ICP2025

32nd International Conference on Photochemistry

13th – 18th July 2025

# Book of Abstracts

# for Poster Presentations

Status: July 8, 2025

RWTH AACHEN UNIVERSITY

FAU Friedrich-Alexander-Universität Erlangen-Nürnberg

**Welcome to the 32nd International Conference on Photochemistry in Aachen**

We are delighted to host this esteemed conference in Aachen, the westernmost city in Germany and a vibrant hub in the heart of Europe, nestled near the borders of Belgium and the Netherlands. Historically significant, Aachen has served as the coronation site for kings over the past 600 years. The city's centerpiece, the Aachen Cathedral, stands proudly in the heart of the old town, a testament to its rich history. The city's diverse character encompasses a wealth of historical context, cultural attractions, major events, and an array of museums, alongside its important economic and scientific contributions. We encourage you to explore the many facets of Aachen during your stay at the 32nd International Conference on Photochemistry. The conference will take place from July 13 (Sunday) to July 18 (Friday), 2025, and is jointly organized by RWTH Aachen University (Dominik Wöll) and Friedrich-Alexander-Universität Erlangen-Nürnberg (Dirk M. Guldi). We will dive into a range of relevant scientific topics, including:

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| Frontiers in Photochemical Sciences |
| The Photophysics and Photochemistry of Solar Energy Conversion |
| Pushing the Spectroscopic and Microscopic Limits of Single Molecules |
| Plasmonics & Photonics |
| Photochemical Reaction Kinetics and Mechanisms |
| Industrial Photochemistry |
| Photochemistry and the Sustainable Environment |
| Photoswitches for Super-resolution Fluorescence Microscopy |
| New Theoretical Tools in Photochemistry |
| Advanced Spectroscopic Methods |
| Molecular Photomedicine |
| Photoredox Catalysis |
| Enriching Materials Science with Photochemistry |
| Light-Driven Functional Molecular Systems |

The poster sessions are set to take place on Monday, July 14, 2025 (Poster Session I), and Tuesday, July 15, 2025 (Poster Session II), from 6:00 PM to 8:00 PM. These events will be held in the foyer of the Eurogress Aachen building.

**Information for Poster Presenters:** The maximum poster size permitted is DIN A0 (84.1 cm x 118.9 cm). Please print your posters in portrait orientation. They will be attached to the poster boards using pins, which will be provided by the organizers. Posters can be set up on the designated poster wall starting at 11 a.m. on Monday for Poster Session I and on Tuesday for Poster Session II. If you require assistance, our staff will be more than happy to help. We kindly ask that you remove your poster immediately after the poster session to ensure that the poster walls remain available for the subsequent presentations. Thank you!

We look forward to welcoming you in Aachen. For more information and to access the registration form, please visit the official conference website at www.icp2025.de.

Dominik Wöll (RWTH Aachen University)
Dirk M. Guldi (FAU Erlangen-Nürnberg)

## Poster Session I: Monday, July 14 (18:00 – 20:00)

### Frontiers in Photochemical Sciences

**A1:** Angerer, Simon (University of Regensburg), “Exploring New Bond Insertions of Photogenerated Donor Donor Diazo Compounds”

**A2:** Avila-Serna, Michelle (Instituto de Química UNAM), “Design and Photochemical properties of donor-π-acceptor asymmetric Stenhouse salts”

**A3:** Cora, Diego (Universidade de Santiago de Compostela), “Cas9 aggregation studied at the single-molecule level”

**A4:** Govind, Chinju (University of Geneva), “Excited state symmetry breaking with a twist”

**A5:** Heitmann, Mara (Saarland University), “Unsymmetrically Substituted Pyrene-based Photoacids”

**A6:** Jana, Madhurima (University of Bologna), “Electrochemiluminescence-based detection of clinically relevant pathogens”

**A7:** Jiménez, María Consuelo (Universitat Politècnica de València), “Photoinduced Labeling of Cysteine with Fluorescent Probes”

**A8:** Larios, Alejandro (Instituto de Quimica, Universidad Nacional Autonoma de Mexico), “Experimental and theoretical insight into the nature of the intersystem crossing pathway in 9-nitroanthracene, an extension to the El-Sayed’s rules”

**A9:** Law, Tsz-Kit (The Hong Kong Polytechnic University), “Hemi-Protonated Cytosine-Cytosine Base Pair Controls Ultrafast Excited State Dynamics in Human Telomere and c-MYC Promoter i-Motifs”

**A10:** Lazarevski, Bruno (University of Basel - Department Of Chemistry), “Long-Lived Metal-to-Ligand Charge-Transfer Excited States in Nickel(II) Complexes”

**A11:** Marin, Maria Luisa (Instituto de Tecnología Química, Universitat Politècnica de València-Consejo, Superior de Investigaciones Científicas), “New $TiO_2$-Coated Sand Composite for Scalable Continuous-Flow Photocatalytic Degradation of Microplastics”

**A12:** Markovitsi, Dimitra (CNRS), “Studying UV-induced electronic relaxation in DNA at the frontier of time-resolution”

**A13:** Mejia, Mariana (Massachusetts Institute of Technology), “Primary Photophysics of Nicotinamide Chromophores in Their Oxidized and Reduced Forms”

**A14:** Morgan, Luca (Università Degli Studi di Padova), “Regenerative chemiluminescence from reduction reactions with amino-pyrene derivatives”

**A15:** Olivier, Wesley (RWTH Aachen University), “A photochemical method for the selective oxidative cleavage of arenes over alkenes”

**A16:** Ortega Valdovinos, Luis Ramón (Insitituto de Química, UNAM), “Synthesis and study of amphiphilic photo-switches controlled by two-photon absorption applied to carrier systems.”

**A17:** Paczelt, Viktor (Ruhr-Universität Bochum), “Generation and UV-photolysis of N-methyleneformamide”

**A18:** Tsutskiridze, Armaz (Universität Regensburg), “Advances in Photoinduced Catalysis and Photochemistry Enabled by Near-Infrared Light”

**A20:** Wenzel, Jonas Oliver (Karlsruhe Institute of Technology), "BPI Ligands for Visible-Light Homolysis of E–C Bonds in Main Group Chemistry"

**A21:** Wong, Man-Sing (The University of Edinburgh), “Fluorogenic and Photocatalytic Amino Acids for Imaging T Cell Activity”

**A22:** Zank, Simon (FAU Erlangen-Nürnberg), “Nanohoops Favour Light-Induced Energy Transfer over Charge Separation in Porphyrin/[10]CPP/Fullerene Rotaxanes”

**A23:** De, Arijit (Indian Institute Of Science Education & Research, Mohali), “Dissecting triple emission from a fluorescent protein” (poster presented by Kumari, Anita)

**A24:** Paul, Sasthi (Indian Institute of Science Education and Research Mohali), “New insights into ultrafast excited-state dynamics of green fluorescent protein” (poster presented by Kumari, Anita)

## Poster Session I: Monday, July 14 (18:00 – 20:00)

### Industrial Photochemistry

**B1:** Itoh, Akichika (Gifu Pharmaceutical University), "Development of an automation system of ibuprofen synthesis through flow photo Favorskii reaction with robot"

**B2:** Petko, Filip (Cracow University of Technology), “Photoinduced Cationic Frontal Polymerization as a New Method for Curing Thick Composites Materials Using Visible Light”

**B3:** Yen, Shun-Chang (National Taiwan Ocean University), “Applying optical systems for chemical combustion and physical property analyses: Schlieren, Shadowgraph, and Mie Scattering”

## Poster Session I: Monday, July 14 (18:00 – 20:00)

### Light-Driven Functional Molecular Systems

**C1:** Banerjee, Debarshi (International Centre for Theoretical Physics (ICTP)), “Heavy Water Induces Intrinsic Fluorescence in Bioorganic Crystals”

**C2:** Basquill, Cody (Florida State University), “Excimer Formation in Solution and Surface-Bound Pyrene Dicarboxylic Acids”

**C3:** Boonmong, Nutnicha (Kyushu University), “Enhancing photon upconversion efficiency via steric protection of π-electron systems with sterically controlled intermolecular interaction”

**C4:** Bravo-Romero, Melissa (Universidad Nacional Autónoma de México), “Indirect Photo-transformation of Molecular Switches using a Pyrrolo-pyrrole Two-Photon Absorbing Antenna”

**C6:** Cingolani, Matteo (Università di Bologna - Dipartimento di Chimica "G. Ciamician"), “Detection of early protein aggregates with fluorogenic hyaluronan nanogels”

**C7:** Drichel, Alwin (DWI – Leibniz Institute for Interactive Materials), “Dynamic Covalent Spiropyran Exchange Systems”

**C8:** Dvoracek, Metodej (TU Dublin), “Unprecedented visible light-initiated topochemical [2+2] cycloaddition in a functionalized bimane dye”

**C9:** Schwarz, Denise (RWTH Aachen University), “Computational Investigation of Photochemistry and Reactivity in Macrocyclic Diarylethenes Photoswitches”

**C10:** Hernandez Mejias, Sara (IMDEA Nanoscience), “Protein-promoted chromophore excited state decay modulation”

**C11:** Hruzíková, Anna (Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences), “Towards a Unified Methodology for Half-life Determination of Photoswitches with Highly Stable Z isomer”

**C12:** Kuevda, Alexey (University of Groningen), “Polarization-Sensitive Single-Object Microscopy Resolves Theoretical Debate on the Structure of a Synthetic Light-Harvesting Complex”

**C13:** Kumar, Rohit (ISM, Université de Bordeaux), “Photochemical Control of Gel Disassembly mediated by Singlet Oxygen”

**C14:** Lienert, Jonas (Goethe University Frankfurt), “Multistate Dihydroazulene-Spiropyran Dyads: Path-Dependent Switchings and Refinement of the “Meta-rule” of Photoactivity”

**C15:** Maity, Nishith (Christian Albrechts University of Kiel), “Unraveling Excited-State Intramolecular PCET in a Dinuclear Ir(III) Complex via Ultrafast Spectroscopy and Strategic Hydroquinone Core Modifications”

**C16:** Matasovic, Lujo (University of Cambridge), “Role of Molecular Topology on Quartet-Derived Luminescence in Emissive Radicals”

**C17:** Metzen, Christian (RWTH Aachen University), “Photoswitchably Crosslinked Microgels and their Super-resolved Visualization”

**C18:** Moghtader, Julian Amir (JGU Mainz, Kerzig Group), "At the “peak” of TTA upconversion: clear advantages of TIPS substituents"

**C19:** Nakase, Kotaro (Ritsumeikan University), “Multistep Photochromic Reactions of a Stilbene-Anthraquinone Conjugate Based on Self-Accelerating Photoreduction”

**C20:** Omist, Alicia (DIPC), “Non-kasha photo-emission behavior in organic molecules”

**C21:** Orozco-Barrera, Diego (Instituto de Química, UNAM), “One Excitation, Two Isomerizations: Second Generation Oxazolones Photochemistry.”

**C22:** Pereira, Ana Margarida (Maastricht University), “Synthesis of red light photoswitches – The case of Konrad’s azobenzene”

**C23:** Raffy, Guillaume (Institut des Sciences Moléculaires (ISM) - UMR5255), “Structural and Dynamic Studies of Low Molecular Weight Molecular Organogels using Multimodal FLIM, Hyperspectral, Polarization and Super-Resolution Fluorescence Microscopy”

**C24:** Reza-González, Francisco A. (UNAM), “Developing novel two-photon switching systems for non-linear optical super-resolution microscopy”

**C25:** Ricci, Gaetano (Donostia International Physics Center), “Optically addressability of the arylnitrene spin triplet”

**C26:** Rodriguez, Aolani (Instituto de Química, UNAM), “Two-photon release of a radical species and generation of a highly fluorescent probe”

**C27:** Seinfeld, Mathilde (Laboratoire de Chimie, ENS de Lyon), “Unraveling the AIE Mechanism in Red-Emitting Fluorophores: Stereoselective Synthesis and Physicochemical Studies”

**C28:** Shahsavari, Hamid Reza (Institute for Advanced Studies in Basic Sciences (IASBS)), “Luminescent cycloplatinated(II)-thiolate complex stabilized by interaction with a borane compound”

**C29:** Sucre-Rosales, Estefania (University of Geneva), “Ultrafast charge transfer photodynamics in polymeric materials”

**C30:** Thielert, Philipp (University of Freiburg), “Supramolecular light-induced multi-spin systems as qubit candidates”

**C31:** Tideland, Hannah (University of Gothenburg), “Synergetic Photoinduced Electron Transfer and triplet-triplet annihilation upconversion for highly sensitive $K^+$ detection”

**C32:** Wang, Qunying (Niederrhein University of Applied Sciences), “Pattern of Cyanines Controls Photopolymerization via Activated Photoinduced Electron Transfer between 700-1100nm”

**C33:** Yagi, Masayuki (Niigata University), “Non-electric bias hydrogen peroxide production by visible light in a photoelectrochemical cell using an organic polymer photocathode”

**C34:** Yoshioka, Rengo (Okinawa Institute of Science and Technology), “Efficient Organic Long-Persistent Luminescence Enabled by Thermally Activated Delayed Fluorescence Molecule”

## Poster Session I: Monday, July 14 (18:00 – 20:00)

New Theoretical Tools in Photochemistry

**D1:** Guhl, Jasper (Heinrich Heine Universität Düsseldorf), “Design of efficient, NIR-luminescent Pd/Pt(0) complexes”

**D2:** Kremper, Jennifer (Heinrich-Heine University), “Photophysical Properties of a TADF Emitter in Complex Environments”

**D3:** Olivier, Yoann (University of Namur), “Optically addressable organic radicals for quantum information and photochemical upconversion applications: A computational perspective.”

**D4:** Perumal Marisami, Janaarthana Babu (DIPC), "Enhancing RASCI Excitation Energy Accuracy with Second-Order Perturbation Theory"

**D5:** Ueda, Sakuya (The University of Electro-communications), “Deciphering carbon–sulfur rotational distribution in a crystalline host for enhanced red persistent organic phosphorescence”

**D6:** Valverde, Danillo (University Of Namur), “Theoretical Investigation on the Reverse Intersystem Crossing Mechanism in Inverted Singlet-Triplet Gap Molecules”

## Poster Session I: Monday, July 14 (18:00 – 20:00)

Photochemistry and the Sustainable Environment

**E1:** Avcu, M. Tuğrul (Koç University), “Photocatalytic Water Splitting with Ta and Ti Doped 2D Niobate Perovskites”

**E2:** Brettschneider, Sarah (RWTH Aachen University), “Modular Solid-State Sono-Piezo-Photocatalysts for Efficient Hydrogen Peroxide Production”

**E3:** Duong, Thi Thanh Hoa (Leibniz Institute For Catalysis e.V. (LIKAT)), “Boosting photocatalytic performance of bismuth molybdate in DCF degradation by controlling the molar Bi to Mo synthesis ratio”

**E4:** Eggenweiler, Henri (Universität Basel), “Copper(I) Isocyanide Complexes Featuring High Triplet Energies”

**E5:** Fan, Yu (City University of Hong Kong), “Design and Study of Luminescent Re(I) Complexes with Strong $\pi$-Accepting Anionic Ligands”

**E6:** Fischer, Alexander (JGU Mainz AK Heinze), “A blessing and a curse: remote ligand functionalization modulates 3MLCT relaxation in group 6 tricarbonyl complexes”

**E7:** Förster, Moritz (Johannes Gutenberg-Universität Mainz), “Luminescent Octahedral Group 14 Complexes”

**E8:** Gao, Mengyue (The University of Hong Kong), “Dinuclear Cyclometalated Pincer Nickel(II) Complexes with Metal-Metal-to-Ligand Charge Transfer Excited States and Near-Infrared Emission”

**E9:** Grigoras, Amalia Malina (University of Perugia), “Adsorption and Light dating: photocatalytic water remediation based on $\alpha$-$Bi_2O_3$”

**E10:** Hartkorn, Marco (Ulm University), “Photocatalytic On-demand Hydrogen Evolution - A Water-soluble Copolymer for Storage and Catalytic Conversion of Electrons”

**E11:** Häser, Leonie S. (ITMC, RWTH Aachen University), “Accessing Photocatalytically Active Covalent Triazine-based Frameworks by Ball Milling: A Fast and Facile Synthesis Method”

**E12:** Hübner, Daniella (Universität Osnabrück), “Red-to-blue photon upconversion nanoparticles and their photocatalytic activity for polymerization in water”

**E13:** Kabeer K, Adhil (IMDEA Nanoscience, Madrid), “Towards Orchestrating TADF Properties with Proteins as Scaffolds”

**E14:** Lee, Byeong-Kyu (University of Ulsan), “Internal electric field engineering for boosting visible-light-driven $H_2$ production”

**E15:** Leistikow, Georg (University of Heidelberg), "Light-Induced Metal-Free Generation of Cyanocarbenes from Alkynyl Triazenes for the Synthesis of Nitrile Derivatives"

**E16:** Leśniewicz, Aleksandra (Adam Mickiewicz University in Poznan), "Probing Mechanism of Rhodamine B Decolorization under Homogeneous Conditions via pH-Controlled Photocatalysis with Anionic Porphyrin"

**E17:** Liu, Wu-Han (ITRI), "Exploring $Al_2O_3$–ZnO Composite Coatings as Photocatalysts: A Novel Approach Using Thermal Spraying Technique"

**E18:** Marlina, Dini (University of Potsdam), "Polymer-Peptide Conjugates for Enhanced Lanthanide Recovery: A Comparative Study Using Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLFS)"

**E19:** Rahman, Atikur (IIMDEA Nanociencia), "Harnessing Energy and Electron Transfer Processes in Engineered Bio-Hybrids for Enantioselective Photocatalysis"

**E20:** Rein, Alexandra Stefanie Jessica (Ulm University), "Supramolecular manipulation of heteroleptic iron(II) chromophores"

**E21:** Säbb, Emil (Uppsala University), "Photophysical properties of monobenzopentalene and its derivatives"

**E22:** Sethi, Mukul (Ulm University), "Designing B-$TiO_2$ photoelectrodes for efficient photochemical water splitting with an operando focus on the modular photoreactor"

**E23:** Takagi, Toranosuke (Institute of Science Tokyo), "Ligand exchange of $CsPbBr_3$ perovskite nanocrystals and observation of single-particle electroluminescence"

**E24:** Tamay, Ilayda Meltem (Koç University), "Investigation on the Photocatalytic Methanol Oxidation Activity of Layered Niobate Perovskites Coupled with Metal Sulfide Nanoparticles"

**E25:** Tran, Phuong Anh (Leibniz Institute for Catalysis. e.V.), "Synthesis and photocatalytic applications of carbon dots/polymeric carbon nitride composites"

**E26:** Valaei, Akbar (Ulm University), "Integrating Photocharging of $TiO_2$ Aerogels and $N_2$-Reduction in Taylor Flow for On-Demand Ammonia Synthesis"

**E28:** Witas, Kamil (Ulm University), "Beyond the First Coordination Sphere – Manipulating Excited States in Heteroleptic Iron(II) Chromophores with Protons"

**E29:** Wu, Minghui (Maastricht University), "Non-Innocent Behavior of Aromatic Isocyanides under Visible Light: A Pathway to Thioformimidates"

## Poster Session I: Monday, July 14 (18:00 – 20:00)

### Pushing the Spectroscopic and Microscopic Limits of Single Molecules

**F1:** Chen, Xiong (KU Leuven University), "Sequence-Specific Fluorescent Labeling of DNA Leveraging Natural Mechanisms"

**F2:** Höche, Hannah (RWTH Aachen University), "Estimating the local water content in polymer systems using super-resolution fluorescence microscopy"

**F3:** Malsbenden, David (RWTH Aachen University), "Formation of Three-Dimensional Cross-Linked Polymer Networks Studied by Single Molecule Tracking"

**F4:** Schöngen, Damian (RWTH Aachen University), "FEDUP: extending the range of feasible diffusion imaging"

**F5:** Shimura, Riku (The University of Electro-Communications), "Oxygen quantification based on the persistent phosphorescence lifetime of host–guest nanocrystals"

**F6:** Trottenberg, Leon (RWTH Aachen University), "Influence of Nile Red on the internal structure of pNIPAM microgels investigated with combined spectral and lifetime measurements"

## Poster Session I: Monday, July 14 (18:00 – 20:00)

### The Photophysics and Photochemistry of Solar Energy Conversion

**G1:** Ahn, Da Hee (Chungbuk National University), "Enhancement of the Photoelectrochemical Performance of CoreShell Structured Hematite Photoanode with Homojunction Configuration"

**G2:** Beneventi, Giovanni Mariano (FAU Erlangen-Nürnberg), "Length-Dependent Optoelectronic Behavior in Nanographenes"

**G3:** Biebl, Sonja Maria (Eberhard Karls Universität Tübingen), "Functionalized 1,2-dihydro-1,2-azaborinines for Molecular Solar Thermal energy storage"

**G4:** Bisht, Jyoti (Friedrich Schiller University Jena), "Insight into excited state dynamics of PM6:Y6 Bulk-Heterojunction: deposited via Langmuir Schaefer deposition technique"

**G5:** Bo, Yifan (FAU Erlangen-Nürnberg), "Intramolecular Down- and Up-Conversion in Dimeric Tetracene Complexes Centered via Platinum(II) and Palladium(II)"

**G6:** Burgoyne Morris, Georgina (University of Cambridge), "Effect of Host Oxygen Permeability on the Efficiency of Solid-State Photon Upconverters for Photovoltaics"

**G7:** Cantoni, Roberto (University of Perugia), "Aggregation-Induced Singlet Fission in Push-Pull Diketopyrrolopyrrole Water Dispersed Nanoaggregates and Thin Films"

**G8:** Choi, Seoung Heon (Chungbuk National University), "Revealing the Origin of the Improved OER Activity of Ni-Based ZIFs on α-$Fe_2O_3$ Photoanode using NF-HD-TG Spectroscopic and PEIS Techniques"

**G9:** Das, Shirsendu (University of Twente), "The mechanism of hole diffusion and the role of coherent phonon modes in lithium doped bismuth vanadate photoanodes"

**G10:** Dumitrascu, Alexandru George (LEMPI), "Photo-assisted recharge of Lithium Ion battery"

**G11:** Dunlop, David (Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences), "Positional Isomerism of Sulfur Determines Which $C_8H_6S$-Heterocycles are Candidates for Anti-Kasha $S_2$-$T_1$ Singlet Fission"

**G12:** Eberhart, Michael (New Jersey Institute of Technology), "Controlling Electron Transfer Reactions for Artificial Photosynthesis"

**G13:** Furube, Akihiro (Tokushima Univ.), "Enhanced Visible Light Response and Photoinduced Charge Transfer Dynamics of Gold/SiC Nano-Composite Photocatalysts"

**G14:** García González, Asier (IMDEA Nanoscience), "Understanding the impact of aminoacid networks on protein-based artificial photosystems"

**G15:** Gómez, Roberto (University of Alicante), "Metal tungstates as photoanodes for water oxidation: computational and experimental results"

**G16:** Greißel, Phillip (FAU Erlangen-Nürnberg), "Intramolecular Singlet Fission in Individual Graphene Nanoribbons–Competition with Charge Transfer"

**G17:** Herm, Maximilian (FAU Erlangen-Nürnberg), "The Photochemical E/Z-Isomerization Pathway of the NIR Photoswitch peri-Anthracenethioindigo"

**G18:** Hong, Aram (Chungbuk National University), "Photoelectrochemical Water Splitting and Charge Transfer Dynamics of Bismuth Vanadate ($BiVO_4$) Photoanode with Chiral Perovskite"

**G19:** Itagaki, Ren (Kyoto University), "Phase-Migrating Z-Scheme Charge Transportation Enables Photoredox Catalysis Harnessing Water as an Electron Source"

**G20:** Jana, Bikash (CIC biomaGUNE), "Mechanism of photocatalytic hydrogen generation in carbon nanodots photocatalysts"

**G21:** Jang, Seong Kyu (Chungbuk National University), "Estimations of the Activation Energies for the Charge Transfers of the Long-Lived Holes at the Semiconductor/Electrolyte Interfaces of α-$Fe_2O_3$ and α-$Fe_2O_3$/Co-Pi Photoanodes."

**G22:** Jeong, Seung Hyeon (Chungbuk National University), "Investigation of Hole Transfer Efficiency in $MAPbI_3$ Perovskite Solar Cells with Various Copper-based Hole Transport Materials Using Near-Field Heterodyne Transient Grating Spectroscopy"

**G23:** Kandappa, Sunil (Uppsala University), "Understanding the Mediator Enhanced Triplet-Triplet Annihilation Upconversion"

**G24:** Kim, Gun Woo (Chungbuk National University), "Investigation of the Charge Carrier Dynamics in $MAPbBr_3$ and $MAPbI_3$ Perovskites Using a Near-Field Heterodyne Transient Grating Spectroscopic Technique"

**G25:** Kippes, Mathieu (FAU Erlangen-Nürnberg), "Influence of linkers between norbornadiene and perylenediimide at the N-position on photoswitching and photochemical properties"

**G26:** Krishna, Swathi (FAU Erlangen-Nürnberg), "Pushing the Limits Towards Long-Lived Charge Separation in Ruthenium (II) Phthalocyanine-Subporphyrazine Conjugates"

**G27:** Leung, Chi-Fai (Department of Science and Environmental Studies, The Education University of Hong Kong), "Function-integrated Cyclometalated Diruthenium Photocatalyst for $CO_2$ Reduction"

**G28:** Li, Yi (Technical Institute of Physics and Chemistry, Chinese Academy of Sciences), "Crystalline hydrogen-bonded organic framework for air-tolerant triplet-triplet annihilation upconversion"

**G29:** Mikie, Tsubasa (Hiroshima University), "Impact of semiconducting polymer crystallinity on hydrogen evolution in organic p/n heterojunction nanoparticle photocatalysts"

**G30:** Odutola, Jokotadeola (Tampere University), "Just add Salmiakki: Photophysics of $NH_4Cl$-Modified Potassium Poly (Heptazine Imide) for Enhanced Photocatalytic Hydrogen Peroxide Production"

**G31:** Thiel, Dominik (FAU Erlangen-Nürnberg), „Intramolecular Triplet Diffusion Facilitates Triplet Dissociation in a Pentacene Hexamer"

**G32:** Raj, Amar (Nanoscience Center, University of Jyväskylä), "Ultrafast Insights into Monohybrid CN- via femtosecond-TA and In-Situ Gaseous Raman Spectroscopy"

**G33:** Reimann, Louise (ICIQ), "De novo protein design for efficient solar energy conversion"

**G34:** Seth, Sudipta (KU Leuven), "Unveiling Microscopic Charge Carrier Dynamics of Perovskite Solar Cells in Action"

**G35**: Shim, Yeon Gyo (Chungbuk National University), "Anodic Potential Shift in Hematite Photoanode Induced by $TiO_2$ Underlayer: Origin and Mitigation"

**G36:** Sivanarayanan, Jibin (IISER Thiruvananthapuram), "Unlocking the Room Temperature Phosphorescence through Halogen Engineering in Carbazole Dimer"

**G37:** Suzuki, Hajime (Kyoto University), "Interface Engineering between Layered Oxyhalide Photocatalyst and Cocatalyst for Enhancing Water Oxidation"

**G38:** Szychta, Kamil (University of Warsaw), "Aromatic α-hydroxy Schiff bases for Molecular Solar Thermal Energy Storage applications"

**G39:** Takahashi, Reiya (Kyoto University), "Enhancing Photocatalytic $O_2$ Evolution over Double-Layered Perovskite Oxyiodide through Flux Synthesis and Surface Modifications"

**G40:** Tingare, Yogesh (National Taipei University of Technology), "Fluorinated Nitrogen-rich heterocycle-based hole transport materials for defect passivation in inverted perovskite solar cells"

**G41:** V. Muralidharan, Anjana (IISER Thiruvananthapuram), "Long-Lived Intramolecular Charge Transfer in Persubstituted Perylenediimide"

**G42:** Yoosefi, Sahar (Ulm University), "Ruthenium(II) Complexes with Functionalized Phenanthroline Ligands: Synthesis, Structural Characterization"

**G43:** Sheeja Sury, Adhra (Indian Institute of Science Education and Research), "Triplet-Triplet Annihilation Upconversion Mediated Photocatalysis Using Quantum Dots"

## Poster Session II: Tuesday, July 15 (18:00 – 20:00)

### Advanced Spectroscopic Methods

**H1:** Alebardi, Martina (University of Perugia, Department of Chemistry, Biology and Biotechnology), "Ultrafast Features of Intermolecular Singlet Fission in Quinoidal Push-Pull Molecules"

**H2:** Gensch, Thomas (Institute of Biological Information Processing 1 (IBI-1; Molecular And Cellular Physiology); Forschungszentrum Jülich), "Molecular Basis of Nitric Oxide Sensing by a Blue Fluorescent Protein"

**H3:** Hou, Yuqi (Dalian University of Technology), "Efficient intersystem crossing in donor-Bodipy dyads/triads and photon upconversion application"

**H4:** Kalal, Bhavika (Indian Institute of Technology, Hyderabad), "Spectroscopic Characterization of 2-(2'-pyridyl)-benzimidazole-(water)1,2 Complexes Isolated in the Gas Phase"

**H5:** Li, Chunyu (The Institute of Photonic Sciences-ICFO), "A novel ultrafast spectroscopic method to determine how and how fast the light-harvesting complexes sense and respond to changes in pH: proof of principle"

**H6:** Montanari, Chiara (University of Perugia), "Red Thermally Activated Delayed Fluorescence with nearly zero gap in phenothiazine-naphthalimide derivatives"

**H7:** Pal, Chandrani (Indian Institute of Technology Kanpur), "Conformational Switching of a Nano-Size Urea-bridged Zn(II)Porphyrin Dimer by External Stimuli"

**H8:** Saha, Abhijit (Indian Institute of Technology Kanpur), "Fine-tuning the Excited State Dynamics of Ruthenium(II) Polypyridyl Complexes with Benzazole-Substituted 8-Hydroxyquinolines"

**H9:** Wega, Johannes (University of Geneva), "Ground-State Structure and Excited-State Dynamics of a Donor-Acceptor Complex with Two Charge-Transfer Bands"

**H10:** Zhang, Xue, (Dalian University of Technology), "The spatial distribution of triplet state wave function in molecules with large π-conjugated systems"

**H11:** Zimmermann, Simon L. (Heinrich Heine University Düsseldorf), "Assignment of Transient States in Copper(I) Complexes by Femtosecond Near Infrared Spectroscopy"

**H12:** Arvanitakis, Georgios (Edinburgh Instruments Ltd.), "Probing Excited-State Dynamics in $TiO_2$ and $TiO_2$/rGO Hybrids via Transient Absorption"

## Poster Session II: Tuesday, July 15 (18:00 – 20:00)

### Enriching Materials Science with Photochemistry

**I1:** Auria-luna, Fernando (Universidad del País Vasco (UPV/EHU)), "The BOLD project: Applying organic chemistry and photochemistry to particle physics by means of Barium tagging"

**I2:** Casnati, Francesco (Università di Bologna), "Photoinduced cleavage of triarylmethane crosslinked polymers with photoacid"

**I3:** Coccimiglio, Mariafrancesca (University of Salento - University of Perugia), "Integrating deployment of bio-waste based complex-nanosystem' photo-active modulable behavior in colloidal aqueous solution"

**I4:** de Lange, Robert Dirk (Institute of Physical Chemistry, RWTH Aachen University), "UV-Induced Response of Dual Stimuli-Responsive pNIPAM Microgels Functionalized with Photolabile Protected Amines"

**I5:** Duarte, Luís (Institute of Chemical Research of Catalonia (ICIQ)), "Bio-Inspired Chromophore-Protein Complexes as Color Converting Layers of LEDs"

**I6:** Hauza, Karol (Adam Mickiewicz University), "Photochemistry of chiral porphyrin assemblies on thin ferromagnetic films"

**I7:** Hicguet, Matthieu (Institut des Sciences de Chimie de Rennes), “Synthesis and optoelectronic properties of original bicarbazole-based π-conjugated helical chiral structures”

**I8:** Hirai, Yuichi (NIMS), “Photofunctional Behavior and Tunability of Molecular Solids under Mechanical Stimuli”

**I9:** Huang, Shufang (The University of Osaka), “Tuning phosphorescence through molecular rigidity: role of intramolecular hydrogen bonding in trans-bis(iminopyrazolato)platinum(II) complexes”

**I10:** Jiang, Lanting (UBC), “Photoactive stimuli-responsive flexible Lewis pair oligomers”

**I11:** Kundu, Sangita (Institut Lumière Matière, CNRS), “Ligand Effects on Photothermal Properties of Atomically Precise $Au_{25}$ Nanoclusters”

**I12:** Kunnumma Chelladath, Krishnapriya (Gothenburg University), “The effect of HOMO-FRET on the donor-acceptor FRET efficiency in thin films”

**I13:** Leray, Isabelle (ENS Paris Saclay PPSM), “Fluorescent sensor for monitoring pH in cementitious materials”

**I14:** Llanes Montesino, Luis Enrique (Physical-Chemistry Department, University of Geneva), “Au-25 atomically precise nanoclusters: on the way to elucidate a complex photophysics”

**I15:** Mack, Elena (FAU Erlangen-Nürnberg), “Morphological and electronic control of interfacial charge transfer in 2D transition metal dichalcogenides”

**I16:** Meng, Xinyue (Saarland University), “All-Carbon Mixed Valency: Thiele’s, Chichibabin’s, and Müller’s Radical Cations”

**I17:** Middelhoff, Christoph (FH Münster), “Efficient Blue to UV Up-Conversion through Energy Transfer between $Pr^{3+}$ and $Gd^{3+}$”

**I18:** Moll, Lena (JMU Wuerzburg), “Axially chiral NIR emitters”

**I19:** Moshniaha, Liliia (OIST), “Organic Long-Persistent Luminescence Enhanced by Charge-Transfer States in Donor–Acceptor Molecules”

**I20:** Murugesan, Chandran (Gachon University), “Electrochemical and fluorescence dual-mode detection of norepinephrine with a portable smartphone assay by nitrogen-doped $Ti_3C_2$ MXene quantum dots”

**I21:** Nagai, Kanato (Ritsumeikan University), “Excited-state dynamics of indium-doped zinc oxide nanocrystals”

**I22:** Nuti, Silvia (Alma Mater Studiorum – Università di Bologna - Dipartimento di Chimica "Giacomo Ciamician"), “Studying Thermochemiluminescence through rational design and nanoparticle integration”

**I23:** Park, Jungjin (Yonsei University), “Stabilizing Diketopyrrolopyrrole Radical Cations Through Carbazoles: Substitution Pattern vs. Spin-Delocalization”

**I24:** Pelorosso, Elisa (Università di Padova), “Enhancing Self-Assembly Complexity via Ligand Exchange in Luminescence Pt(II) Complexes”

**I25:** Ranieri, Donato (University of Perugia), “Encapsulation of silver nanoclusters to increase their luminescent properties”

**I26:** Takayama, Dai (Osaka Metropolitan University), “Exciton dynamics in CdTe quantum dot superlattices with minibands”

**I27:** Tong, Ka-Ming (University of British Columbia), “Photophysics of Platinum(II) Flexible Lewis Pairs Compounds”

**I28:** Uji, Masanori (Department of Chemistry, Graduate School of Science, The University of Tokyo), “In Vivo Optogenetics Based on Heavy Metal-Free Photon Upconversion Nanoparticles”

**I29:** Van Hout, Bob (KU Leuven), “Boosting the Stability and Optoelectronic Performance of $CsPbI_3$ Nanocrystals for the Design of Advanced Red-Emitting LEDs”

**I30:** Völlmecke, Katharina (Paderborn University), “Targeted therapy at the speed of light”

**I31:** Zeng, Yimin (University of British Columbia), “Antimicrobial textiles based on photocrosslinked poly(ethylene-co-acrylic acid)”

**I32:** Zhang, Wenhao (Institute of Science Tokyo), “From mechanosensitive to locked: environment-induced structural diversity in dendronized anthracene nanofibers”

## Poster Session II: Tuesday, July 15 (18:00 – 20:00)

| Molecular Photomedicine |
| --- |
| **J1:** Barczyk, Dominik (Jagiellonian University), “Modification of Tetrapyrrolic Photosensitizers as a Strategy to Enhance Photodynamic Therapy Efficiency” |
| **J2:** Dochtermann, Hannah (University of Cologne), “Fluorescent coumarins for the photoinduced activation of Artemisinin – A photopharmacological approach” |
| **J3:** Guo, Xudong (Institute of Chemistry, Chinese Academy of Sciences), “Chalcone Derivatives for β-gal and Aminopeptidase N Detection” |
| **J4:** Harris, Mariah (Institut des Sciences Molécularies d'Orsay (ISMO) - Université Paris Saclay), “Fluorescent Organic Nanoparticles: A Bright Nanotool for Early Detection in Biological Systems” |
| **J5:** Holovan, Denys (McGill University), “Development of a mitochondria-targeted fluorogenic probe for monitoring LDE reactivity during ferroptosis” |
| **J6:** Jeong, Hyunsun (Ewha Womans University), “Tumor-Targeted Exosome-based Heavy Atom-Free Nano-sensitizer for effective Sono-Photodynamic Therapy of Solid Tumors” |
| **J7:** Kolman, Aleksander (Adam Mickiewicz University, Poznań), “Spectroscopic insights into photophysical properties and interactions of m-THPC with Pluronic P123” |
| **J8:** Méndez, Erandi (UNAM), "Time-resolved fluorescence NADH signals as a tool to investigate the adaptative capacity of cell-lines towards changes in available metabolic substrates" |
| **J9:** Ossanna, Riccardo (Institut des Sciences Moléculaires d'Orsay (ISMO UMR 8214)), “Control of the optical absorption properties of nanovectors for photoacoustic imaging (CAP-PHOTOAC)” |
| **J10:** Ott, A. Theresa (Heinrich Heine University), “Photoreaction vs. Electron Transfer: Time-Resolved Spectroscopy on Amotosalen and Mixed DNA Oligomers” |
| **J11:** Rademacher, Michelle P. (HHU Düsseldorf), “(Time-Resolved) Spectroscopy on the Interaction of Novel Angelicins with DNA” |
| **J12:** Repetowski, Paweł (Uniwersytet Jagielloński), “Modified Zn(II) and Pt(II) Sulfonyl Phthalocyanines for Photodynamic and Theranostic Applications” |
| **J13:** van Stiphoudt, Jan (University of Cologne), “Illuminating Artemisinin: A Photochemical Approach to Unlock Its Pharmacological Potential Beyond Malaria” |
| **J14:** Wang, Lan (Leiden University), "Comparison of cis and trans cyclometalated Palladium photosensitizers on the photophysics and supramolecular self-assembly" |
| **J15:** Warszyńska, Marta (Jagiellonian University), “Enhancing Antitumor Immunity with Bacteriochlorin-Based Photodynamic Therapy and Immune Checkpoint Inhibition” |
| **J16:** Yoshihara, Toshitada (Gunma University), “Intracellular oxygen sensing based on time-resolved emission measurements using phosphorescent Ir(III) complexes” |

## Poster Session II: Tuesday, July 15 (18:00 – 20:00)

### Photochemical Reaction Kinetics and Mechanisms

**K1:** Arpa, Enrique Manuel (RWTH Aachen University), “Turning nitroarenes into photocatalysts for energy transfer: triplet energies and beyond”

**K2:** Berger, Julia (Saarland University), “Single-Molecule Spectroscopy of the Excited-State Proton Transfer”

**K3:** Diepold, Niklas (Bielefeld University), “Enhancing the Efficiency of Flavin Photoreduction Inside Enzymes for Application in Biocatalytic Halogenation”

**K4:** Drabkin, Vladimir (Ruhr-Universität Bochum), “H-Tunneling Rotamerization in Glycine Imine”

**K5:** Drizhinin, Sergey (Uni Siegen), “Fluorescent water-sensitive probes for dynamic polymer wetting”

**K6:** Einholz, Christopher (Institute of Physical Chemistry, University of Freiburg), “Unraveling biological magnetoreception by modulating cryptochrome photochemistry”

**K7:** El Moqaouil, Zineb (CEA-I2BC), “Mechanistic Insight into the Photocatalytic Deoxygenation of N–O Bonds Using $[Re(CO)_3bpyCl]$ Photocatalyst”

**K8:** Feldmann, Gereon (RWTH Aachen University), "Ab initio photochemical reaction modeling of the relaxation of $S_1$ photoexcited azobenzene to the ground state using RRK theory"

**K9:** Fella, Fabian (University of Würzburg), "$^{15}$N-labeling of Donor-Acceptor-Dyads for Investigations of the Magnetic Field Dependent Spin Interconversion"

**K10:** Fu, Xingjie (Institut de Physique et de Chimie des Matériaux de Strasbourg), "Effect of the Substitution Groups on the Excited-state Dynamics of Oxindole-based Photoswiches Revealed by Ultrafast Spectroscopies"

**K11:** Groß, Tobias (University of Wuerzburg), “Magnetic field dependent fluorescence in donor-acceptor-dyads”

**K12:** Heger, Dominik (Masaryk University), “Excimer of 1-Methylnaphthalene Originates in Ground State Dimer”

**K13:** Hoffmann, Norbert (CNRS, University of Strasbourg), “Photochemical reactions of oxazolones – Insights in the reaction mechanism”

**K14:** Hou, Yuxuan (University of Copenhagen), “Light in the Garratt–Braverman/[1,5]-H Shift of Ene-diallenes”

**K15:** Kang, Byeongjoo (Yonsei University), “Janus-Type Photophysics of Rotational Isomers in a Diphenylanthracene Dimer”

**K16:** Klaverkamp, David (Heinrich Heine Universität), “The Addition of Photoexcited Nitroarenes to Alkenes traced by Femtosecond Spectroscopy”

**K17:** Kobeleva, Elizaveta (Freie Universität Berlin), "Photo-induced electron transfer in [FeFe] hydrogenases studied by multiscale time resolved infrared spectroscopy"

**K18:** Kölbel, Joseph (Department of Physical Chemistry, University of Geneva), “Illuminating Single- and Multi-Branched Donor–Acceptor Systems with Multidimensional Spectroscopies: Intrinsic Asymmetry, Torsional Disorder and their Redox Dependence”

**K19:** Mahankudo, Sanat Kumar (Institute of Physical Chemistry, Polish Academy Of Sciences), “Early Time Photophysics of Atomically Precise Gold Nanoclusters”

**K20:** Mamusi, Fatemeh (Universitat de Barcelona), “Towards Understanding the Mechanism of Magnetoluminescence in Triarylmethyl-Based Diradicals”

**K21:** Mitra, Prajoy Kumar (IISER Thiruvananthapuram), “Ultrafast Charge Transfer Dynamics in Excited-state Donor-acceptor Benzylideneaniline”

**K22:** Niederst, Léo (LPIM - Université de Haute-Alsace), “An unexpected way to boost Type I photoinitiator reactivity: singlet-singlet energy transfer”

**K23:** Noguchi, Hikaru (University of British Columbia), “Substituent Effects on the Photochemistry of Sulfoxide-Bridged Anthracenes”

**K24:** Nozawa, Shunsuke (High Energy Accelerator Research Organization), "Structural Dynamics of Photo-functional Metal Complexes Studied by Time-resolved XAFS"

**K25:** Peterka, Lukáš (University of Chemistry and Technology, Prague), "Photoinduced Electron Transfer in Bilirubin Model - Oxygen Complex"

**K26:** Pfund, Björn (Michigan State University), "Breaking Kasha's rule to unlock higher excited state reactivity in photoredox catalysis"

**K27:** Putra, Miftahussurur Hamidi (Institute of Theoretical Chemistry Ulm University), "The Mechanistic Process of Catalyst Degradation on RuPt-Based Photochemical Molecular Devices: From Theoretical Perspective"

**K28:** Rabatinová, Kristína (Friedrich Schiller Universität Jena), "In-situ measurement cell integrated into photocatalytic setup for automated exploration of photocatalytic reactions"

**K29:** Santiago Diaz, Lukas (FAU Erlangen-Nürnberg), "Investigation of Iridium(III) Complexes for Organic Photocatalysis via Triplet-Triplet Energy Transfer"

**K30:** Spierling, Leander (University of Basel), "Phenothiazine Sulfoxides as Active Photocatalysts for the Synthesis of γ-Lactones"

**K31:** Toledo, Gabriela (Universidad Nacional Autónoma de México), "Intersystem Crossing in Nitroaromatics Through a $^{1}(\pi\pi^{*})$ to a Twisted $^{3}(\pi\,\pi^{*})$ Mechanism"

**K32:** Verma, Preetika (Indian Institute of Science Education And Research, Thiruvanthapuram), "Ultrafast Excited-state Dynamics of 4-Hydroxychalcone: Role of Intramolecular Charge Transfer and Photoacidity"

**K33:** Werner, Johannes (Karlsruhe Institute of Technology), "Ultrafast Bond Cleavage in Diorganyl Bis(pyridyl)imino Isoindolide Aluminum Complexes"

**K34:** Pauls, Mike (RWTH Aachen University), "Computational Investigation of Relaxation Pathways in Organic Donor-Functionalized Doublet Emitters"

## Poster Session II: Tuesday, July 15 (18:00 – 20:00)

### Photoredox Catalysis

**L1:** Ahuja, Sapna (CSIRO), "Breaking Energy Barriers: Red Light ConPET Photoredox Catalysis"

**L2:** Angelov, Plamen (University of Greenwich), "Iron-Catalysed LMCT Activation of Alcohol Derivatives for Sustainable Radical Alkylation"

**L3:** Bignardi, Camila, (Unesp), "Visible-Light Photocatalysis with Iron(II) Pyridine–NHC Complexes in Radical and Cationic Photopolymerizations"

**L4:** Chaudhuri, Amrita (University of Bonn), "Harnessing LMCT in Fe-Photocatalyzed Chlorooxygenation of Alkenes: A Gateway to Access Orthogonally Functionalized Synthetic Intermediates"

**L5:** Chen, Chiing-Chang (National Taichung University of Education), "Highly Selective Photocatalytic Conversion of C1 to C2+ Hydrocarbons, $H_2$ Evolution, and Photodegradation of CV Dye Using SbSI and SbSeI as Catalysts"

**L6:** Cristofaro, Silvia (University of Namur), "Controlling Cage Escape Yields of Transition Metal Complexes in Photoinduced Electron Transfer Processes"

**L7:** Gocht, Benedikt (University of Helsinki), "Visible-Light Mediated Synthesis of Substituted Furanones"

**L8:** Göcke, Cornelia (Universität Bielefeld), "Photoredox-catalysed cross-coupling reactions with halogenated amino acids"

**L9:** Heinz, Killiann (University of Chemistry and Technology of Prague), "Tri-oxo-triangulene: a new versatile photocatalyst of highly selective photoredox systems."

**L10:** Huth, Philipp (RWTH Aachen University), "Mechanistic Investigation and Optimisation of the Photocatalytic Production of Hydrogen Peroxide"

**L11:** Kanao, Shuhei (Ritsumeikan University), “Near-UV driven photocatalytic defluorination of PFAS by ZnO nanocrystals”

**L12:** Kumari, Anita (IISER Mohali), “Enhancing Visible-Light Driven Photocatalytic Hydrogen Evolution through Organic Conjugates Integrated with Graphitic Carbon Nitride”

**L13:** Laface, Zoe (University of Milan "la Statale"), “Advanced metal-free photocatalytic strategies for on-resin and in-solution synthesis of peptidomimetics”

**L14:** Merico, Dalila (University of Greenwich), "Supramolecular control of selectivity in photocatalytic C-H bond functionalisation"

**L15:** Nabiyan, Afshin (University of Potsdam), “Polypeptoid Micellar Photocatalysts for Visible-Light-Driven Arene Cyanation in Water”

**L16:** Nakada, Akinobu (Kyoto University), “Conjugated polymers with a built-in metal complex catalyst for visible-light-driven $CO_2$ reduction”

**L17:** Neuner, Julian (Johannes Gutenberg-Universität Mainz), “$[Cr(tpPO)_2]^{3+}$ – a highly photooxidizing and photostable photoredox catalyst”

**L18:** Nikitin, Maksim (University of Regensburg), “Photoredox-Assisted Nickel-Catalyzed Cross-Couplings Facilitated by Brønsted Acid”

**L19:** Nogueira, André (Aeronautics Institute of Technology), “Influence of cobalt precursors on the photocatalytic activity of $Nb_2O_5$-based composites for $CO_2$ reduction”

**L20:** Pérez-Ruiz, Raúl (Universitat Politècnica de València), “HIGHLY EFFICIENT TRIPLET PHOTOSENSITIZERS BASED ON BORON-CENTERED DYES”

**L21:** Seitz, Tobias (RWTH Aachen University), “Entatic State Model Systems in Photochemistry”

**L22:** Sharma, Sushil (The University of British Columbia, Vancouver, Canada), “Photoredox O-ATRP of Styrene via Molecular Design of Imidazole-based Organic TADF Photocatalysts”

**L23:** Toigo, Jessica (University of British Columbia), “Photophysical Properties of Tunable Co(III) Photosensitizers with Phenothiazine-based Ligands”

**L24:** Toyota, Yuto (Ritsumeikan University), “UVA-light induced photocatalytic defluorination of perfluoroalkyl substances by silver-loaded titanium dioxide”

**L25:** Treuheit, Johanna (Johannes Gutenberg University), “Visible light-driven hydrogen production by hydrated electrons in aqueous solutions using a single-molecule catalyst”

**L26:** Varma, Naisargi (Adam Mickiewicz University), “Novel Deazaalloxazine Derivatives for Photo-reductive Catalysis: Synthesis and Photophysical Insights”

**L27:** Zhang, Shen (Queen Mary University of London), “Photoredox catalysed difluoromethylation–triggered transformations of styrene derivatives”

**L28:** Zhang, Yuming (Imperial College London), “Heterostructured Redox Mediator for Photoelectrochemical HMF Oxidation with Simultaneous Hydrogen Production”

## Poster Session II: Tuesday, July 15 (18:00 – 20:00)

### Plasmonics & Photonics

**M1:** Chen, Jui-Kai (KU Leuven), “Exploring optical binding inside and outside laser irradiation area toward a rational design of optical matters”

**M3:** Li, Mu-En (National Yang Ming Chiao Tung University), “Optical binding and assembly outside irradiation area: gold nanoparticles guided by gold nanodisk pattern”

**M4:** Lin, Kuanjiuh (National Chung-Hsing University), “Nonoplasmonic Hybrid Photoelectrodes for One-step Immunosensing Devices“

**M5:** Matsumoto, Reiko (Kanagawa University), “Fabrication of a Plasmonic Tapered Fiber Probe using Gold Nanoparticle Assemblies for Surface-enhanced Raman Scattering”

**M6:** Nara, Ryuga (Kanagawa Univ), “Fabrication of Tapered Optical Fibers Modified with Gold Nanoparticle Assemblies toward Plasmonic Optical Trapping”

**M7:** Nayak, Samir Kumar (IIT MADRAS), “Achieving PFAS Degradation through Plasmon-Induced Hot Carrier Generation in Metal Nanoparticles”

**M9:** Satpathy, Jagannath (KU Leuven), “High-resolution imaging of non-equilibrium colloidal self-assembly by photo-fixation”

**M10:** Schaap, Jorik (University of Twente), “In-situ Transient Absorption Spectroscopy of the Photoreduction of $CO_2$ on Silver Nanoparticles”

**M11:** Shoji, Tatsuya (Kanagawa Univ.), “Development of Photofixation for Polymer Nanoparticles Trapped by Plasmonic Optical Tweezers”

**M12:** Skała, Karolina (Institute of Physical Chemistry, Polish Academy of Sciences), “Resonant enhancement of vibrational signal around atomically precise gold nanoclusters seen with stimulated Raman scattering”

**M13:** Steinke, Michael (Leibniz University Hannover), “Fiber-based Plasmonic Microreactor for Flow Chemistry”

**M14:** Willemsen, Andes (Brown University), “Ultrafast Hot Carrier Decay in Aggregated Plasmonic Systems”

# Exploring New Bond Insertions of Photogenerated Donor-Donor Diazo Compounds

Simon Angerer[1], Vincent George[1], Aryaman Pattanik[1], Julia Rehbein[1], Burkhard König* [1]

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Diazo compounds are highly reactive versatile reagents, showing a broad spectrum of chemical transformations such as carbene generation, cycloadditions and bond insertions, making them invaluable for the synthesis of complex molecular architectures[1] Despite their synthetic utility, diazo compounds pose significant safety challenges due to their potential explosiveness and toxicity, necessitating careful handling and stringent safety protocols[2] Therefore, numerous methods have been developed to generate diazo compounds in-situ to circumvent these associated dangers. One example is the photogeneration of donor-donor diazo compounds from tosylhydrazones as demonstrated by the König group[3]

These donor-donor diazo compounds have shown to be very nucleophilic on the neighbouring carbon, which can formally insert into the C-H bond of formyl groups allowing them to be used in the Büchner-Curtius-Schlotterbeck reaction[3] However, many more bond insertions can be envisioned utilizing these very reactive, nucleophilic diazo compounds[4]

**Funding:** National Research Agency (12354) (Arial 9)

**Acknowledgement:** We thank all the contributors for using this template and allow a nice and coherent presentation of the conference papers. (Arial 9)

**References:**

[1] L. W. Ciszewski, K. Rybicka-Jasińska, D. Gryko, Org. Biomol. Chem., **2019**, 17, 432-448.

[2] S. P. Green, K. M. Wheelhouse, A. D. Payne, J. P. Hallett, P. W. Miller, J. A. Bull, Org. Process Res. Dev. **2020**, 24, 67–84.

[3] H. Wang, S. Wang, V. George, G. Llorente, B. König, *Angew. Chem., Int. Ed.*, **2022**, y, e202211578

[4] S. Angerer, V. George, A. Pattanik, J. Rehbein, B. König, **Manuscript in preparation**

# Design and Photochemical properties of donor-π-acceptor asymmetric Stenhouse salts

Francisco Reza[1], Melissa Bravo[1], Luis Ortega [1], Michelle Avila[1], Oscar Guzmán, Jorge Peon[1,2]

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Stenhouse's salts (**SS**) are molecular switches with important negative photochromism. These systems can be derived from furfural and aromatic amines in one-pot reactions.[1] In the presence of visible light, these molecules undergo a Z/E isomerization reaction followed by a 4π-electrocyclic ring closure[2] in the manner donor-acceptor Stenhouse adducts do.[3] The photo-switching properties of **SS** have recently been demonstrated in aqueous mixtures of polar protic organic solvents.[1] Despite the important structural change shown in aqueous media, currently these systems have only been produced for cases where the same amino-group is included on the two sides of the molecule (see Figure 1). In this work, we present the first synthesis of Stenhouse salts where the two amino end-groups are different, thus creating appropriate push-pull systems with different electron-withdrawing (**EW**) or electron-donating (**ED**) groups on each side of the polymethine chain. This donor-acceptor (**D-π-A**) design enables control over the optical properties of **SS** while keeping their photo switching performance in certain solvent systems.

For the synthesis of these new asymmetric **SS**, the first step involved the reaction of a phenylamine derivative substituted with an **EW** group (acceptor side) with furfural to obtain the corresponding imine. This is followed by a furane-mediated condensation of the imine with indoline hydrochloride (donor side), which is formed *in situ*. This two-step procedure enabled the synthesis for the first time a family of **SS** with a variety of different donor and acceptor groups. Additionally, we successfully characterized their photo-switching properties using UV-visible spectroscopy in different solvent systems.

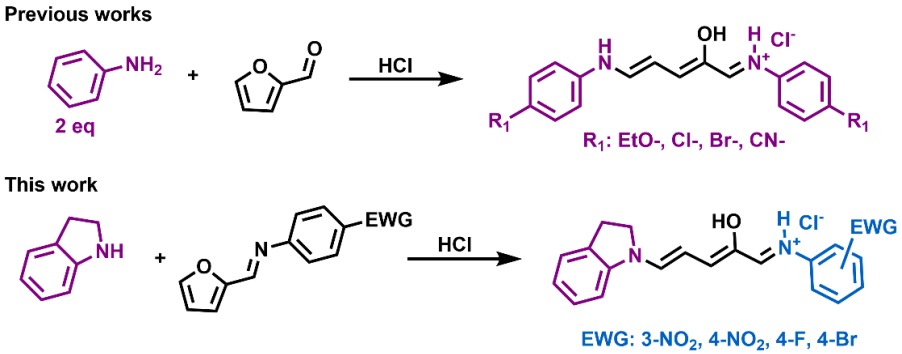


Figure 1. Design and synthesis of asymmetric Stenhouse salts. Previews works have studied the properties of **SS** formed with the same aniline on both sides of the molecule. The present contribution explores the effect of different donor and acceptor aromatic amino groups on the **SS** photo-switching properties.

The indoline donor moiety allowed these systems to keep their characteristic photochemistry in polar protic solvents while varying the acceptor side with groups of different electron-withdrawing power. The synthesis of a new family of **D-π-A** Stenhouse salts represents an effort towards the design and application of isomerizable systems with important structural changes upon photo-switching.

**Funding:** CONAHCyT-México grant Ciencia de Frontera 2019-51496 and PAPIIT/DGAPA/UNAM IG200824.

**Acknowledgement:** CONAHCyT-México grant Ciencia de Frontera 2019-51496 and PAPIIT/DGAPA/UNAM IG200824. Francisco A. Reza-Gonzalez to CONAHCyT for scholarship no. CVU: 1100683.

**References:**

[1] D. Puthoff, H. Kuttiyil, J. A. Peterson, *J. Am. Chem. Soc.* **2024**, *146*, 34008–34013.
[2] R. F. A. Gomes, J. A. S. Coelho, C. A. M. Afonso, *Chemistry – A European Journal* **2018**, *24*, 9170–9186.
[3] F. A. Reza-González, E. Villatoro, M. M. Reza, J. Jara-Cortés, H. García-Ortega, E. F. Blanco-Acuña, J. G. López-Cortés, N. Esturau-Escofet, A. Aguirre-Soto, J. Peon, *Chem. Sci.* **2023**, *14*, 5783–5794.

# Cas9 aggregation studied at the single-molecule level

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CRISPR/Cas9 is a well-known genome editing tool that enables precise DNA modifications through the action of Cas9 endonuclease guided by a specific RNA sequence (gRNA).[1] During our investigation of Cas9 internalization into liposomes as a model delivery system, we observed unexpected aggregation behavior of the Cas9 protein. This prompted a detailed study using single-molecule detection (SMD) and fluorescence correlation spectroscopy (FCS) (Fig. 1).

Although previous reports have noted some level of Cas9 aggregation,[2–4] its physicochemical characterization remains limited. Here, we systematically examined Cas9 aggregation under varying conditions, including changes in salt concentration (NaCl and $MgCl_2$) and the presence of gRNA. Aggregation was found to be strongly influenced by these components, highlighting the importance of buffer composition for maintaining protein stability. This aggregation behavior may have critical implications for delivery efficiency, as protein aggregation can hinder encapsulation into carriers such as liposomes and affect genome editing outcomes.[5]

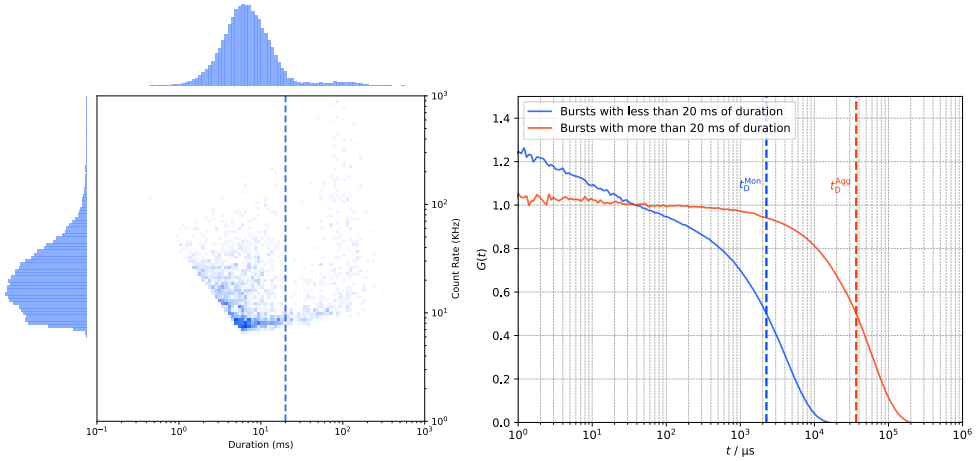


Figure 1. *Left panel:* Two-dimensional burst number histograms of count rate versus burst duration from SMD analysis of Cy5-labeled Cas9 in Tris buffer (pH 7.4, no salt). A vertical line distinguishes populations based on burst duration, corresponding to monomeric and aggregated forms. *Right panel:* Normalized fluorescence correlation curves for the two populations, showing distinct diffusion times characteristic of monomer and aggregate species, highlighted with vertical lines.

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**Acknowledgement:** D.C. thanks the Xunta de Galicia for his research scholarship “Campus de Especialización Campus Terra”.

**References:**

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# Excited state symmetry breaking with a twist

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Interest in symmetry-breaking (SB) charge transfer processes in multibranched donor-acceptor (D-A) systems has been steadily growing due to their promising applications in photovoltaics and sensing. It has been observed that, during excited-state symmetry breaking (ES-SB), the electronic excitation redistributes unevenly over the two D-A branches depending on the solvent polarity[1]. Real-time visualization of ES-SB in many A-D-A-type molecules has been intensively investigated in our group by various spectroscopic techniques[2]. To the best of our knowledge, ES-SB in a helically tethered twisted molecule have never been studied so far. Here, we investigate how the twist of the aromatic core of a symmetric double-branched donor-π-acceptor (D-π-A, ADA4 and ADA8, Fig.1) molecule affects the nature and dynamics of its lower singlet excited state by ultrafast electronic and vibrational absorption spectroscopies. TRIR absorption spectra were obtained by probing the -C≡C- stretching region of the $\pi$ linkers in solvents of varying polarity. In nonpolar CHX, the TRIR spectra of ADA4 and ADA8 display a single −C≡C− band at 2060 cm–1, attributed to a quadrupolar excited state. In a medium polar solvent (THF), the non-distorted ADA8 show two bands characteristic of partial symmetry breaking, and corresponding to an intermediate state with an uneven distribution of excitation on the two branches. By contrast, the spectra of the distorted ADA4 exhibit an additional band that is attributed to a dipolar state with the excitation localised on a single branch. This band is also present with ADA8 but only in more polar environments. These results demonstrate that, along with solvent polarity, the distortion of the core plays a major role in ES-SB in A-D-A systems. This difference is attributed to the larger interbranch coupling in non-distorted ADA8 compared to distorted ADA4. Additionally, the effect of twisting on the singlet and triplet dynamics of the A-D-A systems revealed by transient electronic absorption spectroscopy will also be discussed.

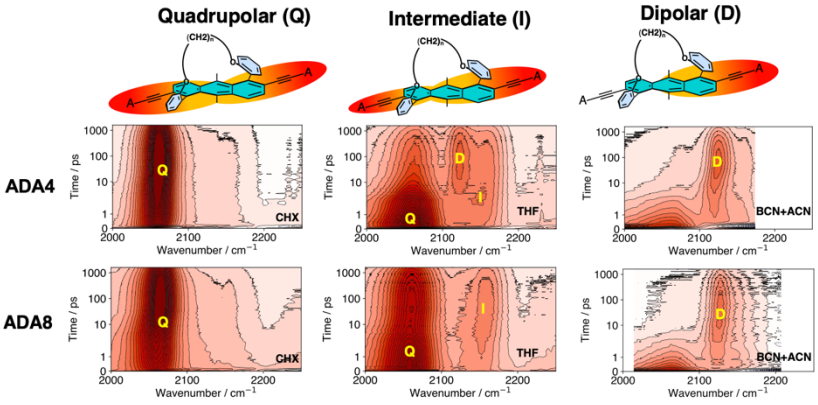


**Figure 1.** Chemical structure of the tethered A-D-A system with n=4 or 8 (top) and transient infrared spectra of ADA4 (n=4) and ADA8 (n=8) in solvents of increasing polarity (left to right). Single −C≡C− band in CHX suggests a quadrupolar excited state and the appearance of new −C≡C− at 2120 $cm^{-1}$ in more polar solvents indicates the localisation of the excitation on a single branch.

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# Unsymmetrically Substituted Pyrene-based Photoacids

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Pyrene-based photoacids with either a hydroxy or amino moiety as the photoacidic group are interesting tools not only for the investigation of proton-transfer reactions. Upon excitation, they experience an increase in acidity by several orders of magnitude. The introduction of electron-withdrawing sulfonamide or sulfonic ester groups thus entails $pK_a$ values below 0 in the excited state.[1-4]

Our aim is the synthesis of pyrene-based photoacids with two different kinds of substituents in addition to the respective photoacidic group. However, the synthesis of these unsymmetrically substituted hydroxy- and aminopyrene derivatives has proven to be challenging, due to low yields and side reactions. While previous work from our group has focused on unsymmetric substitution in position 3, our recent work on the bromination of aminopyrene derivatives has opened a route for the substitution in position 2 (Fig. 1). Substituents in position 3, in contrast to those in position 6 or 8, appear to have only a minor influence on the photophysical properties of the photoacid. It is therefore interesting to investigate the electronic influence of a substitution in position 2.[5]

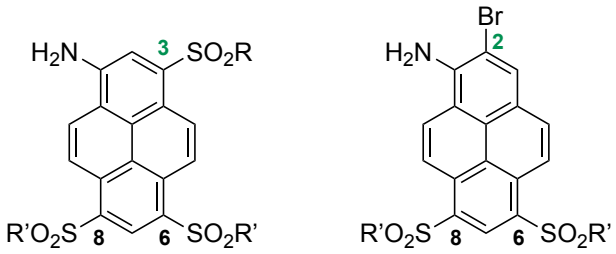


Figure 1. Substitiution pattern of aminopyrene photoacids, left: previous focus, right: current focus.

Conversion of the bromine moiety to another nitrogen bearing group, e.g. an amidine, in close proximity to the amino group, may allow the complexation of metal ions such as Cu(I). This conversion therefore opens the investigation of a putative photo Lewis acidity of the coordinated ion. Pyrenol-derivatives with this substitution pattern could be accessed through the already established diazotization of the amino group followed by decomposition of the diazonium salt to the phenol in an aqueous environment.

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# Electrochemiluminescence-based detection of clinically relevant pathogens

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Luminescent-based techniques have made significant contributions to the sensitive detection and imaging of clinically relevant chemicals and biochemicals.[1] Among them, electrochemiluminescence (ECL) has emerged as a unique approach for biodiagnostics. ECL is a light emission process that occurs by excitation of a luminescent material through electron transfer reactions at an electrode surface.[2-4] Because of the high sensitivity and low background noise offered by ECL, the development of ECL active materials with strong and stable ECL signals and their biosensing applications are under extensive research.

We have conducted ECL-based quantitative detection of clinically relevant bacteria (*Pseudomonas aeruginosa)* and parasites *(Leishmania infantum*) using their nucleic acid as the target analyte.[5] We have selected different Ru (II) complexes as luminophores as they are known to have a strong ECL signal, good water solubility and reactivity, that could interact with double-strand DNA (compound **1**, Fig. 1a) or derivatize anti-double strand antibodies (compound **2**, Fig. 1b, respectively). In order to achieve selectivity, the electrode surface was functionalized with capture oligonucleotide probes and then exposed to the target nucleic acid. The electrode was then incubated with either **1** or the antibody conjugated with **2**, followed by ECL measurement. Our results showed that ECL detected *L. infantum* and *P. aeruginosa* with sensitivity in the ng/µL range, and that using the luminophore-antibody conjugate offered a stronger ECL signal as compared to **1**. Thus, these findings demonstrate that ECL can be used for the sensitive detection of clinically relevant bacteria and parasites.

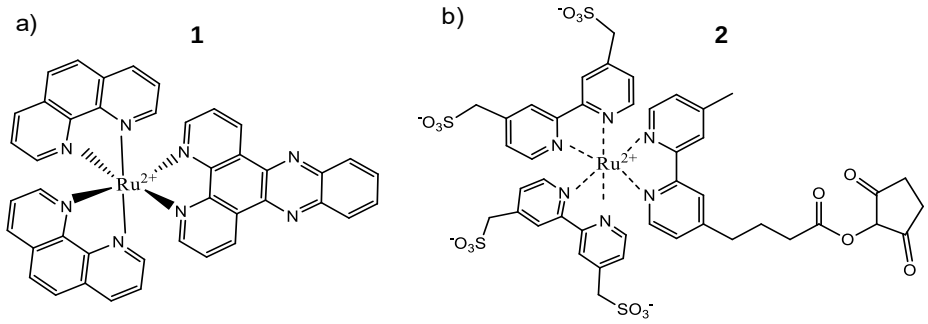


Figure 1. Chemical structures of ECL luminophores used in our study. a) Luminophore used to intercalate into DNA double strand. b) Luminophore used to conjugate with antibody.

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# Photoinduced Labeling of Cysteine with Fluorescent Probes

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The chemical modification of proteins enables a wide spectrum of applications, ranging from targeted drug delivery and biosensing to protein imaging and the development of multifunctional bioconjugates for therapeutic and diagnostic purposes. A major goal in this field is to develop selective, efficient, and biocompatible functionalization strategies that allow precise control over protein structure and function. In particular, fluorescent labeling serves as a powerful tool for investigating protein localization, dynamics, and interactions in complex biological environments. [1,2]

Although click chemistry has provided a versatile platform for the site-specific introduction of functional groups into proteins, alternative strategies that exploit different activation modes are gaining increasing attention. Among the naturally occurring amino acids, cysteine stands out as a privileged site for selective modification due to the unique nucleophilicity of its thiol side chain. In this context, the development of thiol-specific reactions that proceed under mild conditions, with high chemoselectivity and minimal byproduct formation, remains an ongoing challenge.

In this work, we investigate a photocatalyzed thiol-ene reaction for the labeling of protected cysteine (CysP) with fluorescent probes, using visible light as a clean and energy-efficient activation source.[3] Two complementary approaches are presented (Figure 1): a) direct irradiation of a fluorescent probe that also acts as an organophotocatalyst (PC), enabling its excited state to react with CysP and form a covalent adduct; and b) selective excitation of a PC, which mediates the coupling between CysP and an independent fluorescent probe.

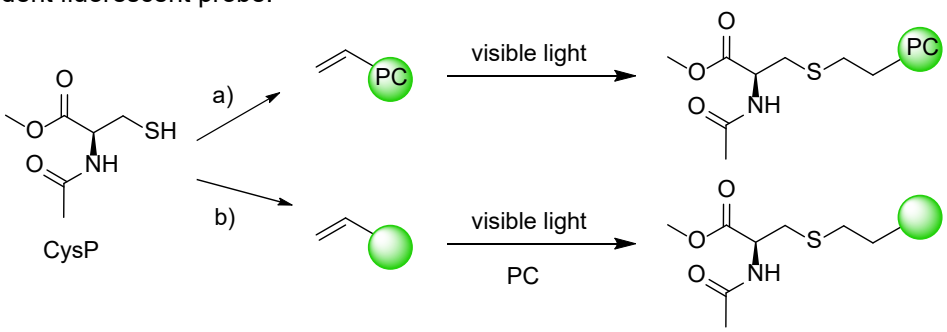


Figure 1. Proposed modifications of CysP with fluorescent probes

**Funding:** Spanish Government (PID2022-1381890NB-I00) funded by MCIN/AEI/10.13039/501100011033 and "ERDF A way of making Europe".

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# Experimental and theoretical insight into the nature of the intersystem crossing pathway in 9-nitroanthracene, an extension to the El-Sayed's rules

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Nitroaromatic compounds (NACs) in their first singlet excited state exhibit arguably the strongest spin-orbit coupling amongst organic molecules.[1] As a result, their photophysics is dominated by a sub-picosecond manifold-crossing pathway. In this contribution we present a computational study at the highest possible level of theory on the excited state dynamics of 9-nitroanthracene (9-NA). The computational results were supported by femtosecond-resolved studies in multiple solvent environments.

The computational studies were made at the XMS-RASPT2/cc-pVDZ level with a formal active space of 16e,16o which corresponds to an appropriate compromise from complete-active space methods. These calculations indicate that the $S_1$, $T_1$ and $T_2$ states of 9-NA are of $\pi\pi^*$ character. Such results are consistent with calculations at the STEOM-DLPNO-CCSD or ADC(2) levels of theory but differ from calculations that use the TDDFT method due to the multiconfigurational nature of the mentioned states.[2] The calculations indicate a rapid evolution in the $S_1$ potential energy surface which leads to a region with large spin-orbit couplings with the $T_2$ state. This coupling is enhanced by vibronic-spin-orbit interactions involving a low-frequency vibrational mode associated with motions around the dihedral angle defined between the $NO_2$ plane and the aromatic system. The tilting or twisting of the $NO_2$ $\pi$ and $\pi^*$ orbitals from the aromatic plane allows for a strong spin-orbit interaction even though this triplet state is not of $n\pi^*$ character. Such characters of the first singlet state and the receiver $T_2$ state (both of $\pi\pi^*$ character but involving a twisted conformation) correspond to an extension of El-Sayed´s rules for rapid intersystem crossings.

The experimental results are consistent with a rapid manifold change as evidenced by the sub-picosecond decay of the emissive $S_1$ state and the transient formation of the receiver $T_2$ state which is followed by internal conversion to the phosphorescent $T_1$ state. The experimental results also indicate that such mechanism is present in both polar and non-polar solvents, where the latter are more appropriate for comparisons with the abovementioned calculations which correspond to the gas-phase predictions.[2]

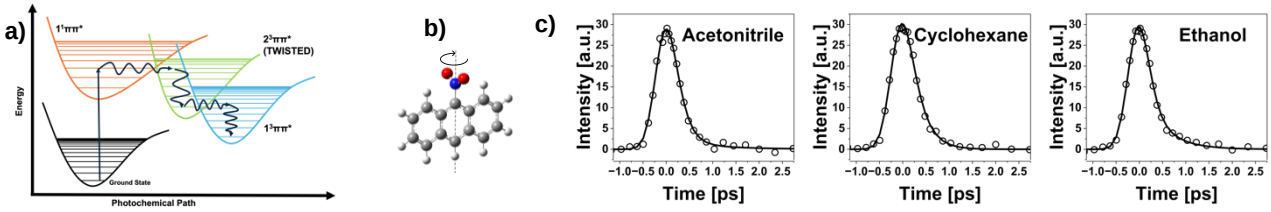


Figure 1. a) PES displaying the transition $1^1\pi\pi^* \rightarrow 2^3\pi\pi^*$, which in accordance with El-Sayed's rules should not be favored for a fast ISC process, b) Molecular structure of 9-NA portraying the $NO_2$ twisted dihedral angle responsible for the large singlet-triplet coupling between this kind of singlet and triplet states, c) Fluorescence up-conversion transients of 9-NA at 480 nm showing that the rapid $S_1$-$T_2$ crossing is independent of the solvent environment

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**Acknowledgement:** CONAHCyT-México grant Ciencia de Frontera 2019-51496 and PAPIIT/DGAPA/ UNAM IG200824

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# Hemi-Protonated Cytosine-Cytosine Base Pair Controls Ultrafast Excited State Dynamics in Human Telomere and c-MYC Promoter i-Motifs

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Sequences that adopt i-motif structures are widespread throughout the human genome, encompassing gene promoters and telomeres. Their in vivo presence has been verified, particularly in proximity to the G1/S boundary during the cell cycle.[1] Consecutive cytosine-rich DNA i-motifs are known for their susceptibility to forming cyclobutene pyrimidine dimers (CPDs), which are highly mutagenic and directly associated with skin cancer.[2] Notwithstanding this connection, the influence of i-motif structures on electron dynamics remains incompletely understood within the scientific community. In our preliminary investigation, we meticulously examined the excited-state dynamics of the homo-oligomer $dC_{20}$ i-motifs.[3] To further elucidate their excited-state behavior, we conducted a detailed analysis of i-motifs originating from human telomeric and c-MYC promoter sequences, employing a comprehensive approach that encompassed steady-state, femtosecond time-resolved fluorescence, and transient absorption spectroscopy. Our research uncovers a complex multichannel deactivation pathway characterized by charge recombination (CR) occurring within tens of picoseconds and proton-coupled electron transfer (PCET) within the hundreds of picoseconds timescale. A notable discovery from our research is that the charge transfer (CT) and PCET processes in the excited state of i-motifs predominantly transpire within the hemi-protonated (C–C+) base pair environment. Moreover, our investigations have revealed that the characteristics of CT states within the C–C+ base pairs are significantly influenced by the number of these base pairs present.

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# Long-Lived Metal-to-Ligand Charge-Transfer Excited States in Nickel(II) Complexes

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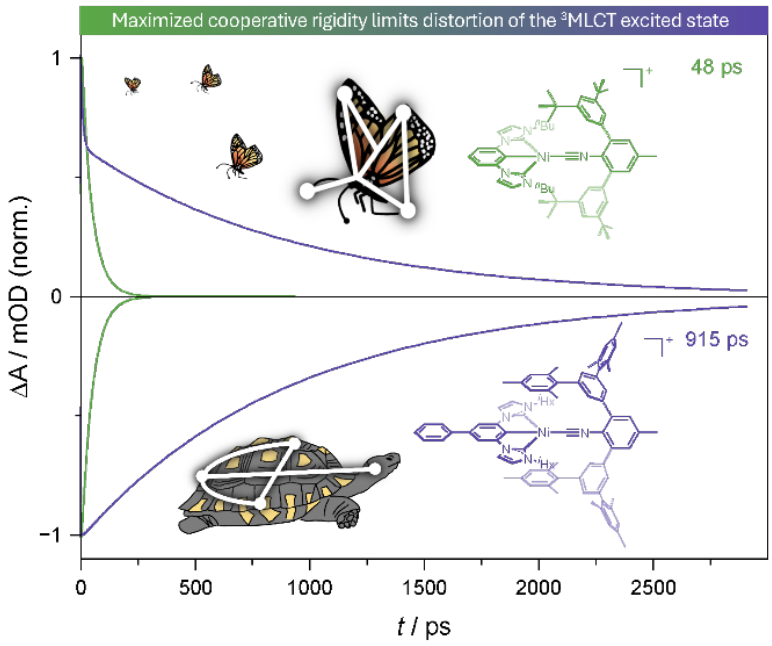
We report here a molecular design strategy to slow the relaxation of photoactive higher excited states of nickel(II) coordination complexes from the sub-ps to the ns timescale.

Metal-to-ligand charge transfer (MLCT) excited states and their deactivation pathways through metal-centered (d-d) states play important roles in square planar $Ni^{II}$ complexes.[1][2] Our approach is to suppress these nonradiative deactivation pathways by exploiting cooperative rigidity. The excited-state behavior of three novel nickel(II) complexes were probed via fs UV-Vis and IR transient absorption spectroscopy. The combination of a structurally rigid tridentate chelate with a bulky mesitylene-substituted monodentate isocyanide ligand resulted in an extension of the photoactive $^3$MLCT state lifetime from roughly 48 ps to 915 ps in aerated $CH_2Cl_2$ at room temperature.[3] The concept of cooperative rigidity and the resulting elongated $^3$MLCT lifetime enables bimolecular photochemistry from a higher excited state.

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# New $TiO_2$-Coated Sand Composite for Scalable Continuous-Flow Photocatalytic Degradation of Microplastics

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Microplastic (MP) pollution in aquatic environments poses a significant and growing environmental threat, with millions of tons accumulating in water bodies each year due to the extensive use of plastics. The persistence of MPs and their resistance to conventional removal methods underscore the urgent need for innovative treatment strategies. Among these, photocatalysis has emerged as a promising approach, offering efficient degradation of MPs [1].

Herein, we present a novel heterogeneous photocatalyst based on $TiO_2$-coated silica sand, engineered for effective and sustainable mineralization of MPs. The design also facilitates easy separation and reuse, supporting its application in large-scale water treatment processes. The photocatalyst was synthesized by coating silica sand with an optimized $TiO_2$ layer and enhancing the surface area through the incorporation of $TiO_2$-coated $SiO_2$ microspheres. The millimetric size of the sand conferred operational advantages [2,3], such as mitigating pressure build-up in the photoreactor and enabling simple recovery and reuse. Detailed material characterization using TEM, FESEM, EDX, and UV diffuse reflectance spectroscopy confirmed the desired photophysical properties. Batch experiments were conducted to optimize coating thickness for maximum photocatalytic efficiency. Furthermore, a modified rotary evaporator was employed to scale up the synthesis, demonstrating its feasibility for practical deployment. A laboratory-scale continuous-flow photoreactor was then designed and constructed (Fig. 1A), consisting of a tubular glass column packed with the photocatalyst and surrounded by UV-A LED modules. The system was tested using real wastewater containing PET microfibers derived from the domestic washing of polyester textiles. Chemical Oxygen Demand (COD) measurements at the reactor inlet and outlet showed negligible MP adsorption in the absence of light but revealed more than 95% COD reduction under UV illumination. This substantial decline confirmed the effective mineralization of organic matter and validated the photocatalyst's performance (Fig. 1B).

Overall, this work highlights the potential of the developed $TiO_2$-coated sand composite as a scalable and eco-friendly solution for microplastic degradation. By delivering high photocatalytic efficiency, operational scalability, and alignment with key Sustainable Development Goals, the technology addresses critical environmental challenges and offers a practical route for industrial adoption.

A) B)

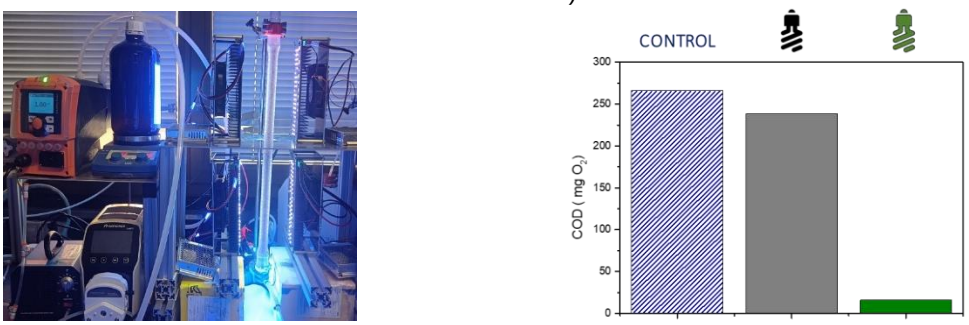


Figure 1. A) Homemade continuous flow photoreactor. B) COD values at the inlet (control under dark) and outlet under irradiated conditions. Values are referred to a 2 L sample.

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# Studying UV-induced electronic relaxation in DNA at the frontier of time-resolution

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The photoactivated relaxation of the DNA electronic excited states is studied in connection with the UV-induced damage of the genetic code and may contribute to the development of optoelectronic applications using nucleic acids. Since the beginning of the century, transient absorption spectroscopy brought valuable information on the fate of photon energy absorbed by DNA. A key finding has been that an important population of the Franck-Condon states evolves toward excited charge transfer (*CT*) states. The decays of the *CT* states, whose lifetime ranges from tens to hundreds of ps, are well documented, but their formation has not been observed so far.

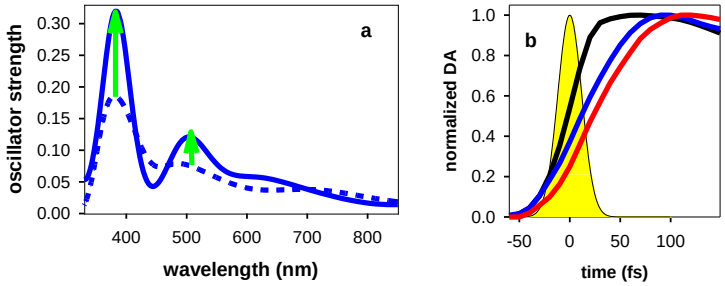


Figure 1. (a) Transient absorption spectra computed for the *CT* state (solid line) and the initial Franck-Condon state (dashed line) of the *anti-syn* conformer of **GT**. (b) Transient absorption signals recorded for the dinucleotides **GT** (red), **TG** (blue) and an equimolar mixture of monomeric chromophores (black) at 570 nm. The instrumental response function is shown in yellow; excitation: 266 nm.

Focusing on two pairs of DNA dinucleotides, **AG**/**GA** and **TG**/**GT** (**A**: adenine; **G**: guanine; **T**: thymine), we explored, for the first time, the excited state relaxation from the Franck-Condon states to the minima of the potential energy surfaces (*PES*). Our study was conducted using broadband transient absorption spectroscopy with sub-30-fs time-resolution. The results were interpreted by means of quantum chemistry methods, which determined the most stable ground state conformation of each dinucleotide, computed the Franck-Condon states that are likely to be populated by the exciting laser pulse, followed their evolution along the *PES* and calculated the transient absorption spectra (Fig. 1a). This approach allowed us to overcome the difficulty of global fits with multiexponential functions, which fail to correctly describe parallel relaxation pathways along *PES*.

We showed that both the Franck-Condon states and their evolution strongly depend on the way in which the two chromophores are connected (**AG**≠**GA**; **TG**≠**GT**) and the stacking conformation. The time needed for the stabilization of the $\mathbf{G}^{+}\rightarrow\mathbf{A}^{-}$ or $\mathbf{G}^{+}\rightarrow\mathbf{T}^{-}$ *CT* states ranges from 90 to 130 fs (Fig. 1b). We also detected a minimum associated with the $\pi\pi^{*}$ state of **G**, but not with those of **A** or **T**. We observed instead an ultrafast (~100 fs) energy transfer toward **G**, facilitated by the existence of electronic coupling between stacked nucleobases.

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# Primary Photophysics of Nicotinamide Chromophores in Their Oxidized and Reduced Forms

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Nicotinamide adenine dinucleotide (NADH) is a key enzymatic cofactor with fluorescent properties that make it useful for studying cellular metabolism through fluorescence microscopy. In contrast, its oxidized counterpart, $NAD^+$, exhibits minimal fluorescence[1,2]. The biological importance of this enzymatic cofactor makes understanding the photophysics behind the corresponding relaxation pathways of the reduced and oxidized forms essential. In this study, we explore the photophysical behavior of the nicotinamide moiety in both its reduced and oxidized forms. To isolate the photophysics of the nicotinamide system without interference from the adenine group-whose absorption overlaps with that of the nicotinamide chromophores-we examined model compounds lacking the adenine nucleotide. Three model molecules were studied: nicotinamide (also known as niacinamide, an unsubstituted oxidized form), 1-benzyl-3-carbamoyl-pyridinium bromide (NBzOx, an oxidized chromophore), and its reduced analogue, 1-benzyl-1,4-dihydronicotinamide (NBz). To understand their excited-state dynamics, we employed femtosecond-resolved emission and transient absorption spectroscopy. [3,4]

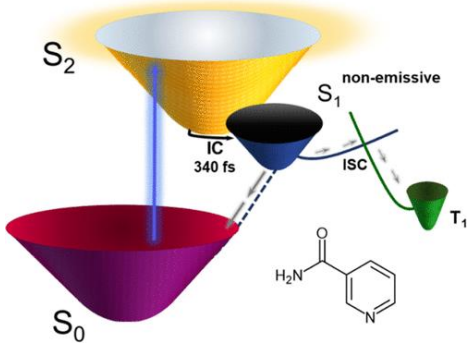


**Figure 1. Relaxation pathways of nicotinamide.** Upon UV excitation, nicotinamide accesses a bright excited singlet state, which rapidly relaxes to a lower-lying dark singlet state via a conical intersection. From this dark state, the molecule can return to the ground state through internal conversion or transition to the triplet state ($T_1$) via intersystem crossing.

Both oxidized systems—nicotinamide and NBzOx—exhibit similar behavior: an initially excited bright state decays in under 400 femtoseconds. This is followed by positive transient absorption signals that evolve on two timescales. The first occurs within 1 to several picoseconds, and the second is a slower decay with time constants of 480 ps for nicotinamide in water, and 80–90 ps for nicotinamide in methanol and NBzOx in water. These slower decays are attributed to $S_1$ states populated from higher-lying bright singlets. Though these $S_1$ states are nonemissive, they are detectable via transient absorption. In the case of NBzOx and methanolic nicotinamide, the $S_1$ signal returns to the baseline after decay. However, for nicotinamide in aqueous solution, a weak transient signal remains even after the 480 ps decay, indicating a small population of triplet states formed during the slower $S_1$ relaxation.

**Funding:** CONAHCyT-México grant Ciencia de Frontera 2019-51496 and PAPIIT/DGAPA/UNAM IG208824.

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# Regenerative chemiluminescence from reduction reactions with amino-pyrene derivatives

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Electronically excited states play a crucial role as reactants in electron transfer (ET) processes, such as converting light into chemical energy[1]. Far less attention has been given to the reverse process, exploit ET reactions to harness chemical energy for generating excited states in solution. Within this framework, highly exergonic ET reactions involving luminescent compounds happen to produce chemiluminescence. Light generation is observed from the oxidation of diphenylanthracene radical anions[2], or from the reduction of rubrene and diamino-pyrene radical cations[3,4]. Chemiluminescence from ET reactions is recorded also using luminescent metal complexes - from the reduction of Ru(III) polypyridine complexes by OH-, forming Ru(II) complexes[4]. This process is referred as “regenerative chemiluminescence” (RCL) to highlight the luminophores ability to remain chemically intact after subsequent redox steps and potentially undergo multiple cycles. This marks a significant difference with traditional chemiluminescence (e.g. luminol) where the driving force required to generate the excited state comes from bond breaking, with the luminophore becoming effectively a waste product. However, the harsh conditions required to obtain luminophore radical ions limited further developments of such systems.
In our work, we show that strategic chemical design of a reported chemiluminescence dye, diamino-pyrene (**DAP**)[4], to obtain triamino-pyrene (**TAP**), allows a control over its ground state oxidation potential, enabling the use of oxygen as mild oxidant for RCL.

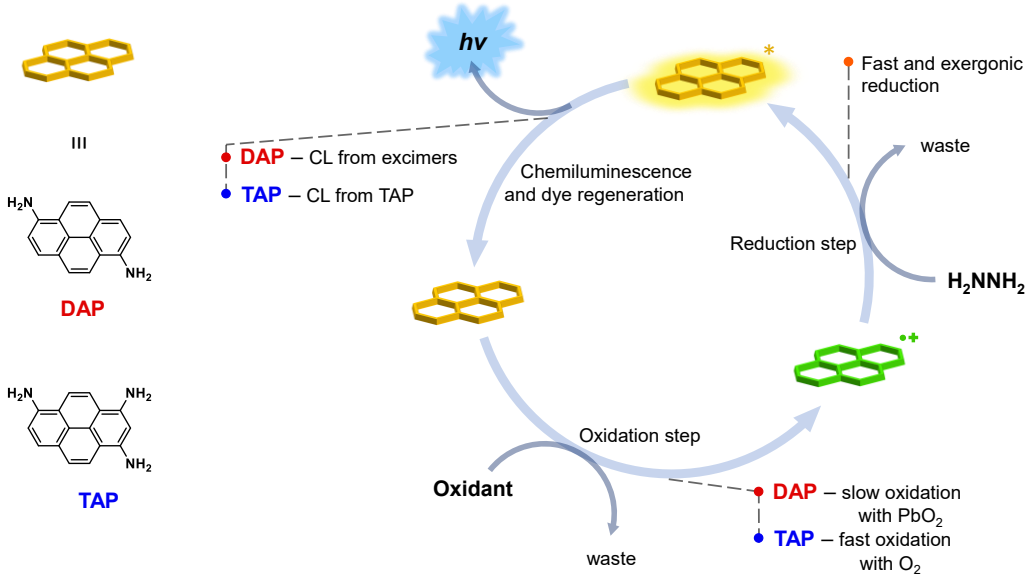


Figure 1. Schematic representation of regenerative chemiluminescence with DAP and TAP

**Funding:** European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement no. 949087).

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# A photochemical method for the selective oxidative cleavage of arenes over alkenes

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The ozonolytic deconstruction of aromatics remains a challenge in organic chemistry. Ozone preferentially reacts with alkenes over arenes, meaning that once the initial aromatic cleavage occurs, the dearomatized products are inherently more reactive than the starting materials. Consequently, the process cannot be halted, resulting in full oxidation. Overcoming this challenge requires subverting intrinsic rules of chemoselectivity to transform a less reactive substrate in the presence of a more reactive one. In this presentation, I show how this concept has been realized using photoexcited nitroarenes.[1] Crucial to the success of this process is the use of a nitroarene that is preferentially excitable to a triplet $\pi,\pi^*$ state over the $n,\pi^*$ state. This $\pi,\pi^*$ triplet state provides an otherwise inaccessible manifold, in which oxidative cleavage of aromatics occurs chemoselectively, even in the presence of alkenes.

**Funding & Acknowledgements:** D.L. acknowledges the European Research Council for a fellowship (101086901). W.J.O and E.M.A thank the Marie Skłodowska-Curie Actions for fellowships (101102820 & 101150311 respectively). The authors gratefully acknowledge the computing time provided to them at the NHR Center NHR4CES at RWTH Aachen University (project number p0021519). This is funded by the Federal Ministry of Education and Research, and the state governments participating on the basis of the resolutions of the GWK for national high-performance computing at universities (www.nhr-verein.de/unsere-partner). M.G.-M. and V.d.l.P.O'S. acknowledge financial support from the Spanish national project SolarChem 5.0 (TED2021-130173B-C41) and SOL-Future (PLEC2021-0079069). I.M. and T.P. acknowledge the API program supported by the European Union through the operational program (ERDF/FSE2014–2020, no. 20E04976), the RIN ZIRCO_PHOTO_COP program (ERDF/FSE 2021–2027, no. 21E05645) and FNADT-DRACCARE [program 2020–2023 (N)15179] for funding, as well as Normandie Univ. (NU), Région Normandie, CNRS, Univ. Rouen Normandie, INSA Rouen Normandie, Labex SynOrg (ANR-11-LABX0029), the Graduate School for Research XL–Chem (ANR-18- EURE-0020XL CHEM) and Innovation Chimie Carnot (I2C) for support. K.H. acknowledges the JSPS Overseas Challenge Program for Young Researchers.

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# Synthesis and study of amphiphilic photo-switches controlled by two-photon absorption applied to carrier systems.

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Two-photon absorption (2PA) involves the simultaneous absorption of two photons, resulting in a non-linear dependence on light intensity. This property requires tightly focused beams, enabling excitation within highly localized volumes and providing exceptional spatial resolution. These characteristics make 2PA a powerful tool for applications such as microscopy, microfabrication, three-dimensional data storage, and photodynamic therapy.[1]

In this context, molecular switches such as Donor-Acceptor Stenhouse Adducts (DASAs) have emerged as promising candidates due to their high non-linear optical response to light stimuli.[2] DASAs feature a push-pull system connected by a triene bridge, imparting unique photochromic properties.[3] This structure allows DASAs to undergo reversible isomerization from a hydrophobic to a hydrophilic state upon irradiation, making them ideal for light-controlled applications. On the other hand, amphiphilic molecules are capable of self-assembly into nanostructures such as micelles and liposomes. These systems have shown significant potential in drug delivery, enabling the encapsulation and controlled release of therapeutic agents.

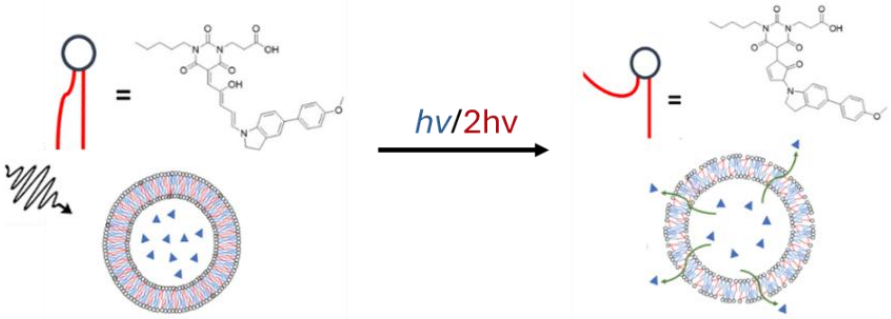


Figure 1. Photoisomerization of the 5MicDASA system from its open (hydrophobic) form to its closed (hydrophilic) form.

Building on these principles, this contribution shows the development of DASA-based amphiphilic systems as targeted drug carriers, leveraging their photochromic properties and self-assembly capabilities Fig. 1. Our studies have demonstrated efficient photoconversion under controlled irradiation, confirming the isomerization behavior of the system. It was also demonstrated that when these non-linear optical photos-witches are included as constituents of liposome constructs, these can be efficiently disassembled from the photoinduced geometry-changes of the amphiphilic DASA, allowing for highly localized drug delivery.

**Funding:** CONAHCyT-México grant Ciencia de Frontera 2019-51496, the Postdoctoral Fellowship Program at UNAM and PAPIIT/DGAPA/ UNAM IG200824.

**Acknowledgement:** This work was supported by the Postdoctoral Fellowship Program at UNAM. I sincerely thank the program for its invaluable support during this research.

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# Generation and UV-photolysis of N-methyleneformamide[1]

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Simple imines have been detected in space and are considered as building blocks to larger heteroaromatic, cyclic and biological relevant compounds. Herein we revisited the formation of the simplest acylimine, namely N-methyleneformamide, by high-vacuum flash pyrolysis (HVFP) as well as its spectroscopic characterization by cryogenic matrix isolation infrared (IR) and UV/Vis spectroscopy. N-methyleneformamide prefers a gauche over a s-trans conformation in contrast to parent 1,3-butadiene. In UV-photolysis experiments we identified formaldehyde:HCN and formaldimine:CO complexes as the major decomposition products. As further photolysis products we observed the HCN:CO and HNC:CO complexes. All experimental findings are supported by deuterium labeling experiments and high-level ab initio coupled cluster calculations. N-methyleneformamide should be considered as a candidate for an interstellar search. The sequence $R_2C{=}N{-}RC{=}O$ also occurs in cytosine making the title compound highly relevant for prebiotic chemistry and the search for the molecular origins of life.

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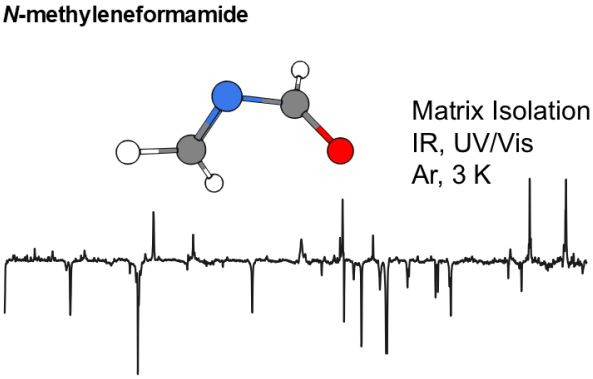


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**Acknowledgement:** Continuous and generous support by all organic chemistry professors at RUB is acknowledged.

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# Advances in Photoinduced Catalysis and Photochemistry Enabled by Near-Infrared Light

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Multiphoton upconversion processes have attracted growing interest due to their broad applicability in photonic and biochemical systems.[1] Here, we demonstrate that near-infrared (NIR) light can drive acid-catalyzed transformations through two-photon absorption, activating blue-light-sensitive, merocyanine-based metastable photoacids.[2]

We also explored NIR-to-UV upconversion to enable classical UV-driven photochemistry under near-infrared light. Sensitized upconversion nanoparticles (UCNPs) served as photocatalysts, converting multiple NIR photons triggered UV-A-induced [2+2] photocycloadditions. The UCNPs showed high efficiency, with turnover numbers exceeding 290,000 and turnover frequencies up to 8.52 $s^{-1}$, and were easily recovered and reused. This strategy provides a versatile approach for performing UV photochemistry under low-energy light, expanding the potential of light-mediated catalysis in complex systems.

These approaches offer a potentially versatile strategies for remotely controlling chemical reactivity with low-energy light, expanding the possibilities for light-mediated catalysis in complex environments.

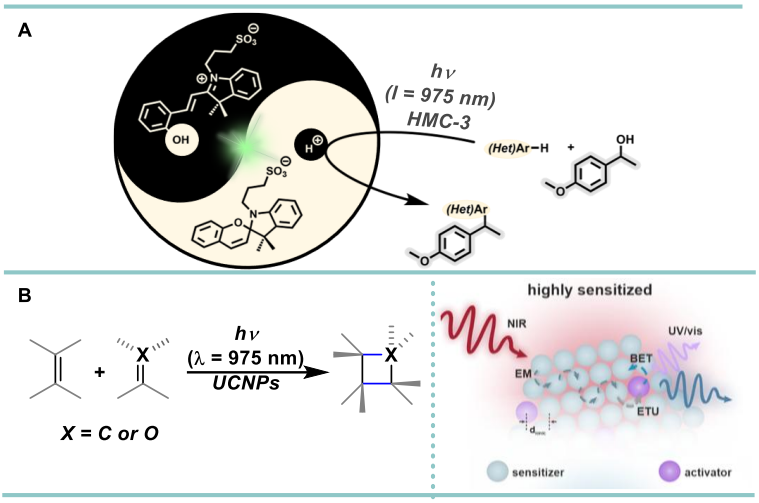


Figure 1. A) NIR driven Photoacid Catalysis, B) UCNP-s photocatalysis - NIR induced UV-A photochemistry.

**Funding:** Elite Network of Bavaria

**Acknowledgement:** We thank our collaborators Naomi Weitzel and Thomas Hirsch for their contributions to the development of UCNPs as NIR-sensitized photocatalysts for UV-A-driven transformations.

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# BPI Ligands for Visible-Light Homolysis of E–C Bonds in Main Group Chemistry

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The radical reactivity of organometallic compounds is highly beneficial for applications in homogeneous catalysis and radical organic synthesis[1] or polymer chemistry.[2] Typically, the homolysis of E–C bonds within main group organometallics is thermally not feasible, due to the high energetics of subvalent main group radicals, thus high bond dissociation energies of the E–C bond. Even photochemically, homolytic reactivity is mostly only induced by using very harsh UV irradiation.[3,4] The redox-active bis(pyridylimino) isoindolide (BPI) ligand system enables the charge-transfer induced cleavage of E–C bonds, initiated by visible light.[5] In the case of aluminum organometallics, this was investigated by means of stationary and transient UV/Vis spectroscopy, spin trapping experiments, kinetic measurements, DFT calculations and further isolation of reduced BPI compounds[6] to obtain fundamental insights into the molecular processes. Utilization of the formed radicals in C–C-coupling reactions was investigated, which revealed a rare example of radical-polar-crossover reactivity in main group chemistry and highlights the potential of organometallic radical sources.

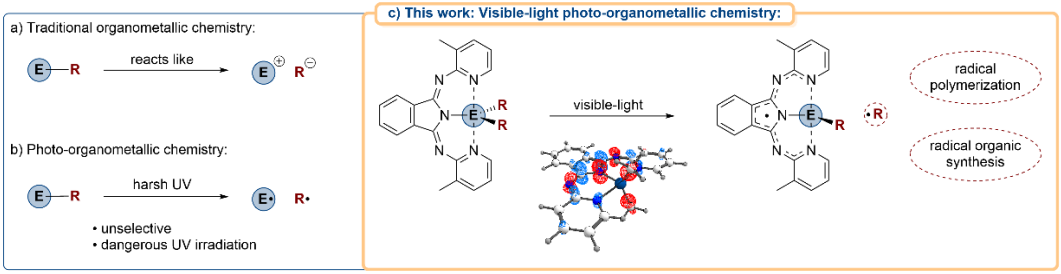


Figure 1. a) Schematic depiction of ionic reactivity, typically observed in organometallic chemistry. b) The homolysis of organometallic E–C bonds by UV irradiation. c) Homolysis of organometallic E–C bonds by the aid of visible-light.

**Funding:** Kekulé Scholarships by Verband der Chemischen Industrie (VCI) for JOW and JW.

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# Fluorogenic and Photocatalytic Amino Acids for Imaging T Cell Activity

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T cells are important contributors to the adaptive immune system by activating B cells, directly killing infected or cancerous cells and providing long-term protective immunity. The biological activity of T cells is tightly regulated by the expression of cell-surface receptors such as programmed cell death protein 1 (PD-1), which acts as an immune checkpoint receptor (ICR) on the surface of active T cells.[1] The overexpression of PD-1 receptors on T cells leads to reduced production of effector cytokines and diminished cytotoxic activity. Immune checkpoint therapy (ICT) has been suggested to restore T cell activities, by blocking these ICRs. Currently, PD-1 blockade strategies primarily rely on antibodies, with few reports on peptides or small molecules.[2] Additionally, imaging approaches often depend on conventional 'always-on' fluorescent dyes, which require additional washing steps and typically suffer from low signal-to-noise ratios (SNR). These limitations highlight the need for the development of innovative imaging tools to both monitor and modulate T-cell responses.

The incorporation of non-natural fluorogenic AAs into peptides and proteins represents a valuable tool for imaging defined immune cell populations due to their tunability and target specificity.[3] Given the excellent properties of fluorogenic probes (i.e. environmental sensitivity, high SNRs and real-time monitoring etc.), over the last years, our group has designed novel amino acids (AAs) as fluorogenic building blocks to optically label peptides and proteins without affecting their functionality and biological activity.[4] In this work, we have transformed conventional 'always-on' fluorophores into fluorogenic amino acids by direct linkage of the amino acid tryptophan through simple metal-catalysed C-H activation, and prepared a library of multi-coloured fluorogenic probes, showing distinct quenching effects and turn-on properties. By using this general approach, we have incorporated near-infrared (NIR) fluorogenic amino acid into PD-1-targeting peptides to monitor the function of T cells. We have demonstrated the good fluorogenic properties of the peptides in labelling PD-1 receptors on the surface of activated T cells and their potential to be applied in drug screening platforms.

In addition, we have genetically encoded a silicon rhodamine (SiR) photocatalytic amino acid into PD-L1 protein for targeted photocatalysis in T cells expressing PD-1 receptors.[5] We proved the excellent photocatalytic properties and therapeutic potential of these SiR-PD-L1 proteins by uncaging pro-fluorophores in activated T cells. The encoding of the SiR photocatalyst into other model proteins also highlighted the versatility of the approach. To our knowledge, this is the first example of genetically encoding a photocatalytic amino acid into protein structures, showing great potential for the simultaneous labelling and treatment of specific immune cells.

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# Nanohoops Favour Light-Induced Energy Transfer over Charge Separation in Porphyrin/[10]CPP/Fullerene Rotaxanes

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[2]Rotaxanes offer unique opportunities for studying and modulating charge separation and energy transfer, because the mechanical bond allows the robust, yet spatially dynamic tethering of photoactive groups. In this work, we synthesized [2]rotaxane triads comprising a central (aza)[10]CPP⊃$C_{60}$ bis-adduct complex and two zinc porphyrin stoppers to address how the movable nanohoop affects light-induced charge separation and energy transfer between the rotaxane subcomponents. We found that neither the parent nanohoop [10]CPP nor its electron-deficient analogue aza[10]CPP actively participate in charge separation. In contrast, the nanohoops completely prevented through-space charge separation. This result is likely due to supramolecular "shielding", because charge separation was observed in the thread that acted as reference dyad. On the other hand, the suppression of electron transfer allowed the observation of energy transfer from the porphyrin triplet to the fullerene triplet state with a lifetime of ca. 25 µs. The presence of the interlocked nanohoops therefore leads to a dramatic switch between charge separation and energy transfer. We suggest that our results explain observations made by others in photovoltaic devices comprising nanohoops and may pave the way toward strategic uses of mechanically interlocked architectures in devices that feature (triplet) energy transfer.[1]

**Acknowledgement:** N.G. and P.E.B. are grateful for the President's Doctoral Scholar Award by The University of Manchester (to N.G.), as well as Waters Corporation for their continued support of mass spectrometry research within the Michael Barber Centre for Collaborative Mass Spectrometry. We are grateful to under graduate students L. Hinrichs, L. Reiser, J. Schießl and S. Hieber for assistance with precursor syntheses.

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Excited state proton transfer (ESPT) is essential for the bright fluorescence of wild-type green fluorescent protein, while the large Stokes shifts in certain red fluorescent proteins (LSS-RFP) imply a more intricate excited-state photophysical behavior [1-2]. This study describes the intriguing observation of temperature-sensitive local and distant emissions as well as dual and triple fluorescence in the LSS-RFP mBeRFP [3], marking it as the first known example of triple fluorescence in a chromophore. An electronic structure calculation also performed in ground and excited states (GS & ES) to understand the nature of these absorbing and emissive conformers of mBeRFP. Further, to gain insight into ultrafast relaxation of different conformers in excited state, we performed femtosecond transient absorption spectroscopy (fs-TAS) studies in both normal buffer and deuterated buffer, as well as varying pH of the buffer. Combining the results, we conclude that branching of excited-state population through multiple conical intersections leads to LSS in mBeRFP.

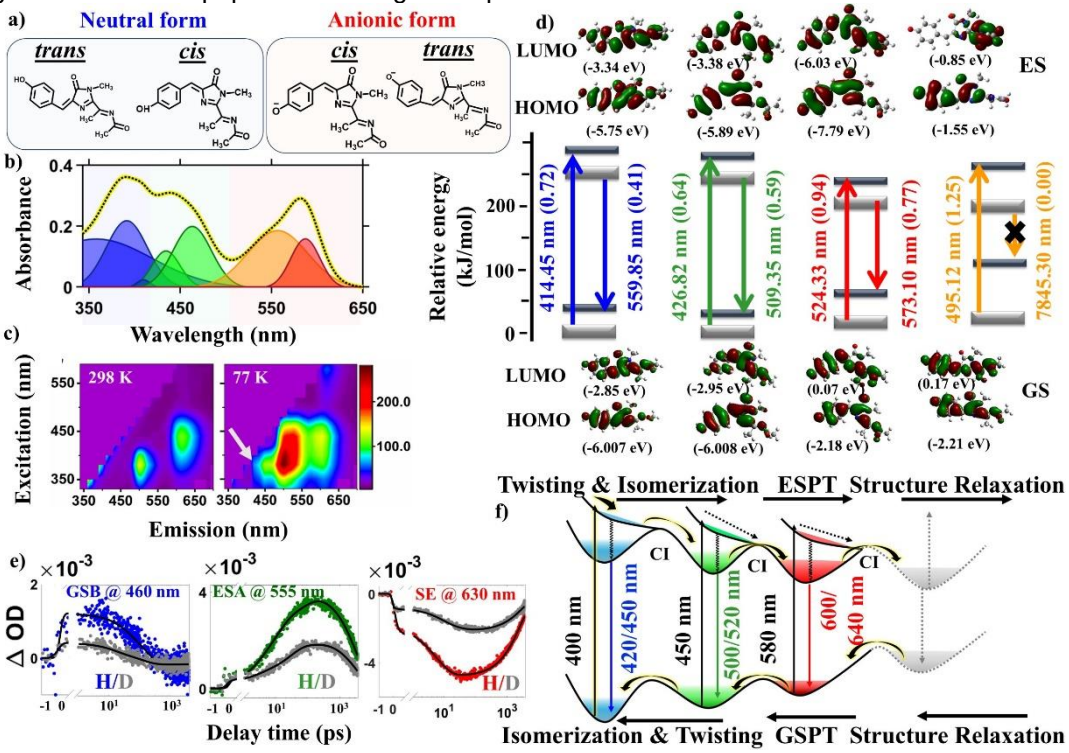


Figure 1. a) Structure of possible conformers, b) Decomposed absorption spectra with cumulative spectra (yellow dotted) over the absorption spectra (black line), c) Fluorescence excitation-emission contour map, d) Electronic structure calculation, e) Kinetic traces at GSB, ESA & SE and their fits, f) Proposed schematic of potential energy surfaces of different conformers of mBeRFP.

**Funding:** IISER Mohali, SERB, DST (CRG/2021/003981), MHRD (MHRD-14-0064, to PG) and CSIR.

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# New insights into ultrafast excited-state dynamics of green fluorescent protein

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The discovery of bioluminescent proteins in jellyfish and the development of a panchromatic library of fluorescent proteins revolutionized live cell imaging, earning the Nobel Prize in Chemistry in 2008. The pioneering experimental study revealed that excited-state proton transfer (ESPT), occurring in a few picoseconds was the main mechanism behind the bright fluorescence of green fluorescent protein (GFP) [1]. Based on some recent studies on dynamic Stokes shift during polar solvation [2] we revisited the mechanism of photocycle in wild-type GFP (avGFP) and revealed that ESPT happens quite fast and that reorganization of the local environment is the key process underlying the observed picosecond kinetics. Presence of a proton-wire, i.e. a hydrogen-bonded network that includes the chromophore, water molecules, and nearby residues, is essential for facilitating proton transfer in both the ground and the excited states. To simulate the movement of protons through the proton-wire, a computational study also carried out, based on reaction force and WBI (Wiberg Bond Index) analysis, we show that proton transfer is initiated in the far-end of proton wire (Ser205 to Glu222) and is completed in a concerted and asynchronous manner as also shown by others [3]. The proposed model summarizes that after photo-excitation of cis-neutral form of avGFP leads to two pathways: rapid, barrierless proton transfer with structural reorganization or instant radiative decay.

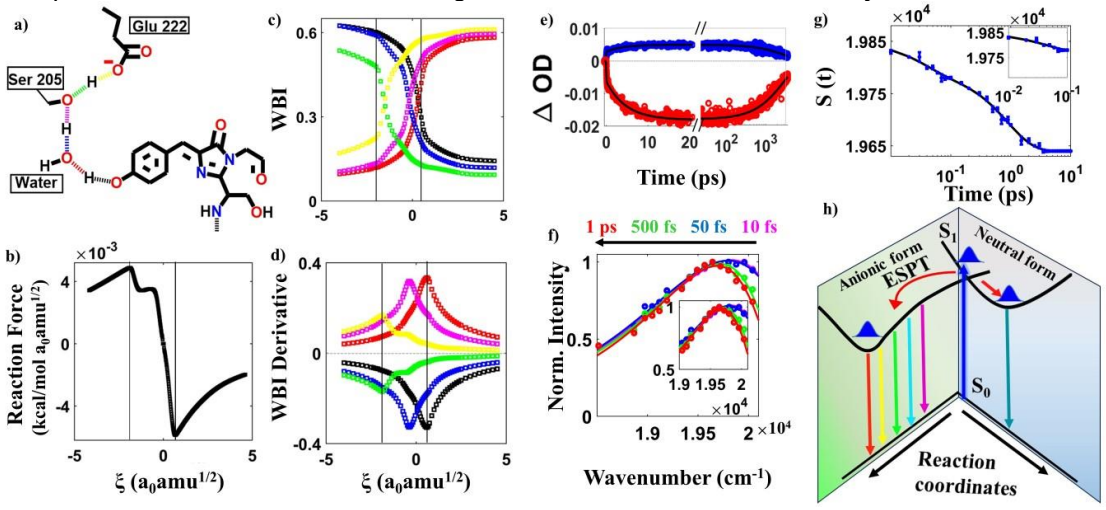


Figure 1. a) Schematic of GFP's proton wire, b) Reaction force representing the intrinsic reaction coordinate, c,d) Wiberg bond indices and derivative analysis, e) Kinetic traces at ESA (blue) & SE (red) and their fits, f) Time-resolved emission spectra following temporal deconvolution along with the log normal fits, g) Stokes' shift function and fits, h) Proposed schematic of potential energy surfaces of avGFP.

**Funding:** IISER Mohali, SERB, DST (CRG/2021/003981), MHRD (MHRD-14-0064, to PG) and CSIR-UGC.

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# Development of an automation system of ibuprofen synthesis through flow photo Favorskii reaction with robot

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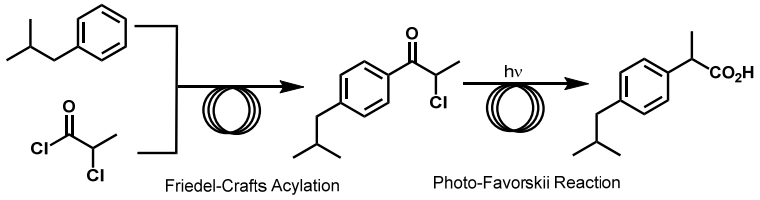
The continuous-flow synthesis has attracted considerable research attention as a method for drastically improving the production efficiency of small-molecule drugs. This is because the method can allow the continuous mixing and reaction of phases in a small and defined volume under highly controlled conditions; however, the effect will be limited if it only improves a portion of these processes. On the other hand, in general, it is well known that photoreaction and the flow reactor as a device are compatible, and can help minimize energy loss. Therefore, we aimed to develop a continuous, integrated production system for all reaction processes for the manufacture of ibuprofen that involves two distinct steps: the Friedel–Crafts acylation reaction and the metal-free photo-Favorskii reaction without human help (Scheme 1).




Scheme 1. Strategy for synthesis of ibuprofen

The Friedel-Crafts reaction and the photo-Favorskii reaction, as well as their respective post-treatments and purification processes, were individually optimized, and integration of the entire flow system under the optimized conditions was examined. Finally, the time between each step was adjusted to feed the entire flow smoothly. Specifically, by utilizing 2 h for the initial Friedel–Crafts reaction, including the work-up, as a benchmark, the reaction conditions were examined to ensure that the passage (reaction) time of each subsequent step was less than 2 h to prevent the accumulation of the reaction solution. After carefully examining the liquid mixing feed speed, the optimal conditions for running the reaction solution and extraction solvent were identified. We were able to obtain the desired ibuprofen at a total yield of 38% for all steps, with a production efficiency of 47 mg $h^{-1}$ (Fig.1). [1]

Figure 1. Fully automated flow system

**Funding:** Japan Agency for Medical Research and Development (19ak0101114h0001, 20ak0101114h0002 and 21ak0101114h0003).

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# Photoinduced Cationic Frontal Polymerization as a New Method for Curing Thick Composites Materials Using Visible Light

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Currently, various energy sources are used to cure composite materials, of which light-based methods - photopolymerization - have recently gained the most popularity (Fig. 1A). They have numerous advantages over classical thermal methods or electron-beam curing, such as low energy cost and high productivity.[1] In addition, photopolymerization is environmentally friendly because it eliminates volatile organic compounds (VOCs) from the curing process of materials. Unfortunately, the use of light as an energy source to initiate polymerization also brings disadvantages, such as low penetration of higher energy light such as the ultraviolet.[2]

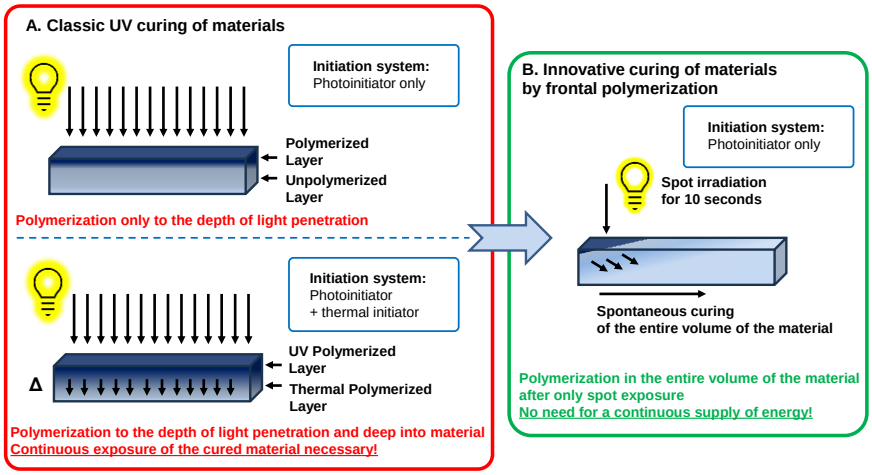


Figure 1. Curing of composite materials using classical methods (A) and photoinduced cationic frontal polymerization (B).

An interesting and recently gaining popularity alternative to classical photopolymerization processes is the so-called frontal polymerization (Fig. 1B).[3] The process involves using the heat that is released during the monomer polymerization reaction to decompose successive initiator molecules. The process is initiated by spot delivery of energy, such as light, to the sample and leads to spontaneous curing of the entire material. In this study, we present a new approach to curing composite materials using a photoinduced cationic frontal polymerization process.

**Funding:** Research funding from the project “Innovative iodonium initiators for curing prepreg composite materials by photoinduced frontal polymerization” carried out within the Proof of Concept programme of the Foundation for Polish Science co-financed by the European Union under the European Funds for Smart Economy 2021-2027 (FENG). Grant agreement number: FENG.02.07-IP.05-0074/23.

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# Applying optical systems for chemical combustion and physical property analyses: Schlieren, Shadowgraph, and Mie Scattering

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With the goal of investigating the chemical layout and physical properties of chemical combustion, this study utilized Schlieren, Shadowgraph, and Mie Scattering optical systems to visualize the combustion field. This enables the measurement and observation of the flame effect, flow/flame characteristics, density, temperature, and the concentration of reaction products, which serve as key indicators for assessing combustion efficiency. As shown in Fig. 1(a), the combustion experiment setup included a combustor and a nozzle. The outer-flow consisted of air, whereas the central jet used propane ($C_3H_8$) as fuel [1,2]. When the air and fuel mixture is ignited, the flame characteristics would appear as in Fig. 1 (b), which includes red, orange, yellow, blue, and other flame colors [3]. A pulse laser is then utilized for triggering the flame field. This led to better observations of the variations in temperatures, as it allows the implementation of Mie scattering—the flow/flame visualization method—which illustrates the interaction between the outer cold airflow and the central fuel jet [4] (Fig. 1 (c)). Eventually, the Shadowgraph optical systems were incorporated for evaluating the density for different flames. The Schlieren system, which involves the use of a knife edge, allowed the measurement of the first derivative of density on the direction of its knife-edge (Fig. 1 (d, e)). The use of the Shadowgraph system—which does not utilize a knife-edge—provided measurements of the second derivative of density (Fig. 1 (f, g)). Collectively, the Schlieren and the Shadowgraph systems illustrated the changes and differences in density between the cold airflow and the central fuel jet, which is significant for measuring the temperature of the combustion field. Collectively, the combination of three optical and instrumental methods illustrated a clearer picture of the combustion field. This would be beneficial in chemical combustion analyses in industrial applications for achieving better energy efficiency.

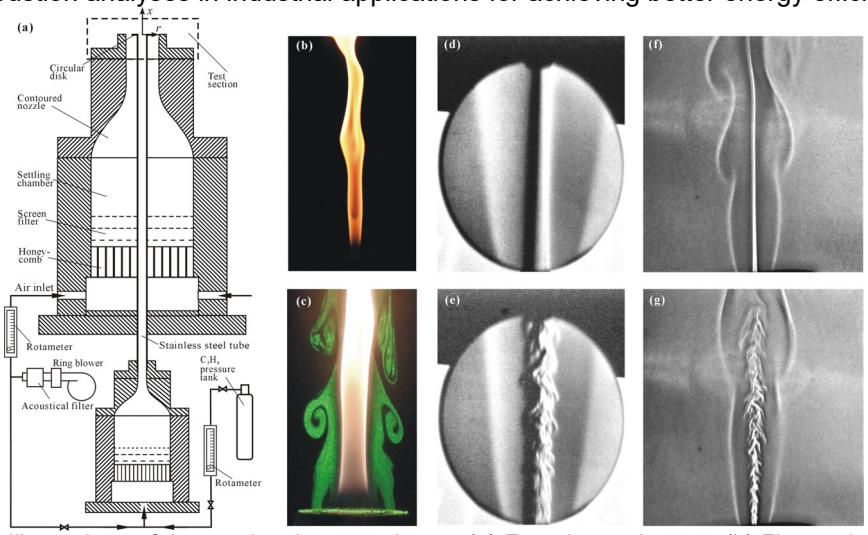


Figure 1. Illustrations of the combustion experiment: (a) Experimental setup, (b) Flame photograph, (c) Flow/flame Mie scattering photograph, (d, e) Schlieren system photographs, and (f, g) Shadowgraph system photographs.

**Funding:** National Science and Technology Council (Taiwan), under Grant No. MOST 105-2221-E-019-038.

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# Heavy Water Induces Intrinsic Fluorescence in Bioorganic Crystals

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The field of aggregation-induced emission (AIE) and non-traditional intrinsic luminescence (NTIL) has been developing rapidly over the past few years. Prior work done by our group[1-5], using a variety of theoretical and experimental approaches, has studied the occurrence of NTIL in the absence of aromatic moieties in amino acids and even larger proteins, such as amyloids. We term this phenomenon *Non-Aromatic Fluorescence* (NAF), and it appears to violate common chemical wisdom, which holds that fluorescence typically requires the presence of conjugated/aromatic groups. We have uncovered some key design principles to explain the microscopic origins of NAF, and in the present work we expand on this by focusing on how subtle structural differences and solvent isotope effects can influence NAF.

Developing non-invasive techniques that can probe how solvents modulate the nucleation pathways of bioorganic molecules in solution remains an active and open area of research. In this paper[6], we investigate the crystallization of the amino acid L-cysteine and show that both the structure of the crystal and its intrinsic fluorescence can be drastically altered by solvent isotope effects. Crystals formed in heavy water exhibit markedly different intermolecular packing as well as strikingly different monomer conformations compared to those in light water. Remarkably, these differences in the supramolecular packing result in significantly elevated intrinsic fluorescence in the crystal that is formed in heavy water.

Using a combination of experimental techniques (confocal microscopy and FLIM) and advanced electronic structure approaches (non-adiabatic molecular dynamics simulations), we elucidate the molecular interactions within the crystals that govern both the electronic origins and the intensity of their emission. These findings demonstrate how tuning the solvent by changing its isotope leads to the emergence of design principles for new intrinsic fluorophores that could serve as novel sensing probes for biomedical applications.

**Funding:** ERC Grant HyBOP 101043272 and EURO HPC Grant EHPC-EXT-2023E01-02.

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# Excimer Formation in Solution and Surface-Bound Pyrene Dicarboxylic Acids

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The interactions between molecular chromophores/fluorophores can have a profound impact on their utility in a variety of applications including solar energy conversion, light emitting diodes, and biochemical sensing. In many cases, processes like aggregation and excimer formation lower the excited state energy and provide an alternate pathway to relaxation that competes with desirable events like the generation of light or electrical current.[1] Here, we investigate how concentration, orientation, and surface coverage of two pyrene molecules substituted with carboxylic acid surface-binding groups at the 1,6- and 2,7-positions (Figure 1) impact its photophysical properties in solution and on a $ZrO_2$ surface.

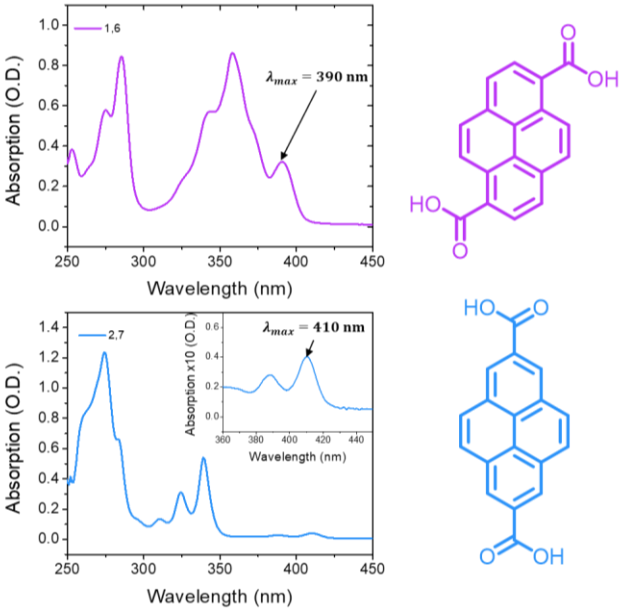


Figure 1. Absorption spectra of pyrene-1,6-dicarboxylic acid (top) and pyrene-2,7-dicarboxylic acid (bottom), 16 μM in DMSO

In dilute solution the 2,7-derivative, like parent pyrene, has an optically forbidden $S_0 \rightarrow S_1$ transition that is, alternatively, allowed in the 1,6-derivative (Figure 1). At higher concentrations, the 1,6-derivative readily forms excimers while no excimer formation was observed in the 2,7-substituted molecules. However, steady-state and time resolved spectroscopy indicates that the geometric restriction imparted by surface binding (i.e., orientation and spacing) notably impacts the likelihood of aggregation and excimer formation. This work will provide insights into how both molecular substitution and interfacial structure impacts intermolecular interactions at organic-inorganic interfaces.

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# Enhancing photon upconversion efficiency via steric protection of π-electron systems with sterically controlled intermolecular interaction

**Nutnicha Boonmong[1], Naoyuki Harada[1], Hayato Shoyama[1], Kiichi Mizukami[1], Yuya Watanabe[1], Pei Zhao[3], Masahiro Ehara[3], Yoichi Sasaki*[1,2], Nobuo Kimizuka*[1,2]**

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Photon upconversion is a photophysical process that converts **low-energy photons into higher-energy photons**. Especially **triplet-triplet annihilation-based photon upconversion (TTA-UC)** has attracted significant attention due to its high efficiency under relatively low excitation intensity. In TTA-UC, excited triplet donors (sensitizers) transfer energy to acceptors (emitters) via Dexter-type triplet energy transfer (TET). Subsequently, two excited acceptors undergo triplet-triplet annihilation (TTA), forming one ground state and one emissive excited singlet state (Fig. 1a). This study focuses on **visible-to-ultraviolet (Vis-to-UV) upconversion**, which is expected to be applied to blue light-induced photocatalysis and aims to develop high-performance acceptors that efficiently convert visible light (λ > 400 nm) to UV light (*l* < 400 nm).

To date, the most efficient acceptor for Vis-to-UV TTA-UC reported is triisopropylsilyl substituted naphthalene (TIPS-Nph) paired with a sensitizer Ir(C6)$_2$(acac), showing the highest TTA-UC efficiency of 20%[1]. Despite the superiority, low photoluminescence quantum yield (PLQY = 66% in 10mM/THF) due to intersystem crossing and excimer formation in the solid state persists. In addition, although recent efforts have demonstrated the role of bulky substituents in suppressing nonradiative decay[2], a further systematic study of bulkiness and their relevance to solid-state TTA-UC is necessary. To overcome these limitations, designing a new π-conjugated backbone that can achieve both high PLQY (>90%) and effectively suppress intermolecular interactions in condensed systems is essential. In this study, we focused on modification of **DiHydroIndenoindene (DHI)** chromophore and developed a methodology to systematically and precisely control the net p-interplanar distances by a novel side-chain modification method using sp$^3$ alkyl substitution (Fig. 1b). We report our findings that these novel DHI chromophores withthe optimal bulky substituents is an excellent acceptor, showing the consistent high PLQY (≒90% in 10mM/THF) and **highest ever UC efficiency of over 26%** in THF solution and a low threshold excitation intensity comparable to solar irradiance[3].

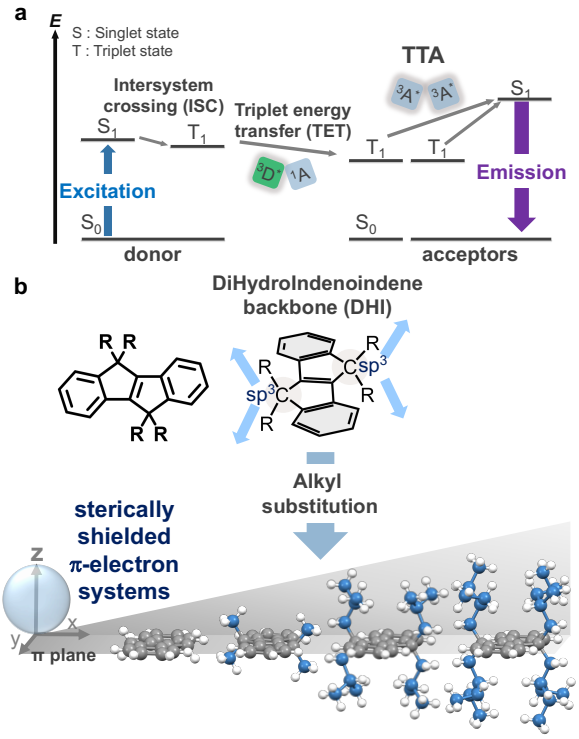


Figure 1. a) Energy diagram of TTA–UC, and b) sterically shielded π-electron systems of triplet acceptors systems.

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**Acknowledgement:** The authors thank HAMAMATSU Photonics, Takuma Yasuda, and Taisuke Matsumoto, for supporting the solid-state absolute UCQY measurements with a reabsorption correction, XRD measurement, and crystal structure analysis, respectively.

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# Indirect Photo-transformation of Molecular Switches using a Pyrrolo-pyrrole Two-Photon Absorbing Antenna

**Melissa Bravo-Romero[1], Óscar Guzmán-Méndez[1], Mariana M. Reza[2], Jorge Peon[1]**

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Highly localized photo-transformations are efficient methods to modify the environment within a material or a biological system[1,2]. When the photoactivation is made through a non-linear optical interaction, these effects can be localized in volumes of the order of a single femtoliter at a variable depth. We have developed a new antenna-molecular switching modular system comprised of a two-photon absorbing pyrrolo-pyrrole antenna section and two azo-isomerizable units (Fig 1.).

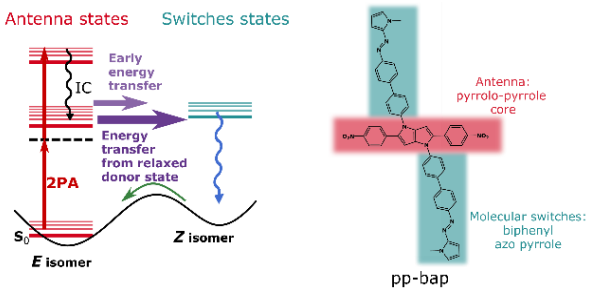


Figure 1. Two-photon pyrrolo–pyrrole molecular antenna indirectly activates azo molecular switches (green) bonded to the antenna core (red). The E-Z isomerization is induced indirectly through an energy migration step from the antenna to the switches. The energy transfer process presents a biphasic nature, happening both from the pre-relaxed and relaxed singlet excited state.

In these systems, the non-lineal light absorption event is localized at the pyrrolo-pyrrole unit. After this, the indirect *E* to *Z* photoisomerization of the azo units occurs via an energy transfer process due to the energy coincidence between the electronic transitions of the modules.[3] We also have studied the femtosecond and picosecond photo-induced processes in these systems in order to identify the dynamics of the relaxation and energy transfer steps. It was found that in solvents of mild polarity, as toluene and 1,4-dioxane, the antenna-localized excited states transfer energy from its pre-relaxed and relaxed $S_1$ state. Moreover, a temperature dependent study showed that the energy transfer step can be activated and has an activation energy of 0.16 eV.[4]

With this kind of molecular architecture, the large two-photon cross section of the pyrrolo-pyrrole section (near 500 GM) can be used to indirectly activate with high spatial precision a variety of molecular actuators which otherwise would not be two-photon-active. This includes dissociating fragments and photocatalysis reaction centers.

**Funding:** CONAHCyT-México grant Ciencia de Frontera 2019-51496 and PAPIIT/DGAPA/UNAM IG200824.

**Acknowledgement:** Thanks to CONAHCyT-México and PAPIIT/DGAPA/UNAM for the funding.

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# Detection of early protein aggregates with fluorogenic hyaluronan nanogels

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Proteins are natural polymers based on a library of 20 L-a-amino acids and they undergo a complex folding process into specific tertiary structures essential for their biological activity. While the native state represents the thermodynamically most stable conformation, environmental perturbations such as alterations in pH, temperature, oxidative stress, macromolecular crowding, or interactions with other biomolecules can induce the formation of metastable conformations. These non-native states exhibit reduced colloidal stability, predisposing them to aggregation and/or phase separation phenomena [1]. Protein aggregation is a process critically implicated in the etiology of severe human neurological disorders [2] and has also been observed under stress conditions in diverse model systems, including bacteria and plant cell cultures. Consequently, the development of methodologies for the comprehensive monitoring and mechanistic elucidation of protein aggregation pathways is crucial for the early detection of pathological indicators and for a thorough understanding of the cellular implications of this phenomenon.
In this study [3], we investigated the interaction between a model plant-derived metabolic enzyme, GAPC1, undergoing oxidative stress-induced aggregation, and the fluorogenic biopolymer HA-RB obtained functionalized hyaluronan with Rhodamine B. In aqueous media, HA-RB self-assembles into nanogel structures. Within these nanogels, the constrained microenvironment induces heavy fluorescence self-quenching of Rhodamine B moieties due to both inter- and intra-filament fluorophore interactions. Upon interaction with the aggregating protein species, the HA-RB nanogels undergo conformational changes, disrupting the self-quenching interactions and resulting in a substantial increase in fluorescence emission. This fluorescence enhancement enables the real-time monitoring of the protein aggregation kinetics via spectrofluorometric and microscopic assays, allowing monitoring of individual pre-aggregates of ca. 50 nm (Figure 1).
Notably, in comparison to conventional fluorescent probes such as Thioflavin-T (ThT) and light scattering techniques, the HA-RB emission signal exhibits an earlier onset of increase, specifically during the lag phase of aggregation. This early diagnostic capability of HA-RB suggests its potential to interact with early-stage oligomeric and pre-fibrillar protein assemblies, a significant attribute for both diagnostic and therapeutic applications. We propose that the unique sensing mechanism of HA-RB arises from a synergistic effect between the polymeric nature of the hyaluronan scaffold and the specific fluorogenic response of the Rhodamine B derivative upon interaction with the protein aggregates.

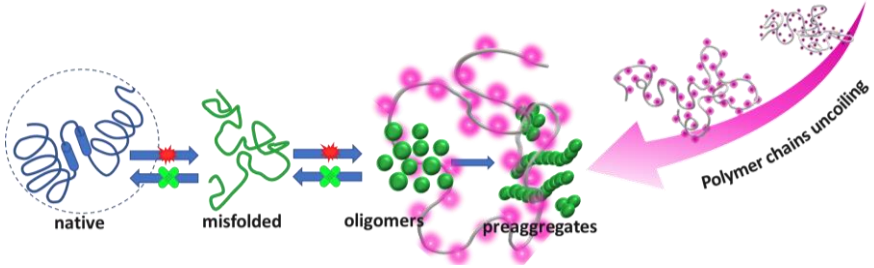


Figure 1. Cartoon representation of the fluorescence enhancing of the HA-RB in presence of early stage protein aggregates

**Funding**: PRIN Project 2022WAKTFR - NoveL approaches to mIcro- and nAno-plastIcS detectiOn iN water (LIAISON)

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# Dynamic Covalent Spiropyran Exchange Systems

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Dynamic covalent chemistry is a powerful tool for rapid structural diversification. We discovered that spiropyrans – or more precisely, their open merocyanine forms – are able to participate in a dynamic covalent exchange process, in which the indoline moiety is replaced *via* Michael addition and elimination. Depending on the reaction conditions and the nature of the substitution, the exchange with another methylene indoline either results in an equal formation of both spiropyrans or can be shifted to the spiropyran containing the stronger acceptor group on the indole moiety (**Figure 1**).[1]

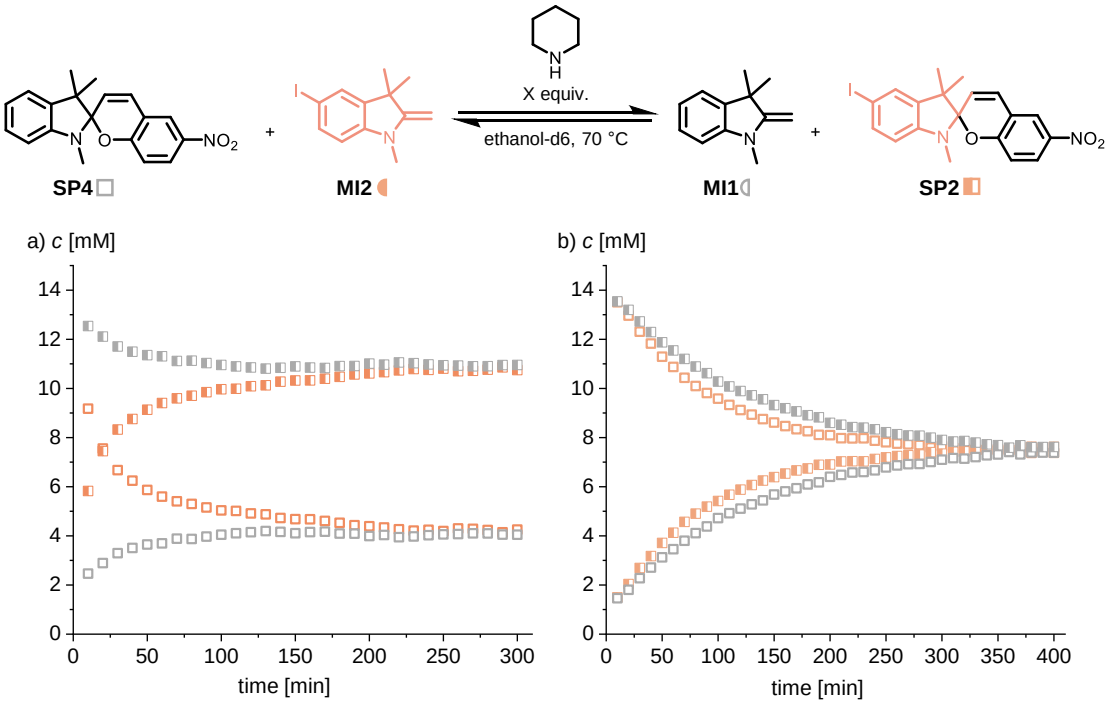


**Figure 1**. Spiropyran exchange between **SP1** + **MI2** (orange curve) and **SP2** + **MI1** (gray curve) ([**SP**] = [**MI**] = 15 mM) as monitored by *in-situ* $^1$H NMR a) without and b) with 4 equiv. of piperidine.

The dynamic properties of the merocyanine compounds are usable in a variety of applications, such as the synthesis of novel spiropyrans, which are promising candidates as dual-color photo initiators in xolography yet cannot be obtained otherwise. Moreover, the exchange conditions can be used to generate dynamic constitutional libraries, which allow rapid screening of spiropyran photoswitches. Currently, we are working towards controlling the developed exchange process by light.

**Funding:** Deutsche Forschungsgemeinschaft (DFG via SPP2363 “Molecular Machine Learning“)

**Acknowledgement:** We thank Ines Bachmann-Remy for help with the *in-situ* $^1$H NMR measurements as well as Jutta Schwarz, Jannes Leonhard, and Linos Madalo for synthesis support.

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# Unprecedented visible light-initiated topochemical [2+2] cycloaddition in a functionalized bimane dye

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Bimanes, a class of molecules based on the 1*H*,7*H*-pyrazolo[1,2-*a*]pyrazole-1,7-dione scaffold. Two isomers exist, with *syn*-bimanes often characterized by high fluorescence quantum yields (60-100%) [1] while *anti*-isomers often exhibit phosphorescence.[2] These properties, along with their small structure make them an attractive candidate for the development of fluorescence probes.[3]

In this work, a series of bimane molecules were synthesized to explore functionalization of the bimane scaffold for modulating their optical properties. Example structures are shown in Figure 1a. It was unexpectedly found that the compound **$Cl_2$B** underwent a topochemical [2+2] cycloaddition, initiated by visible light (Figure 1b and 1c), which is the focus of this presentation. A notable aspect of this reaction is that it occurs only in the solid state – not in the solution phase. We found that the reaction is selective to **$Cl_2$B**, as **$Me_2$B** and **$Me_4$B** did not react in the same way. The alignment of the potentially reactive double bonds in all compounds was examined with X-ray crystallography, showing that they are parallel and coplanar in **$Cl_2$B** and **$Me_2$B** but not **$Me_4$B**. Despite this **$Me_2$B** did not undergo the cycloaddition, likely due to the steric effects.[4]

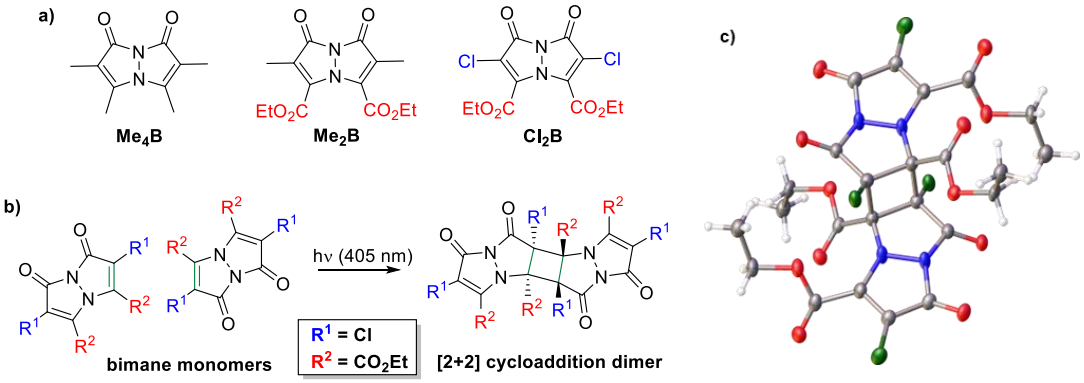


Figure 1. a) Structures of the bimanes studied and b) reaction scheme of the [2+2] photocycloaddition of $Cl_2$B and c) X-ray structure of the dimer.

Our findings suggest that strategically functionalizing bimanes to redshift their absorption bands into the visible region provides a promising strategy for synthesizing substituted cyclobutanes without the need for ultraviolet irradiation.

**Funding:** The authors acknowledge support from Taighde Éireann – Research Ireland (SFI award 21/FFP-A/9214 (DyeSICPhoto) for this work.

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# Computational Investigation of Photochemistry and Reactivity in Macrocyclic Diarylethenes Photoswitches

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Diarylethene (DAE) photoswitches hold significant potential for applications in materials science and biology due to their ability to undergo a reversible light-induced ring-closing/opening reaction.[1] This study investigates the effect of embedding them into a cyclic topology on their absorption properties and behavior on the first excited state $S_1$ in a series of synthesized DAE macrocycles (see Fig. 1).

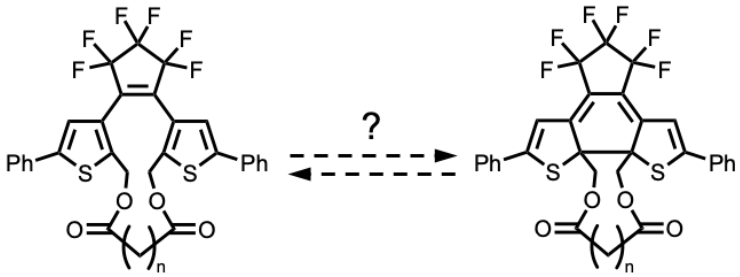


Figure 1. The photoswitching of DAE macrocycles with different linker lengths n is investigated using computational methods in this study. Our results are compared to the experimentally observed photoswitching behavior.

The photocyclization of the DAE generates the corresponding ring-closed isomer, which experiences some geometric perturbation in the macrocyclic derivative due to the presence of the linker.
Here, we discuss the influence of the linker size on the absorption energy and the photoswitching process of the DAE derivatives in comparison with the experiment.
Furthermore, we show that functionalized macrocycles reveal a photoswitchable reactivity in [3+2] cycloaddition reactions. The experimental observations are explained with quantum chemical and thermostatistical calculations, suggesting that the reaction trajectory of the open DAE form provides a more favorable pathway that is not available for the closed form.

**Funding:** Federal Ministry of Education and Research (BMBF) and the Ministry of Culture and Science of the German State of North Rhine-Westphalia under the Excellence Strategy of the Federal Government and the *Länder*

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# Protein-promoted chromophore´s excited state modulation

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In natural photosynthesis, light energy is transferred through a dynamic protein-pigment network with remarkably high quantum efficiency. Local fluctuations in protein structure and conformational changes play a crucial role in shaping the chromophore's energy landscape for efficient light harvesting. However, the precise mechanistic role of these conformational changes remains unclear due to the complexity of natural photosystems, making them difficult to control. Photoactive biohybrids (Fig.1)—synthetic systems that incorporate the key components of natural photosystems, such as proteins and chromophores—offer a promising approach for applying these natural principles in man-made technologies[1]. However, designing these biohybrids presents significant challenges, particularly in controlling the protein-chromophore interaction network, which unpredictably affects the electronic and conformational states of the chromophores[2]. In our lab, we have developed biohybrids based on optimized de novo proteins with well-defined cavities and flexible conformational states[3]. This design enables precise tuning of the biohybrid's response through single-point mutations. Our biohybrids provide a powerful platform for studying the fundamental role of protein amino acids in chromophore relaxation, offering new insights for bio-inspired nanotechnology and photonics.

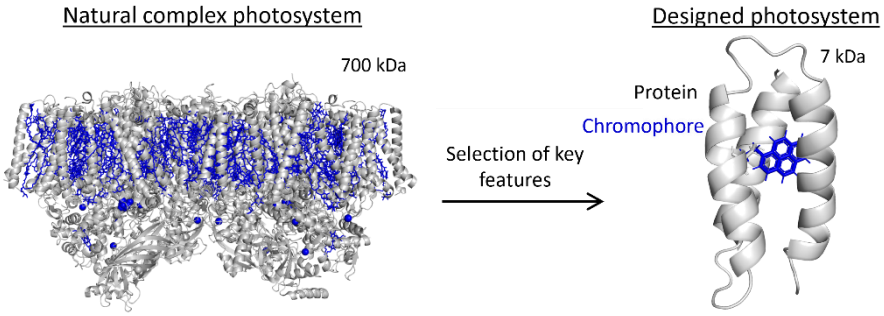


Figure 1. Simplified photosystem to study the role of protein amino acids in chromophore relaxation dynamics.

**Funding:** Cesar Nomberla atracción de Talento grant (REf 2023-T2/ECO-28965. Ayudas I+D en tecnologías (ref TEC2024/TEC85)

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# Towards a Unified Methodology for Half-life Determination of Photoswitches with Highly Stable *Z* isomer

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In the rapidly developing field of photoswitchable systems, current design strategies target at their several desirable properties, such as quantitative switching, activation by visible light, and tuning the thermal stability of the metastable species. Photoswitches exhibiting long half-lives of metastable forms are promising candidates for future applications in smart responsive materials, controlled drug release, and molecular electronics. One example of such systems is a class of azobenzenes and their derivatives based on well-established *E*–*Z* photoisomerization with rich structural versatility. Half-life ($\tau_{1/2}$ at 25 °C) of their representatives with very stable *Z* isomers can be obtained by extrapolation from Eyring or Arrhenius plots, which are constructed using rate constants measured at several elevated temperatures. However, kinetic analysis is often not straightforward, requiring careful data analysis and it can be processed by several different approaches. In this work, we selected compound designed by Fuchter et al.[1] (Fig. 1a) as a model system representing azo-based photoswitches, featuring the longest reported *Z*-isomer half-life of 46 years. We extrapolated $\tau_{1/2}$ at 25 °C from both Eyring as well as Arrhenius plots, using rate constants from four commonly employed methods (Fig. 1b.). We ended up with $\tau_{1/2}$ in the range of 41.9–57.4 years, clearly demonstrating a wide spread of values which can be hardly compared among the laboratories worldwide. We recommend using a unified methodology for evaluation of photoswitch kinetics.[2]

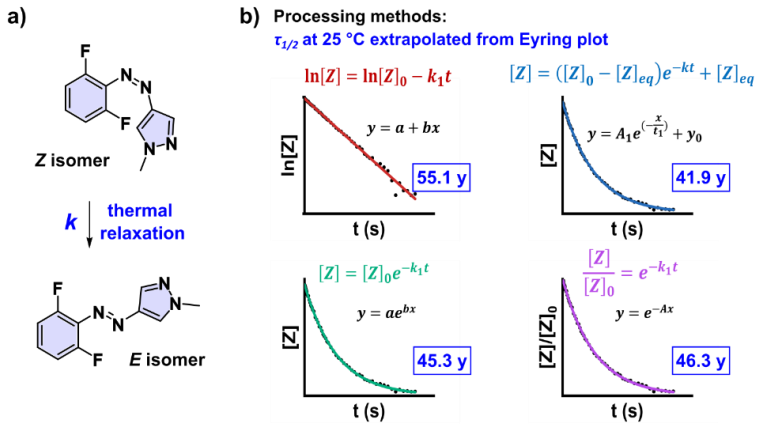


Figure 1. a) Chemical structure and thermal relaxation of model compound, b) methods for processing kinetic data with physically derived equations (in color) and corresponding fitting functions from OriginPro (in black).

**Funding:** This work was financially supported by INTER-COST-LUCES, Ministry of Education, Youth and Sports of the Czech Republic (grant No. LUC24043).

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# Polarization-Sensitive Single-Object Microscopy Resolves Theoretical Debate on the Structure of a Synthetic Light-Harvesting Complex

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Double-walled nanotubes (DWNTs), self-assembled from amphiphilic cyanine dye molecules Cy3 in aqueous environment, have remarkable ability to mimic behavior of highly efficient light-harvesting complexes of green algae bacteria. These bacteria possess extremely efficient photosynthetic multilayered cylindrical antennae, formed by densely packed chromophores, which facilitate energy transfer via delocalized Frenkel excitons [1]. Similarly, DWNTs consist of two concentric tubular layers with diameters of 7 and 14 nm, exhibiting remarkable excitonic properties, such as narrow absorption and photoluminescence (PL) bands.

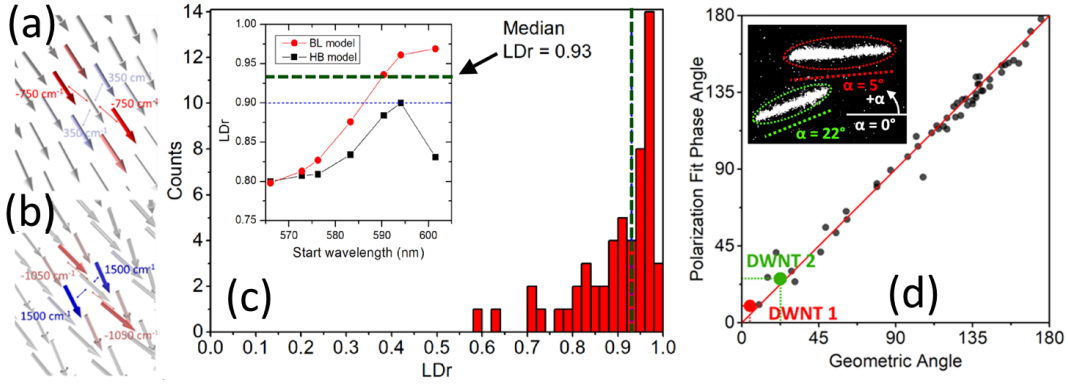


Figure 1. Illustration of the nature of the excitons in the BL (a) and HB (b) models. Blue arrows show a positive coupling with the molecule in the center, while a red color shows a negative coupling. c) Experimental LDr values histogram, showing statistics collected for 54 DWNTs. The inset shows BL, HB and experimental LDr values. d) Correlation plot comparing the geometrical DWNT orientations, extracted from isotropic PL images, with the PL polarization maximum angle. The inset shows polarization-resolved PL of two DWNTs. Straight dashed lines represent the geometrical orientations of the DWNTs.

Two competing structural models have been proposed to explain the excitonic features of DWNTs: the bricklayer [2] (BL) model (Fig.1a), based on a layered brick-like packing of molecules and the herringbone [3] (HB) model (Fig.1b), characterized by a zigzag molecular arrangement. Both models accurately predict absorption and PL spectra of DWNTs, which historically complicated differentiation between two models.

In this work, we resolve this long-standing debate by combining quantum-classical spectral simulations with polarization-resolved wide-field PL microscopy of individual immobilized DWNTs. Theoretical analysis indicates that reduced linear dichroism $\mathrm{LDr} = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ are the PL intensities parallel and perpendicular to the DWNT axis, serves as a threshold benchmark for differentiating the two models. The BL model predicts higher LDr values due to strong, in-phase intermolecular coupling (Fig.1c, inset, red curve).

For experimental validation of both models, we implemented a novel polarization-resolved PL microscopy technique to measure LDr in individual immobilized DWNTs suspended in ultrathin sugar matrix. This approach yielded a median LDr value of 0.93 (Fig.1c), clearly favoring the BL model. Additionally, we showed that the transition dipole moments are confined to a narrow angular range aligned with the nanotube's long axis (Fig.1d), further supporting the BL structural arrangement. This molecular alignment generates large transition dipole moments that are closely oriented along the tube axis, resulting to PL that is almost entirely polarized along the DWNT backbone axis. Overall, we were able to differentiate between competing structural models utilizing polarization-sensitive microscopy supported by simulations, as well as report directly measured LDr value and PL polarization orientation of DWNTs. Thus, our findings offer valuable insights into the mechanisms governing excitonic transitions, particularly in nature-inspired synthetic light-harvesting complexes.

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# Photochemical Control of Gel Disassembly mediated by Singlet Oxygen

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Low Molecular Weight Gelators (LMWGs) are small organic molecules that form gel networks in a solvent through non-covalent interactions like hydrogen bonding, π-π stacking, van der Waals forces, and electrostatic interactions.[1] This results in a fibrous network that traps solvent molecules. Our group previously studied the gel formation from the pro-gelator [α-diketone-2,3-didecycloxyanthracene (dkDDOA)] to the well-studied 2,3-didecyloxyanthracene (DDOA)[2] supergelator by a clean photochemical reaction. The use of light to control this molecular organization presents a promising approach in material science and nanotechnology.

This study investigates the reversible self-assembly of DDOA, using a combination of two independent photochemical reactions. First, a blue light source at 455 nm is used to convert the pro-gelator (dkDDOA) into the DDOA gelator. DDOA self-assembles in polar solvents such as propylene carbonate, DMSO or acetonitrile to form a gel, which is a non-equilibrium state stable at r.t.. Then, a red-light source at 635 nm is used to excite Methylene Blue which acts as a photosensitizer for singlet oxygen formation.[3] Singlet oxygen oxidizes and decomposes DDOA, as demonstrated by NMR spectroscopy of the photo-products. An efficient photosensitization has been obtained in acetonitrile and propylene carbonate. When this reaction is applied to a gel of DDOA, the molecules are also decomposed, leading to an irreversible disassembly of the gel as demonstrated by absorption spectroscopy. In conclusion, the gel of DDOA could be formed and disassembled dynamically by photochemical control. In perspective, the structural evolution of these gels will be studied by confocal fluorescence microscopy.

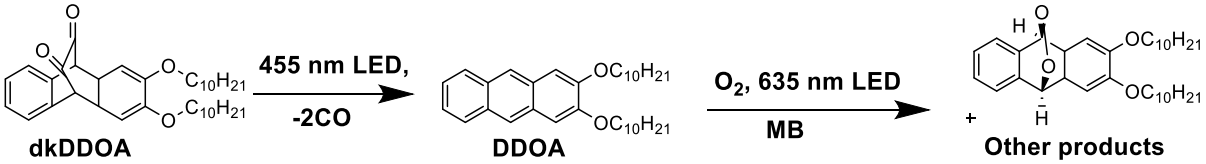


Figure 1: Schemes of the photodecomposition of dkDDOA into DDOA, and of the photooxidation of DDOA into DDOA-endoperoxide.

**Funding:** CEFIPRA Project No. 6708-2 titled “MicroMat: Light- and Bio-Sensitive Soft Micro-Materials.”

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# Multistate Dihydroazulene-Spiropyran Dyads: Path-Dependent Switchings and Refinement of the "Meta-rule" of Photoactivity

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Multistate switches are interesting systems for a plethora of potential applications, such as for data storage involving many different states or for logic operations characterized by specific outputs. The main challenge is to achieve a precise control of accessibility to a specific state via a given sequence of multiple stimuli. Here we have connected dihydroazulene (DHA) and spiropyran (SP) photoswitches in dyads to elucidate differences in optical and switching properties between *ortho*-, *meta*-, and *para*-phenylene bridged dyads.[1,2] Dyads were studied in detail by stationary and ultrafast spectroscopies. The results show path-dependent switchings of the dyads using light in combination with other stimuli (acid/base/heat), allowing access to eight distinct states. By changing the bridging unit and connectivity between the photoswitches, various properties (outputs) were finely tuned such as absorption and fluorescence behaviors, lifetime of metastable states, and photoisomerization dynamics. Overall, the so-called *meta*-rule is applicable to the DHA-to-VHF photoswitching because only the *meta* connected dyad presents similar dynamics to the monomer, whereas the *ortho* and *para* dyads exert additional ICT emission – a novel property not exhibited by the individual units. In contrast, for the SP-to-MC conversion connectivity is less important since all dyads show similar behaviour. Our results illustrate that the electronic communication between the DHA and the SP units can be finely tuned by the type of linker and connectivity, always maintaining reversible photoswitching ability between four (to eight) distinct states.

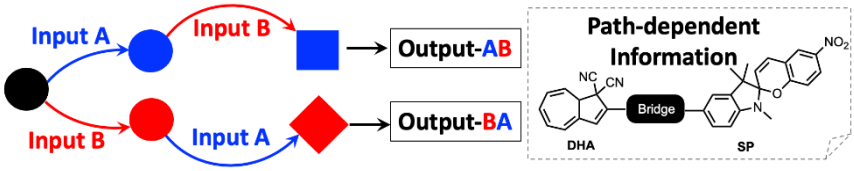


Figure 1. Scheme of multistate photoswitches where Input A and Input B switch the two moieties dihydroazulene (DHA) and spiropyran (SP) in a path-dependent manner, giving different outputs.

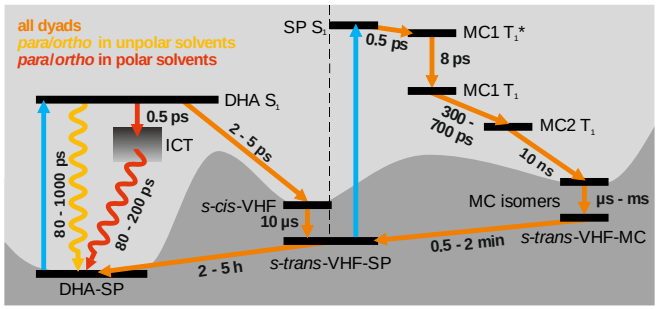


Figure 2. General reaction scheme of DHA-SP dyads; when excited with a 400-nm pulse to trigger the DHA-to-VHF photoconversion (left) and with 360 nm from the 400-nm photostationary state to isolate the SP-to-MC switching.

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# Unraveling Excited-State Intramolecular PCET in a Dinuclear Ir(III) Complex via Ultrafast Spectroscopy and Strategic Hydroquinone Core Modifications

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The dinuclear Ir(III) complex $I_2^+$, bridged by a redox-active Phen–Im–hydroquinone–Im–Phen ligand, exhibits complex excited-state dynamics driven by intramolecular excited-state proton-coupled electron transfer (PCET), facilitated through ESIPT (Excited state intramolecular proton transfer).[1] To dissect the role of PCET in its photophysics, we employed femtosecond transient absorption spectroscopy (fs-TAS) alongside DFT calculations, using varied excitation wavelengths to map excited-state dynamics across spectral and temporal domains. The presence of multiple relaxation pathways including intersystem crossing, vibrational relaxation, PCET, and electron transfer channels challenges the assignment of the time constants to the single steps in the mechanism.

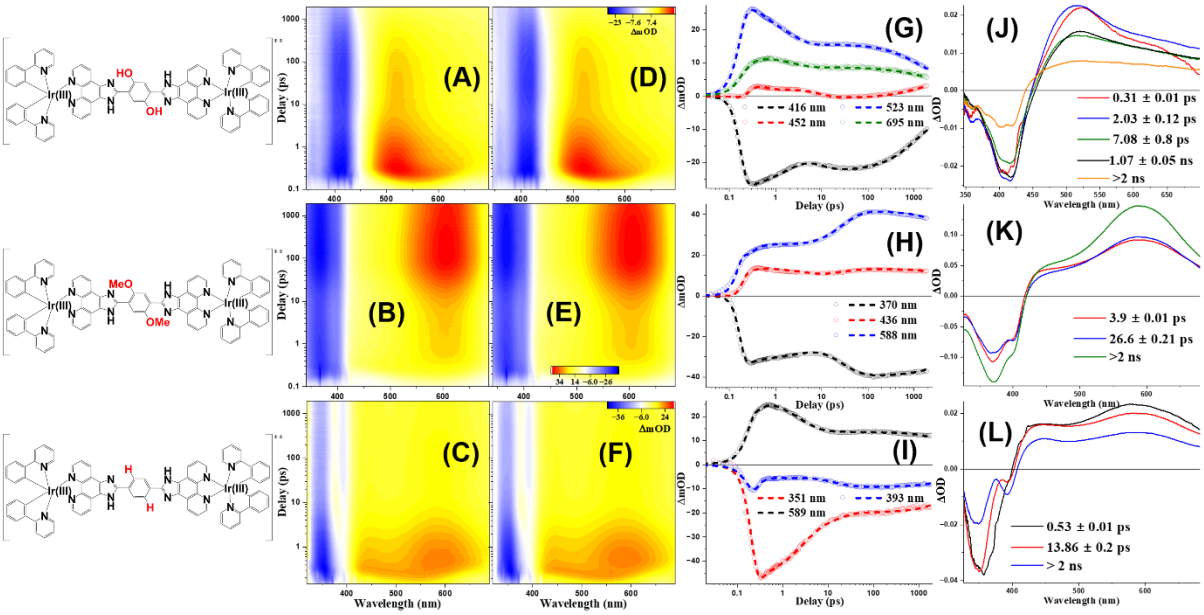


Figure 1. Experimental (A),(B),(C) and fitted (D),(E),(F) fs-transient absorption data, experimental and fitted kinetics (G),(H),(I) and evolution-associated difference spectra (J),(K),(L) of $I_2^+$ (A),(D),(G),(J) and its -OMe (B),(E),(H),(K) and -H derivatives (C),(F),(I),(L).

To probe the contribution of PCET, we synthesized two analogues where the hydroquinone –OH groups were replaced with –H and –OMe (Fig. 1.). The substitutions disrupt the ESIPT pathway. Additionally, ligand redox properties are tuned (-OH/-OMe vs. H). Comparative fs-TAS data [Fig. 1(A) - 1(L)] across all three complexes reveal distinct excited-state dynamics, with $I_2^+$ (bearing the –OH group) showing evidence of faster charge separation and longer-lived transient species. While these findings suggest a possible role of PCET, ongoing nanosecond TA studies and bimolecular electron transfer measurements are required to characterize the properties of the long-lived compounds and determine whether PCET facilitates the formation of charge-separation.
These studies will reveal how subtle electronic tuning of the hydroquinone core governs PCET behavior, offering design principles for tailoring excited-state reactivity in dinuclear Ir(III) systems with relevance for light-driven catalysis, artificial photosynthesis, and photomedicine. [1,2,3]

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# Role of Molecular Topology on Quartet-Derived Luminescence in Emissive Radicals

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Trityl radical semiconductors (TTMs) can exhibit efficient photoluminescence via doublet charge-transfer (CT) excitons between electron-accepting TTM units and donor chromophores, such as carbazole, enabling their use in light-emitting devices. When coupled to near-resonant triplet excitons, quartet states form via intersystem crossing (ISC). If reverse-ISC is also efficient, these high-spin states can emit through the bright doublet channel. Here, we report on three molecular architectures with varying connectivity between TTM, carbazole and acene. We investigate how the electronic coupling strength between acene and TTM dictates luminescence and ISC efficiencies. Direct acene-TTM coupling introduces a dark, low-lying CT state that quenches emission via non-radiative decay, yielding weak luminescence with limited quartet formation (Fig. 1. *left*).

In contrast, weak electronic coupling between acene and TTM via carbazole raises the energy of the same CT state, which promotes ISC and reverse-ISC processes (Fig. 1. *right*). Using this TTM-carbazole-acene topology, we design a molecule achieving 55% luminescence yield, with 94% of photons originating from the quartet state with a lifetime of 1.03 µs, revealing the critical role of molecular topology for quartet-derived luminescence in tuneable quantum materials.

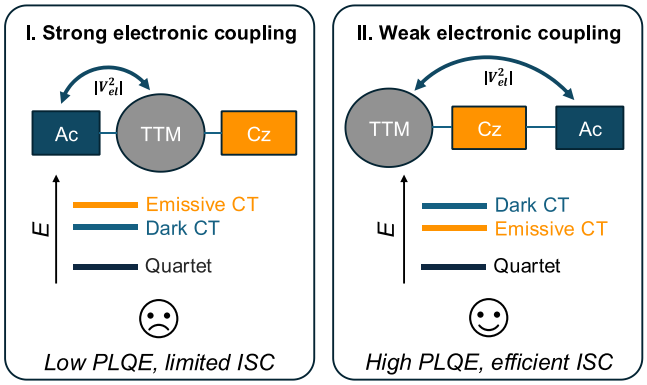


Figure 1. The electronic coupling strength between acene and radical-donor dyad can be chemically modulated by connectivity. It dictates the emission efficiency and intersystem crossing rates via the energy of dark acene to radical CT state.

**Funding:** European Research Council, European Union's Horizon 2020 research and innovation programme (no. 10102016), Winton Programme, Harding Distinguished Postgraduate Scholarship, European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreements (No. 891167, No. 886066), Emmanuel College, Cambridge, Research Fellowship.

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# Photoswitchably Crosslinked Microgels and their Super-resolved Visualization

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Due to their distinctive architecture, functional microgels offer exceptional versatility by rapidly adapting to various external stimuli such as temperature, pH, ionic strength, solvent composition, and light.[1] In this work, we describe the synthesis of poly(*N*-isopropylacrylamide) (PNiPAM) microgels that are responsive to both light and temperature. Their photoresponse is achieved through a supramolecular crosslinker based on a host-guest complex between azobenzene and β-cyclodextrin (β-CD).[2] In the thermal equilibrium, the majority of azobenzene exists in the *trans* form, resulting in the predominant formation of the host-guest complex. Upon exposure to UV light, azobenzene undergoes a *trans*-to-*cis* isomerization until reaching its photostationary state (PSS). This isomerization reduces its binding affinity with β-CD due to a lower association constant,[3] thereby causing a reversible dissociation of the crosslinker. The intrinsic polarity of β-CD increases the volume phase transition temperature (VPTT) of PNiPAM microgels.[4] Moreover, when azobenzene is encapsulated within the cavity of β-CD, its apolarity is effectively masked, leading to a net increase in polarity and, consequently, an elevated VPTT. Conversely, the release of azobenzene upon UV irradiation decreases the net polarity and thus the VPTT. Since the *trans*-*cis* ratio in the PSS is highly wavelength dependent, it is possible to finely tune the VPTT between approximately 33 °C and 37 °C. Thermal equilibrium is recovered either over time or via irradiation at 455 nm, which supports the reversible dissociation of the crosslinker. The photoswitching behavior was characterized using NMR, light scattering, viscosimetry, and absorption spectroscopy.

Furthermore, employing the super-resolution fluorescence microscopy technique direct stochastic optical reconstruction microscopy (dSTORM) allows for a detailed investigation of both the global and local morphological changes of the microgels in response to irradiation.[5] In this context, ongoing research focuses on modifying the crosslinker to enable fluorescent dye labeling.

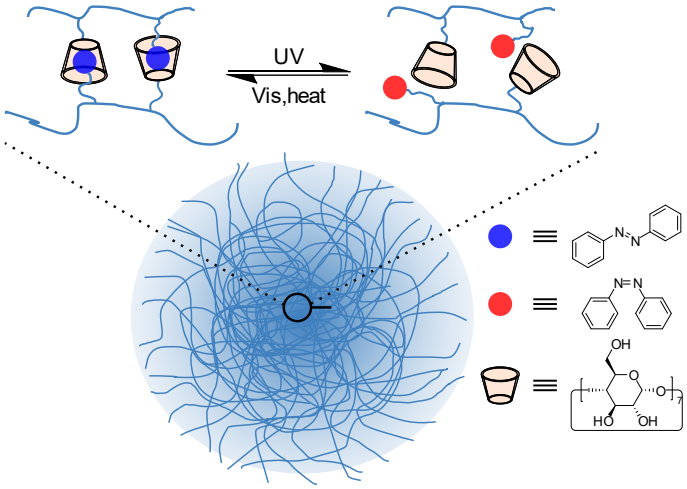


Figure 1. Schematic visualization of photoswitchable crosslinked microgels based on β-cyclodextrin and azobenzene host-guest complexation. The cone represents β-cyclodextrin and the blue and red dots represent the *trans*- or *cis*-azobenzene, respectively.

**Funding:** German Research Foundation (DFG) through the collaborative research center SFB 985

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# At the "peak" of TTA upconversion: clear advantages of TIPS substituents

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With the increasing importance of triplet-triplet annihilation upconversion in applications such as light-driven catalysis, bio-imaging and 3d-printing, the need for highly efficient annihilators has increased significantly.[1] The attachment of the triisopropylsilylethynyl group (TIPS) to an aromatic core unit has led to the development of many annihilators with high annihilation quantum yields.[2,3] One major aspect of the TIPS substitution is to prevent excimer formation and therefore reduce unproductive competitive quenching pathways. [4,5] In our study, we synthesized a series of biphenyls with silyl substituents of varying size and employed them in blue-to-UV upconversion systems to explore the respective influence on the triplet energy transfer (TET) and the following triplet-triplet annihilation. We demonstrate that, in comparison to trimethlysilyl- (TMS), tritethylsilyl- (TES) or triphenylsilyl (TPhS)-derivatives, the TIPS-subsituted biphenyl shows the longest triplet liefetime as well as high-lying, inaccessible $T_2$ and $T_3$ states, thereby reducing energy-wasting processes. Exploiting our findings, we developed a highly efficient UC system with the doubly TIPS-substitued biphenyl (bTIPS-BP) as annihilator. We employed the best-performing system for initiating the release of fluorescein from a photocage by blue-to-UV upconversion.

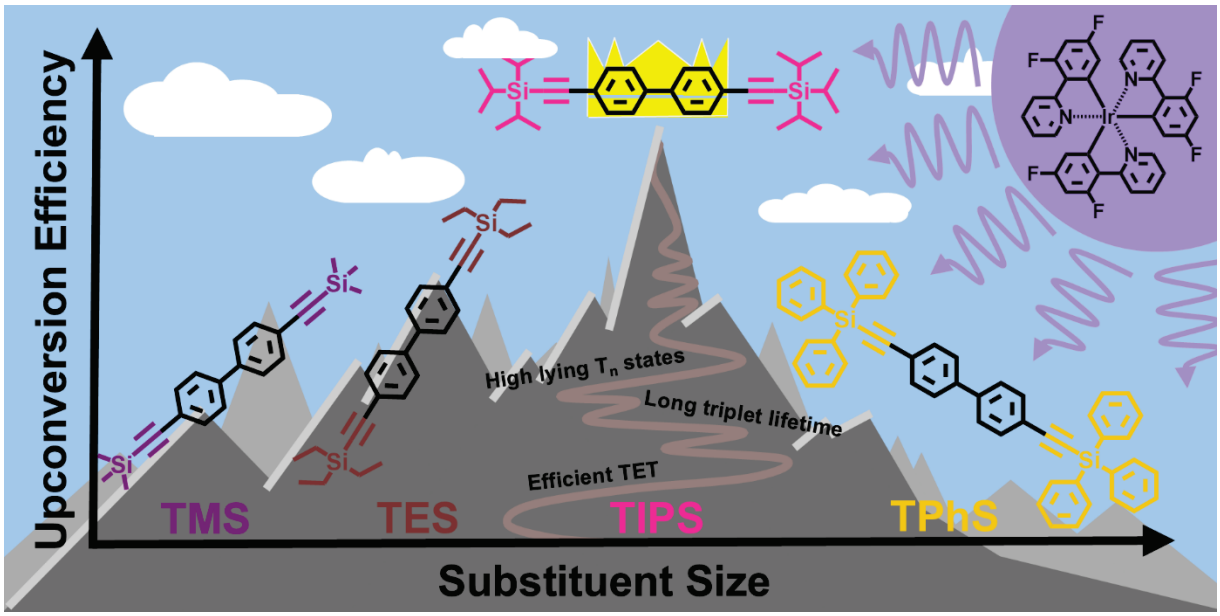


Figure 1. Schematic illustration of the physical properties of bTIPS-BP (pink) compared to its substituted derivatives with *tris*[3,5-difluoro-2-(2-pyridinyl)phenyl]-iridium ($Ir(dFppy)_3$, black) as sensitizer that lead to highly efficient sensitized triplet-triplet annihilation upconversion.

**Funding:** Johannes Gutenberg University Mainz, The University of Tokyo, Max Planck Graduate Center with the Johannes Gutenberg-Universität Mainz (MPGC).

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# Multistep Photochromic Reactions of a Stilbene-Anthraquinone Conjugate Based on Self-Accelerating Photoreduction

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Photochromic reactions are phenomena in which the color and/or structure of materials changes reversibly upon light irradiation, serving as a fundamental technology in designing photoresponsive materials. Conventional photochromic reactions are controlled between two states. In contrast, controlling photochromic reactions among three or more states by light irradiation is essential for developing advanced photofunctional materials. Recent studies have achieved multi-step photochromic control by linking several photoswitches that respond to different wavelengths of light.[1] However, achieving multiple states requires excitation at several different wavelengths, leading to the complexity of applications.

In this study, we synthesized a stilbene-anthraquinone conjugate (St-AQ, Fig. 1a) and investigated its photochromic properties. As a result, stepwise photochromic reactions were observed upon constant light irradiation with a single wavelength in the presence of a reducing agent. This finding is expected to contribute to the development of temporally-programmed photofunctions such as spatiotemporal photopatterning.[2]

UV light (365 nm) irradiation to the St-AQ in nitrogen-purged acetonitrile with triethylamine (TEA) as a reducing agent caused *trans*-to-*cis* photoisomerization of the stilbene moiety at first, followed by photoreduction of the quinone moiety after an induction period of 35 s (Fig. 1b). Supplying the air into the solution caused aerobic oxidation of the quinone moiety to recover the original form of St-AQ. Higher concentrations of TEA brought shorter induction periods until the photoreduction. Time-resolved absorption spectroscopic studies suggested that the induction period is likely attributed to the accumulation of any photoproduct; The accumulated species is presumed to facilitate the subsequent photoreduction process of St-AQ. The induction period was reset upon air supply, indicating the catalytic photoproduct is quenched by oxygen.

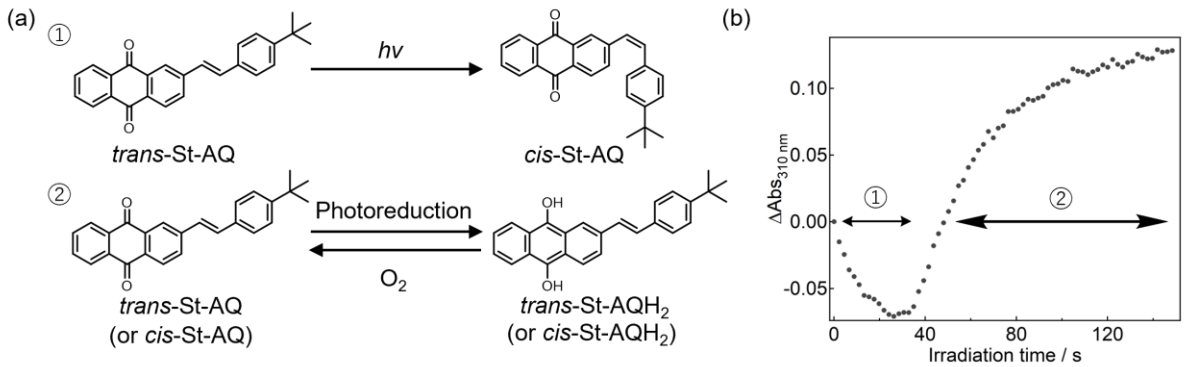


Figure 1. (a) Plausible photochromic reaction scheme of St-AQ: (1) *trans*-to-*cis* photoisomerization, (2) photoreduction, (b) Absorption change at 310 nm of 250 μM St-AQ with 2.5 mM TEA in nitrogen-purged acetonitrile under 365-nm light irradiation.

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# Non-kasha photo-emission behavior in organic molecules

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The well-known Kasha's rule states that in complex organic molecules, light emission occurs from the lowest excited state of a given multiplicity, no matter which excited electronic state is initially populated. [1] However, few systems have shown some anomalous emission processes which violate this rule. The study of non-kasha processes enables the development of tools for designing new materials with tailored optical properties, offering potential technological impact across various fields.[2] Most of these systems are organic molecules containing heteroatoms or non-benzenoid aromatic hydrocarbons, such as azulene and its derivatives.[3] Here, we investigate the emission properties of an azulene-based molecule which shows non-kasha behavior using time-dependent density functional theory (TD-DFT). We explore the different radiative and non-radiative processes demonstrated via molecular orbital diagrams, oscillator strength and spin-orbit coupling values.

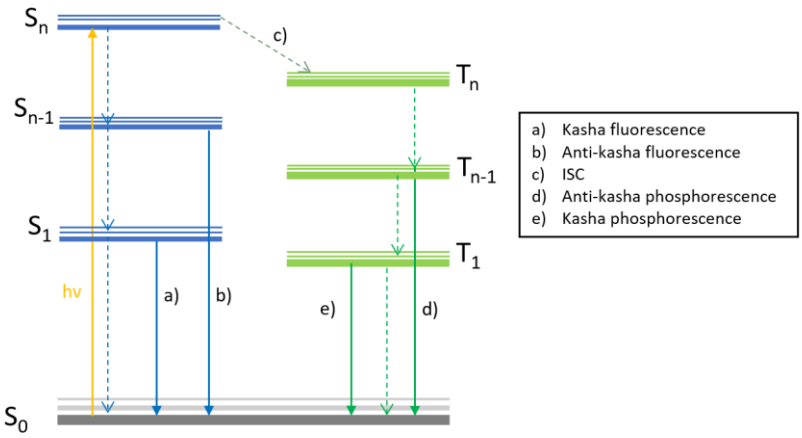


Figure 1. Suggested mechanisms for the azulene-based molecule studied.

**Funding:** PID2022-136231NB-I00

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# One Excitation, Two Isomerizations: Second Generation Oxazolones Photochemistry

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Oxazolones are versatile five-membered heterocycles whose physicochemical properties can be tuned through conjugation extension and strategic functionalization. This allows for precise control over their linear and non-linear optical proprieties, making them valuable candidates for diverse applications. We have explored several new push-pull oxazolones with an extended conjugation and studied the effects of different substitution patterns on their photophysical and photochemical behavior.[1] The photo-switching and excited-state dynamics were studied through steady state and femtosecond-resolved spectroscopies to examine the interplay between electronic structure and photoinduced transformations.

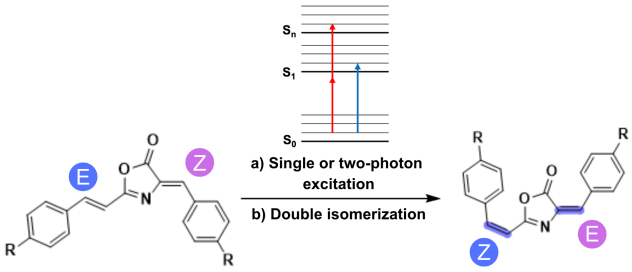


Figure 1. Oxazolone general structure capable of a) notable single and two-photon absorption properties and b) double isomerization form the E/Z isomer to the Z/E.

We observed that certain derivatives show and enhanced the two-photon absorption cross-sections to the level of hundreds of GM units. Importantly, several of these systems show an unprecedented dual photoisomerization process upon linear or two-photon excitation (Fig. 1.). The observed photochemistry was monitored through NMR spectroscopies, confirming that a single excitation event produces a simultaneous isomerization of two spatially separated, electronically conjugated –but non-connected– double bonds. Such kinds of double photoisomerization processes are scarce in current literature, highlighting a novel mechanism for non-adjacent bond isomerization with implications for molecular design in optically responsive materials.

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# Synthesis of red light photoswitches – The case of Konrad's azobenzene

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Azobenzenes are widely applied as photoswitches in several fields such as material sciences and pharmaceuticals. However, for in vivo applications, light has to be able to reach the azobenzene moiety. It has been shown that red light and ideally near infrared light penetrates deeper within tissue than radiation with shorter wavelengths.[1] In this regard, the work of Konrad *et al*. is worthy to be highlighted because the authors reported on an azobenzene derivative that can be switched to the *cis*-state upon irradiation with 660 nm light yielding a 17:83 *trans*:*cis* ratio, while the *trans*-state can be obtained upon irradiation with blue light (440 nm) yielding a 95:5 *trans*:*cis* ratio. Moreover, the thermal relaxation half-life is 5h at 25 °C in DMSO.[2]

In this work, we have optimized the synthesis of Konrad's azobenzene (**Fig. 1**). Various reaction conditions and purification conditions were tested. For the oxidation condition, we replaced the reported potassium permanganate[2] by N-chlorosuccinimide/DBU[3] which increased the yield from 5% to 22%. Additionally, various reaction temperatures were screened for this reaction, in which it was observed that higher temperatures promote a slight increase in chemical yield (at -78 °C, η=22%/ at -20 °C, η= 25%). In the chlorination reaction, no product was formed when a lower concentration of the starting material was used, therefore unravelling an important effect of the starting material concentration on product formation. Overall, our optimized synthesis protocol allows the synthesis of this interesting azobenzene building block in 14% overall yield on a 200 mg scale.

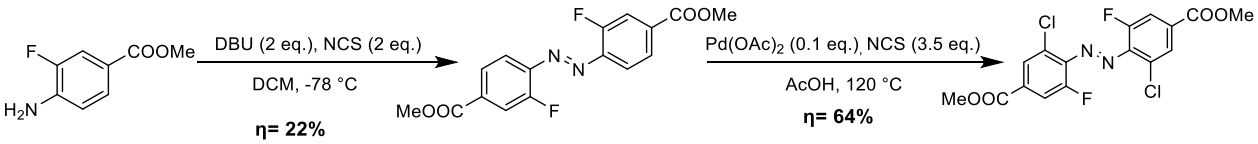


Figure 1. Optimization of Konrad's azobenzene synthesis.

**Funding:** ZonMw (04510242410025).

**Acknowledgement:** We would like to thank Evi Timmer who worked on this project for her bachelor thesis.

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# Structural and Dynamic Studies of Low Molecular Weight Molecular Organogels using Multimodal FLIM, Hyperspectral, Polarization and Super-Resolution Fluorescence Microscopy

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Low molecular weight organogels are fascinating materials that have recently garnered significant interest in the scientific community. These materials are formed from small organic molecules that self-assemble into a three-dimensional structure, capable of entrapping organic solvents and forming a gel. Unlike traditional gels formed from polymers or biopolymers, low molecular weight organogels offer unique advantages such as flexibility in designing the structure, ease of synthesis, and a wide range of physicochemical properties. They have potential applications in various fields such as materials science, chemistry, biology, medicine, or organic electronics[1-3]. In this context, understanding the self-assembly mechanisms and properties of low molecular weight organogels is crucial for developing new applications and improving the performance of these materials.

We present current studies that make extensive use of multimodal fluorescence microscopies, including hyperspectral, time resolved, polarization resolved[1,3] and super-resolved microscopy, in view of (i) understanding the photoconversion mechanisms of a pro-gelator molecule, dkDDOA[2], leading to the spatio-temporal control of the gel nanofibers formation, (ii) using the PAINT super-resolution approach to get insight into the nano-heterogeneities of a small peptide based gel and the dynamics of nanofibers.

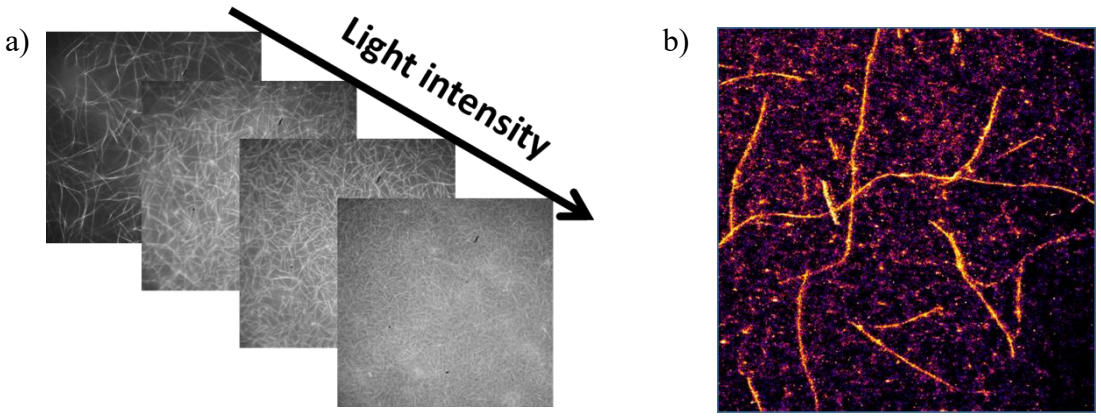


Figure: a) dkDDOA photo-converting to DDOA and self-assembling into DMSO gel nanofibers with density controlled by the light intensity (74 x 74 µm fluorescence images), b) PAINT image of FFmoc nanofibers with ca. 20nm spatial resolution (11 x 11 µm).

**Funding**: European Union's Marie Skłodowska-Curie Actions (MSCA) Doctoral Networks (DN) HORIZON-MSCA-2021-DN-01 under the grant agreement N°101072585, within the network MultiSMART, funded as aforementioned and by the UKRI (grant agreement N° EP/X029980/1 and EP/X02895X/1).

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# Developing novel two-photon switching systems for non-linear optical super-resolution microscopy

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Super-resolution microscopy techniques like PALM require molecular probes that can transition between bright and dark states after excitation. The fluorescence of single molecules allows for the reconstruction of cellular images with a resolution of tens of nanometers. A key aspect of designing these probes is the control over their *on/off* states.[1] Photo-switches, like donor-acceptor Stenhouse adducts (DASA) undergo a significant structural change after excitation, transitioning from an open polymethinic-type colored isomer to a closed cyclopentenone non-colored form (figure 1a)[2]. The spectral change which accompanies the isomerization reaction of DASAs can be exploited to control fluorescent dyes through an energy transfer process. In this work, we synthesized a modular molecular probe based on a FRET pair that utilizes DASA isomerization to modulate fluorescence response of a BODIPY dye (figure 1a). While the DASA module remains open, the probe is in the *off* state due to deactivation of bright BODIPY states by the FRET process. Once the DASA system is photo-switched to the "closed" form (cyclopentenone isomer), the emission property of the BODIPY moiety is in the *on* state. The recently demonstrated two-photon absorption (TPA) properties of DASAs[3], with their quadratic dependence on laser pulse intensities, enable this isomerization reaction to be localized within volumes of the order of a single femtoliter, thereby activating the fluorescent probe with high spatial localization.

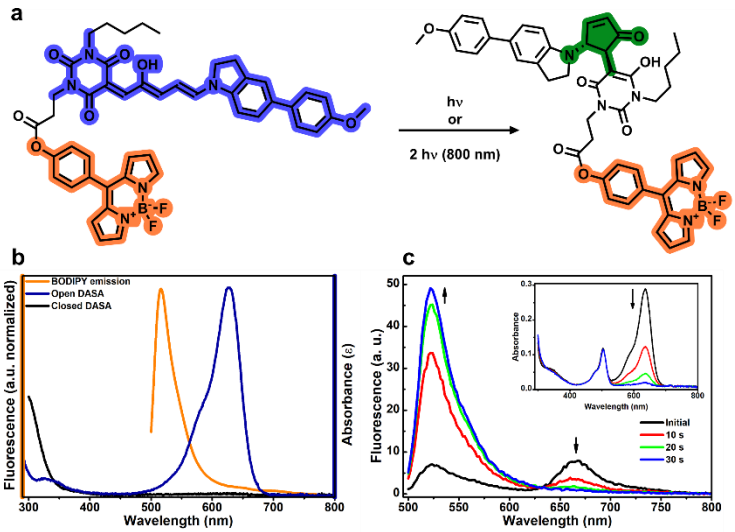


Figure 1. Molecular TPA probe constituted by DASA (blue) and BODIPY moieties (orange). **a**. Photo-transformation of the DASA switch by TPA. **b**. Change in absorption spectra between open and closed forms of the DASA moiety. The emission spectra from the BODIPY section is shown in orange to highlight the overlap between the open DASA absorptive transitions and the BODIPY´s emissive transitions. **c**. Increase in BODIPY´s fluorescence intensity upon photo-conversion of the DASA switch to the closed isomer. Inset: Same change measured through absorption spectroscopy.

**Funding:** CONAHCyT-México grant Ciencia de Frontera 2019-51496 and PAPIIT/DGAPA/UNAM IG200824.

**Acknowledgement:** CONAHCyT-México grant Ciencia de Frontera 2019-51496 and PAPIIT/DGAPA/UNAM IG200824. Francisco A. Reza-Gonzalez to CONAHCyT for scholarship no. CVU: 1100683.

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# Optically addressability of the arylnitrene spin triplet

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The development of quantum interfaces to control the interaction between spins and photons is essential to accomplish an efficient implementation of devices for quantum networks and quantum information. Optically addressable spin systems (OASSs)[1] are promising candidates that allow establishing quantum bits (qubits) initialization through spectroscopic means. The nitrogen-vacancy ($NV^-$) centres in diamond[2] have represented a first valid strategy to accomplish this goal, but their solid-state nature faces challenges in terms of scalability and tunability.

In this work[3], we explore from a computational perspective arylnitrene systems (Fig. 1) to assess their potential application as molecular alternatives to $NV^-$ centres. Specifically, we employed high-level quantum chemistry methodologies to study the electronic structure and the spin conversion processes characterizing these systems. The resulting triplet ground state of the pristine compound and the vibronically assisted spin-polarized intersystem crossing paths enable an efficient spin initialization. Furthermore, targeted chemical modifications allowed increasing the photoluminescence properties of the arylnitrene systems, facilitating the optical read-out process and making them promising candidates for molecular qubits.

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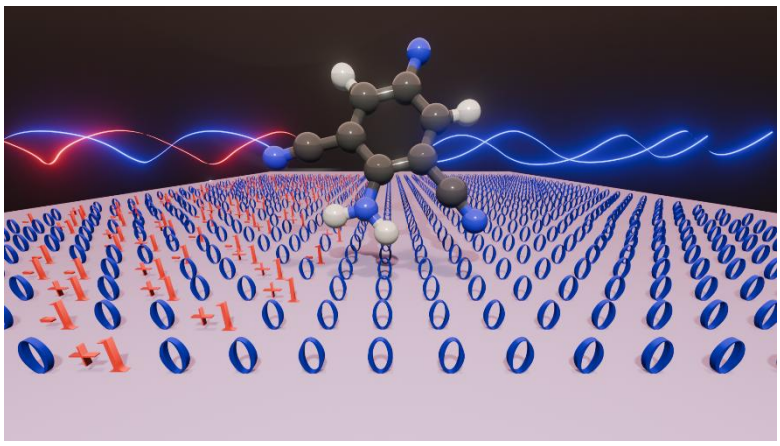

Figure 1. Arylnitrene derivative studied in this work.

**Funding:** Programa Mujer y Ciencia 2025

**Acknowledgement:** (DIPC) Computer Center

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# Two-photon release of a radical species and generation of a highly fluorescent probe

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**Abstract**

The control of molecular events with a spatial precision of the order a single femtoliter requires a non-linear excitation step to focus these processes at a variable depth. We have previously reported the synthesis and general properties of a system which can release a radical fragment from a two-photon absorbing antenna based on a polymethinic chromophore [1]. In this contribution we describe a new synthetic process that improves the yield of this antenna-releasable group by a factor of 10 which was required for further studies of this system. We also describe the two-photon release properties and general behavior of the non-linear photo-detachment in different media.

Specifically, the molecule AntOIR in Figure 1 releases a radical fragment (AntO·) after two-photon excitation with 850 nm pulses (two-photon cross section maximum of more than 2000 GM units). The AntO· fragment can rapidly abstracts a hydrogen atom from its environment to generate a highly emissive chromophore AntOH. Both the highly localized release of a pair of radical species and the ability of one of the fragments to generate a highly emissive fluorophore can have interesting applications for biological systems regarding potential photodynamic therapies. Also, the highly controlled localization of fluorophores within cells can serve to follow biological pathways. We include studies of several tissues and live cells where a femtosecond pulse train induces the aforementioned release, which's effects are followed by high resolution fluorescence microscopies. The latter required new instrumental designs for microscopic control and observation which combines two-photon release followed immediately by single cell observations. The ability to precisely control the release of radicals and fluorophores in living cells opens new possibilities for studying dynamic cellular processes in real-time with minimized photonic damage.

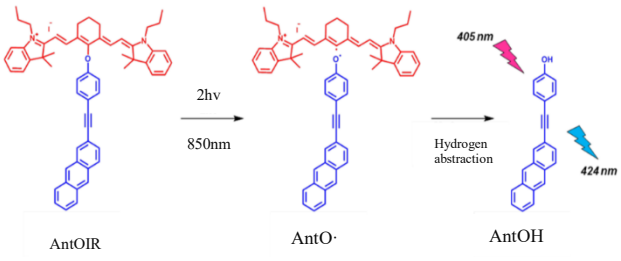


Figure 1. Schematic representation of the photodissociation of the AntO· fragment from the AntOIR molecule after two-photon excitation.

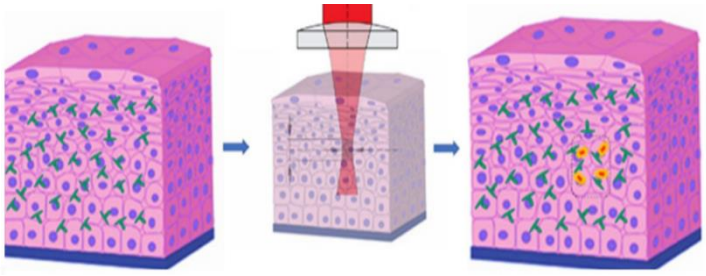

Figure 2. Biphotonic activation irradiation by a 860 nm femtosecond pulse train at a variable depth.

**Funding:** CONAHCyT-México grant Ciencia de Frontera 2019-51496 and PAPIIT/DGAPA/ UNAM IG200824

**Acknowledgement:** CONAHCyT-México grant Ciencia de Frontera 2019-51496 and PAPIIT/DGAPA/UNAM IG200824.

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# Unraveling the AIE Mechanism in Red-Emitting Fluorophores: Stereoselective Synthesis and Physicochemical Studies

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While nowadays ubiquitous in a variety of optoelectronic applications, fluorophores displaying emission exclusively in solid state and in particular those constructed around the tetraphenylethylene (TPE) core suffer severe limitations. In particular, although it has been reported in many instances[1,2] that the stereoconfiguration around the central double bond may severely impact the solid state luminescence, a stereoselective synthesis of extended TPE cores remains challenging, and separation of diastereoisomer mixtures is generally tedious.

Thanks to a stereoselective McMurry coupling[3] followed by a click cycloaddition, we introduce a new chemical group to induce AIE. Although closely related to TPE, the new molecules can easily be synthesized in a pure (E) configuration with 100% stereoselectivity. Comparison of the spectroscopic properties with the (Z) isomer, obtained by photoisomerization, revealed important difference in solid state emission efficiency ($\Phi_E$=14%, $\Phi_z$=54%) underlining the importance of the stereochemistry in the AIE properties. Through a combined set of spectroscopic experiments, crystal structure resolution and computational modeling, we also show that the photophysical basis of these AIE properties is due to the flexibility at the excited state around the central C=C bond, allowing fast relaxation to the ground state via a conical intersection in solution, which is blocked in the solid.

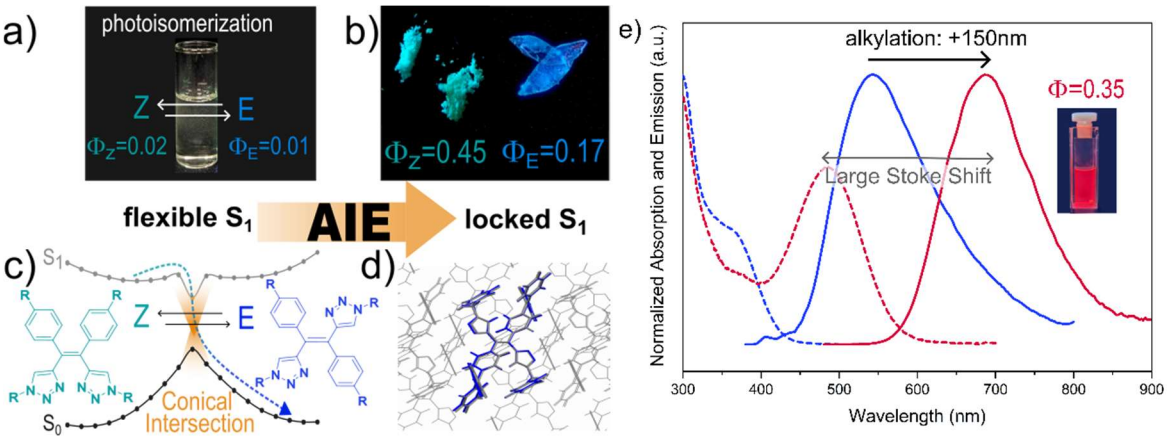


Figure 1. a) Emission quantum yield (QY) in solution, b) QY in solid, c) Potential energy surface scan around the central carbon double bond ((TD)-DFT), d) Superposition of the optimized $S_0$ (grey) and $S_1$ (blue) structures in (E)-isomer crystal (periodic (TD)-DFT) e) Absorption (dashed line) and emission spectra (solid line) of non-alkylated (blue) and alkylated (red) compound. QY for nanoprecipitate in water.

By alkylation of the introduced triazole moieties, a large red-shift in emission is obtained, which can be further tuned, owing to counterion exchange, to reach a solid state emission maxima of 700 nm. The resulting fluorescent organic nanoparticules constitute a very valuable platform for *in vivo* imaging.

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# Luminescent cycloplatinated(II)-thiolate complex stabilized by interaction with a borane compound

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One of the notable classes of organoplatinum(II) compounds with remarkable photophysical properties is cycloplatinated(II) complexes, which can be electrically and structurally modified with the help of supporting ligands.[1] Thiolates, for instance, are crucial in the ability to tune the steric and electronic characteristics of transition metal complexes as supporting ligands by coupling strong σ-donating. This would increase the metal center's electron-richness (based on the aromatic ring's ability to donate electrons when coordinated to the S atom) and, in turn, enhance the complexes' luminescence properties by raising the energy of the d-d* states.[2] One or more covalent changes to the supporting ligand environment typically cause a complex to change, necessitating the synthesis of the changed ligand and complex from scratch. Beyond that, however, postsynthetic addition is a synthetic technique that enhances covalent modification and adjusts the optical and electrochemical characteristics of cycloplatinated(II) complexes by changing Lewis acid-base interactions. Compared to the standard covalent substituent modification, this tuning procedure is quicker and more methodical.[3]

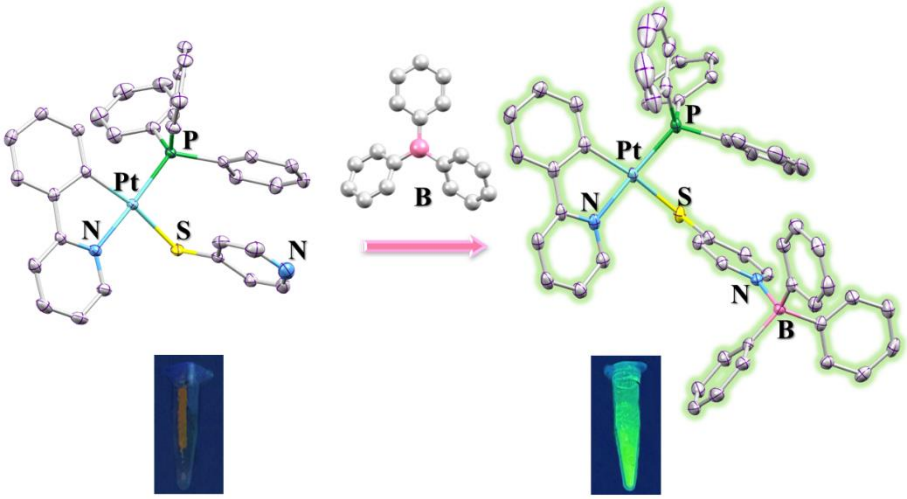


**Figure 1.** ORTEP view of the molecular structures of Pt(II) complexes and their emission under a UV lamp (down).

In this study, we aim to illustrate how borane-pyridine thiolate Lewis acid-base interactions in the secondary coordination sphere can affect the photophysical characteristics of cycloplatinated(II) complexes that contain ppy (2-phenylpyridine) as a cyclometalated ligand. The general formula for this complex is [Pt(ppy)($\kappa^1$-S-Spy)($PPh_3$)], where Spy = 4-pyridine thiolate. The compound was found mainly by NMR, HR ESI-MS, and X-ray crystallography after being titrated with $BPh_3$ as a Lewis acid at room temperature. Photophysical investigations were conducted using UV-Vis and photoluminescence spectroscopies (Fig. 1.), and DFT (density functional theory) calculations were used in support of the results.

**Funding:** Iran National Science Foundation (Grant Number: 99023593)

**Acknowledgement:** The Institute for Advanced Studies in Basic Sciences (IASBS) Research Council is gratefully acknowledged.

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# Ultrafast charge transfer photodynamics in polymeric materials

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Novel polymeric materials that display tunable aggregation-induced emission using trough-space charge transfer (TSCT) polymeric materials had been developed recently[1,2]. These polymers and copolymers are constituted by a single naphthalene diimide (NDI) unit as an acceptor, polystyrene (PS) chains as primary donor ($D_1$), and secondary stronger-donor chains ($D_2$) (Fig. 1.a). Theoretical studies show that the emission color tunability originated from the structurally dependent TSCT energies, but experimental evidence was still missing. Hence, in this work we provide an in-depth study of the photodynamics of CT processes in these materials.

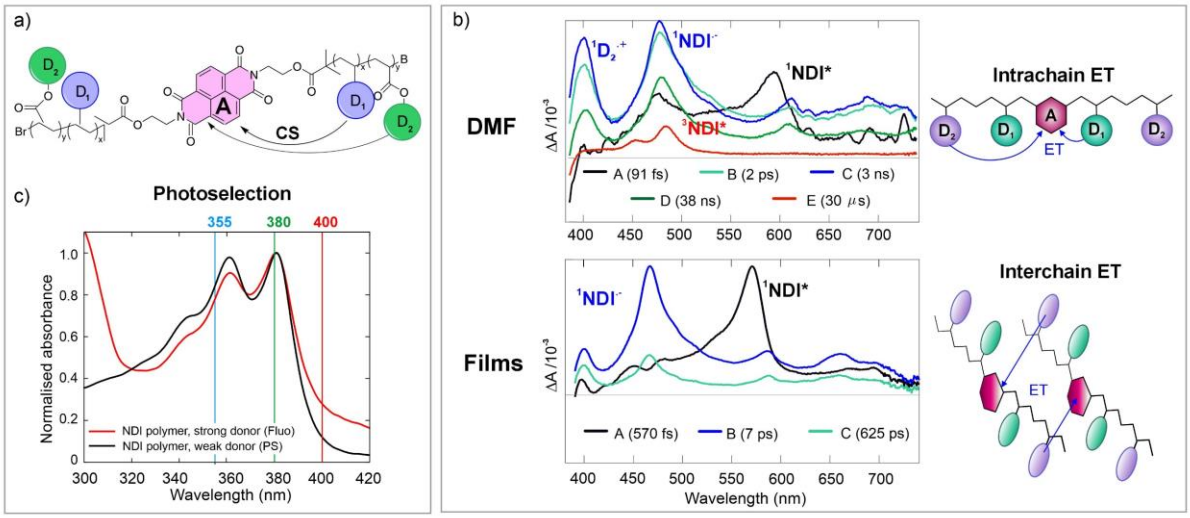


Figure 1. Charge transfer photodynamics in NDI-based copolymers a) General structure b) Evolution-associated spectra from a sequential global analysis of the photodynamics of the copolymer with $D_2$= biphenyl in DMF solution and in films. c) Steady state electronic absorption spectra of the copolymer with $D_2$= Fluorene (Fluo) vs. the polymer with only $D_1$ (PS), showing selected wavelengths for photoselection.

We used transient absorption spectroscopy to demonstrate the sub-picosecond electron transfer between the NDI and $D_1$ in solution and to both $D_1$ and $D_2$ in films, *via* the direct observation of the spectral signatures of the NDI radical anion and the radical cation at $D_2$. While in solution the ultrafast recombination points out to intrachain charge transfer, the slower recombination of the charge-separated state (CSS) in the solid suggests that interchain CT is dominant in this case (Fig. 1.b). The recombination of the CSS is found to occur both through emission and to the population of the triplet manifold of NDI *via* a spin-orbit charge-transfer intersystem crossing mechanism. Additionally, we show that it is possible to selectively populate the CSS when exciting at the red-edge absorption of the NDI (Fig. 1.c). Our results allow for a better understanding of the underlying CT mechanisms in these polymers, and pave the way to the tailored design of new emissive polymer materials.

**Acknowledgement:** We thank the Swiss National Science Foundation (SNSF) and the University of Geneva for supporting this research.

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# Supramolecular light–induced multi–spin systems as qubit candidates

Philipp Thielert[1], Ivan V. Khariushin[2], Elisa Zöllner[1], Maximilian Mayländer[1], Theresia Quintes[1], Andreas Vargas Jentzsch[2], Sabine Richert[1].

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Supramolecular chemistry utilizes intermolecular interactions for the design of highly ordered complex structures or molecular devices, which is especially valuable in nanotechnology and could potentially be exploited for quantum information science (QIS).[1]

Assemblies consisting of an organic chromophore, a linker and a radical, are excellent model systems to investigate structure property relationships in light–induced multi–spin systems, which recently receive increased attention due to their exceptional properties and their potential for applications in molecular spintronics, including QIS.[2-4] Light excitation generates a triplet state at the chromophore site, which may then interact with the stable organic radical, leading to spin mixing and the formation of high–spin (quartet) states.[2]

This study, combines the two fields of supramolecular chemistry and molecular spintronics by exploring the properties of hydrogen-bonded chromophore–radical pairs, shown in Fig. 1a. Titration experiments followed by UV-Vis spectroscopy verify 1:1 binding with high association. The transient EPR data confirm quartet state formation and thereby efficient spin mixing through the triple-hydrogen-bonding motif. The results demonstrate that supramolecular chemistry may be exploited for exploring, developing and scaling up materials for QIS.[1]

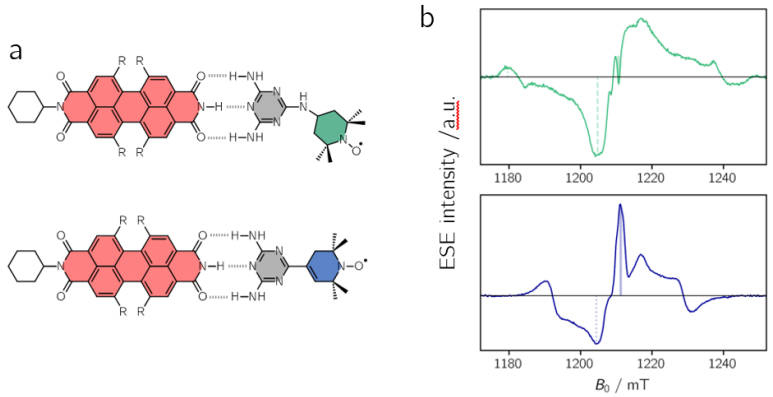


Figure 1. a) Structures of the investigated hydrogen-bonded chromophore–radical pairs and b) their electron-spin-echo (ESE) detected field-sweep EPR spectra.

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Agence Nationale de la Recherche (25-CE92-0009-01)

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# Synergetic Photoinduced Electron Transfer and triplet-triplet annihilation upconversion for excitation-dependent $K^+$ detection

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Triplet-triplet annihilation photon upconversion (TTA-UC) combines two low-energy photons into one of higher energy, offering highly selective detection by minimizing scattering and autofluorescence. Given the biological significance of ions, quantitative, all-optical flow sensing is highly desirable. In this work, we develop an anthracene-crown ether molecule (Fig 1a) with dual functionality as a TTA-UC emitter and a photoinduced electron transfer (PET) based ion sensor. This integration enables $K^+$ detection at biologically relevant concentrations. Notably, we observe a difference between the ion binding constants of electronic ground and excited states. Due to the similar timescale of triplet lifetimes and the ion dissociation from the crown ether, the observed equilibrium constant is significantly influenced by the excitation conditions (Fig. 1b), highlighting the need careful analysis of these factors. Finally, we demonstrate upconversion sensing in a microfluidic device (Fig. 1c) achieving scattering-free signals and predictable binding constants in controlled flow conditions (Fig. 1d). This work provides a thorough evaluation of TTA-UC-based ion sensing, from fundamental mechanisms to application, paving the way for quantitative, all-optical flow sensing of biologically relevant ions.

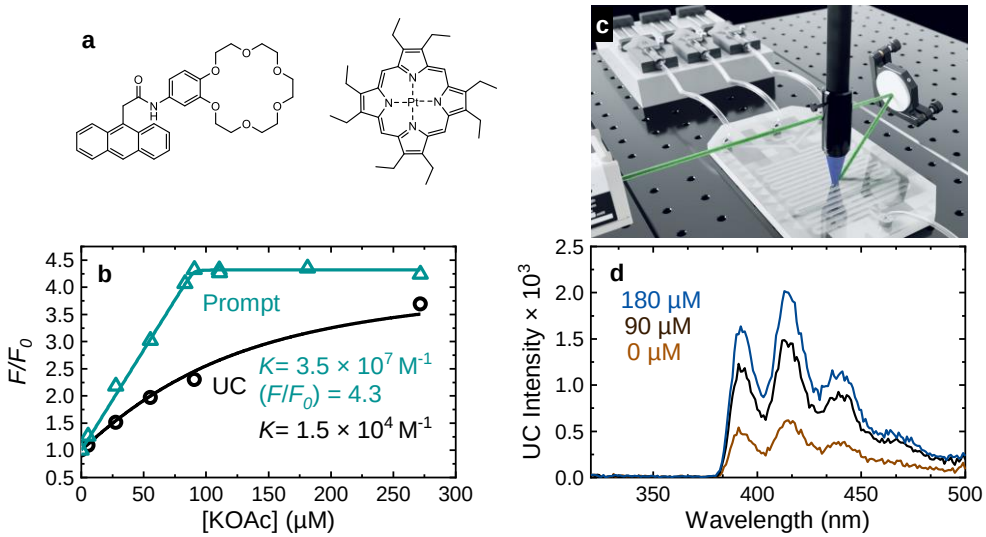


Figure 1. a) Molecular structures of the emitter, and the sensitizer Pt(II)octaethylporphyrine (PtOEP) in the TTA-UC system. b) Relative integrated emission, $F/F_0$ from prompt fluorescence (teal, 350 nm excitation) and upconversion (black, 532 nm excitation) in a 1:1 DCM:methanol solution of 90 μM emitter and 5 μM sensitizer at different concentrations of potassium acetate (KOAc) at high excitation intensity (~5.3 W/cm$^2$, or about 6 times the threshold intensity). c) Illustration of the microfluidic setup with CAD files of optical component from Edmund Optics and ThorLabs websites.[1,2] d) TTA-UC emission spectrum obtained with the microfluidic setup.

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# Pattern of Cyanines Controls Photopolymerization via Activated Photoinduced Electron Transfer between 700-1100nm

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A series of cyanine dyes were selected to explore the relation between their structural pattern and performance in the light-driven systems as photosensitizers in the NIR. They comprise distinct terminal groups, namely benzoindolium, benzo[*e*]indolium, benzo[*g*]indolium, and benzo[*c,d*]indolium moieties with distinct connecting middle chains. Their photophysical properties such as fluorescence decay time and quantum yield as well as photochemical performance for photobleaching and initiation of radical/cationic photopolymerization were investigated considering their distinct structures. The iodonium salt served as coinitiator to react with the excited state of the cyanine sensitizer based on an activated photoinduced electron transfer (**PET**). Variation of connecting methine chain and terminal groups resulted in distinguished reactivity to generate initiating moieties such free radicals and conjugate acid, which enabled to initiate conventional radical and cationic photopolymerization, respectively. Photophysical data obtained by TCSPC study in the NIR indicated the relation between the structure and the decay time (between 25 ps-1.5 ns) of excited states (radiative deactivation) and the contribution of nonradiative deactivation resulting in generation of additional heat, which is needed within activated **PET**. This system worked well with high-power LED light sources emitting up to 1050 nm[1,2]. Electrochemical studies complement the pattern of activated **PET**, which mostly requested to expose with a high intensity NIR light source; that is a high-power LED.
The terminal moieties of the cyanines surprisingly demonstrated strong impact on the performance of radiative and nonradiative deactivation upon exposure. Here, benzo[*c,d*]indolium derivatives showed high efficient non-radiative deactivation and therefore efficient conversion of heat with respect to the absorbed light quants. The technology of high-intensity NIR-LED prototypes also pushed the boundaries of applications in the field of photochemistry under **PET** reaction. The utilization of such light source successfully started this reaction while the low-power devices failed, except those barbiturate group in the *meso*-position. The combination of cyanines and iodonium salt as initiator system significantly initiated free radical photopolymerization of acrylates of **UDMA**, **TPGDA** and **TMPTA**[3]. Furthermore, cyanines carrying heptamethine and nonamethine also initiated the photo-induced crosslinking of cationic monomers with efficient reactivity and solidification of expoxy-based sol-gels comprising nanoparticles from silanization reaction. These obtained photopolymers exhibited higher $T_g$ than that of UV exposure samples.

In addition, the heat from nonradiative deactivation upon excitation in the system served as a novel tool for physical drying in water-based coating dispersions functioned as a replacement of oven technology[4]. These findings show the potential to design tailor-made materials on demand, also provide new insights into the reformation of high-energy consuming technologies to more environmentally friendly setups for the applications in practice following a demand of the society.

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# Non-electric bias hydrogen peroxide production by visible light in a photoelectrochemical cell using an organic polymer photocathode

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Hydrogen peroxide ($H_2O_2$) is a clean oxidant that emits only water as a by-product and is widely used in organic synthesis, medical disinfection, and wastewater treatment. Currently, $H_2O_2$ is mainly manufactured by the anthraquinone method, which is energy-intensive and non-ecofriendly. Photoelectrochemical two-electron oxygen reduction reaction (ORR) using a photocathode has attracted attention as an alternative to produce $H_2O_2$ in an environmentally benign way. However, there are only a few reports of efficient photocathodes that can selectively produce $H_2O_2$.[1,2] Herein, we report an organic polymer photocathode consisting of a donor-acceptor type covalent triazine framework (CTF) for $H_2O_2$ production with nearly 100% Faradaic efficiency in aqueous media. Furthermore, a photoelectrochemical cell using the CTF photocathode and an inorganic photoanode enabled bias-free solar $H_2O_2$ production ($O_2 + 2H_2O \rightarrow 2H_2O_2$).

The CTF photocathode was prepared using an in-situ polymerization method. A mesoporous ITO electrode was immersed in a DMSO solution containing monomers and heated for polymerization. After cooling to room temperature, the substrate was washed with DMSO and water, and then dried under air to give a CTF modified electrode. Under visible light irradiation (100 mW $cm^{-2}$, $\lambda$ > 390 nm), the CTF photocathode showed satisfactory ORR performance with a high onset potential of ~1.3 V vs. RHE in a wide pH range. Bulk photoelectrolysis at 1.05 V in $O_2$-saturated phosphate buffer solutions at pH 3 and 7 provided steady photocurrent densities of -0.14 and -0.06 mA $cm^{-2}$ respectively, with nearly 100% Faradaic efficiency for $H_2O_2$ production. A bias-free solar $H_2O_2$ production system was constructed by connecting the CTF photocathode with a $BiVO_4$ photoanode in neutral media under parallel illumination. The system generated a stable photocurrent with stoichiometric evolution of $H_2O_2$ and $O_2$.

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# Efficient Organic Long-Persistent Luminescence Enabled by Thermally Activated Delayed Fluorescence Molecule

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Long-persistent luminescence (LPL) is a phenomenon where emission persists long after the removal of an excitation source, enabled by the storage and gradual release of charge carriers trapped within a host matrix. Although inorganic phosphors have traditionally dominated LPL research and applications, organic LPL (OLPL) materials made by mixing donor and acceptor molecules in unequal ratios are gaining increasing attention. Their advantages, such as flexible molecular design, mechanical softness, and compatibility with solution processing, suggest their potential for use in various luminescent applications[1,2].

The OLPL mechanism typically involves three key steps (Fig. 1a): (i) upon photoexcitation, a donor/acceptor pair forms an intermolecular charge transfer excited state ($CT_{D/A}$); (ii) the $CT_{D/A}$ excited state undergoes charge separation (CS), during which electrons and holes are spatially separated and trapped by the surrounding host matrix or intrinsic traps; (iii) after sufficient trapping time, charge recombination occurs, leading to delayed luminescence. In conventional OLPL systems, the emission mainly arises from the $CT_{D/A}$ excited state (Fig. 1b), which often suffers from a low photoluminescence quantum yield (PLQY) and broad emission profiles. Furthermore, achieving blue OLPL remains challenging, with most systems showing green to red emissions.

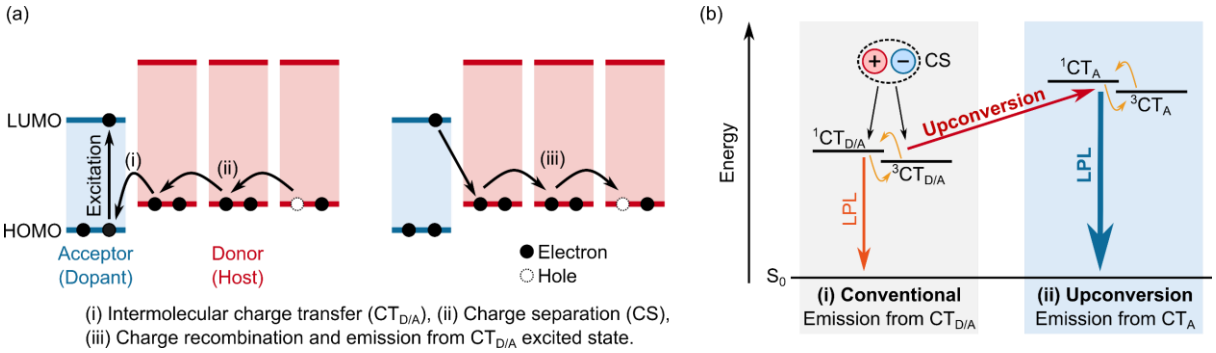


Figure 1. a) Emission mechanism of OLPL, b) Jablonski diagram of (i) conventional OLPL system and (ii) upconversion OLPL system. Superscripts indicate spin multiplicity of the excited states: $^1$ = singlet, $^3$ = triplet.

In this study, we propose a novel OLPL system employing a thermally activated delayed fluorescence (TADF) molecule. By utilizing TADF material as an acceptor and dispersing it within a donor matrix, charge separation and recombination can occur via the $CT_{D/A}$ excited state, with the final emission site upconverted from the $CT_{D/A}$ excited state to the intramolecular charge transfer excited state of the TADF molecule ($CT_A$). This approach enables the simultaneous achievement of high charge separation efficiency and high PLQY. By mixing trifluoromethyl-substituted 4CzIPN with semiconducting organic host matrices, we successfully achieved an efficient blue OLPL with a higher PLQY compared to conventional $CT_{D/A}$-based systems. Furthermore, temperature-dependent LPL spectroscopy revealed that the upconversion from the $CT_{D/A}$ to the $CT_A$ excited states is promoted by thermal energy.

**Funding:** Japan Science and Technology Agency (JST) FOREST project (grant number JPMJFR201H); JSPS KAKENHI (grant number 21H02020 and 24K01575); and OIST Proof of Concept program.

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# Design of efficient, NIR-luminescent Pd/Pt(0) complexes

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At the doorstep to the near infrared region (NIR), the energy gap law greets.[1] It states that the nonradiative decay rate knr increases exponentially with decreasing energy difference. Unfortunately, the radiative rate shrinks cubically with the energy gap. Additionally, non-adiabatic coupling and direct spin—orbit coupling (SOC) can affect knr. Efficient luminescence requires thus a) weak direct coupling to the ground state S0, but b) sizeable transition dipole moments to achieve sufficient radiative rates.

A reliable prediction of NIR luminescent molecules requires a quantitative description of the electronic state landscape, for which we use the DFT/MRCI method.[2] It combines the description of dynamic correlation via density functional theory (DFT) and static correlation via the multireference configuration interaction (MRCI) component. SOC is described in SOCI, which treats spin-free and spin-dependant operators on the same footing.[3]

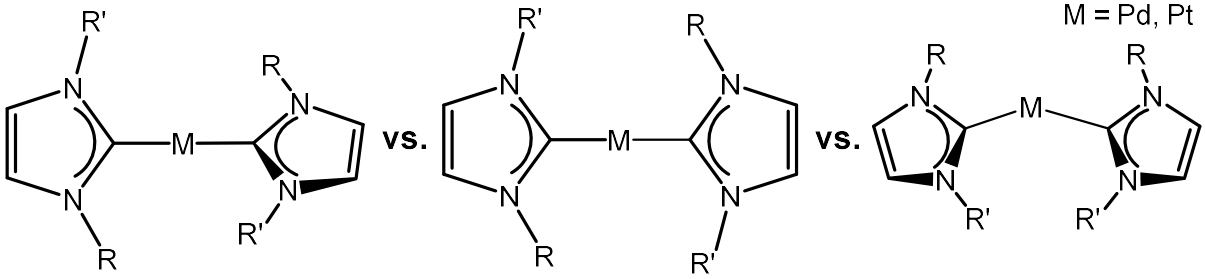


Figure 1: Different conformers of linear bis-carbene Pd-complexes.

Counterintuitively, metal to ligand charge transfer (MLCT) states of neutral d10-complexes may fulfil all listed requirements, provided that the underlying complex is designed well. Linear bis-carbene complexes can possess low direct coupling to S0 and sizeable radiation rates, but at first sight, their linearity conflicts with low-lying carbene orbitals and NIR luminescent states.[4] Careful construction of the employed carbenes can overcome the challenges and enable efficient IR-luminescence. Literature and own results support the underlying theoretical model for the design guide lines.[5,6]

**Funding:** Deutsche Forschungsgemeinschaft (SPP 2102: LCRMC)

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# Photophysical Properties of a TADF Emitter in Complex Environments

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Thermally activated delayed fluorescence (TADF) emitters are crucial for highly efficient organic light-emitting diodes OLEDs, because they boost light emission by converting triplet excitons into fluorescent singlet excitons without relying on heavy metals. The efficiency of TADF emitters is largely determined by the energy gap between singlet ($S_1$) and triplet ($T_1$) states ($\Delta E_{ST}$), as well as key factors like oscillator strength and spin-orbit coupling.[1]

Furthermore, the accurate treatment of the chemical surrounding is essential to predict their photophysical behavior in optoelectronic applications. In this study, we employ a hybrid computational approach[2] combining quantum mechanics/molecular mechanics (QM/MM) with density functional theory (DFT), time-dependent (TDDFT), and multireference configuration interaction (DFT/MRCI[3]) to investigate the excited-state behavior of a well-known TADF emitter (DiKTA[4]) in various solvents (acetonitrile, cyclohexane, water) and polymethylmethacrylate (PMMA) as polymer matrix (Fig. 1).

To account for environmental effects on molecular geometries, we perform QM/MM optimizations using DFT and TDDFT to obtain realistic excited-state conformations.[2] The photophysical properties are subsequently calculated with DFT/MRCI to accurately compute the electronic excitation energies.[3] By applying this method to different environments, we quantify the impact of polarity and rigidity on the above mentioned key TADF parameters.

This computational framework can assist in tailoring TADF emitters for specific applications, guiding experimental efforts in material selection for organic light-emitting diodes OLEDs and other optoelectronic devices. Our findings highlight the necessity of incorporating environmental effects in theoretical models to achieve accurate predictions of photophysical behavior in real-world applications.

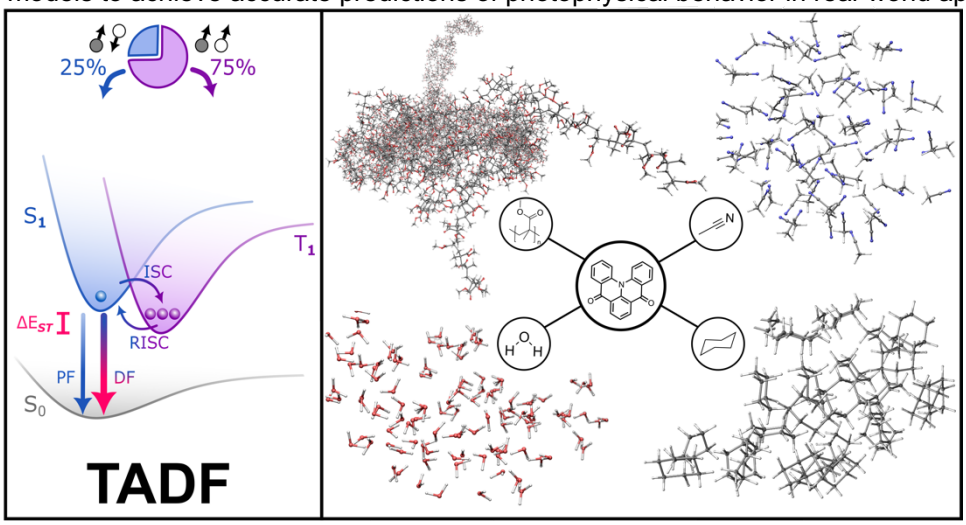


Figure 1. Characterization of the TADF emitter DiKTA in complex environments like acetonitrile, cyclohexane, water and PMMA by using QM/MM and DFT/MRCI calculations. On the left, the schematic approach of the TADF mechanism.

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**Acknowledgement:** The authors cordially thank the DFG and the computational infrastructure and support, which are provided by the Centre for Information and Media Technology at Heinrich Heine University Düsseldorf.

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# Optically addressable organic radicals for quantum information and photochemical upconversion applications: A computational perspective.

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Organic open-shell materials have demonstrated over the last years their capability to be used in a broad range of applications going from organic spintronics, quantum information and organic light-emitting diodes (OLEDs). Recent efforts considering a stable tris(2,4,6-trichlorophenyl)methyl radical (TTM) decorated with different classes of electron-donating groups have allowed to design new emitters for OLEDs alleviating the spin statistics issue encountered with closed-shell emitters that limits the internal quantum efficiency of OLEDs to 25 percents because light emission only takes place from the lower-lying singlet state while triplets are dark. Here, we will discuss the case of TTM-carbazole (TTM-Cz based radicals decorated with either an anthracene (An) or a derivative of it, diphenyl-An (DPA) that display optical features making them prone for applications in the fields of quantum information and photochemical upconversion. Especially, we will rationalize, based on computational modeling, how:

- Upon photoexciation of a TTM-Cz-An radical (see Fig. 1a), a spin-allowed energy transfer process, occurring on the picosecond timescale can generate a low-spin trip-doublet state (a locally triplet excitation on the An with the radical spin in an overall spin doublet state) that subsequently converts into a high-spin quartet state that can be coherently addressed and that can serve as molecular spin qudit for quantum information applications.
- Triplet-triplet annihilation (TTA) can occur in solution containing a TTM-Cz-DPA triplet sensitizer and a DPA annihilator (see Fig. 1b) and how the Dexter-type triplet energy transfer from the sensitizer to the annihilator is ruled out by the formation of the trip-doublet state upon fast energy transfer opening perspectives for biomaging applications.

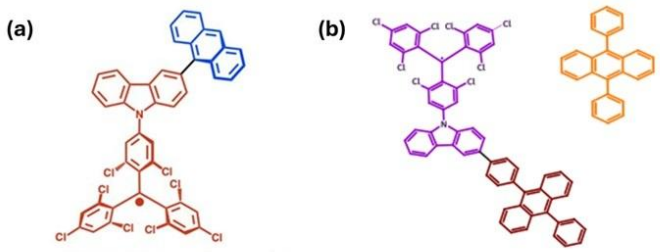


Figure 1. Chemical structures of **(a)** TTM-1Cz-An radical for quantum information application and **(b)** TTM-1Cz-DPA triplet sensitizer and DPA annihilator for bioimaging applications.

**Acknowledgement:** This work was funded by the Fonds de la Recherche Scientifique-FNRS under Grant n°T.0226.24 (OMLED). Computational resources were also provided by the ‘‘Consortium des Équipements de Calcul Intensif’’ (CÉCI), funded by the ‘‘Fonds de la Recherche Scientifiques de Belgique’’ (FRS-FNRS) under Grant No. 2.5020.11.

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# Enhancing RASCI Excitation Energy Accuracy with Second-Order Perturbation Theory

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Multiconfigurational (MC) wave function methods effectively describe large regions of the molecular potential surface, especially in degenerate systems[1]. Unfortunately, in most cases, relative energies obtained at this level of theory are not sufficiently accurate due to the lack of dynamic correlation. To address this, dynamic correlation is typically added perturbatively. The application of perturbative approaches to MC methods is often limited by the intrinsic computational cost derived from the optimization of the reference orbitals[2]. Alternatively, restricted active space configuration interaction (RASCI(h,p)) method, which doesn't include orbital optimization, significantly lowers computational costs. RASCI(h,p) divides orbital space into three subsets: RAS1 (doubly occupied), RAS2 (electrons distributed in occupied/unoccupied), and RAS3 (unoccupied) [Fig.1]. This approach introduces most of the static correlation of the molecular system, but it does not properly account for dynamic correlation[3].

To overcome this limitation, we introduce the second order MC perturbation theory scheme (RASCI(2)), which improves the performance of RASCI(h,p) in the evaluation of vertical transition energies by adding contributions from higher-order hole/particle excitations[3]. In some cases, this approach might be affected by the presence of intruder states, causing energy singularities that reduce performance. To address this, level shifts are applied in the second-order energy correction. Applying RASCI(2) to medium-sized organic molecules, we find that it produces excitation energies comparable to CASPT2 and NEVPT2. Thus, we conclude that RASCI(2) is a promising method for strong-correlation effects in complex molecular systems.

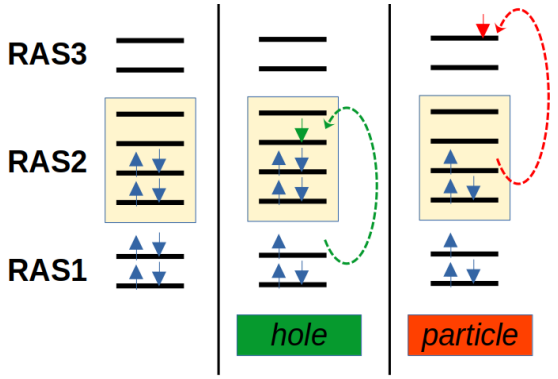


Figure 1. Schematic representation of the RASCI orbital partitioning into RAS1, RAS2, and RAS3 subspaces.

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**Acknowledgement:** https://molecular-electronic-structure-group.github.io/team/

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# Deciphering carbon–sulfur rotational distribution in a crystalline host for enhanced red persistent organic phosphorescence

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Persistent room-temperature phosphorescence (*p*RTP) materials are a promising technology for bioimaging without detecting auto-fluorescence. Although various studies on the development of *p*RTP materials suitable for bioimaging have been reported, achieving both red-shifted RTP and high RTP quantum yield ($\Phi_p$) remains a challenge[1,2]. Here, we report enhanced red *p*RTP emission from a conjugated chromophore directly substituted with a sulfur element in crystalline host. By comparing experimental results with quantum chemical calculations, we revealed molecular geometry distribution of the *p*RTP emitter in the crystalline host.

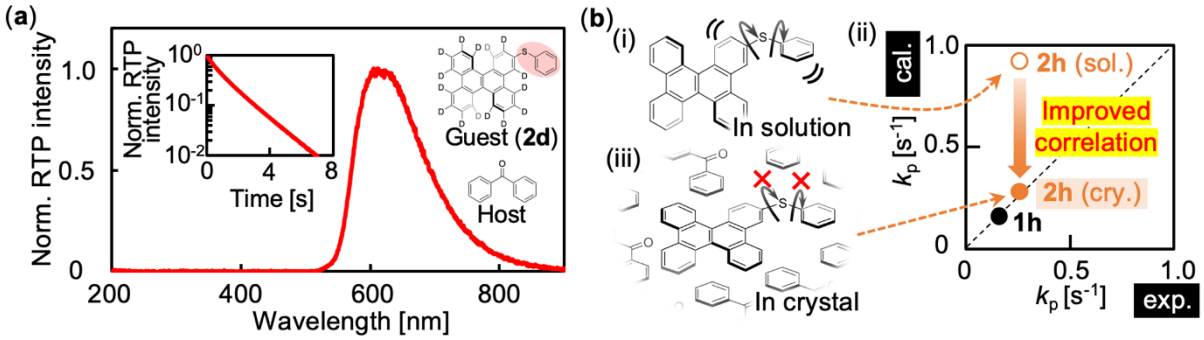


Figure 1. a) RTP spectra and decay (inset) characteristics of **2d** dispersed in crystalline benzophenone host. b) (i) The C–S bond of **2h** rotates freely as in solution. (ii) The relationship between experimental and calculated $k_p$ values for **1h** and **2h**. (iii) The rotation of the C–S bond in **2h** is confined in crystalline host.

Specifically, dibenzo[*g*,*p*]chrysene (**1h**) was used as a starting material, and its phenylthio-substituted derivatives (**2h** and deuterated **2d**) were synthesized as guest chromophores. Each of the guests was dispersed into crystalline benzophenone host to form films showing red *p*RTP. Guests **2d** showed a $\Phi_p$ of 29% and a long lifetime of 1.4 s (Fig. 1a). Undeuterated form of **2d** (**2h**) had $\Phi_p$ = 12% which was 1.6 times compared with that of **1h**. The improvement of $\Phi_p$ of **2h** is due to enhancement of the phosphorescence rate constant ($k_p$). Since **2h** has a flexible C–S bond, it is expected to adopt various rotational conformations. Therefore, to investigate the reason for the enhanced $k_p$, we considered the rotational distribution. First, assuming that the C–S bond rotates freely as in solution, we rotated the bond every 10° and examined the total bonding energy and $k_p$ for each conformer (Fig. 1b(i)). Taking into account the conformational stability based on the total bonding energy, the averaged $k_p$ was calculated to be 0.92 $s^{-1}$. However, this value was significantly overestimated compared to the experimental $k_p$ of 0.26 $s^{-1}$ (Fig. 1b(ii)), suggesting that **2h** does not behave as if it rotates freely like in solution. In the crystalline host, the rotation of the C–S bond should be logically restricted due to steric hindrance between the host and the guest (Fig. 1b(iii)). Indeed, assuming this rotational restriction, we recalculated the average $k_p$, which resulted in a value of 0.26 $s^{-1}$. Compared with the unsubstituted compound **1h**, a good correlation between the experimental and calculated $k_p$ values was observed (Fig. 1b(ii)). These results indicate that the rotation of the C–S bond is restricted and the rotational distribution of **2h** is confined in the crystalline host[3].

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**Acknowledgement:** Fusion Oriented REsearch for disruptive Science and Technology (FOREST) scholarship

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# Theoretical Investigation on the Reverse Intersystem Crossing Mechanism in Inverted Singlet-Triplet Gap Molecules

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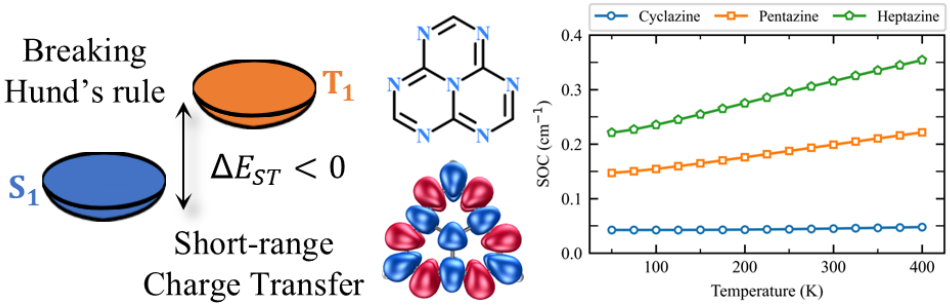
One of the major challenges in Organic Light Emitting Diodes (OLED) is related to the improvement of the internal quantum efficiency (IQE) in closed-shell fluorescent emitters since upon charge injection 75% of the generated excitons are dark triplets and thus limiting the IQE of up to 25%.[1] Several experimental and theoretical strategies have been designed over the years to harvest the lost triplet population. Among these strategies, inverted singlet-triplet gap materials (INVEST) have emerged as potential candidates as OLED emitters because their lowest singlet excited state ($S_1$) is energetically lower than their lowest triplet excited state ($T_1$), making the reverse intersystem crossing (rISC) from triplet to singlet manifolds an exothermetic path that can therefore potentially enhance the triplet-to-singlet conversion. The present work aims at understanding the excited state relaxation mechanisms from a theoretical point of view of three workhorse INVEST triangle-shaped compounds (cyclazine, pentazine, and heptazine). By doing so, the most relevant critical point structures (minima, conical intersection, etc) in different potentials energy surfaces (PES) were optimized using the RMS-CASPT2 and SCS-ADC(2) methods.[2] Our results indicate that the lower-lying singlet and triplet excited states have a short-range charge-transfer character (SRCT). In addition, only $S_1$ and $T_1$ state are involved in the ISC and rISC mechanisms since other high-lying excited states are much higher in energy. We also rationalize the experimentally-observed anti-Kasha emission of cyclazine,[3] which is a consequence of the high-energy conical intersection between the $S_2$ (the first bright state) and $S_1$ states, therefore precluding the nonradiative decay to the $S_1$ state. By including non-Condon effects within a linear vibronic coupling model, we identified which normal modes contribute to the increase of the spin-orbit coupling (SOC) and thus to the ISC and rISC mechanisms. Additionally, within the Herzberg Teller (HT) approximation, we rationalize which higher-lying singlet (triplets) are vibronically coupled with the lower-lying singlet (triplet), which helps us to better understand the magnitude of the electron-phonon coupling constants modulating the three components of the SOC.

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# Photocatalytic Water Splitting with Ta and Ti Doped 2D Niobate Perovskites

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Photocatalytic water splitting under sunlight using semiconductor materials offers a promising route toward sustainable energy production. Perovskite structures are particularly attractive due to their tunable bandgaps, flexible chemical compositions, and adaptable morphologies. Following the discovery of $TiO_2$'s photocatalytic activity[1], research expanded into perovskites like $SrTiO_3$[2]. In 1998, the exfoliation of layered perovskite oxides into single nanosheets was achieved[3], opening new possibilities for 2D semiconductor photocatalysts.

In this study, the effect of Ta and Ti doping at the B-site of the $KCa_2Nb_3O_{10}$ layered perovskite oxide structure was investigated. Ta doping is particularly noteworthy since layered structures containing Nb and Ta are known for their high photocatalytic activities. While tantalates exhibit superior charge separation properties, they are much more challenging to exfoliate compared to niobates. Ti doping was also explored to further tailor the electronic structure and optimize the photocatalytic response, as Ti is known to enhance photocatalytic activity through its role in adjusting the electronic band structure, as seen in titanates. By doping both Ta and Ti into the niobate structure, it is aimed to combine the desired properties of the B-site incorporated atoms.

The materials, $KCa_2Nb_2TaO_{10}$, $KCa_2NbTa_2O_{10}$, and $KCaLaNbTaTiO_{10}$, were synthesized via solid state reaction, followed by proton exchange to replace interlayer $K^+$ ions with protons, thereby enhancing photocatalytic activity through hydronium intercalation. Exfoliation into 2D nanosheets subsequently increased surface area and reduced charge recombination, further improving photocatalytic efficiency. Results indicate that pristine structures exhibit poor photocatalytic activity, however after protonation, Ta doped niobates exhibit significantly enhanced hydrogen evolution, 4-5 times of protonated $KCa_2Nb_3O_{10}$. Exfoliated Ta doped nanosheets show 3-5 times the photocatalytic activity of exfoliated $KCa_2Nb_3O_{10}$, producing up to 5.6 mmol $H_2$ per gram of catalyst.

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# Modular Solid-State Sono-Piezo-Photocatalysts for Efficient Hydrogen Peroxide Production

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An emerging strategy toward a more sustainable future is the implementation of multi-energy piezo-photocatalysis, defined as the integration of piezoelectric effects with semiconducting photocatalysts. [1–3] In these systems, piezoelectric polarization and the resulting piezo-potential facilitate the directional migration of photoinduced charge carriers. This process enhances charge separation and suppresses their recombination, a key deactivation pathway.[1,2] Recently developed piezo-photocatalysts include zinc oxide, bismuth oxides, and metal–organic frameworks.[2–4] Additionally, organic polymers such as PVDF and graphitic carbon nitride, are known piezo-photocatalysts, but only make up a small share of the literature, exhibiting considerable promise due to their modular architectures, which enable rational and tunable structural design.[2] Herein presented is an air-stable solid molecular catalyst (SMC), a molecularly defined organic polymer for metal-free piezo-photocatalysis.

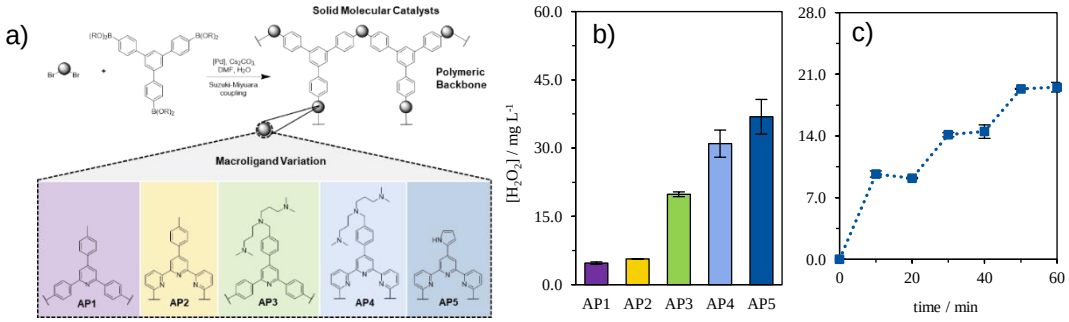


Figure 1 a) Synthesis and structures of SMCs. b) Comparison of the activity of five different SMCs at 45 kHz (0.5 mg mL$^{-1}$, room light, air atmosphere) c) ON-OFF experiments of ultrasonic with 45 kHz and AP5.

The aim of this study was to examine the impact of various structural motifs and backbone functionalities on piezo-photocatalytic hydrogen peroxide production. To this end, a series of five SMCs (Figure 1a) was synthesized. Using the procedure established by Wang *et al.*, the piezo-photocatalytic activity of these materials was evaluated. Our results demonstrate that all synthesized SMCs show piezo-photoresponsive behavior.[5] Through an extensive reaction set-up testing it could be figured out, that the proposed SMCs exhibits the highest efficiency with the simplest reaction set-up: air atmosphere, room light and an ultrasonic bath. Comparison of the structures and catalytic activities of SMCs AP1 with AP2, and AP3 with AP4, reveals that the terpyridine motif demonstrates higher activity than the diphenylpyridine motif. In addition, we could display that the functionalisation of the backbone increases the catalytic activity by at least fourfold (36.9 mg L$^{-1}$). To further demonstrate the potential of this reaction system, a series of switchable ON-OFF experiments were performed, showing that the concentration of hydrogen peroxide can be regulated using ultrasound as an external stimulus. In addition, the reaction works with biocompatible ultrasound, broadening its potential applications.[6]

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# Boosting photocatalytic performance of bismuth molybdate in DCF degradation by controlling the molar Bi to Mo synthesis ratio

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As a visible light responsive photocatalyst with a unique structure, the development of bismuth molybdate (BMO) materials for the efficient degradation of pollutants has drawn extensive attention. In this work, bismuth molybdate (BMO) materials with molar Bi/Mo precursor ratios between 1.1:1 and 3.0:1 was synthesized by a solvothermal method using ethylene glycol as solvent. The structural, textural and optical properties of the BMO materials were comprehensively characterized using complementary methods to investigate the effect of this ratio. The characterization results indicate the formation of a heterojunction between $Bi_2MoO_6$ and a newly formed Bi-rich phase when Bi/Mo ratios of 2.3:1 or higher are used. The photocatalytic properties of the synthesized BMO photocatalyst were evaluated by degrading the model drug diclofenac sodium (DCF) under irradiation of blue LED light ($\lambda max$ = 467 nm). Boosted DCF degradation and mineralization was observed when the Bi/Mo synthesis ratio was 2.3:1 or higher, with DCF degradation of 98% and mineralization of 80.0% achieved upon 3 hours of irradiation. The improved photocatalytic performance of the materials synthesized at a Bi/Mo ratio of 2.3:1 or higher is attributed to the intimate contact between $Bi_2MoO_6$ and the Bi-rich phase formed during the solvothermal process, which leads to improved charge transfer efficiency and suppressed photoelectron-hole recombination. Finally, the possible degradation pathway of DCF via BMO under blue LED light was proposed.

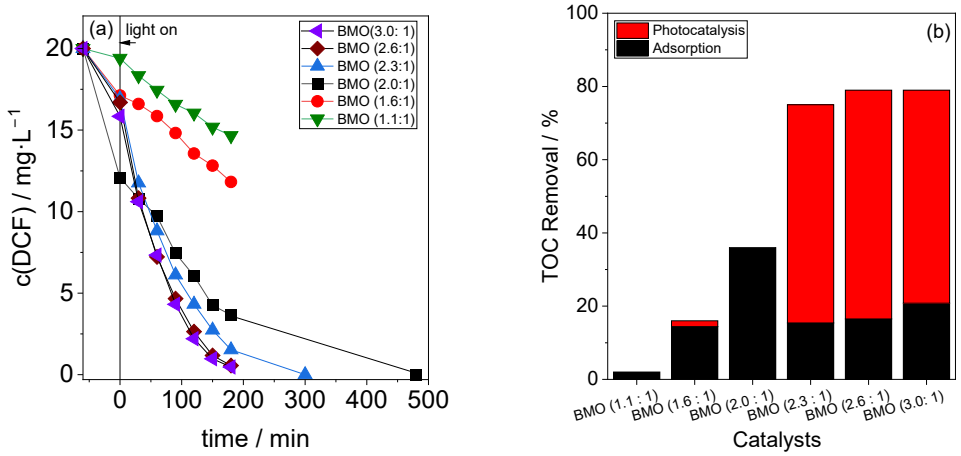


Figure 1. a) Plot of irradiation time versus DCF concentration, b) TOC removal using catalysts synthesized with different Bi/Mo ratios upon irradiation with blue LED light.

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# Copper(I) Isocyanide Complexes Featuring High Triplet Energies

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Complexes of copper(I), a more abundant metal than the precious metals traditionally used, have emerged as a suitable alternative in photochemistry and physics.[1] Tetrahedral copper(I) complexes are characterized by favorable electronic properties, such as long luminescence lifetimes as well as high quantum yields due to their closed $d^{10}$ subshell.[2, 3] $\alpha$-diimine ligands, like 1,10-phenantroline, marked the beginning of the copper(I) photochemistry and could be further improved through heteroleptic designs with electron-rich ligands like diphosphines.[4] Isocyanide ligands are underexplored in the context of photoactive copper(I) complexes and a recently reported copper(I) isocyanide complex featured a high triplet energy and luminescence in the solid state, but the photophysical investigation was incomplete.[5] This motivated us to synthesize and explore copper(I) isocyanide complexes, to understand their photophysical and photochemical properties in greater depth.

Herein we report three new copper(I) complexes exhibiting photoluminescence in solution at room temperature. By combing a phosphine ligand with a chelating isocyanide ligand, we obtained a complex exhibiting a triplet energy over 2.5 eV, comparable to other copper(I) isocyanide complexes, but with an excited-state lifetime of hundreds of nanoseconds.[5, 6] Using DFT calculations a deeper understanding of the nature of the excited state could be gathered. These favorable properties were exploited in a triplet-triplet energy transfer photocatalysis, where we showed the photo-isomerization of norbornadiene to quadricyclane as a proof-of-concept reaction. These results demonstrate the potential for the development of new photocatalysts with high triplet energies based on copper(I) and isocyanide ligands.

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# Design and Study of Luminescent Re(I) Complexes with Strong π-Accepting Anionic Ligands

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Although numerous families of phosphorescent transition metal complexes have been reported, many are cationic in nature and thus exhibit limited processability for device fabrication, particularly due to incompatibility with vacuum sublimation techniques. One strategy to overcome this limitation involves the coordination of anionic ligands to generate charge-neutral analogues. However, such modifications often result in decreased emission efficiency and reduced excited-state energy. We have previously demonstrated the coordination of strong-accepting anionic ligands, such as isocyanoborate ligands, to cationic triplet emitters to develop charge-neutral complexes with enhanced photophysical properties, including increased luminescent quantum yields and blue-shifted emission profile.[1] Several of these complexes exhibit excellent electrochemical and thermal stability, enabling their integration into electroluminescent devices fabricated via vacuum sublimation.[1a] In addition to emission properties, the use of these strong anionic isocyanoborate ligands has also been demonstrated to increase excited-state potentials, thereby facilitating the activation of inert functional groups.[2] In this context, we have developed a new series of luminescent Re(I) phenanthroline complexes with various strong π-accepting anionic ligands such as cyanopentafluorophosphate and its derivatives.

All these complexes have been characterized, including X-ray crystallography (Figure 1). A systematic comparison of their MLCT absorption and emission features as well as the carbonyl stretching frequencies observed in the IR or Raman spectroscopy, the π-acceptor strength of these anionic ligands are investigated. We anticipated that these ligands could be used for developing new classes of charge-neutral vacuum-sublimable emitters and photosensitizers with potential applications in various photocatalytic systems.

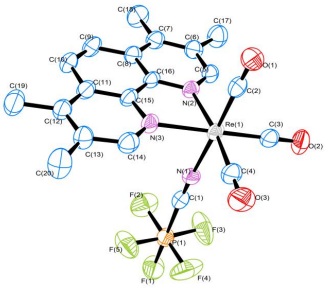

Figure 1. Perspective drawing of a tricarbonyl Re(I) phenanthroline complex with cyanopentafluorophosphate ligand.

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# A blessing and a curse: remote ligand functionalization modulates $^3$MLCT relaxation in group 6 tricarbonyl complexes

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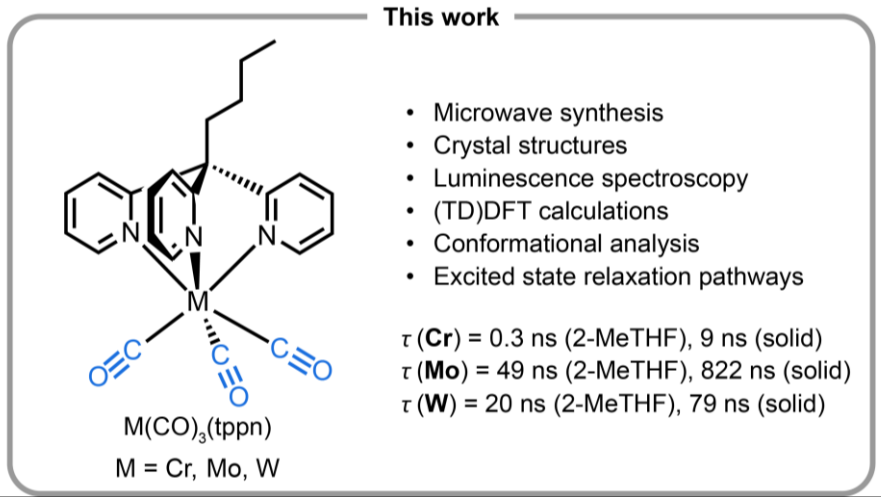
Photoactive complexes with chromium group metals Cr, Mo and W are interesting candidates for replacing established complexes with less abundant metals such as $[Ru(bpy)_3]^{2+}$ or $Ir(ppy)_3$. Although in the last years, some examples of photoactive complexes beyond Ru and Ir complexes were reported, the employed ligands often require a multistep synthesis.[1–3] Recently our group developed a simple and photostable $Mo^0$ complex $Mo(CO)_3$(tpe) with intense red phosphorescence and $^3$MLCT lifetimes of several hundred nanoseconds. Its utility has been demonstrated in triplet-triplet annihilation upconversion and photoredox catalysis experiments.[4]

One drawback of $Mo(CO)_3$(tpe) is its poor solubility in common organic solvents. Here, we describe the novel ligand tppn and its $M(CO)_3$(tppn) complexes with M = Cr, Mo, W. The series of complexes was fully characterized including SC-XRD, IR and NMR spectroscopy as well as absorption and static/time-resolved emission spectroscopy.[5]




The newly introduced *n*-butyl substituent at the ligand shortens triplet metal-to-ligand ($^3$MLCT) lifetimes in solution but improves $^3$MLCT lifetimes in the solid state. By combining temperature-dependent spectroscopy with theoretical calculations, we uncover the dual role of the alkyl chain in excited state relaxation: flattening potential energy surfaces in solution and acting as a protective spacer in the solid state. Our study sheds light on the relation between structure and excited state relaxation to inform the development of photoactive complexes based on earth-abundant metals.[5]

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# Luminescent Octahedral Group 14 Complexes

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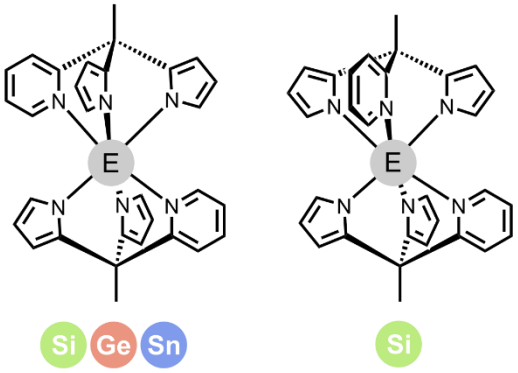
Owing to their photophysical properties precious metal and rare earth metal complexes are well established for photochemical applications. Due to the low earth abundance of these metals, the design of photoactive molecules only consisting of abundant elements is desirable. First row transition metal complexes with unique photophysical properties have been a research focus in recent years.[1] In these, participation of the central atom in electronic transitions generally allows for moderately fast intersystem crossing despite the comparably small spin orbit coupling constants for these lighter elements.

Compared to transition metal complexes, photoactive main group coordination compounds are rare.[2]

Here, we present a series of homoleptic group 14 complexes with silicon(IV), germanium(IV) and tin(IV) as central ions. These compounds were characterized using SC-XRD, NMR, DFT calculations, static and transient absorption spectroscopy and static-/time resolved emission spectroscopy.




- Group 14 series of *trans* isomers
- Emissive
- Calculation and spectroscopy

A special emphasis is put on the photophysical properties of these complexes. They are put in relation to the structure of the scorpionato type ligands. Differences between the configurational isomers are discussed as well.

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# Dinuclear Cyclometalated Pincer Nickel(II) Complexes with Metal-Metal-to-ligand Charge Transfer Excited States and Near-Infrared Emission

**Mengyue Gao[1], Wai-Pong To[1], Glenna So Ming Tong[1], Lili Du[1], Kam-Hung Low[1], Zhou Tang[1,2], Wei Lu[3], and Chi-Ming Che[1,2,3,4]***

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Facile non-radiative decay of low-lying metal-centered (MC) d-d excited states has been well documented to pose a significant obstacle to the development of phosphorescent $Ni^{II}$ complexes due to substantial structural distortions between the dd excited state and the ground state.[1, 2] Herein, dinuclear pincer-type $Ni^{II}$ complexes bridged by formamidinate/α-carbolinato ligands and the dinuclear $Pt^{II}$ and $Pd^{II}$ analogues were studied. These $Ni^{II}$ complexes exhibit short Ni-Ni distances of 2.947-3.054 Å and singlet metal-metal-to-ligand charge transfer transitions at 500-550 nm. At 77 K, these $Ni^{II}$ complexes display phosphorescence (τ=2.6-8.6 μs) in the NIR (800-1400 nm) spectral region in 2-MeTHF and in the solid state, which originates from the $^3$dd excited state as supported by DFT calculations. One example is presented in Fig. 1.

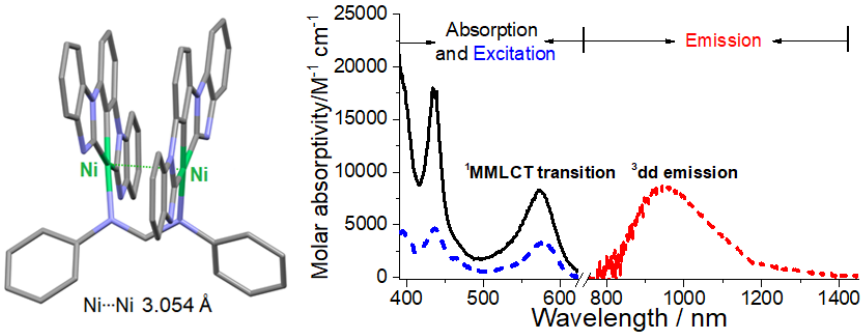


Figure 1. Perspective view of the crystal structure of one example and its corresponding UV/Vis absorption spectra, emission and excitation spectra.

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**Acknowledgement:** We thank Dr. Cheng Yang and Dr. Yinhua Yang from Southern University of Science and Technology for assisting with emission measurements and EPR experiments, respectively.

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# Adsorption and Light dating: photocatalytic water remediation based on α-$Bi_2O_3$

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The uncontrolled discharge of synthetic dyes from textile, cosmetic, and printing industries poses severe environmental challenges due to their high stability, toxicity, and resistance to biodegradation[1]. While adsorption is widely employed for dye removal owing to its simplicity and cost-effectiveness, it typically requires subsequent regeneration or disposal of saturated materials.[2] Photocatalysis offers an alternative through oxidative degradation, but suffers from limited surface contact and recombination losses.[3] In recent years, a synergistic approach combining adsorption and photocatalysis has gained increasing attention for its potential to enhance dye removal efficiency while addressing the limitations of each method individually.[3,4] In such systems, pollutants are first adsorbed onto the material's surface and subsequently degraded through light-activated photocatalysis, promoting a more sustainable remediation process.[4,5]

In this study, rod-like α-$Bi_2O_3$ nanostructures were synthesized via a straightforward aqueous method and evaluated as dual-function materials for the removal of organic dyes. Nile Blue was employed as a representative model compound, chosen for its structural complexity, environmental persistence, and widespread industrial relevance. In addition to assessing optimal adsorption conditions, overall removal efficiency, and material recyclability (Fig. 1), the investigation also focused on the interactions between the dye and the nanostructured surface to gain mechanistic insights into the adsorption process. Notably, the system demonstrated nearly complete removal of the dye, achieving close to 100% total efficiency through the combined action of adsorption and visible-light-driven photodegradation. These findings contribute to a broader understanding of the interfacial phenomena governing synergistic adsorption-photocatalysis systems, supporting the design of more effective and sustainable water treatment technologies.

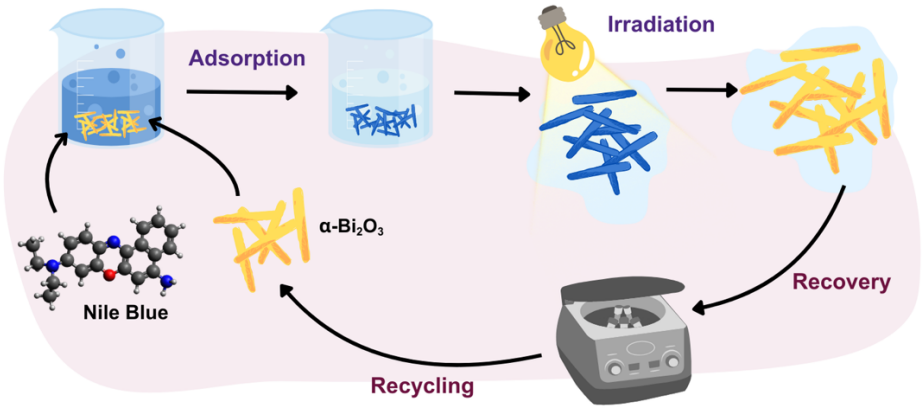


Figure 1. Schematic representation of the adsorption-photocatalytic cycle of α-$Bi_2O_3$ for the degradation of Nile Blue.

**Funding:** "LUminescent modular NAno-composites for Responsive LIGHTing devices (LUNARLIGHT)" project funded by PRIN - Bando 2022 Prot. 2022NHLX2M.

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# Photocatalytic On-demand Hydrogen Evolution - A Water-soluble Copolymer for Storage and Catalytic Conversion of Electrons

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With the energy crisis looming, establishing reliable and renewable energy sources poses one of the most crucial challenges that todays' scientists face. Energy storage is a promising approach to overcome this, which in this research is addressed by a redox-active copolymer[1]. Together with well-known Ru(II)-photochemistry and suitable hydrogen evolving catalysts, a system can be established, which can store energy for several days and generate hydrogen on-demand.

The established process can in general be divided into two half reactions, depicted in Fig.1. First, in the presence of triethylamine as sacrificial electron donor and at neutral pH, by irradiation of the Ru photosensitizer, the redox-active viologen units of the polymer can be charged with electrons to a degree of more than 80%. This charge is fully preserved for multiple days and can be consumed on-demand for catalysis in the dark reaction. For this second half reaction, in presence of an appropriate Rh or Pt hydrogen evolving catalyst (HEC), the stored electrons are used for catalysis with a conversion of up to 72% after establishing an acidic pH. Furthermore, this system shows remarkable reversibility facilitated by this pH switch, enabling multiple charging, storage and catalysis cycles.

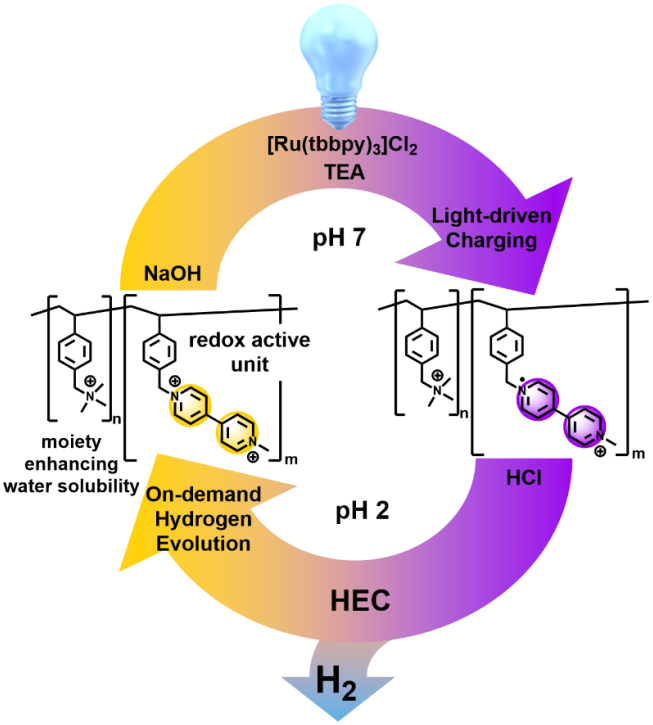


Figure 1. Scheme of the charging and on-demand hydrogen evolution cycle using a viologen unit containing copolymer as electron storage material.

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**Acknowledgement:** TRR 234 [B2] is greatly acknowledged.

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# Accessing Photocatalytically Active Covalent Triazine-based Frameworks by Ball Milling: A Fast and Facile Synthesis Method

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Covalent Triazine-based Frameworks (CTFs) are a promising class of materials in areas such as photocatalysis, energy storage, heterogeneous catalysis, and gas adsorption, conversion, and separation.[1] CTFs offer several advantageous properties, including high chemical and thermal stability, structural tunability, and favorable optoelectronic characteristics. Various synthetic protocols for CTFs have been reported in the literature.[2] However, conventional methods often require high reaction temperatures, long polymerization times, and the use of toxic reagents. These drawbacks can be addressed using mechanochemical synthesis approaches.[3]

In this study, we present a novel and straightforward mechnochemical preparation strategy for CTFs with enhanced functionality and photocatalytic performance using a mixer mill. The synthesis was developed by adapting the literature-known solvothermal polycondensation of amidines and aldehydes (stCTF) to a mechanochemical process in a ball mill (bmCTF).[4] Successful trimerization was confirmed via Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and $^{13}$C-detected solid-state-NMR experiments, also indicating a higher degree of functionalization for the bmCTFs. Additionally, the bmCTFs exhibited a reduced band gap energy relative to the stCTF, reflecting in an increased photocatalytic activity of the bmCTFs compared to the stCTF in the light-driven transformation of water and oxygen to hydrogen peroxide.

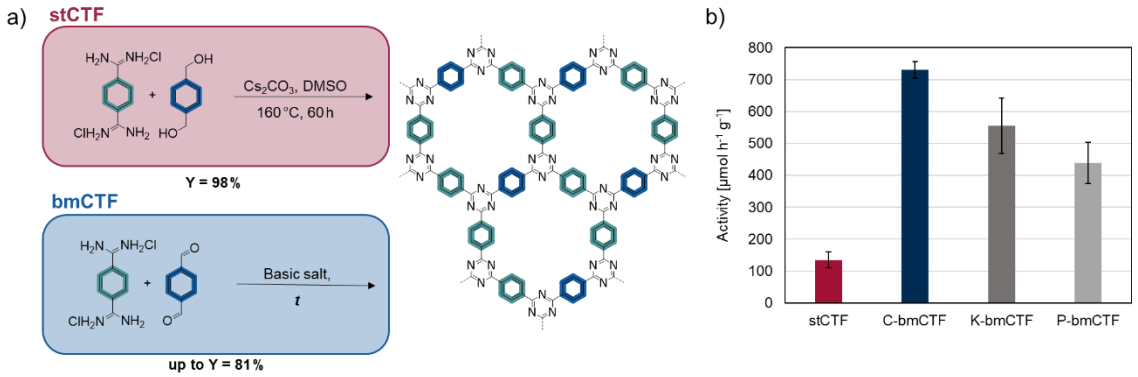


Figure 1. a) Schematic depiction of the solvothermal CTF synthesis (stCTF, red) to the ball milling synthesis (bmCTF, blue to grey) using three different basic salts as grinding additives (C: $Cs_2CO_3$, K: $K_2CO_3$, P: $Na_3PO_4$). B) The respective activities in the photocatalytic production of hydrogen peroxide from water and oxygen.

**Funding:** Fuel Science Center (EXC 3782186, ID: 390919832) funded by the Excellence Initiative of the German federal and state governments; Deutsche Forschungsgesellschaft (project number: 455238107); HC-H2 project funded by the German Federal Ministry of Education and Research and the Ministry of Economic Affairs, Industry, Climate Action and Energy of the State North Rhine-Westphalia.

**Acknowledgement:** We acknowledge beamtime at the beamline I15-1 at Diamond Light Source (Didcot England). L.S.H. also gratefully thanks the German Federal Environmental Foundation for financial support.

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# Red-to-blue photon upconversion nanoparticles and their photocatalytic activity for polymerization in water

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Sensitized triplet-triplet annihilation upconversion (sTTA-UC) converts two low energy incident photons to one output photon of higher energy. Particularly, red-to-blue UC is a favorable approach for biological studies and photocatalysis, due to the deeper penetration depth into samples and reduced photodamage of the irradiation light.[1] The efficiency of sTTA-UC is sensitive to environmental conditions and can be significantly quenched by oxygen, which severely limits the applications.[2] Red-to-blue upconversion that can be used in aqueous solution under ambient conditions seems attractive in this context.

Established research confirms that oxygen quenching in sTTA-UC systems can be effectively reduced by implementing a physical barrier to suppress oxygen diffusion.[3] In this work, we apply this strategy to a red-to-blue upconversion pair consisting of meso-tetraphenyl-tetrabenzoporphine palladium (II) complex (PdTPTBP) as the photosensitizer and 9,10-Bis[(triisopropylsilyl)ethynyl] anthracene (AnTIPS) as the annihilator. The PdTPTBP/AnTIPS pair is encapsulated into 100 nm-sized polystyrene (PS) nanoparticles suspended in water (Fig. 1). Photoexcitation of PdTPTBP at 638 nm gives delayed blue fluorescence from AnTIPS (Fig. 1). Encapsulation of the upconversion pair into PS particles significantly improved the photorobustness of the UC components. Additionally, the shielding effect offered by the PS particles makes UC feasible in aerobic water with an UC quantum yield (UCQY) of 0.02%. In deaerated water, the UCQY achieved 0.09%, which allows efficient photoredox catalytic radical polymerizations of acrylate monomers in water with red light.

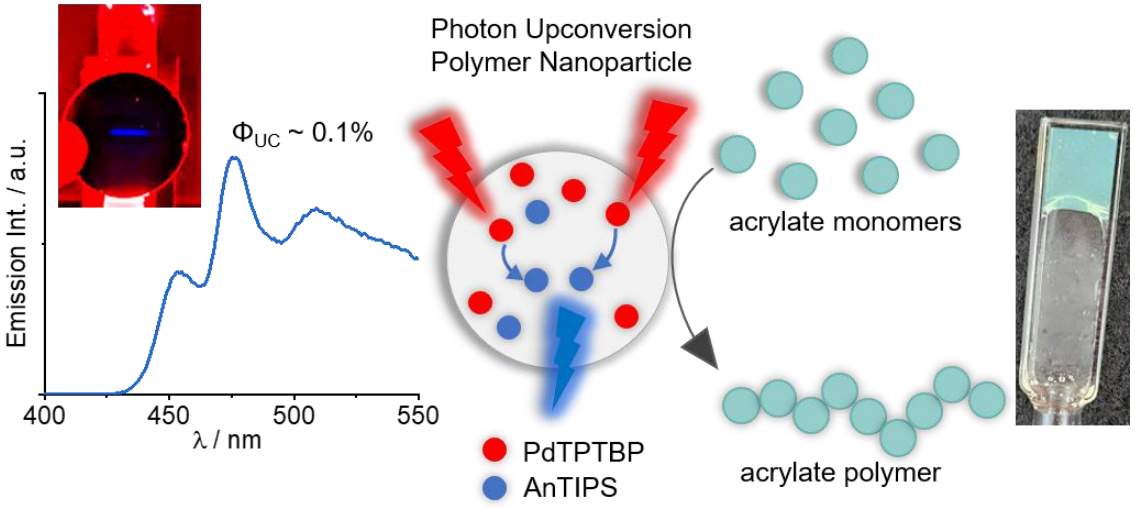


Figure 1: Photon Upconversion luminescence spectrum of PdTPTBP and AnTIPS encapsulated in polymer nanoparticle in water and conversion of acrylate monomer to free-standing polymer gel upon red light irradiation for two minutes.

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# Towards Orchestrating TADF Properties with Proteins as Scaffolds

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Thermally Activated Delayed Fluorescence Chromophores (TADF-C) has earned a burgeoning interest because of their interesting applications in light emitting devices, photocatalysis and sensing. [1,2] This is attributed to their phenomenal properties like prolonged luminescence lifetime and high quantum efficiency. Albeit to it, the non-radiative energy transfer to the host materials, is a major bottleneck limiting its versatility and large-scale applications.[2] Herein, we advocate a novel approach to augment TADF properties enabled by conformationally rigid chiral protein environment [3] (Fig. 1) (chromophore inside the cavity vs outside the cavity), conferring nuanced control of the singlet-triplet energy gap and enhanced solubility. With the advent of site-specific mutagenesis, we infer the possibility of fine-tuning the local excited state, by virtue of polar and charged amino acid residues in proteins. [4]

In the current work, we employ Cu (I) complexes, being cost effective and electron rich emissive center have a psuedotetrahedral geometry; yet they are susceptible to non-radiative flattening distortion in their excited states.[2] Of note, phenanthroline Cu(I) based systems, 2,9 substitution aids rigidity of the optimal geometry, but in the solution state they undergo rapid equilibrium, between homoleptic and heteroleptic complexes. We rely on the protein labeled TADF-Cs molecules in the cavity to unravel the influence of proteins on this dynamic equilibrium and thereby the emissive properties. On the contrary, we employ homoleptic Cu(I) phenanthroline derivatives to be sandwiched in between two proteins. To incorporate these TADF-Cs we take advantage of click chemistry and Micheal reaction. [4,5] Our initial results indicate the successful expression of protein with desired mutations and synthesis of Cu(I) homoleptic complexes. Taken together, this current work shall underscore a molecular understanding of how the protein environment influences the photo-physics of these molecules and hence can set directions towards new protein-based materials.

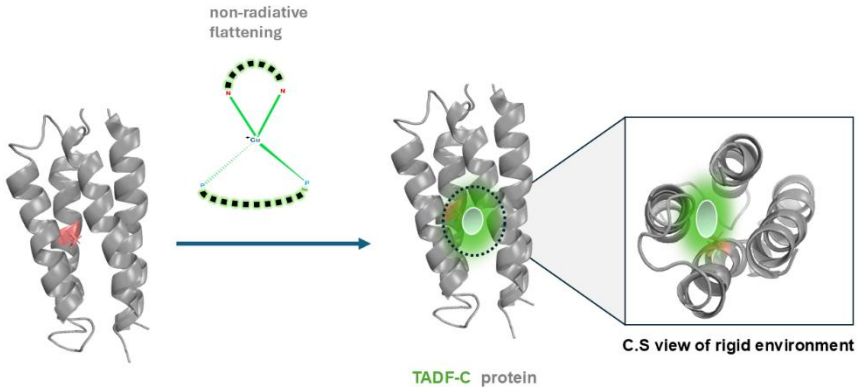


Figure 1. Schematic of TADF-C in protein environment. Protein environment provides rigidity and enhances TADF properties, by taking care of non-radiative flattening distortion.

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**Acknowledgement:** AK acknowledge contributions of all authors, of note, DD and LL with synthetic hands of chromophores; JC and SH for guidance.

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# Internal electric field engineering for boosting visible-light-driven $H_2$ production

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Direct solar-to-hydrogen ($H_2$) conversion is an intriguing approach and one of the most promising ways to tackle the challenges of global energy shortages and environmental deterioration [1].
Heterogeneous photocatalysts have gained considerable attention and research focus due to their potential to convert solar energy into chemical energy. Graphitic carbon nitride (g-$C_3N_4$) has exhibited great potential in visible-light photocatalysis due to its appropriate band structure, morphology regulation, facile preparation, good stability, and natural abundance [2]. Nevertheless, limited light absorption and severe charge recombination hinder g-$C_3N_4$ from achieving high photocatalytic activity. To address these issues, various strategies, such as morphology regulation, element doping, and heterojunction design, have been applied to modify g-$C_3N_4$ [3].
In this study, a sheet-like structure of the $CNWO_3$ composite was successfully synthesized using a simple and eco-friendly method. The $H_2$ evolution performance of the samples was evaluated under a 300 W Xe lamp equipped with a cutoff filter (λ > 400 nm). The generated $H_2$ gas was analyzed using gas chromatography equipped with a thermal conductivity detector. The optimized composite exhibits enhanced visible-light harvesting ability and a higher surface area than pure CN. **Figure 1a** displays the surface morphology of $CNWO_3$, revealing a highly ordered sheet-like structure composed of thin layers that promote light absorption. The hydrogen evolution rate (HER) over CN and $CNWO_3$ is presented in **Figure 1b**, showing that after the modification of CN by building an internal electric field, the HER is enhanced by 84% in $CNWO_3$. This significant improvement results from the increased surface area, improved light harvesting, and enhanced charge carrier transfer.

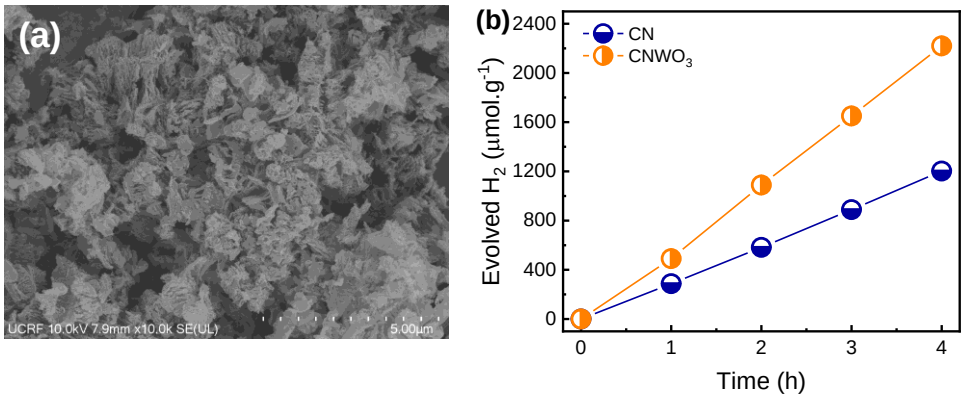


Figure 1. (a) SEM image of $CNWO_3$; (b) Photocatalytic $H_2$ production of CN and $CNWO_3$.

**Funding:** National Research Foundation of Korea (NRF)

**Acknowledgement:** This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT*) (RS-2025-00555613). *MSIT: Ministry of Science and ICT

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# Light-Induced Metal-Free Generation of Cyanocarbenes from Alkynyl Triazenes for the Synthesis of Nitrile Derivatives

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The chemistry of alkynyl triazenes is an emerging and exciting area in organic chemistry, especially in the field of acid-induced nucleophilic functionalizations.[1] Traditionally, the main synthetic application of triazenes involves the cleavage of the N2-N3 bond in the presence of a Lewis acid, which activates the triazene for further reactions with nucleophiles, accompanied by the release of nitrogen gas.[1-2]

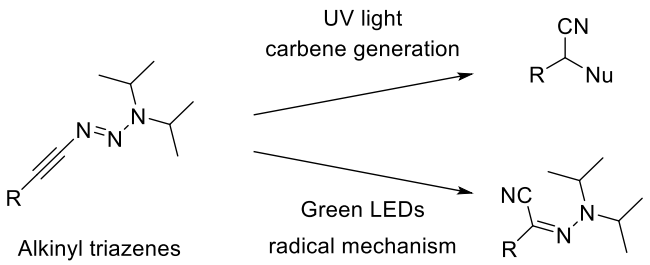


Figure 1. Photo-induced reactivity patterns of alkynyl triazenes.

Under photoirradiation, alkynyl triazenes have revealed a “reactivity switch” depending on the light source used. Under UV light irradiation, an unusual reactivity pattern is triggered which involves N1-N2 bond fissure in the triazene group liberating the reactive cyanocarbene intermediate which is intercepted by insertion of the carbene in the alcohol being used as solvent for the reaction. The method allows the synthesis of nitrile compounds without using toxic cyanating agents. By adjusting reaction conditions and light sources, a different reactivity can be achieved in combination with Eosin Y as photosensitizer enabling a radical mechanism. This approach enabled the synthesis of α-alkoxynitriles, α-aminonitriles and α-cyanohydrazones which serve as valuable intermediates for the synthesis of pharmaceuticals and total synthesis.[3]

**Funding:** We thank Carl-Zeiss foundation for financial support.

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# Probing Mechanism of Rhodamine B Decolorization under Homogeneous Conditions via pH-Controlled Photocatalysis with Anionic Porphyrin

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Porphyrins are known photosensitizers with promising applications in water treatment.[1] This study investigates the efficiency of meso-tetra(4-sulfonatophenyl)porphyrin (TPPS) for the photodecolorization of rhodamine B (RhB) in aqueous solutions under visible light.[2] We demonstrate that the decolorization rate is highly dependent on the pH of the solution. Under homogeneous conditions, approximately 95% of RhB was rapidly decolorized within 120 minutes at pH 3.0, whereas only 12% decolorization was observed at pH 6.0. Comprehensive photophysical studies, including absorption and fluorescence spectroscopy, fluorescence quantum yields, triplet absorption spectra, triplet lifetimes, and singlet oxygen quantum yields, were conducted at both pH values to elucidate the underlying mechanism. Surprisingly, reactive oxygen species and singlet oxygen were found not to play a significant role in the RhB decolorization process. Instead, the primary mechanism involves electron transfer from photoexcited TPPS to RhB, followed by proton transfer at pH 3.0, resulting in the formation of a colorless leuco dye. These findings provide valuable insights into the pH-dependent behavior of porphyrin photosensitizers in dye degradation and contribute to the development of efficient photocatalytic water treatment technologies.

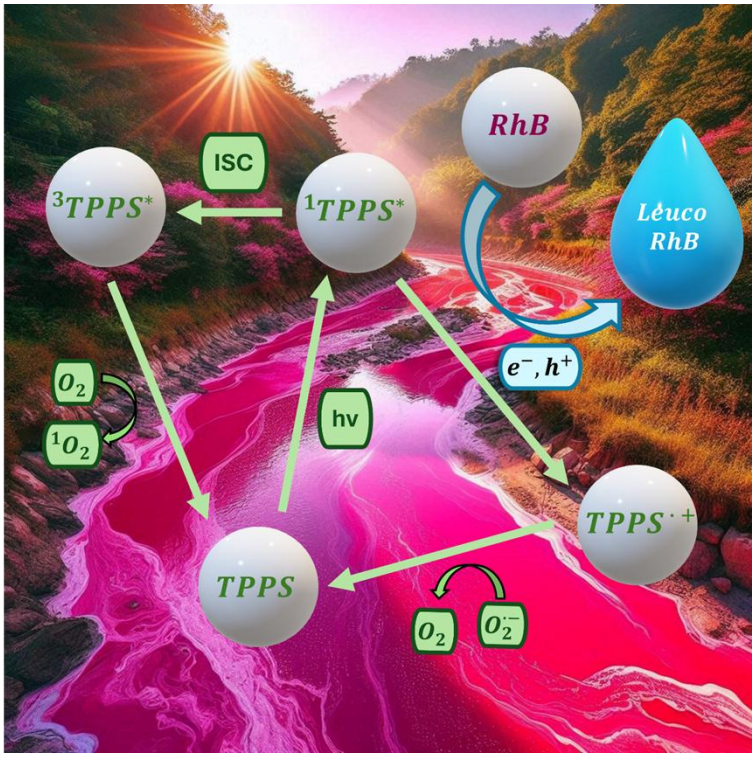


Figure 1. Schematic illustration of RhB decolorization by TSPP at pH=3.0

**Funding:** AMU “Excellence Initiative - Research University" (054/13/SNŚ/0025)

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# Exploring $Al_2O_3$–ZnO Composite Coatings as Photocatalysts: A Novel Approach Using Thermal Spraying Technique

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It is well known that ZnO doped with $Al_2O_3$ exhibits catalytic activity under direct solar irradiation and is considered one of the most promising photocatalysts for green environmental applications[1,2,3]. However, the performance of heterogeneous photocatalysts strongly depends on the exposed crystal facets during interactions with organic pollutants. In this study, a composite coating composed of $Al_2O_3$ and AZO (ZnO doped with 3 wt.% $Al_2O_3$) powders was deposited on a 304 stainless steel substrate using the thermal spraying technique. A hierarchical nanostructured morphology was observed (Fig. 1), notably featuring nanosheets—an uncommon structure resulting from flame spraying—alongside more typical whisker-like features. This morphology is attributed to the high concentration of $Al_2O_3$ splashes, which serve as nanostructured templates that enable the adhesion of AZO nanosheets to microparticles during the spraying process. The coating morphology characterized by XRD and SEM indicates structural with characteristics that are likely to promote defect formation, which may be beneficial for photocatalytic activity. Photocatalytic performance under UV-A irradiation was evaluated using a UV-Vis spectrometer. The results suggest that the AZO crystallites within the composite coating expose multiple high surface-energy facets, thereby enhancing photocatalytic efficiency. Furthermore, the measured water contact angle of approximately 145° indicates that the $Al_2O_3$-50wt.% AZO (ZnO-3wt.%$Al_2O_3$) coating possesses excellent hydrophobicity, which enhances its potential for practical industrial applications. This study provides a simple and effective strategy for environmental pollution control through advanced surface engineering of photocatalytic materials.

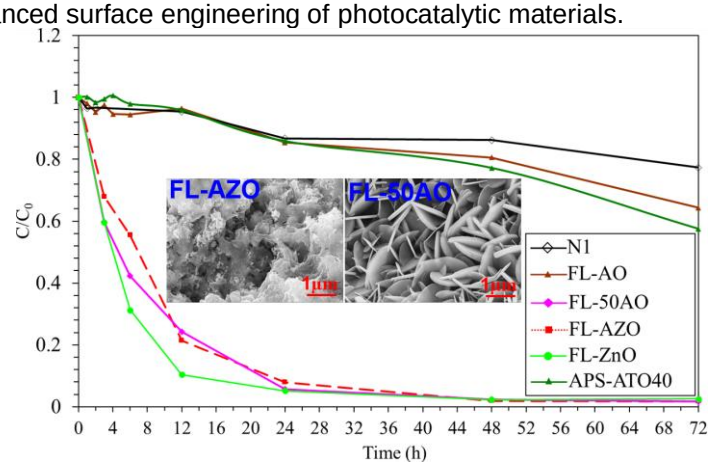


Figure 1. Degradation of methylene blue (MB) under UV irradiation as a function of time for the tested samples. N1: MB under light without sample. FL-AO: Flame-sprayed $Al_2O_3$. FL-50AO: Flame-sprayed $Al_2O_3$–50 wt.% AZO (ZnO–3 wt.% $Al_2O_3$). FL-AZO: Flame-sprayed ZnO–3 wt.% $Al_2O_3$. APS-ATO40: Air plasma–sprayed $Al_2O_3$–40 wt.% $TiO_2$. Inset SEM images show nanoparticle aggregates with whisker-like structures (FL-AZO) and nanosheet morphologies (FL-50AZO), respectively.

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# Polymer-Peptide Conjugates for Enhanced Lanthanide Recovery: A Comparative Study Using Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLFS)

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Peptides are promising candidates for lanthanides recovery, but their performance can be influenced by structural limitations and environmental conditions. To address this, we conjugated a peptide with three different polymers to assess their impact on lanthanide coordination behavior. The peptide is originally from metal binding site of Calmodulin with additional glycine at N-terminal which was conjugated via solid phase peptide synthesis (SPPS) to polymers (pDMA, pNAM, or pNIPAM). We also investigated two different polymers' weight, 5 and 30 kDa. To monitor the complexation of lanthanides with the conjugate, time-resolved laser-induced fluorescence spectroscopy (TRLFS) was used (Fig. 1), taking advantage of its high sensitivity that allows measurement at micromolar concentrations and europium was chosen as the spectroscopic probe. This approach enabled precise comparison of conjugates under minimal sample conditions. Our results show that conjugation of peptide to pNAM and pDMA enhanced peptide affinity (up to 10-fold) ($K_D$ ~0.2 - 0.8 µM) in comparison to free peptide ($K_D$ = 1.9 µM) while pNIPAM ($K_D$ ~1 - 2 µM) had the least effect on peptide affinity. It has been demonstrated that peptide affinity is unaffected by the molecular weight, suggesting that as low as 5 kDa polymers are sufficient to enhance peptide binding affinity. In a competition titration, a mixture of europium and pNAM 5 kDa conjugate was titrated with $La^{3+}$/$Lu^{3+}$/$Ca^{2+}$. Results indicated that europium bound to conjugates is not easily replaced by other lanthanides, suggesting possible lanthanide selectivity. Europium remains bound to conjugates even at high $Ca^{2+}$ concentrations, indicating a stronger affinity for trivalent ions than divalent ones. This work supports the development of modular biomimetic systems for lanthanide recovery in low concentration environments.

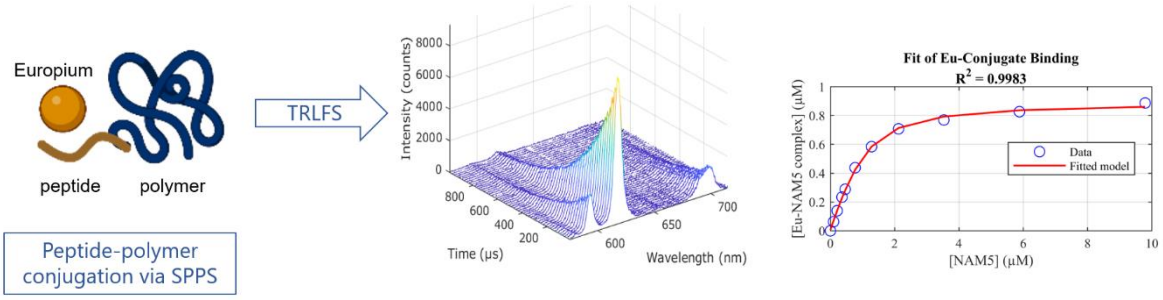


Figure 1. Schematic representation of the complexation of europium with peptide-polymer conjugate monitored with TRLFS

**Funding:** German Federal Ministry of Education and Research (031B1122B)

# Harnessing Energy and Electron Transfer Processes in Engineered Bio-Hybrids for Enantioselective Photocatalysis

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Photoactivation of catalysts allows access to various reactive intermediates via photoinduced energy and electron transfer processes.[1] On the contrary, enantioselective catalysis has been renowned for the selective preparation of enantiomerically pure compounds as pharmaceutical ingredients and drug molecules.[2] Over the past decade, BODIPY (Boron-dipyrromethene) dyes have emerged as promising metal-free catalysts encompassing different tactics to achieve several photochemical transformations under visible light irradiation.[3] However, selectivity and asymmetric photochemical conversion of BODIPY-based photocatalysis remain challenging because creating the chiral center on BODIPY derivatives will give synthetic difficulty as low product yield. Furthermore, the required activation of reactive intermediates during substrate binding to the chiral center and deactivating them when no substrate is present makes these reactions even more challenging. Within this context, we are willing to use the protein microchiral environment, which will provide high chemo-, regio-, and stereoselective catalysis under sustainable reaction conditions. Herein, we used the Lactococcal Multidrug Resistance Regulator (LmrR) protein because of its promiscuous dimeric hydrophobic pocket that can bind planar organic molecules through multiple supramolecular interactions.[4] Previously, it has been shown that recruiting BODIPY into LmrR_W96 protein facilitated the photoinduced electron transfer between the tryptophan unit of LmrR_W96 and BODIPY, quenching its photochemistry.[4] To overcome this challenge, we synthesized the diiodo substituted BODIPY to favour the triplet state formation, a reactive state that competes with the fast-quenching electron transfer process in the case of unsubstituted one. This approach allows us to take advantage of the protein´s chiral environment and the BODIPY´s photochemistry. We characterized the dissociation constants (Kd) for our LmrR-[BODIPY] complexes, and they were relatively high, confirming that the aromatic interactions between tryptophan and the BODIPY unit played a significant role in their binding affinity. We also studied their excited-state photophysical properties using steady-state and ultrafast spectroscopic techniques. All these studies helped us understand the photoinduced energy or electron transfer processes of developed LmrR-[BODIPY] complexes to select the best candidate for enantioselective photoconversion. This novel strategy will have an impact on tuning the photoredox properties of LmrR-[BODIPY] complexes for generating regio- and stereoselective chiral products that could potentially be used as synthetic precursors and drugs under sustainable reaction conditions shown in Fig. 1.

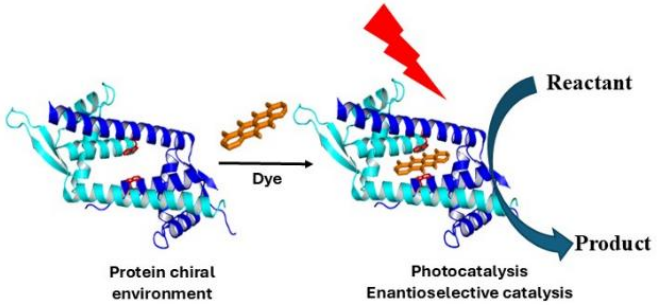


Figure 1. General Schematic for generating artificial photoenzymes for enantioselective photoconversion.

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# Supramolecular manipulation of heteroleptic iron(II) chromophores

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Transition metal complexes play a central role in many photochemical applications including dye-sensitized solar cells (DSSDs), photocatalysis and photodynamic therapy. Due to their beneficial photophysical properties, heavy metal-based complexes like $[Ru(bpy)_3]^{2+}$ have been used predominantly in these fields.[1,2] Transition from the rare and expensive 4d transition metal ruthenium to cheaper and more abundant 3d metals such as iron is highly desirable for the further development and sustainable application of transition metal complexes. However, the use of iron brings challenges, such as the short-lived nature of metal-ligand charge transfer (MLCT) states due to low-lying metal-centred (MC) states. Recently, a wide variety of ligand concepts based on N-heterocyclic carbenes (NHCs) have been used to optimize the photophysical properties of iron chromophores. However, the supramolecular manipulation of excited states remains still largely unexplored. By introducing the functional 2,2'-bibenzimidazole ligand in the coordination sphere of a heteroleptic iron(II) complex we are now able to manipulate the photophysical properties through interactions in the second coordination sphere.[3] Here, we demonstrate how protonation and deprotonation as well as cation coordination influence the principal photophysics of this new class of iron(II) chromophores, enabling new opportunities for the development of functional chromophores based on iron.[4,5]

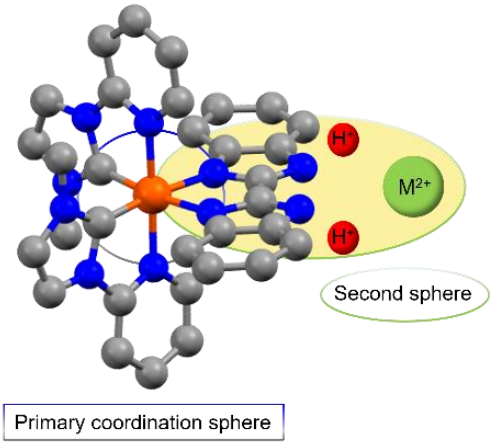


Figure 1: Second-sphere manipulation of the bibenzimidazole ligand enables manipulation of photophysical properties of heteroleptic iron(II) chromophores of the general formula $[(^{Me}NHCpy)_2Fe(BBi)]$.

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# Photophysical properties of monobenzopentalene and its derivatives

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In the search for new and photostable singlet fission (SF) chromophores, monobenzopentalene (MBP) (Figure 1A) with a Baird aromatic $T_1$ state was proposed as a candidate for SF. [1] The compound should be more stable in the excited state and avoid detrimental side reactions in the excited state. [1] However, earlier investigations into the $S_1$ state of MBP and its derivatives indicated a low amount of excitation to the $S_1$ state, and the only observable emission arises due to emissions from higher excited states ($S_n$).[2] Extended analysis of these excited states shows that the emission lifetime is dependent on concentration (Figure 1B). [2] Further exploration of these excited states shows that they eventually give rise to another long-lived excited state at higher sample concentration, with optical characteristics different from $S_n$ states. Comparisons with data from spectro-electrochemical measurements show that these states do not arise from a charge-separated state. Instead, due to their long-lived nature, they may be attributed to triplet state formation on a fast time-scale, which can indicate SF from higher excited states. However, this requires further confirmation via measurements on the long-lived excited state.

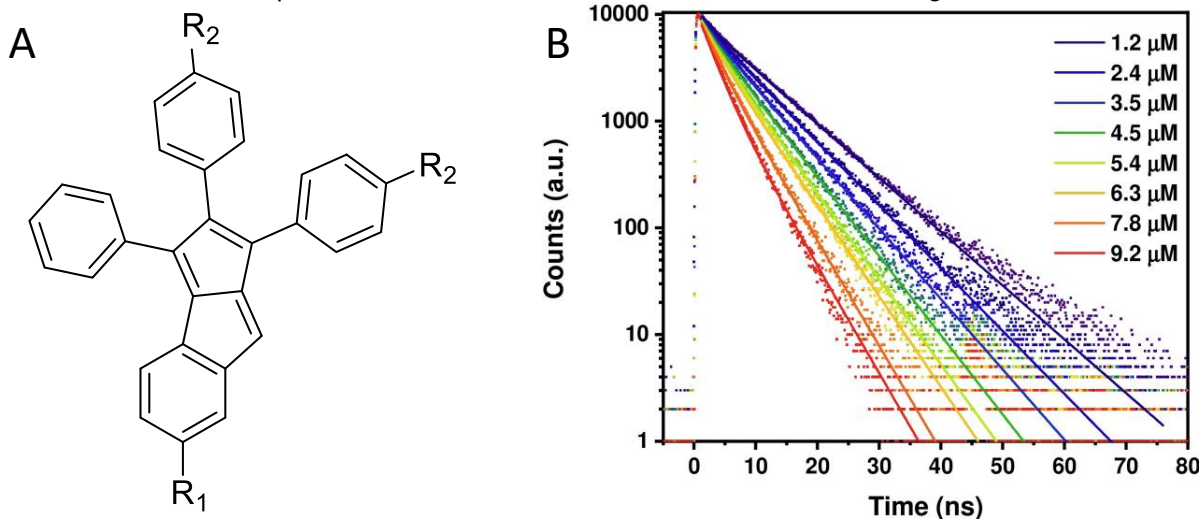


Figure 1: (A). Monobenzopentalene and the most common substitution patterns are specified. (1B) The TCSPC of MBP with $R_1$= OMe and $R_2$= H, after excitation at 377nm in $CH_3CN$. The difference in lifetime due to higher concentration, repurposed from [2]

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# Designing B-$TiO_2$ photoelectrodes for efficient photochemical water splitting with an operando focus on the modular photoreactor

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Photocatalytic water splitting (PCWS) is a crucial approach of producing hydrogen and oxygen from water, and it contributes greatly to the development of carbon-neutral energy sources, even though water electrolysis is thermodynamically unfavorable with a Gibbs free energy of $\Delta G_0$ = +237.2 kJ $mol^{-1}$.·Since the groundbreaking discovery of PCWS on $TiO_2$ by Fujishima and Honda, extensive research has focused on $TiO_2$ due to its low cost and high chemical stability, making it a leading candidate for photoelectrodes in PECWS.[1] However, the utilization of $TiO_2$ particles has been hampered by electron transport inefficiencies, recombination losses, and the requirement for appropriate substrate support. Nonetheless, the efficiency of $TiO_2$ is limited by its wide band gap (3.2 eV), which restricts photoexcitation to UV light, representing only 4-5% of the solar spectrum.[2] Several techniques have been developed recently to improve $TiO_2$ intrinsically poor photon absorption efficiency in the visible light spectrum. One of these strategies that has shown promise is the engineering of $TiO_2$ to have a higher density of oxygen vacancies.

In this study, black $TiO_2$ (B-$TiO_2$) with abundant oxygen vacancies was synthesized on a titanium plate via an anodic spark deposition process using the SOLECTRO technique. The structural and optical properties of the catalyst were comprehensively characterized through XRD, SEM, and UV-Vis spectroscopy.[3] The introduction of oxygen vacancies significantly altered the optical properties of $TiO_2$, shifting its absorption edge into the visible spectrum.[4] Consequently, B-$TiO_2$ exhibited an enhanced light-harvesting capability with a reduced bandgap of 2.3 eV compared to the 3.2 eV bandgap of pristine $TiO_2$. These findings underscore the potential of oxygen-vacancy-engineered $TiO_2$ materials in photocatalytic applications, particularly for hydrogen evolution.

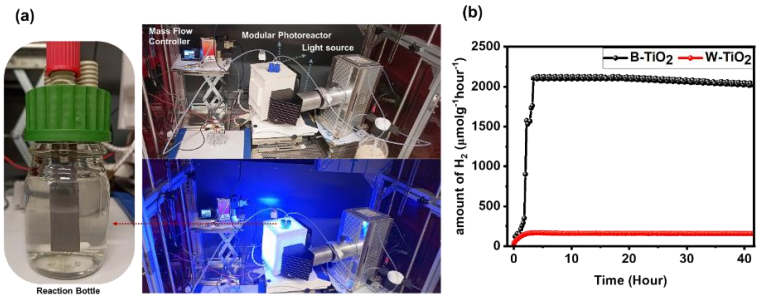


**Figure 1.** (a) Modular Photoreactor setup for photocatalytic hydrogen production (b) amount of hydrogen production

To evaluate the photocatalytic activity of B-$TiO_2$ for hydrogen production under visible light, a modular photoreactor system was employed. This system was designed to ensure precise control over critical operational parameters, including the active catalytic surface area, photon flux, light intensity, and carrier gas flow rate, allowing for systematic optimization and reproducibility of the experimental conditions.

The optimized photocatalytic system demonstrated a remarkable hydrogen evolution rate of 2100 µmol $g^{-1}$ $h^{-1}$, a ninefold increase compared to the 280 µmol $g^{-1}$ $h^{-1}$ achieved with standard W-$TiO_2$. The performance of the optimized catalyst represents a significant advancement over previous studies, which reported a maximum hydrogen production rate of 200 µmol $g^{-1}$ $h^{-1}$ over a 10-hour period. [4,5] This work highlights the potential of B-$TiO_2$ as a highly efficient and stable photocatalyst for visible-light-driven hydrogen generation, paving the way for further advancements in sustainable energy technologies.

**Acknowledgement:** Mukul Sethi thanks Ulm University for granting an LGFG scholarship to support this work.

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# Ligand exchange of $CsPbBr_3$ perovskite nanocrystals and observation of single-particle electroluminescence

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$CsPbBr_3$ perovskite nanocrystals are semiconductor quantum dots (QDs) that combine excellent luminescence properties with the ability to emit high-purity single photons at room temperature, making them promising candidates for single-photon sources. Although extensive research has focused on single-photon emission and single-particle-level phenomena in these materials, nearly all studies to date have been confined to photoluminescence under optical excitation[1]. For practical device applications, however, electroluminescence (EL), i.e., emission under electrical excitation, is indispensable. Here, we report the first observation of single-particle EL achieved due to successful surface ligand exchange.

The $CsPbBr_3$ nanocrystals were synthesized via a hot-injection method and ligand exchange in solution was carried out using the quaternary ammonium ligand didodecyldimethylammonium bromide (DDAB) and the zwitterionic ligand 3-(decyldimethylammonio)propanesulfonate (sulfobetaine 10, DLPS). The ligand exchange leads to significant increase in PL quantum efficiency and in suppressed PL blinking[2]. Single-particle spectroscopy measurements were carried out with an epi-fluorescence microscope coupled to an EM-CCD camera.

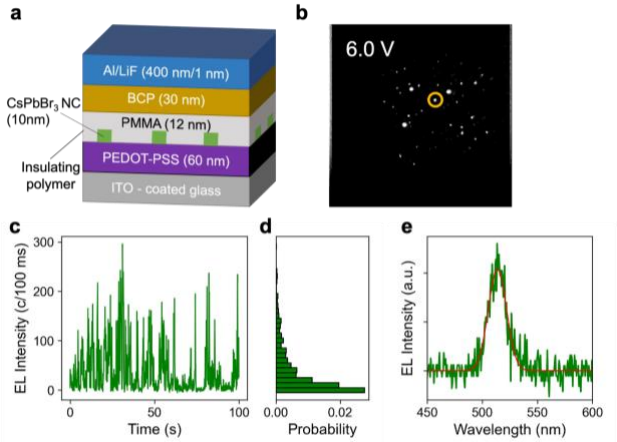


Figure 1. (a) Scheme of the multilayer EL device, showing well-dispersed $CsPbBr_3$ nanocrystals covered with insulating polymer. (b) Electroluminescence image recorded using ligand exchanged nanocrystals. (c) Representative single-particle EL blinking trace. (d) Emission-intensity histogram. (e) EL emission spectrum, featuring a sharp band-edge peak at ~510 nm.

To address selectively the emission of individual QDs within the EL device (Fig. 1a) and to ensure efficient charge injection, the $CsPbBr_3$ nanocrystals were dispersed on the PEDOT:PSS layer and covered with a thin film of an insulating polymer PMMA[3]. When using as-synthesized QDs, almost no emission spots were observed in the EL microscopic images. In contrast, the DDAB ligand-exchanged QDs with passivated surface defects exhibited numerous EL spots (Fig. 1b). Their blinking behavior (shown in Fig. 1c) and the emission-intensity distribution (Fig. 1d) indicate that nanocrystals remained predominantly in low-intensity grey states, punctuated by brief and random "on" events. The EL emission spectrum (Fig. 1e) exhibits a peak at approximately 510 nm, consistent with band-edge emission of $CsPbBr_3$ QDs. Further improvement is expected from a two-step ligand-exchange strategy[4]. Partly replacing DDAB with DLPS, which binds more strongly to the QD surface, is expected to enhance surface stability and improve the single-particle EL performance.

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# Investigation On The Photocatalytic Methanol Oxidation Activity of Layered Niobate Perovskites Coupled With Metal Sulfide Nanoparticles

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Methanol is a highly versatile and widely available chemical that can be sourced not only from fossil-based materials like biogas, shale gas, and coal, but also from more sustainable options such as atmospheric carbon dioxide and industrial wastewater with the recent advances in renewable catalytic conversion technologies. Its abundance makes methanol a key building block for producing a range of valuable C1 and C2 compounds, including formaldehyde, formic acid, ethylene glycol, and methyl formate. These, in turn, serve as essential precursors in the manufacture of numerous industrial materials.

While traditional thermocatalytic methods are effective at converting methanol into these high-value chemicals, they typically rely on high temperatures and pressures, expensive or hazardous catalysts, and often produce toxic by-products, contributing significantly to greenhouse gas emissions. In contrast, semiconductor photocatalysis offers a cleaner, more sustainable alternative. By harnessing renewable energy, it enables more precise control over reaction pathways through selective adsorption and bond activation. This not only minimizes harmful by-products but also reduces energy costs by eliminating the need for high-temperature conditions for catalysis[1].

The methanol oxidation reaction (MOR) is a complex process involving multiple competing pathways, each influenced by the choice of catalyst and reaction conditions. Among these, the most thermodynamically favorable route involves the cleavage of O–H bonds, leading to carbon dioxide ($CO_2$) as the final product, with species such as formaldehyde and formic acid serving as key intermediates. However, the synthesis of higher-carbon compounds requires a more challenging pathway—specifically, the activation of C–H bonds followed by C–C coupling between two hydroxymethyl groups[2]. This route demands a higher activation energy and carefully controlled adsorption/desorption behavior for methanol molecules on the catalyst surface[3].

Recent studies have highlighted metal sulfides as promising materials due to their selective activation of C–H bonds[2,4]. Their reduced affinity for O–H groups and their ability to facilitate oxidation via a concerted electron-hole transfer mechanism make them highly suitable for selective MOR. Another class of materials attracting significant attention is layered perovskites, which offer easy synthesis and highly tunable electronic properties. These properties can be further enhanced by doping or coupling with noble metals or metal oxide nanoparticles[5]. When exfoliated, layered perovskites yield two-dimensional nanosheets with high surface-to-volume ratios and high amount of surface active sites, substantially boosting their photocatalytic efficiency. However, their activity is often limited to the UV range, reducing their effectiveness under natural sunlight. To overcome this, coupling layered niobate perovskites with noble metal or transition metal nanoparticles or co-catalysts has emerged as a promising strategy. This hybrid structure can improve light absorption, enhance charge separation, and promote selective activation of C–H bonds.

In this study, the synthesis and photocatalytic performance of such hybrid materials are investigated. By leveraging the negatively charged exfoliated niobate nanosheets in the synthesis medium, cationic metal sulfide nanoparticles are introduced during restacking[6]. This straightforward method not only simplifies fabrication but also improves catalytic efficiency. Overall, this study demonstrates the potential of metal sulfide-coupled layered niobate nanosheets as efficient photocatalysts for selective methanol photooxidation, offering a sustainable pathway for the synthesis of high-value chemicals and advancing environmentally conscious technologies.

# Synthesis and photocatalytic applications of carbon dots/polymeric carbon nitride composites

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Polymeric carbon nitride (pCN) has been widely studied for photocatalytic application of water pollution treatment. However, the photocatalytic activity of pure pCN is still limited because of the fast charge carrier recombination. In this study, pure pCN was synthesized by heating urea at 550°C in static air and applied for the photocatalytic degradation of Ciprofloxacin (CIP) under irradiation with visible light. The pure pCN shows 20% CIP adsorption and 45% CIP degradation without changing the TOC content. To enhance its photocatalytic performance, carbon dots (CDs) were introduced to form a metal-free CDs/pCN composite. Pure carbon dots were synthesized by hydrothermal treatment of a mixture of lemon juice and urea at 200°C for 3 hours. To prepare the CDs/pCN composite, these CDs were mixed with urea using different CDs amounts (0.5 to 50 wt %) and then heated to 550°C for 2 h. A CDs/pCN composite was also prepared by heating a mixture of different amounts of lemon juice and urea. These samples are named volume lemon juice added in mL_LJ/CN (e.g. 0.02LJ/CN = 0.02 mL lemon juice). The results showed that the CDs/CN and LJ/CN composite samples did not perform photocatalytic better than pure pCN. At low CD content (0.5 wt%) both CIP adsorption as well as photocatalytic degradation occurred. With raising amount of CD added adsorption of CIP increased significantly and photocatalytic activity was negligible. At high amount of CDs loading (50 wt%) about 70% of CIP was adsorbed. When using the sample 2LJ/CN about 85% of CIP was adsorbed in the dark within 30 min. To improve the photocatalytic performance, the composite with low CD content was thermally treated for a second time at different temperatures. After thermal treatment at 500°C in Ar, both 0.5CDs/CN_2 and 0.02LJ/CN_2 samples showed a significantly improved photocatalytic performance, achieving a total CIP removal efficiency of 95%, while pCN only reached 45% (Figure 1a). Moreover, the photocatalytic ability depends strongly on the chosen heating temperature. When the temperature of the second thermal treatment was reduced to 300°C, the activity of 0.5CDs/CN was obviously lower (53 % CIP degradation). PL analysis showed that 0.5CDs/CN_2 has lower photoluminescence (PL) intensity than pCN and 0.5CDs/CN_1, indicating reduced charge carrier recombination of the 0.5CDs/CN_2 sample compared to pCN and 0.5CDs/CN_1 (Figure 1b).

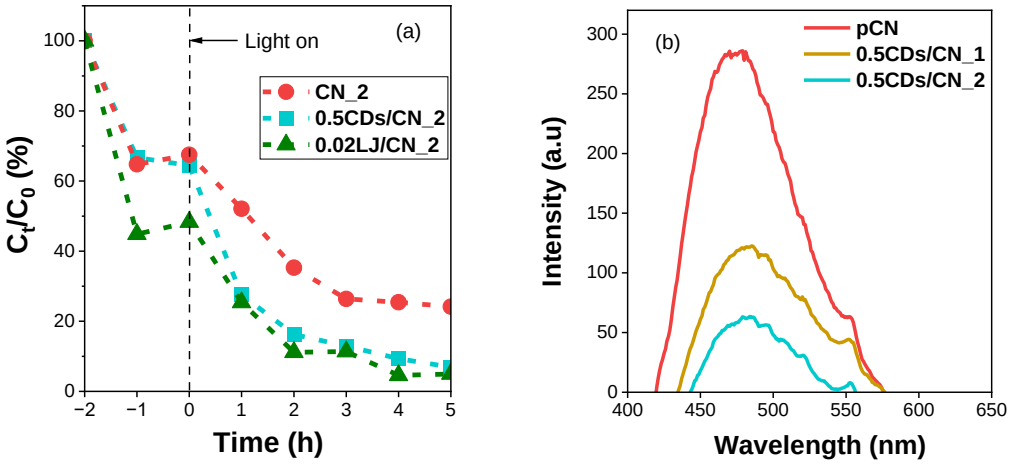


Figure 1. (a) Plot of CIP photocatalytic degradation after 5 hours irradiation under visible light at second thermal decomposition; (b) The photoluminescence spectra of pCN, 0.5CDs/CN_1 and 0.5CDs/CN_2

**Funding:** This work has been supported by the RoHan Project funded by the German AcademicExchange Service (DAAD, No. 57315854) and the Federal Ministry for Economic Cooperation and Development (BMZ) inside the framework “SDG Bilateral Graduate school program”.

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# Integrating Photocharging of $TiO_2$ Aerogels and $N_2$-Reduction in Taylor Flow for On-Demand Ammonia Synthesis

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**Abstract**

Ammonia is not only a necessary feedstock for several industry, like fertilizer, textile, and pharmaceutical, but it is also considered a carbon-neutral energy carrier. Mass production of ammonia contributes to more than 1% of fossil energy consumption and plays a significant role in global greenhouse gas emissions. Therefore, exploring alternative processes to the Haber-Bosch method is of considerable scientific interest [1]. This research presents a two-reactor system designed for the systematic investigation of process parameters in photocatalytic ammonia synthesis, using $TiO_2$ aerogel. $TiO_2$ aerogels are able to store large amounts of photogenerated electrons in surface trap states upon illumination in water−methanol dispersions [2]. The developed system realizes the processes of photocharging and nitrogen reduction in two different capillary reactors. The first reactor is dedicated to photocharging $TiO_2$ aerogels, preparing it for $N_2$ reduction. In this reactor, $TiO_2$ aerogels are exposed to controlled UV-LED lighting conditions, focusing on maximizing the storage of photogenerated charge carriers within the $TiO_2$ structure. The second reactor is dedicated to reducing nitrogen with the stored electrons in the aerogel by utilizing Taylor-flow conditions for enhanced mass transfer and nitrogen reduction efficiency. This reactor is engineered to maximize the contact between nitrogen and the photocharged aerogels, ensuring a more efficient and controlled reduction of nitrogen to ammonia. To regulate impurities in nitrogen reduction, a fixed-volume nitrogen approach has been implemented.

This study includes characterization of the photocharging reactor and an analysis of the operational parameters of both reactors. The number of photons incident on the suspension is the most important factor for determining the photocharging efficiency and comparing batch and capillary reactors. A multidimensional radiometric measurement setup developed by Sender et al.[3], [4] was used to measure the radiation field of the

# Beyond the First Coordination Sphere – Manipulating Excited States in Heteroleptic Iron(II) Chromophores with Protons

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The development of new charge transfer chromophores from cheap and abundant metals is of great interest for the potential upscaling of photochemical transformations, and has gained much traction over the past decade.[1] Iron-based chromophores have shown promising and somewhat unexpected potential in this area once strong σ-donating ligands were introduced that destabilize unwanted metal centered excited states in favor of metal-to-ligand excited states.[2] Here, we describe the first example of a heteroleptic iron(II) chromophore of the functional bibenzimidazole ligand that enables post-synthetic manipulation of the ligand-field and, subsequently, the excited-state landscape. Time-resolved spectroscopy and theory show the formation of short-lived charge transfer states whose location depends on the protonation state of the bibenzimidazole.[3] This creates new opportunities for the manipulation of excited states in iron chromophores and for their use in photochemical reactions through exploitation of the ability to form hydrogen bonds and supramolecular assemblies.[3,4]

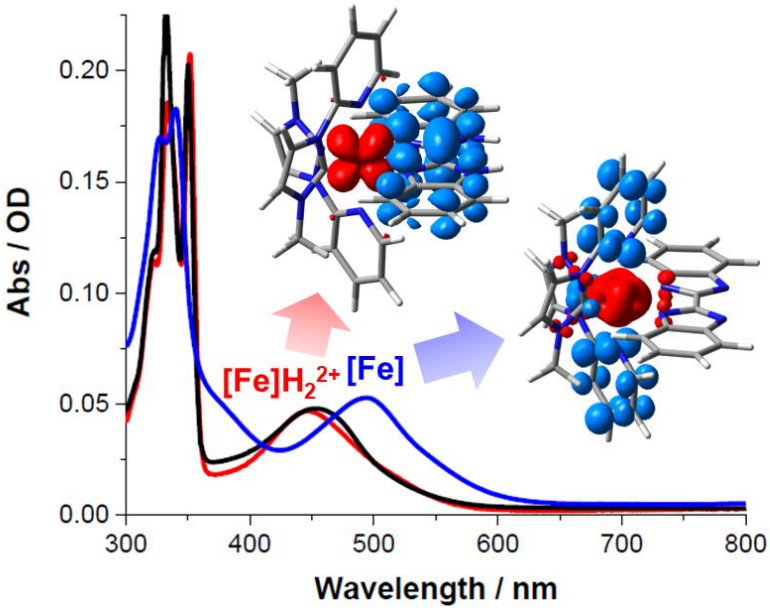


*Figure 1: Protonation-dependent shifts in the steady-state UV-vis absorption spectrum of heteroleptic iron(II) complexes of 2,2'-bibenzimidazole; the underlying MLCT switch is supported by TD-DFT and resonance Raman spectroscopy.*

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**Acknowledgement:** Thanks to T. Bolter and P.G. Porta for gathering CV data of the complexes.

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# Non-Innocent Behavior of Aromatic Isocyanides under Visible Light: A Pathway to Thioformimidates

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Thioformimidates play an important role in peptide modifications as the protection group [1]. The most common method for the synthesis of thioformimidates involves *S*-alkylation of thioformamides with aryl or alkyl halides. However, these processes often suffer from several limitations and purification problems due to the instability of thioformamides and limited substrate scope. Alternatively, thioformimidates can also be synthesized from isocyanides and thiols triggered by UV-light or AIBN initiator [2]. Generally, this reaction proceeds with the formation of a thiyl radical in the presence of UV-light or AIBN followed by thiyl radical addition on the isocyanide to generate an α-thioimidoyl radical [3]. This radical can then undergo H-abstraction from thiols to form the final thioformimidates product. Despite the convenience of this method, less attention has been directed to this pathway due to the following reasons: a) the requirement of UV-light; b) poor reaction efficiency; c) the formation of unwanted side products such as 1,1-bisthiolation; d) C-S bond scission of the intermediate α-thioimidoyl radical, leading to the generation of isothiocyanates.

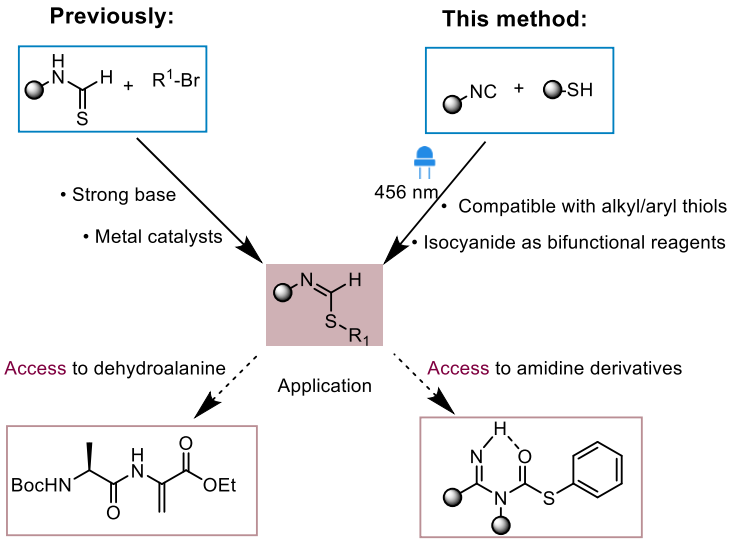


Figure 1. Visible light-mediated synthesis of thioformimidates.

Previously, we desighed a photocatalyst-free pathwy to spirocyclic scaffolds from tryptamine-derived isocyanides by employing blue light [4]. Given the significance of thioformimidates and the current limitations in versatile, sustainable synthetic methods, we focused on developing an innovative, photocatalyst-free, visible-light-driven approach for their synthesis. This study marks a significant advance in the field, as it not only improves existing methods for accessing thioformimidates but also reveals a previously camouflaged role of isocyanides in generation of thiyl radicals.

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# Sequence-Specific Fluorescent Labeling of DNA Leveraging Natural Mechanisms

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**Abstract**

Genetic information is encoded by the sequence of the four DNA nucleobases, intricately organized into double-helical DNA. The ability to address specific sequences within DNA is of tremendous interest in biotechnology and biomedicine, as it unveils invaluable insights into the origin, structure, and functionality underlying the genome. To visualize sequence information, optical detection holds a unique advantage in sensitivity and multiplexing by leveraging multiple fluorophores. Here, building on natural mechanisms, we report two complementary strategies to enable sequence-specific fluorescent labeling of DNA. By modifying the natural cofactor SAM,[1] we achieved multicolor labeling combining well-established methyltransferases and diversified fluorescent enzyme ligands, demonstrating great potential for dye localization and super-resolution imaging. Additionally, inspired by the minor groove binders netropsin and distamycin, we designed and synthesized sequence-programmable, functional pyrrole-imidazole hairpin polyamides as an enzyme-free approach for DNA labeling.[2] Their performance in sequence-specific labeling and single-molecule analysis of DNA was evaluated. These strategies offer versatile tools for sequence-specific DNA recognition and modification.

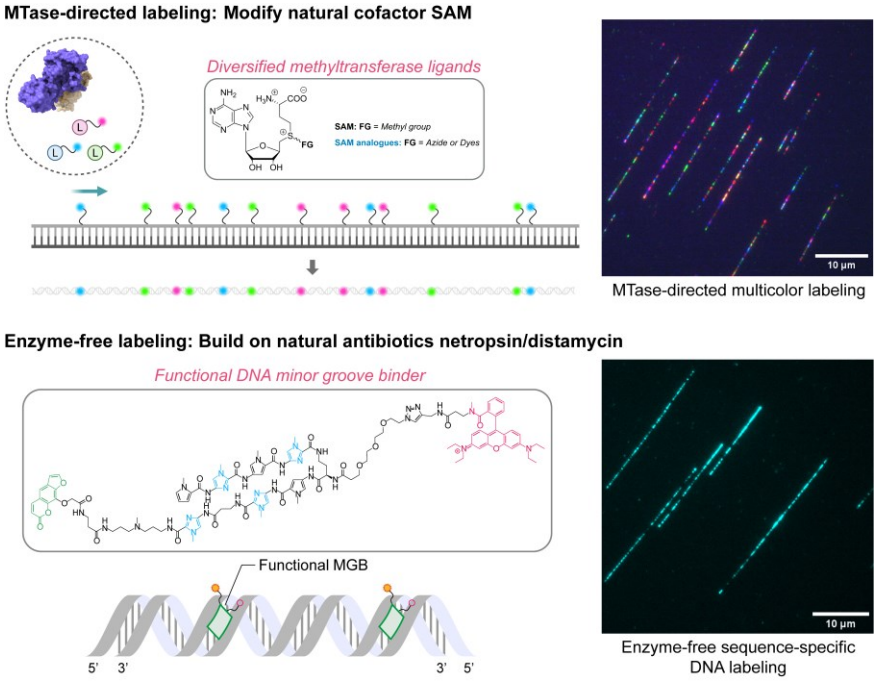


Figure 1. Sequence-specific fluorescent labeling of DNA using two complementary strategies.

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# Estimating the local water content in polymer systems using super-resolution fluorescence microscopy

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In recent years, a significant body of research has been dedicated to the development of environmentally sensitive (fluorescent) probes, many of which can report on physicochemical properties such as viscosity or polarity.[1] Nevertheless, only a limited number of fluorophores have the capacity to detect changes in the local water content. While access to the number of water molecules would provide valuable molecular insights, the investigation of water-containing samples with fluorescence microscopy has proven to be challenging due to the quenching ability of $H_2O$. Indeed, it has been demonstrated that red-emitting dyes are particularly susceptible to this quenching, and it has been postulated that this is due to an effective transfer of energy from the electronically excited dye to the surrounding water molecules.[2] In contrast, when $H_2O$ is replaced with $D_2O$, there is an increase in both the fluorescence quantum yield and the excited-state lifetime (see Fig. 1). Accordingly, the number of water molecules can be estimated by means of fluorescence lifetime imaging microscopy (FLIM).

In the present study, the fluorescence lifetime of ATTO 655, which was covalently embedded into microgels, was measured. These cross-linked polymer networks exhibit intriguing properties that have great potential for applications in medicine and biochemistry.[3] We recorded FLIM images of such labeled microgels in different $H_2O$:$D_2O$ ratios in their swollen state (22 °C) and in their collapsed state (40 °C). A Stern–Volmer analysis was then conducted to determine the water content in microgels at different temperatures. By combining FLIM with localization-based super-resolution microscopy,[4] we were furthermore able to estimate the spatial distribution of water within the microgels, which has not yet been achieved with other techniques.[5] Additionally, an investigation into the moisture changes of these microgels during the drying process could be conducted.[6]

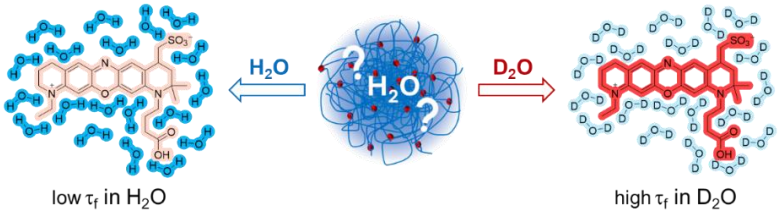


Figure 1. Scheme of fluorescence quenching of ATTO 655 in $H_2O$ and restoration of its fluorescence in the presence of $D_2O$ within the first solvation sphere, which can be used to estimate the water content in microgels.

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# Formation of Three-Dimensional Cross-Linked Polymer Networks Studied by Single Molecule Tracking

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Single molecule tracking (SMT) allows to study the dynamics of single fluorescent dye molecules in a polymer matrix without ensemble averaging. By employing SMT, Ito *et al.* revealed decreasing translational and rotational single molecule mobility with increasing cross-linking density in a thin polymer film.[1] Moreover, SMT has been employed to study the radical polymerization of styrene.[2] Here, we investigate the microstructural formation of a three-dimensional cross-linked polymer network produced by the polycondensation of α-ketoglutaric acid and butane-1,4-diol. Single terrylene diimide (TDI) molecules embedded in a thin film of the educt melt serve as versatile probes to reveal the evolving internal network topology at different stages of the polymerization process. Through a two-dimensional mean-squared displacement (MSD) approach, we monitor the transition from nearly unrestricted single molecule diffusion at early polymerization stages to progressively confined motion as network formation and cross-linking proceeds. Furthermore, segmentation analysis of the single molecule tracks indicates a heterogeneous nature of the polymer network. Next, we plan to study the dependency of the network formation kinetics on the polymerization temperature.

**Funding:** -

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# FEDUP: extending the range of feasible diffusion imaging

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The characterization of diffusion, especially in polymer systems, remains a challenging research topic. A classical (direct) approach relies on fluorescence microscopy, in particular Single Molecule Tracking (SMT).[1] The method, however, is restricted to measurements of diffusion coefficients $D \geq 10^{-17}$ $m^2s^{-1}$. Slower diffusion cannot be resolved accurately due to the effectively achievable localization precision of a widefield microscope and finite measurement times. To combat this lower limit, our group developed a new microscopy technique which we termed FRET Efficiency Diffusion measurement Upon Photocleavage (FEDUP). Our method utilizes the sensitivity of Förster Resonance Energy Transfer (FRET) to intermolecular distances on a nanometer scale.[2] A fluorescent dye dyad is required that can be selectively cleaved into its two dye components. Furthermore, a suitable, at least binary, spectral resolution has to be achieved on a microscopic level. After photocleavage, the two dyes composing the FRET pair diffuse independently resulting in a spatiotemporal decrease of FRET efficiency. The fluorescence intensity of the FRET-donor and FRET-acceptor is consequently monitored and correlated to the relative distance covered by the FRET pair.

We attempted to improve on our previous work[2] by addressing the biggest drawbacks of our original FRET-dyad, namely the low wavelengths required for photocleavage and the water insolubility of the dyad. In this context, we synthesized and characterized a new photocleavable dyad incorporating the well-known photolabile protecting group 2-(2-nitrophenyl)propoxycarbonyl (NPPOC)[3,4] as linker and the cationic dyes ATTO565 and ATTO647N as FRET-donor and FRET-acceptor, respectively.[5] We showed that the linker can be cleaved with wavelengths $\lambda \geq 350$ nm, leading to a gradual decrease of the FRET efficiency. Furthermore, the novel dyad is well soluble in polar solvents.[5]

Here, we present our latest results of single molecule diffusion imaging in different (hydrophilic) polymer systems with our novel FRET-dyad. A few representative frames of an exemplary measurement video in thin PVAc films are shown in Fig. 1.[5]

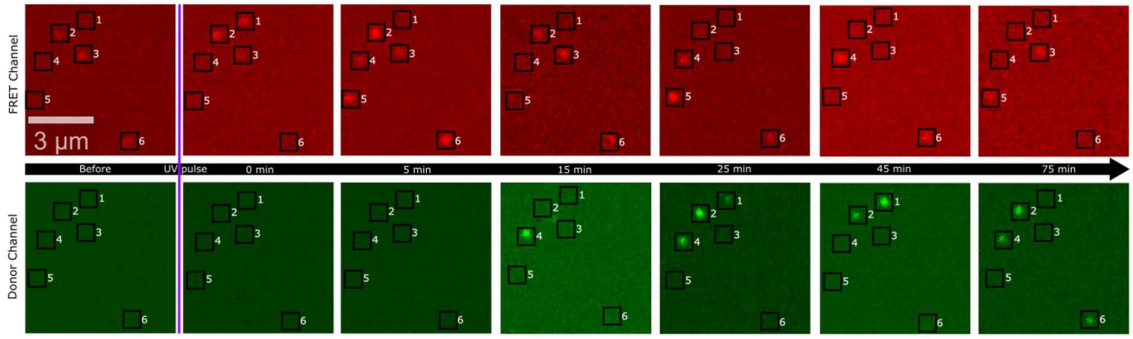


Figure 1. Selected frames during different times of a typical FEDUP measurement in PVAc. The detection channel of wavelengths >655 nm is colored red (FRET channel). The detection channel of wavelength between 570 – 633 nm is colored green (Donor channel). The excitation wavelength was 561 nm.[5]

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# Oxygen quantification based on the persistent phosphorescence lifetime of host−guest nanocrystals

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Phosphorescence lifetime imaging microscopy (PLIM) is a method to accurately measure two-dimensional (2D) oxygen concentration ($[O_2]$)[1]. However, conventional PLIM using room-temperature phosphorescence (RTP) materials with phosphorescence lifetime ($\tau_p$) on the order of μs takes a long time to construct a 2D image regarding $[O_2]$. The persistent RTP with $\tau_p$ > 100 ms (*p*RTP) could be determined using 2D photodetector to allow a fast construction of a PLIM image. However, the range of $[O_2]$ that can be measured with $\tau_p$ > 100 ms, which allows the $\tau_p$-determination using a 2D photodetector, is quite small for previously reported *p*RTP materials[2]. Here, we report a fast and wide-range 2D $[O_2]$ measurement made possible by nanoparticle crystallization.

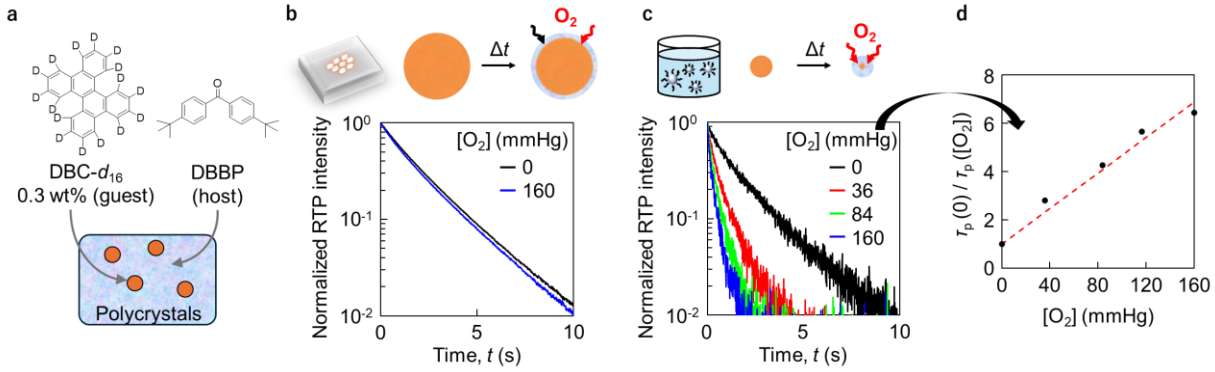


Figure 1. a) Chemical structures of the *p*RTP material (top) and illustration of the guest doped host polycrystal (bottom). b) Illustration of the bulk solid and RTP decay characteristics under air and inert condition. c) Illustration of nano/microparticles and RTP decay characteristics under several $[O_2]$. d) Stern–Volmer plot showing the relationship between $\tau_p$ and $[O_2]$.

The *p*RTP material for the oxygen sensor is composed of deuterated dibenzo[*g*,*p*]chrysene (DBC-$d_{16}$) as the phosphorescence emitter, and 4,4'-di-*tert*-butylbenzophenone (DBBP) as the host crystal (Fig. 1a). In the case of bulk solid of the DBC-$d_{16}$ doped DBBP crystals, it has almost no $\tau_p$ change even with different $[O_2]$. This is because the slow diffusion of oxygen within the crystalline host prevents oxygen from reaching the center of the material within the lifetime, and photons are continually emitted from the anoxic central region (Fig. 1b). On the other hand, RTP decay of nanoparticles becomes shorter with the increase of $[O_2]$ (Fig. 1c) because oxygen reaches the center within the time $\tau_p$. From the lifetime analysis of initial RTP decay of the nano/microparticles, we successfully quantified $[O_2]$ in the range from 0 to 160 mmHg determined at $\tau_p$ > 100 ms. The relationship between $\tau_p$ and $[O_2]$ is usually described as Stern–Volmer plot (Fig. 1d). The slope of the plot is Stern–Volmer oxygen-quenching rate ($k_Q$) that is proportional to the diffusion coefficient of oxygen in the solid. The $k_Q$ value is determined as 0.0027 $mmHg^{-1}s^{-1}$ that is 1/17 that of previously reported *p*RTP crystals which can quantify only 0-15 mmHg[3].

In order to clarify the mechanism by which nanoparticulation induces $[O_2]$ responsiveness shown in Fig. 1b and 1c, we have successfully conducted a discussion on measuring the change in $\tau_p$ of individual nanoparticles, and the results will also be presented in the presentation.

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**Acknowledgement:** We thank Shoei Chemical Inc. for the support regarding electron microscope measurements.

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# Influence of Nile Red on the internal structure of pNIPAM microgels investigated with combined spectral and lifetime measurements

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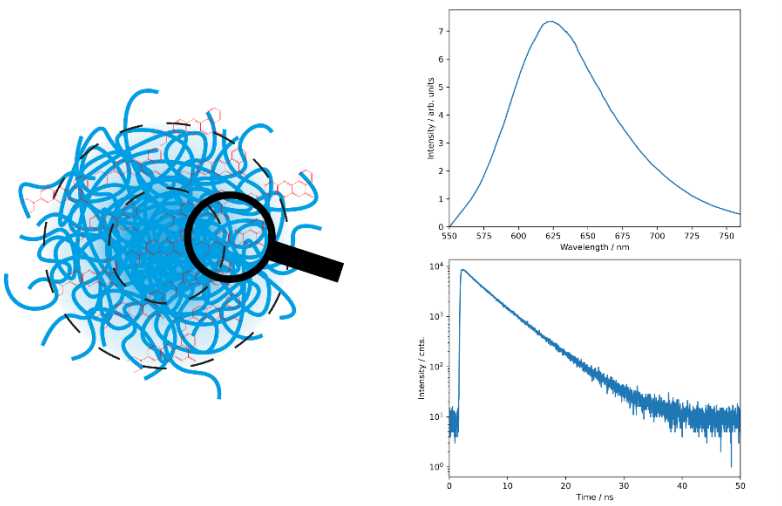
Microgels are three-dimensional cross-linked polymer networks. The properties of microgels depend heavily on the swelling of the microgel in good solvents.[1] The swelling is governed by the local structure of the microgels. To resolve the local structure inside microgels we previously developed a Nile Red PAINT based super resolution method to determine the local polarity inside microgels.[2] In this work we further investigate the interaction between Nile Red and pNIPAM microgels. For this, we combined confocal spectral and lifetime measurements of Nile Red inside single microgels. From these measurements, we conclude that the Nile Red probe changes the local structure of the polymer system. Additionally, we found a preferential solvation in the binary solvent mixture methanol/water around the pNIPAM chains inside microgels, which has also been recently shown in a different work.[3]

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# Enhancement of the Photoelectrochemical Performance of Core-Shell Structured Hematite Photoanode with Homojunction Configuration

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Hematite has been a widely used photoanode material because of its abundant resources, visible light-absorbing band gap, and non-toxicity. However, it has disadvantages such as the fast recombination of photo-generated electrons-holes and a short hole diffusion length. To overcome these issues and enhance PEC performance, in this study, we prepared a core-shell structured hematite sample with the homojunction to facilitate the efficient charge separation. In this study, four types of samples were prepared: a bare sample without any doping; a sample with p-type doping (Zn) introduced into the shell; a sample with p-type doping introduced exclusively into the core; and a sample with n-type doping (Co) in the core combined with p-type doping (Zn) in the shell.

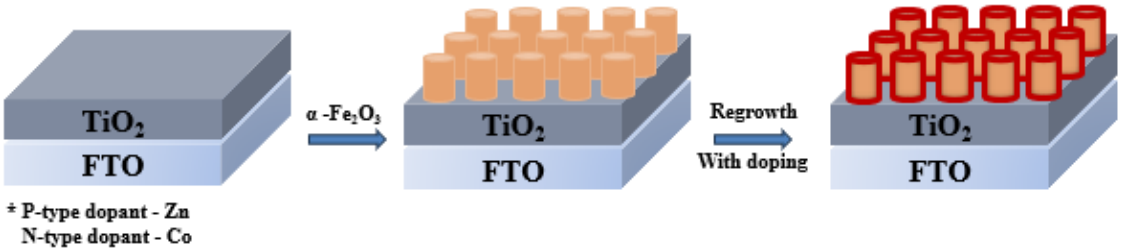


Figure 1. Schematic illustration of the basic synthesis procedure of target samples

For all samples, the $TiO_2$ underlayer was deposited to enhance the photocurrent density and suppress back recombination.[1] By preserving the nanorod morphology of hematite while forming a core–shell structure, the samples exhibit high charge mobility and enable controlled doping strategies. Furthermore, the proposed structure provides a favorable band alignment due to the junction, facilitating efficient charge separation. We doped Zn and Ti through Ti diffusion by $TiO_2$ underlayer the shell and core, respectively, and demonstrated that the PEC performance of the prepared sample was drastically enhanced, compared with that of the undoped one. However, the enhancement in current density was observed, accompanied by the anodic shift in the onset potential. This phenomenon was attributed to Ti diffusion originating from the $TiO_2$ underlayer. To address this issue, an additional experiment was conducted in which a different dopant was doped into the core to suppress Ti diffusion. In this study, cobalt was employed as the n-type dopant, as a result, the cathodic shift in the onset potential was achieved. The origins of the improvements were investigated by the combination of electrochemical and time-resolved spectroscopic methods.[2] As a result, it was confirmed that the structure proposed in this study facilitated efficient charge separation, thereby leading to an enhancement of the PEC performance.

**Funding:** G-LAMP Program of the NRF grant (RS-2024-00445180)

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# Length-Dependent Optoelectronic Behavior in Nanographenes

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Molecular nanographenes are emerging as promising materials for optoelectronic and energy-related applications due to their unique and tunable optical and electrochemical properties.[1] While significant advances have been made over the past decade in the synthesis of atomically precise nanographenes, a comprehensive understanding of their photophysical and electrochemical behavior remains in its early stages.[2,3] In this work, we present a systematic photophysical investigation of a series of molecular nanographenes with varying lengths.[4,5] Furthermore, we explore their interactions with porphyrins and study their behavior in the aggregated state using a broad range of ultrafast spectroscopic techniques.

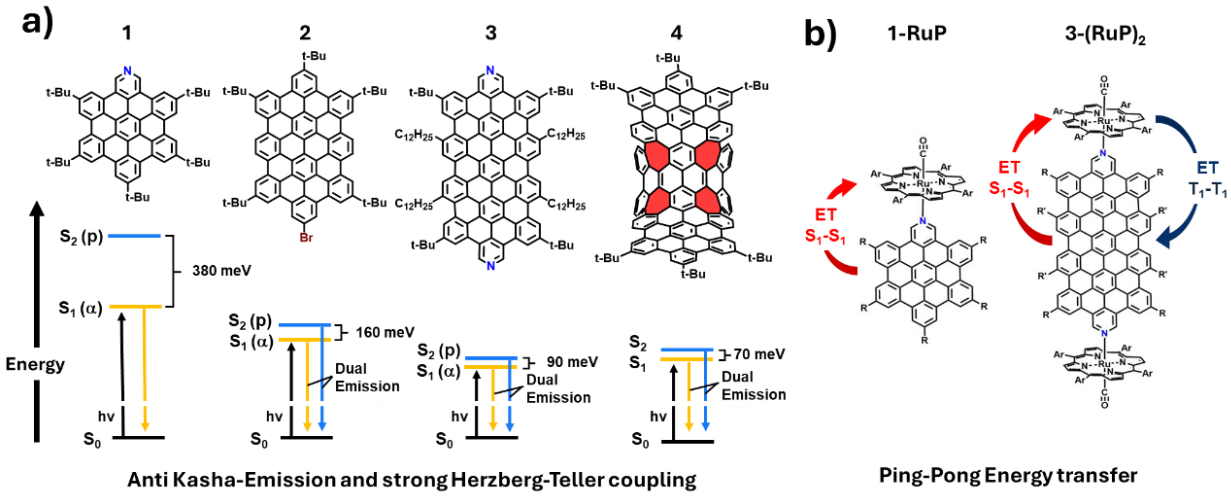


**Figure 1**. **a)** Chemical structure of molecular nanographenes with different lengths, and relative energy scheme with the energy of $S_1$ and $S_2$, leading to Anti-Kasha emission and Herzberg-Teller vibronic couplings. **b)** Chemical structure of nanographene-porphyrin hybrids and their length-dependent excited-state deactivation.

Interestingly, we found that increasing the nanographene length results in an energetic proximity between the $S_1$ and $S_2$ states, giving rise to a rarely observed anti-Kasha fluorescence in **3**. This is accompanied by strong vibronic coupling, which leads to deviations from the widely used Franck–Condon approximation, in favor of Herzberg-Teller activities in **2** and **4**. The nanographene length also influences the excited-state deactivation pathways in their porphyrin (**RuP**) hybrids, as revealed by ultrafast transient absorption spectroscopy. Notably, the hybrid **3-(RuP)$_2$** exhibits a “ping-pong” energy transfer mechanism, where energy is transferred from the nanographene to the porphyrin and then back again—unlike **1-RuP**, where energy transfer occurs unidirectionally from the nanographene to RuP.
Furthermore, the self-assembly behavior of compounds **2** and **3** in solution was examined in detail, revealing the formation of dimers followed by two-dimensional supramolecular polymers. Exciton and charge carrier dynamics within these structures were probed using transient emission microscopy and ultrafast terahertz (THz) spectroscopy. Our findings provide a deeper understanding of the optoelectronic properties of nanographenes and underscore the potential of such assemblies for applications in organic electronics, including solar cells and field-effect transistors (OFETs).

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# Functionalized 1,2-dihydro-1,2-azaborinines for Molecular Solar Thermal energy storage

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In effort to combat climate change in accordance with a stable energy supply, developments of environmentally acceptable energy storage facilities are indispensable. A vibrant research field is given by photo switchable molecules, which enable the storage of solar power in line with valence isomerization, as well as the release of the stored energy on demand.[1] 1,2-Dihydro-1,2-azaborines are six-membered, aromatic heterocycles that are isoelectronic to benzene.[2] Their heterocyclic nature is induced by CC/BN isosterism and gives rise to a unique photoisomerization behavior, assembling exclusively the Dewar isomer (see Fig. 1).[3] With respect to the chosen substituents, the properties of dihydroazaborines can be adjusted, fulfilling many requirements for an application as molecular solar thermal energy storage system.[4] However, one major challenge remains red shifting the absorption wavelength towards the visible spectrum. Until now the functionalization mainly focused on the B-N unit, while protocols considering the substitution of the carbon backbone are rare.[5,6] Our aim is to further optimize key MOST parameters by means of targeted substitution of the carbon backbone e. g. enlargement of the π system or push-pull interdependence.

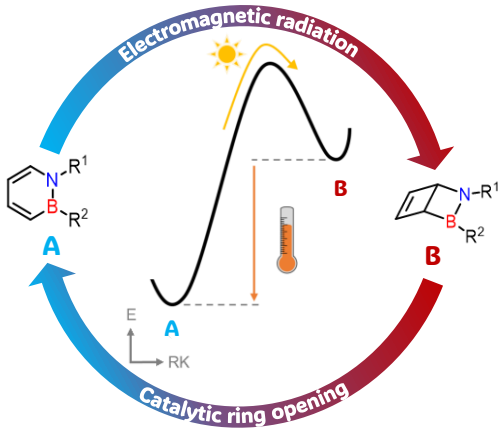


Figure 1. Photoisomerization and catalytic ring opening of 1,2-dihydro-1,2-azaborinines.

**Funding:** Deutsche Forschungsgeselschaft (496207555), Fonds der chemischen Industrie (scholarship)

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# Insight into excited state dynamics of PM6:Y6 Bulk-Heterojunction: deposited via Langmuir Schaefer deposition technique

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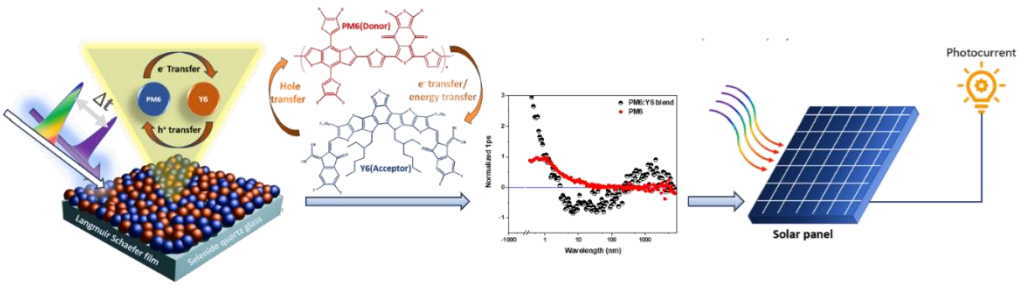
Non-fullerene acceptors along with different donor molecules have driven significant enhancements in device efficiencies for photovoltaic devices based on organic thin films, reaching an impressive 18.01 % efficiency [1]. In particular the combination of PM6[1] as donor and the acceptor Y6[2] presents an active combination of organic compounds to yield efficient active layers in organic photovoltaics.

However, aggregation and non-homogeneous film formation via conventionally used spin- or drop-casting can drastically impact on both the optical absorption and electronic properties. Therefore, we aim to study the optically induced processes in highly organized PM6:Y6 layers. In particular, we utilize Langmuir-Schaefer films, which exhibit organized supramolecular arrangements of both donor and acceptor molecules or mixtures of both compounds. Being able to control the intermolecular interactions might offer a pathway to optimizing the performance of photovoltaic devices built from the highly organized active layer.[2]

In this contribution we utilize steady-state and time-resolved (transient) absorption and emission spectroscopy to study the fate of optical excitations in pristine Langmuir films of PM6 and Y6 and Langmuir-Schäfer of a blends of PM6 and Y6. The accelerated exciton decay observed in PM6:Y6 blend films-compared to pristine PM6 when deposited via Langmuir-Schäfer techniques-reveals efficient energy/electron transfer between donor and acceptor components, driven by optimized molecular packing by providing detailed insights into ultrafast exciton dynamics and charge transfer pathways. transient absorption spectroscopy underscores the importance of advanced fabrication methods like Langmuir-Schäfer in developing high-performance, stable organic photovoltaic devices. This work demonstrates that combining innovative film engineering with state-of-the-art spectroscopic techniques is crucial for advancing the design and scalability of next-generation solar cells.

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Authors acknowledge Deutsche Forschungsgemeinschaft and FuncHeal for supporting and funding this work.

[1] **PM6:** Poly[(2,6-(4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)-benzo[1,2-b:4,5-b’] dithiophene))-alt-(5,5-(1’,3’-di-2-thienyl-5’,7’-bis(2-ethylhexyl) benzo[1’,2’-c:4’,5’-c’] dithiophene-4,8-dione))]

[2] **Y6:**2,2’-((2Z,2’Z)-((12,13-bis(2-butyloctyl)-3,9-diundecyl-12,13-dihydro-125thiadiazolo[3,4-e]thieno[2”,3”:4’,5’]thieno[2’,3’:4,5]pyrrolo[3,2-g]thieno[2’,3’:4,5]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile

# Intramolecular Down- and Up-Conversion in Dimeric Tetracene Complexes Centered via Platinum(II) and Palladium(II)

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Singlet fission, also known as down-conversion, and triplet fusion, also called triplet-triplet annihilation up-conversion, are two reversed multiexcitonic processes that offer the potential to surpass the efficiency limits of conventional solar energy conversion systems.[1–3] In tetracene, where the singlet exciton energy is approximately twice that of the triplet exciton, both SF and TTA-UC processes are thermodynamically feasible.[4] In this study, we design and synthesize tetracene-based dimeric complexes coordinated to Pt(II) and Pd(II) metal centers, employing a one-pot synthetic approach using a pyridyl-terminated tetracene ligand. Remarkably, the Pt(II)-coordinated tetracene dimer exhibits efficient intramolecular down-conversion and up-conversion processes, despite the large spatial separation between the tetracene chromophores. In contrast, Pd(II)-coordinated tetracene dimer exhibits photophysical behavior similar to that of its monomeric complex. Upon photoexcitation, no evidence of singlet fission is observed in Pd(II)-coordinated tetracene dimer. It demonstrates that the metal center plays a crucial role in controlling the excited-state dynamics of tetracene. This approach has the potential to develop new coordination complexes for singlet fission and up-conversion investigations, as well as further applications.

**Funding:** The German Research Foundation (DFG) GU 517/27-1 and GU 517/34-1, and “Solar Energy goes Hybrid” Initiative of the Bavarian Ministry for Science, Culture, and Education (SolTech). The Natural Sciences and Engineering Research Council of Canada (NSERC, grant no. RGPIN-2017-05052 and RGPIN-2023-04000)

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# Effect of Host Oxygen Permeability on the Efficiency of Solid-State Photon Upconverters for Photovoltaics

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Triplet-triplet annihilation upconversion (TTA-UC) has the potential to boost the performance of solar cells by converting sub-bandgap photons to useful energies.[1] However, for the implementation of TTA-UC systems to be practical, solid-state host materials must be developed that give rise to efficient TTA-UC under ambient conditions.[2,3] This poses a series of materials challenges: the host must be mechanically robust, while also allowing sufficient mobility for the upconverting chromophores to undergo the molecular collisions necessary to facilitate the required energy transfers. Furthermore, to avoid necessitating air-free fabrication and encapsulation, the host itself should act as a barrier to prevent oxygen quenching.

This work focuses on a series of TTA-UC hosts based on organic-siliceous hybrid polymers known as *ureasils*. Through the ability to alter the relative contents of flexible organic polymer and oxygen-resistant silica, the properties of ureasils can be tuned such that they act as effective TTA-UC hosts in air (Fig. 1(a).[4] Results will be presented, further investigating the effects of varying the structure and relative proportions of these organic and siliceous components on the host performance. Particular attention will be paid to the characterisation of the oxygen barrier properties of these hosts (Fig. 1(b)), both on a bulk scale through traditional oxygen transmission measurement and in local environments through photophysical analysis, and their role in affecting the overall TTA-UC performance. With this improved understanding, future host materials can be designed to enable greater upconversion efficiencies, increasing viability for applications in solar energy harvesting.

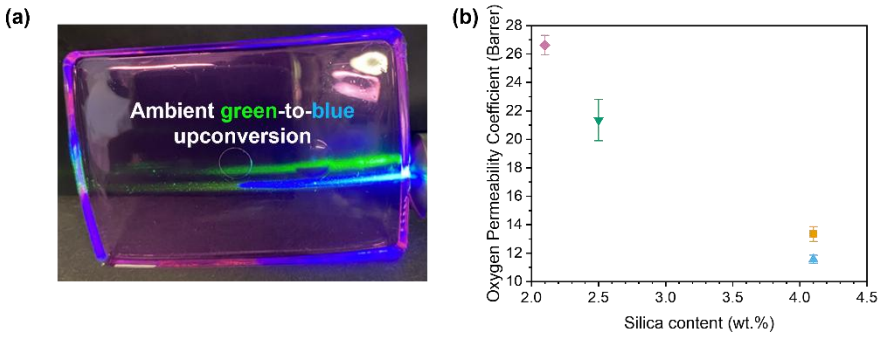


Figure 1. Properties of ureasil TTA-UC hosts. a) Optimisation of ureasil properties allows them to act as effective hosts for green-to-blue upconversion in air. b) By raising the silica content of the ureasils, the oxygen permeability coefficient can be decreased, improving oxygen barrier properties.

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# Aggregation-Induced Singlet Fission in Push-Pull Diketopyrrolopyrrole Water Dispersed Nanoaggregates and Thin Films

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In this work, the phenomenon of singlet fission (SF), interesting for its potential applications in organic photovoltaics[1] and in photodynamic therapy,[2] has been studied. We focused on the effect of aggregation on the intermolecular SF[3] for a set of carbazole functionalized diketopyrrolopyrrole derivatives characterized by dipolar/quadrupolar structures and by meta/para substitutions, confirming the activation of SF upon aggregation. To this aim, their photobehaviour was explored not only as monomers in dilute solution but also as aggregates produced in solid-state thin films and as organic nanoparticles in water.

In water dispersed nanoaggregates and thin films of the investigated compounds, the production of independent triplets through SF has been revealed. This is proved by the observation of bright fluorescence in dilute solutions, while aggregation into thin films and water-dispersed nanoparticles led to strong quenching of the fluorescence quantum yield (from 0.5 to 0.0003) and shortened excited-state lifetimes, indicating the opening of nonradiative pathways. The femtosecond transient absorption (fs-TA) experiments unveiled aggregation induced SF as the non-radiative decay pathway competitive to the emission. In fact, the ultrafast formation of a correlated triplet-pair intermediate and subsequent generation of independent triplets, in contrast to the behaviour observed in solution, with triplet yields larger than 100% in both the organic nanoparticles (108%) and the films (114%) has been found by fs-TA. Consistently, ns-laser flash photolysis confirmed triplet formation only in the aggregates. Interestingly, the fastest SF processes have been observed in para-substituted derivatives, that show stronger intramolecular charge transfer character.

Our study sets the stage for the SF-enhanced use of these highly photostable and strongly visible light-absorbing push-pull diketopyrrolopyrrole-based organic materials for solar and biomedical applications.

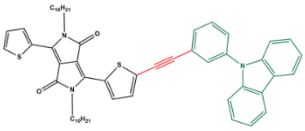

Figure 1: DPP1 structure.

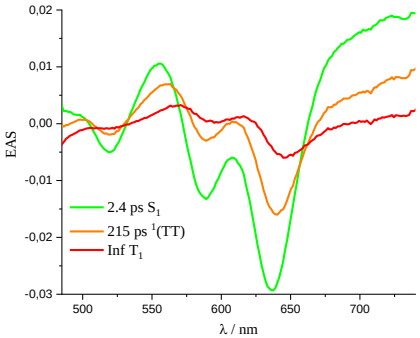


Figure 3: Evolution Associated Spectra of DPP1 nanoaggregate obtained by Global Analysis from fs-TA measurements.

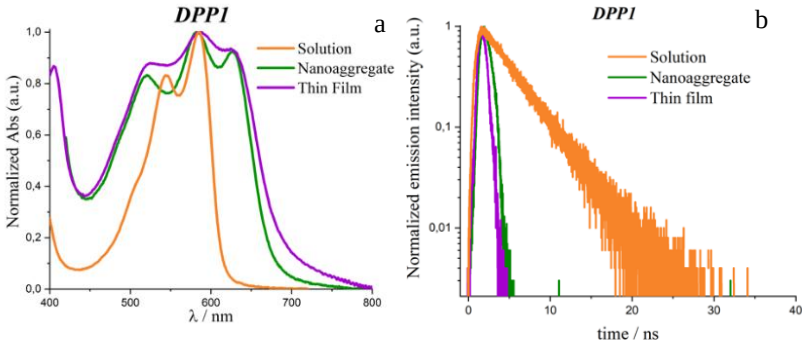


Figure 2: aggregation effect on absorption spectra (a) and on fluorescence lifetime decays (b).

**Funding:** from the European Union - NextGenerationEU under the Italian Ministry of University and Research (MUR) National Innovation Ecosystem grant ECS00000041 – VITALITY and from the MUR under the PRIN 2022 program, grant no. 2022RRFJC4.

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# Revealing the Origin of the Improved OER Activity of Ni-Based ZIFs on α-$Fe_2O_3$ Photoanode using NF-HD-TG Spectroscopic and PEIS Techniques

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Ni-based Zeolitic imidazolate frameworks (ZIFs), a subclasses of metal-organic frameworks (MOFs), were utilized as oxygen evolution reaction (OER) catalysts due to their large surface area, abundant open sites, and ease of tuning.

Nickel is a widely used transition metal catalyst for the OER in photoelectrochemical (PEC) systems. To elucidate the role of various transition metals interacting with the hematite surface, we employed Ni-based ZIF co-catalysts with identical crystal structures. By systematically investigating electrochemical performance and charge carrier dynamics induced by transition metal substitution, we could demonstrate the distinct roles of these metals in interfacial water oxidation processes.

We fabricated Ni-, NiFe-, and NiCo-based ZIFs and deposited them onto the surfaces of the hematite films. We demonstrated that the OER activities of the treated samples could be enhanced, compared to that of the bare sample. In addition, we could successfully reveal the energetic positions of each trap state in the OER catalysts, based on the surface state capacitances ($C_{ss}$) and bulk, transfer resistances ($R_{bulk}$, $R_{transfer}$), obtained by photoelectrochemical impedance spectroscopy (PEIS).[1] These parameters are associated with hole capture and charge transfer processes in the OER reaction. By comparing the $C_{ss}$ and R values of the S2 state, which mediates hole capture at surface-active sites, and the S1 state, which affects charge transfer, it is possible to predict which reaction is more strongly influenced by each transition metal.

Furthermore, using the Near-Field Heterodyne Transient Grating (NF-HD-TG) technique, we could extract the information of the charge carrier dynamics originating from the observed surface trap states.[2]

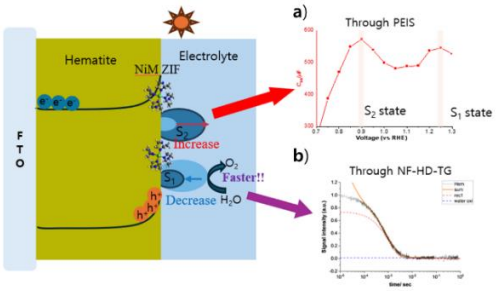


Figure 1. Schematic illustration of α-$Fe_2O_3$ /NiM-ZIF (M = Co,Fe,Ni) a) The surface capacitance obtained from PEIS reveals the energetic position and variation of specific states b) The transfer time constant of specific states derived from NF-HD-TG indicates their efficiency in the OER process.

**Funding:** G-LAMP Program of the NRF grant (RS-2024-00445180)

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# The Mechanism of Hole Diffusion and the Role of Coherent Phonon Modes in Lithium Doped Bismuth Vanadate Photoanodes

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Photoinduced charge separation and transport of holes to the active surface of metal oxide photocatalysts are substantially affected by trapping, leading to the formation of a hole polaron diffusing with the motion of the lattice. Bismuth vanadate ($BiVO_4$) is a promising metal oxide for photocatalytic water splitting, and the hole polaron has been reported to couple to the phonon mode associated with $Bi^{3+}$ and $VO_4^{3-}$ [1,2]. The hole-phonon coupling at early time following light absorption can have diverse effects on the charge separation and mobility of holes from the bulk to the active surface. It is unknown how hole polaron formation relates to the photoinduced charge carrier dynamics and photocatalytic performance, and whether it can be modulated by introducing structural changes in the $BiVO_4$ lattice via e.g. doping[3]. In this work, we address these questions by investigating the effects of Li-doping on the photoinduced charge carrier dynamics by in-situ fs transient absorption spectroscopy, while in parallel the impact on the photocatalytic performance is studied.

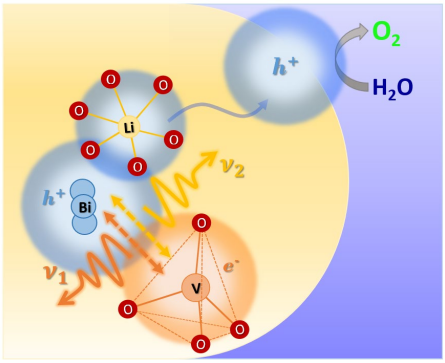


Figure 1: Charge carrier dynamics in Li-doped $BiVO_4$ photoanodes.

**Funding:** Dutch Research Council NWO, Open Competition Domain Science – M-1.

**Acknowledgement:** We thank Mark A. Smithers and Dr. Yibin Bu from the University of Twente for the SEM and XPS measurements.

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# Photo-assisted recharge of Lithium Ion battery

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The presented work is intended to support the energy transition from coal/oil-based production to a more sustainable way of generating electricity in modern society.

The proof of concept we aim to demonstrate is the feasibility and understanding of the chemistry behind a photo-battery that requires less energy to be charged compared to a conventional Lithium-Ion Battery (LIB) (Fig. 1a).

During the charging process of a LIB, the active material at the positive electrode (LFP or LCO) must be oxidized, meaning that $Li^+$ must be de-intercalated, while at the same time, an intercalation of $Li^+$ must occur at the negative electrode. This step requires a certain amount of electrical energy, which depends on the nature of the active materials (AM). The amount of energy supplied by the external circuit to charge the battery can be reduced if the oxidation of the AM at the positive electrode is assisted by a species with a high oxidation potential [1].

The generation of highly oxidative species can be achieved through the interaction of light with specific semiconductors. These materials act as photosensitizers and interact with specific wavelengths of the light spectrum to promote the excitation of an electron ($e^-$) from the valence band (VB) to the conduction band (CB). The energy barrier for this transition is known as the band gap. An external anodic current must be applied to extract the e- from the CB, leaving a hole ($h^+$) in the VB. This overall process requires less energy compared to the direct extraction of $e^-$ directly from the VB. The oxidative potential of the $h^+$ can be tuned by selecting or modifying a semiconductor to oxidize the cathodic material during charging. The photoelectrode consists of a transparent support (glass or PET) on which a thin film of semiconductor is deposited.

The high oxidation potential of the $h^+$ can compromise the stability of the electrolyte (which is stable up to +4.4V vs $Li^+/Li$), drastically reducing the lifespan of a battery. A protective layer can be interposed between the semiconductor and the AM to prevent direct contact between the electrolyte and the photogenerated $h^+$. This protective layer, acting as a charge shuttle, consists of a polymerized organic complex of Fe(II) (Fig. 1b) deposited on the materials via an electrochemical technique. Two different methods are used for this purpose [2].

Several semiconductors were tested and studied to combine their characteristics with LIB technology, with a major focus on ZnO and g-$C_3N_4$.

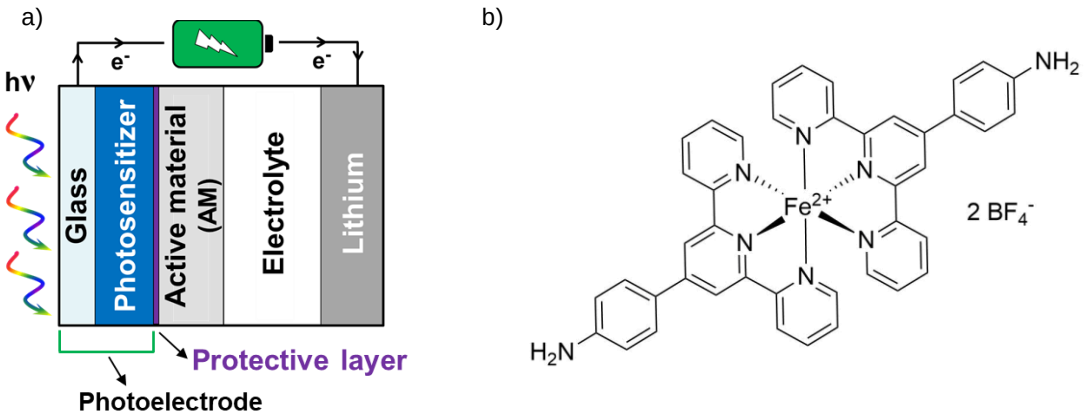


Fig 1 – **a)** Schematic representation of the proposed photodevice and all components of the battery. **b)** Fe(II) complex monomer used as protective layer.

**Funding:** IRGA (Universite Grenoble Alpes) is acknowledged for the financial support of this work.

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# Positional Isomerism of Sulfur Determines Which $C_8H_6S$-Heterocycles are Candidates for Anti-Kasha $S_2$-$T_1$ Singlet Fission

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Singlet fission (SF) is a spin-allowed process in which a photoexcited singlet state molecule transfers energy to a ground-state molecule while generating two triplet excitons, thus increasing solar energy storage efficiency. While most known SF systems undergo SF from their first excited singlet state ($S_1$), recent perspectives have drawn attention towards the feasibility of SF from higher excited singlet states ($S_n$), thereby coining a generalized energy criterion $2\times E(T_1) \approx E(S_n)$ for SF.[1] In support of this new trend, recent computational investigation guided by previous experimental observations suggest that azulene, a 10-membered non-alternant hydrocarbon and an archetypal anti-Kasha fluorophore, may undergo $S_2$ SF.[2] This is because azulene's non-alternant topology results in a large $S_2$-$S_1$ separation and, concomitantly, low $S_1$-$T_1$ separation, thereby satisfying the $2\times E(T_1) \approx E(S_2)$ criterion.[3] However, the same rationale does not apply to azulene's heteroanalogues. Certain heteroanalogues, previously coined as pseudoazulenes[4] (e.g., thialene), exhibit azulene-like optical properties, whereas their positional isomers, referred to here as pseudonaphthalenes (e.g., benzo[*b*]thiophene), do not. Yet, these heterocycles all share the same non-alternant topology, thereby collapsing the established rationale. In this contribution, we present a theoretical framework for distinguishing *S*-pseudoazulenes from *S*-pseudonaphthalenes. Our method relies on DFT and CASSCF calculations, which are distilled down to a qualitative, *pen-and-paper* approach, informed by the concepts of *equiaromaticity*[5] and the *isolobal analogy*.[6] Moreover, we support our model with a time-resolved spectroscopy study of corresponding model compounds. Thus, we identify and, show how to identify heterocyclic candidate molecules for $S_2$-mediated singlet fission.

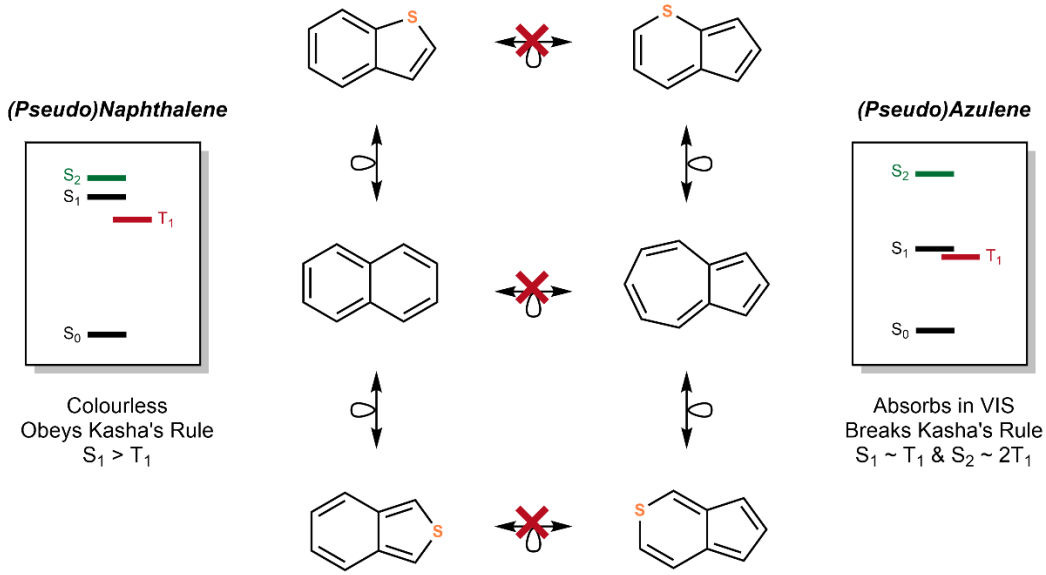


Figure 1: Illustration of the relationship between the electronic structures of (*S*-pseudo)azulenes and (*S*-pseudo)naphthalenes, expressed through isolobal analogy.

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# Controlling Electron Transfer Reactions for Artificial Photosynthesis

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Efficient conversion of sunlight and low energy building blocks such as carbon dioxide and water to higher energy products using artificial systems is highly desirable for meeting future clean energy needs. Photosynthetic organisms are able to capture solar energy and convert it to biologically useful forms, but emulating the processes of biological photosynthesis presents many challenges. Oxidative and reductive chemistry must both occur and multiple electron transfer processes are required. In particular, water oxidation requires four oxidative equivalents which must be delivered sequentially, a kinetically sluggish O---O bond forming step must occur, and the environment is hostile to many molecular species required to facilitate water oxidation. The chemistry of reduction reactions can be similarly challenging. We are interested in synthesis and electron transfer mechanisms of synthetic chemical species which can mimic biological photosynthetic processes. Chemistry for the control, direction, and transient storage of redox equivalents for artificial photosynthesis which model elementary processes that occur in natural photosynthesis will be presented.

# Enhanced Visible Light Response and Photoinduced Charge Transfer Dynamics of Gold/SiC Nano-Composite Photocatalysts

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In recent years, hydrogen—an energy source that is both high-density and clean—has attracted significant attention. Among the various hydrogen production methods, photocatalytic water splitting is considered one of the cleanest approaches. Silicon carbide (SiC), a semiconductor with high durability, is a promising candidate for photocatalytic activity due to its robustness and suitable band positions. However, pristine SiC faces limitations in utilizing visible light and suffers from low photocatalytic efficiency caused by rapid recombination of photoexcited carriers.

To address this issue, we propose enhancing visible-light responsiveness via the plasmonic effect by adsorbing gold (Au) nanoparticles onto the surface of SiC. This modification forms an electric field at the interface of the composite material and enables efficient separation of photoexcited carriers.

In this study, we employed diffuse reflectance transient absorption spectroscopy to observe charge separation under plasmonic excitation on the femtosecond to picosecond timescale, aiming to elucidate the mechanism of photocatalytic reactions under visible light irradiation [1-3].

SiC nanoparticles were purchased from Xiamen Tob New Energy Technology Co., and gold nanoparticles were synthesized via the citrate reduction method. The composite samples were prepared by mixing the gold colloid solution with the SiC aqueous solution, followed by ultrasonic treatment and drying.

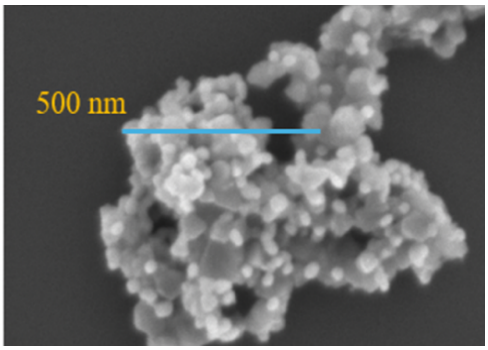

Figure 1. SEM image of Au decorated SiC nanoparticles.

Figure 1 shows a SEM image of the fabricated composite sample. The image confirms that the gold nanoparticles are uniformly adsorbed on the SiC particles. Absorption spectra of the composite samples indicated the occurrence of a plasmonic effect induced by the gold nanoparticles. A red shift in the plasmon peak was observed compared to the original samples, suggesting possible electronic interactions between Au and SiC. Furthermore, diffuse reflectance transient absorption spectroscopy under 400 nm excitation indicated an increase in the average lifetime of charge carriers in Au/SiC compared to pristine SiC, along with a higher proportion of long-lived carriers. This indicates that the effect of the gold nanoparticles suppresses recombination via electron transfer between Au and SiC, thereby enhancing the presence of long-lived components that contribute to the photocatalytic reaction. Also, we have confirmed the occurrence of photocatalytic water splitting reaction under visible light irradiation.

**Funding:** Financial supports by KAKENHI Grants 24K01610 (Grant-in-Aid for Scientific Research B) and 23H00274 (Grant-in-Aid for Scientific Research A) are acknowledged.

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# Understanding the impact of aminoacid networks on protein-based artificial photosystems

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In nature, protein-based structures perform a great diversity of functions with outstanding efficiencies. For this reason, protein-based bio-hybrids are of great interest to technological applications, ranging from green energy generation to electronics[1]. Protein-based artificial photosystems aim to replicate the almost perfect light conversion efficiencies that natural photosystems exhibit. For this, a deep understanding of how each part of the system interacts to generate functional networks is needed, Fig. 1. This presentation proposes an interdisciplinary approach, combining molecular biology and spectroscopy to explore how few mutations on the protein scaffold affect the overall photodynamic properties of artificial photosystems.

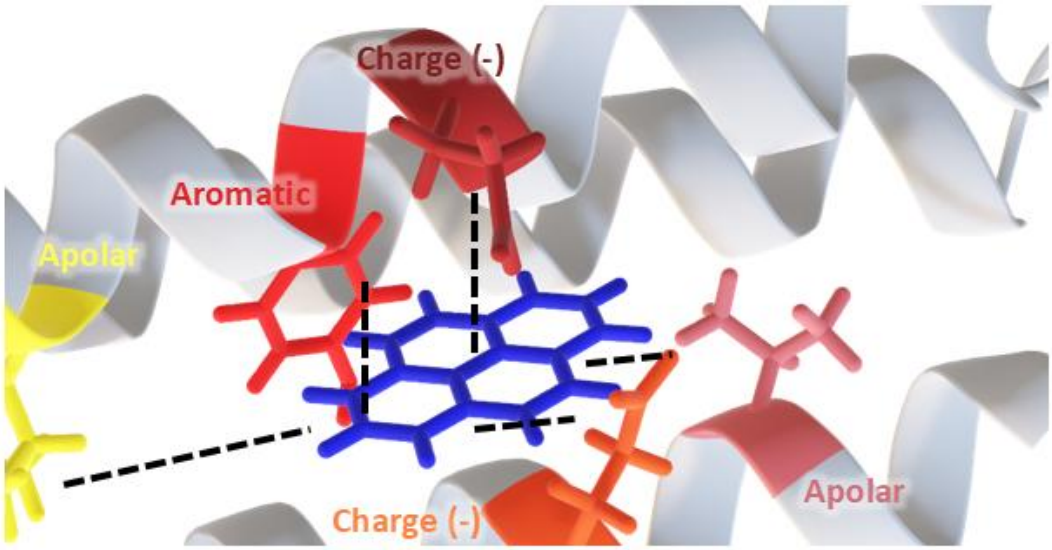


Figure 1. In a protein-based photosystem, the different amino acids inside the protein pocket interact with the dye with different reactivities, affecting the photodynamic behavior of the system.

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# Metal tungstates as photoanodes for water oxidation: computational and experimental results

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Photoelectrochemical water splitting keeps on drawing significant attention as it is a potential way to contribute to energy decarbonization. This approach requires among others the identification of practical photoelectrode materials. In this respect, numerous investigations have been conducted to identify optimal photoanodes capable of promoting water oxidation. This task is though rather challenging due to the extensive array of potential materials to be explored. Among binary oxides, $WO_3$ has garnered attention because of its remarkable photoactivity and stability in acidic media [1,2], although its wide band gap poses a significant drawback. To mitigate this issue, there has been a shift toward exploring related materials, such as $CuWO_4$ [3].

This contribution will focus on summarizing our recent work in this subject, which encompasses both theory and experiments. We have combined computational analysis with experimental validation to screen and benchmark $RWO_4$ materials (where R = Mn, Fe, Co, Ni, Cu, or Zn) as potential photoanodes for water oxidation. Density Functional Theory (DFT) calculations have been used to determine density-of-states profiles as well as electronic structures, which provide estimates for both band gaps and carrier effective masses. Through this theoretical screening, photoanode material candidates as well as their potential limitations have been identified. Subsequently, experimental benchmarking has been implemented, confirming CuWO4 and FeWO4 as promising materials. In-depth photoelectrochemical studies of these tungstates have also been carried out.

Both experimental and theoretical results for this family of materials will be discussed with the aim of uncovering limitations and showing future directions. In more general vein, the advantages of combining theoretical and experimental approaches in the development of photoelectrochemical materials will be highlighted.

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# Intramolecular Singlet Fission in Individual Graphene Nanoribbons—Competition with Charge Transfer

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Graphene nanoribbons (NRs) constitute a versatile platform for developing novel materials, where their structure governs their optical, electronic, and magnetic properties while also shaping their excited-state dynamics. Here, we investigate a set of three twisted N-doped molecular NRs of increasing length, obtained by linearly fusing perylene diimide to pyrene and pyrazino- or thiadiazolo-quinoxaline residues (Fig. 1a).[1] By employing various temperature-dependent time-resolved spectroscopy techniques, we reveal how the flexible twisted NR geometry promotes the formation of a mixed electronic state with varying contributions from locally excited (LE) and charge-transfer (CT) states. The fate of this mixed state is highly sensitive to the molecular geometry, length, and solvent polarity. For the shortest NR, intersystem crossing dominates the deactivation pathway, efficiently generating triplets in low-polarity solvents. In contrast, for the extended NRs, intramolecular singlet fission (*i*-SF) takes place within a single nanoribbon (Fig. 1b). This is enabled by enhanced superexchange coupling, resulting from a pronounced push–pull character and multiple localized π-electron states introduced by heteroatom doping. Hence, this approach circumvents the need for dimeric interactions typically associated with conventional *i*-SF systems.[2] In higher-polarity environments, evidence of a (diabatic) CT state emerges. These findings underscore the intricate relationship between geometry, energy levels, and excited-state dynamics in twisted N-doped NRs.[3]

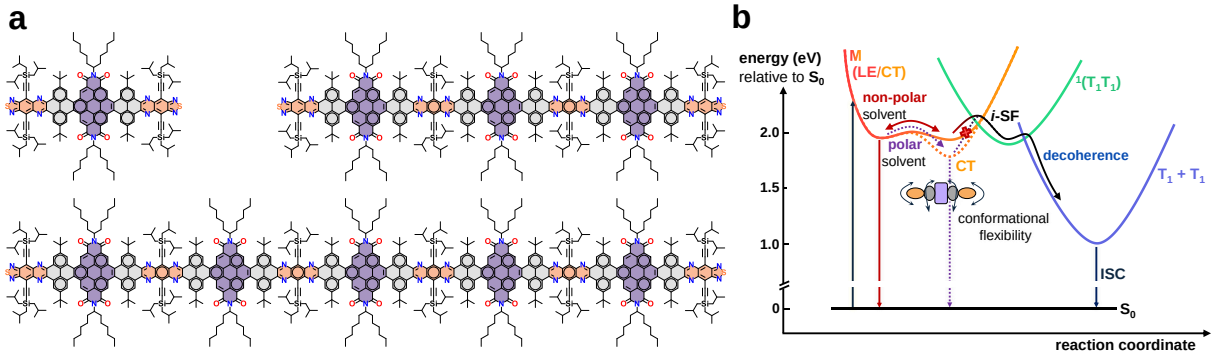


Figure 1. (a) Molecular structures of the investigated graphene nanoribbons (NRs). (b) Proposed excited-state deactivation pathway for the extended NRs, illustrating how solvent polarity, temperature, and conformational flexibility modulate the deactivation cascade. The cascade proceeds from a mixed locally excited/charge-transfer (LE/CT) state via intramolecular singlet fission (*i*-SF) and ultimately through intersystem crossing (ISC), returning to the electronic ground state.

**Funding:** This work was supported by the Deutsche Forschungsgemeinschaft (DFG) under grant nos. GU 517/27-1 and GU 517/32-1.

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# The Photochemical E/Z-Isomerization Pathway of the NIR Photoswitch *peri*-Anthracenethioindigo

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A detailed understanding of the fundamental mechanisms underlying molecular photoswitching is crucial for the further development of this group of molecules. Among the various classes of photoswitches, thioindigoid dyes have attracted significant attention due to their reversible E/Z isomerization and distinctive photochemical behavior. Although these systems have been investigated for decades, important aspects of their photoisomerization mechanisms remain elusive and the recent development of π-extended indigoid photoswitches exhibiting all-red to near-infrared absorption urged the investigation of their excited state isomerization mechanisms to help their further development.

In this study, we take a close look at the recently published *peri*-anthracenethioindigo[1] (**PAT**) (Figure 1). To explore the isomerization pathways of this thioindigoid photoswitch we used a combined theoretical and experimental approach, including (TD-)DFT and ADC(2) calculations as well as steady-state and time-resolved femtosecond and nanosecond spectroscopy.

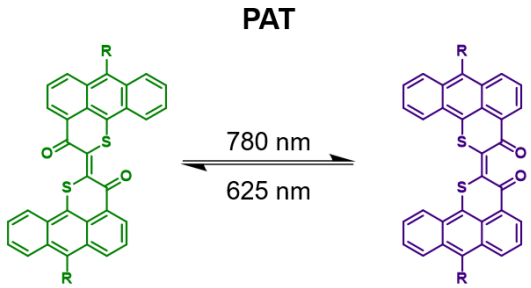


Figure 1: Molecular structure of corresponding E- and Z-**PAT**.

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# Photoelectrochemical Water Splitting and Charge Transfer Dynamics of Bismuth Vanadate ($BiVO_4$) Photoanode with Chiral Perovskite

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Organic-inorganic hybrid perovskites (OIHPs) have emerged as promising light-harvesting materials such as light-emitting diodes and solar cells owing to their significant progress in power conversion efficiency, low cost, and easy fabrication. Nevertheless, their instability to moisture, oxygen, and thermal stress remains a major challenge, leading to material degradation.[1] Recently, Lee et al. reported the integration of chiral OIHPs into the photoanode for PEC water splitting, which demonstrated enhanced PEC performance and excellent stability over 10 h.[2] Bismuth vanadate ($BiVO_4$) based photoanodes are considered among the most promising candidates for photoelectrochemical (PEC) water splitting; however, their poor charge transfer and separation efficiency limit their commercial application. In this study, we fabricated bismuth vanadate ($BiVO_4$)-based photoanode with chiral OIHPs — (R)-(+)-methylbenzyl amine (R-MBA) and (S)-(−)-methylbenzylamine (S-MBA) — to elucidate the origin of the performance enhancement using electrochemical and time-resolved spectroscopic techniques. Figure 1 shows a schematic of the fabricated photoanode structures.

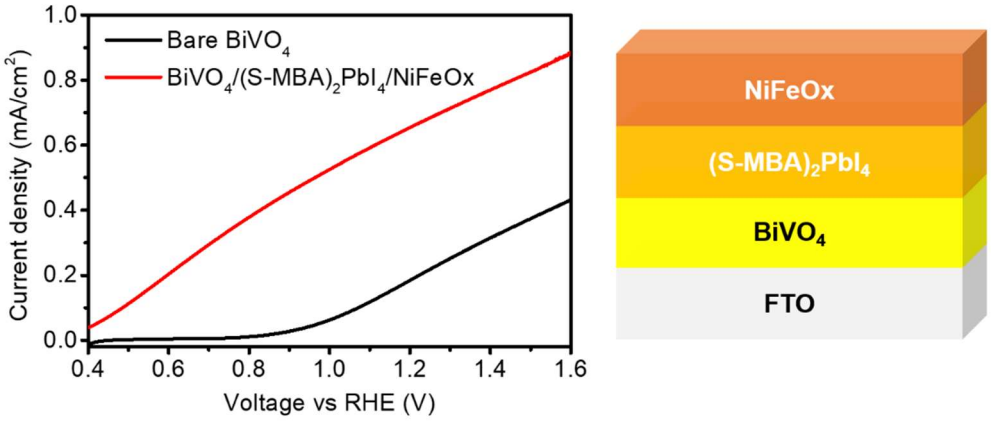


Figure 1. Schematic illustration of the photoanode with chiral perovskite materials

To evaluate PEC performance, we obtained J-V curves of the fabricated films using a linear sweep voltammetry (LSV). Compared to bare $BiVO_4$, the films with chiral OIHPs showed a significant enhancement in photocurrent, as shown in Figure 1. Long-term photo-stability was confirmed by recording the J-t curves of the films at 1.23 $V_{RHE}$ for 1000 seconds. Using a circular dichroism (CD) spectrometer, we demonstrated the chiral properties of the fabricated films. Furthermore, we investigated the photoexcited charge carrier dynamics using a near-field heterodyne transient grating (NF-HD-TG) method, which has been used as a powerful time-resolved spectroscopic technique. In this poster, we will discuss the role of chiral OIHPs and the potential of chiral materials as effective interfacial modifiers for enhancing PEC water splitting.

**Funding:** G-LAMP Program of the NRF grant (RS-2024-00445180)

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# Phase-Migrating Z-Scheme Charge Transportation Enables Photoredox Catalysis Harnessing Water as an Electron Source

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Photocatalytic molecular conversions giving value added product are of great interest. Ideally, it is desirable to utilize water as an electron source for these molecular conversion reactions. Artificial Z-scheme reaction system composed of two-different photocatalysts is a potential strategy to connect various reductive molecular conversions with water oxidation, as demonstrated in overall water splitting.[1] However, it is basically difficult to perform organic molecular conversions integrated with water oxidation due to low solubility of organic reactants in water. In this study, we develop a stepwise Z-scheme photocatalytic system utilizing a water/1,2-dichloroethane (DCE) biphasic solution with a ferrocenium/ferrocene ($Fc^+$/Fc) phase-migrating electron mediator to connect reductive coupling of benzyl bromide in DCE phase and water oxidation (Figure 1a).

Under visible light, a $H_2O$/DCE biphasic solution with Fc as an electron donor, a photoredox catalyst, and benzyl bromide (Bn-Br) undergoes reductive coupling to form dibenzyl ($Bn_2$) in the DCE phase, while $Fc^+$ forms in the aqueous phase (Figure 1a, b).[2] On the other side, $Fc^+$ can be utilized as an electron acceptor for photocatalytic water oxidation with a semiconductor photocatalyst in the aqueous phase (Figure 1a, c). More importantly, the ratio of generated $Bn_2$ and $O_2$ satisfies the stoichiometry corresponding to the overall reaction (Figure 1b, c). Eventually, the $Fc^+$/Fc redox couple transports an electron by the photoredox induced liquid-liquid phase migration to achieve photoreduction of Bn-Br coupled with water oxidation (Eq. 1).[3]

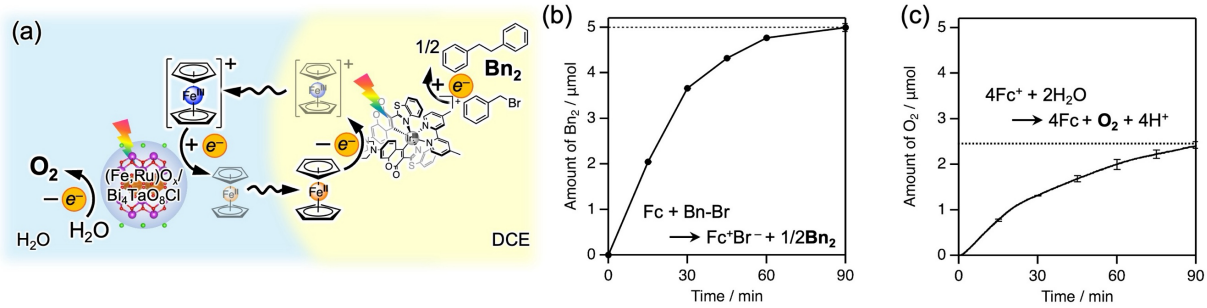
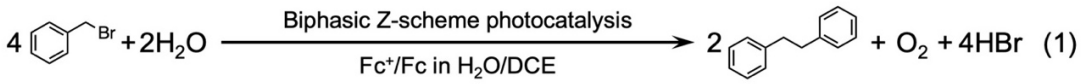



Figure 1. (a) Conceptual scheme of a biphasic Z-scheme photocatalytic system using $Fc^+$/Fc as a phase-migrating electron mediator. Time course of half reactions of (b) $Bn_2$ formation using photoredox catalyst and Fc as an electron donor in a $H_2O$/DCE (2:1, *v*/*v*) biphasic solution under exposure to visible-light ($\lambda$ = 470 nm), and (b) $O_2$ evolution using photogenerated $Fc^+$ by $Bn_2$ production as an electron acceptor and a semiconductor photocatalyst under exposure to visible-light ($\lambda$ = 430 nm) by a stepwise one. The dashed line shows the upper limit of $Bn_2$ and $O_2$ evolution expected from the amount of Fc added to these solutions.

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# Mechanism of photocatalytic hydrogen generation in carbon nanodots photocatalysts

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Recent advancements in photocatalytic hydrogen generation (PHG) using carbon nanodots (CNDs) emphasize the critical need for a deeper understanding of the underlying mechanisms, particularly the intricacies of multiproton-multielectron transfers. While initial efforts utilized simplified microwave-synthesized CNDs to enhance PHG, challenges arose from an unclear grasp of chemical composition and physical properties of the photocatalytic centers.[1] In response, a novel model system was developed featuring well-characterized photoactive centers, demonstrating significant potential for achieving light-driven hydrogen generation from seawater without the need for additional photosensitizers or cocatalysts.[2] This approach not only advances the practical application of PHG but also allows for comprehensive exploration of the catalytic mechanisms at play, facilitated by a combination of spectroscopic and electrochemical measurements that yield valuable insights into the reaction sequences integral to hydrogen generation with CNDs (Summarized in Figure 1).

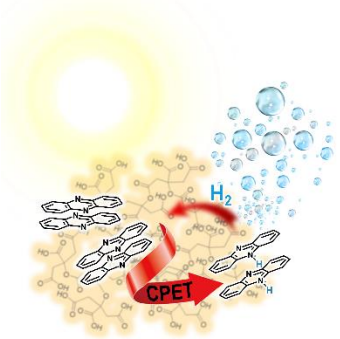


Figure 1. Phenazine-based carbon nanodot for the photocatalytic hydrogen generation through proton coupled hydrogen generation.[2]

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# Estimations of the Activation Energies for the Charge Transfers of the Long-Lived Holes at the Semiconductor/Electrolyte Interfaces of α-$Fe_2O_3$ and α-$Fe_2O_3$/Co-Pi Photoanodes.

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Hematite (α-$Fe_2O_3$) is a promising photoanode material for photoelectrochemical (PEC) water oxidation, but it suffers from sluggish surface water oxidation kinetics.[1] One strategy to address this issue is the surface modification with a co-catalyst. The co-catalyst improves the charge transfer efficiency at the photoanode/electrolyte interface and reduces the activation energy, thereby improving PEC performance.[2] However, to the best of our knowledge, no study has quantitatively evaluated the activation energy after the modification of a co-catalyst on the photoanode. Thus, we fabricated a photoanode by modifying the surface of the α-$Fe_2O_3$ with cobalt phosphate (Co-Pi), a well-known co-catalyst material, and evaluated the activation energy related to hole transfer at the α-$Fe_2O_3$/Co-Pi photoanode/electrolyte interface by varying the temperature under an applied bias voltage, using the Near-Field Heterodyne Transient Grating (NF-HD-TG) technique combined with Arrhenius equation.

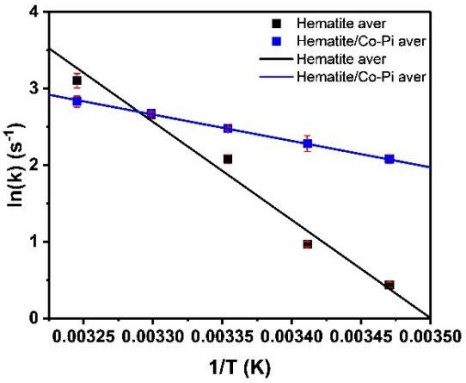


**Figure 1.** Arrhenius plot of the α-$Fe_2O_3$ (black) and α-$Fe_2O_3$/Co-Pi (blue) using Arrhenius equation with error bar.

The activation energy and frequency factor (A) were extracted from the rate constants of hole transfer, which were obtained by varying the temperature. The activation energy was obtained from the slope of the Arrhenius plot, and the frequency factor (A) was determined from the y-intercept, as shown in Fig. 1. The activation energies of α-$Fe_2O_3$ and α-$Fe_2O_3$/Co-Pi were determined 106.4 kJ/mol and 28.6 kJ/mol, respectively. As illustrated in Fig. 1, a significant decrease in activation energy was observed after the surface treatment with Co-Pi, which is consistent with the trends observed in electrochemical measurements. In addition, the frequency factor (A) also exhibited a decreasing trend. This suggests that the water oxidation reaction predominantly occurs on the sparsely deposited Co-Pi sites rather than on the α-$Fe_2O_3$ surface, resulting in a reduction of the overall active surface area. Through the NF-HD-TG method, we quantitatively determined the activation energy for water oxidation after the introduction of Co-Pi onto the α-$Fe_2O_3$ surface. This reduction in activation energy induced by Co-Pi modification indicates that charge transfer is facilitated, thereby accelerating the surface water oxidation kinetics. These findings further confirm that Co-Pi acts as an effective co-catalyst.

**Funding:** G-LAMP Program of the NRF grant (RS-2024-00445180)

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# Investigation of Hole Transfer Efficiency in $MAPbI_3$ Perovskite Solar Cells with Various Copper-based Hole Transport Materials Using Near-Field Heterodyne Transient Grating Spectroscopy

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We fabricated $CH_3NH_3PbI_3$ ($MAPbI_3$) perovskite films using copper-based hole transport materials (CuSCN, CuO, CuS) and investigated their impact on hole transfer efficiency using near-field heterodyne transient grating (NF-HD-TG) spectroscopy.[1, 2]

In our previous study, we inserted CuSCN as the hole transport layer (HTL) in the perovskite film and used NF-HD-TG spectroscopy to determine that the photo-generated electrons in $MAPbI_3$ were transferred to the electron transport layer (ETL), trapped in surface states, while the holes were transferred to the fluorine-doped tin oxide (FTO) substrate via the HTL. This allowed us to observe the time constant of recombination between the electrons trapped at the ETL surface and the holes in the FTO substrate.[3]

Consequently, we observed that the recombination rate between the surface-trapped electrons and the holes transferred to the FTO substrate varied depending on the HTL material, allowing us to compare hole transfer efficiency across different HTLs.

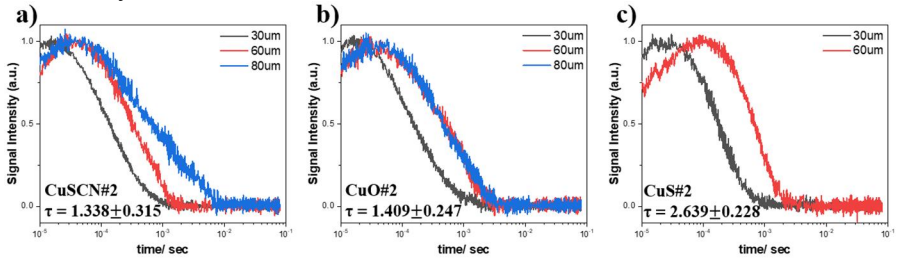


Figure 1 The NF-HD-TG responses of a) FTO/CuSCN/$MAPbI_3$/ZnO, b) FTO/CuO/$MAPbI_3$/ZnO and c) FTO/CuS/$MAPbI_3$/ZnO in toluene with grating spacings (μ) of 30μm (black), 60μm (red) and 80μm (blue).

To determine the optimal HTL thickness for the highest hole transfer efficiency, we varied the spin coating cycles of each HTL material from 1 to 3 times. The highest efficiency was achieved with two spin-coating cycles (HTL#2). The NF-HD-TG responses and time constants of recombination are shown in Figure 1.

By comparing the recombination rates, we identified the best HTL material, and the hole transfer efficiency differences were attributed to the relative valence band gap between the $MAPbI_3$ perovskite and HTL. This approach can be effectively applied to evaluate the hole transfer efficiency of various HTL materials in perovskite-based solar cells.

**Funding:** G-LAMP Program of the NRF grant (RS-2024-00445180)

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# Understanding the Mediator Enhanced Triplet-Triplet Annihilation Upconversion

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Triplet-triplet annihilation photon upconversion (TTA-UC) is a process where the energy of two low energy photons combines to form a photon of high energy. TTA-UC has great potential in solar energy harvesting[1] and water splitting.[2] TTA-UC system consist of triplet sensitizer molecules which absorbs low energy light and transfers its triplet energy to annihilator molecules. The energy of two triplet annihilator molecules then combine to generate one molecule in its singlet excited state, which eventually emits light, whereas the other annihilator molecule returns to the ground state. Minimizing the reabsorption of upconverted light by annihilator molecule would help to achieve high external quantum yield of TTA-UC. Besides minimizing the output photon-flux reabsorption also decreases the effective anti-Stokes shift by mainly re-absorbing the high-energy part of the emission. While traditional TTA-UC system relies on high concentration of annihilator molecules for efficient energy transfer and triplet-triplet annihilation, reabsorption becomes more severe with increasing concentration. Recently, it was suggested that introducing an energy transfer mediator that through columbic interactions with the sensitizer could yield efficient triplet transfer with reduced annihilator concentrations.[3] Here we extend this strategy and show that mediators without columbic interactions can also enhance triplet energy transfer and minimize reabsorption. The energy transfer mediator needs to have a triplet energy in between that of sensitizer and annihilator molecule, and the UV-Vis absorption of mediator molecule should have minimal overlap with the emission of annihilator molecule. This helps to maintain high concentration of mediator molecule for efficient energy transfer even if the concentration of annihilator is reduced to minimize the reabsorption of upconverted light. We were able to achieve over 10-fold increase in the upconversion quantum yield by employing benzothiophen based mediator, TIPS-BT in the presence of TIPS-Nap annihilator and 4CzBN sensitizer compared to the case without mediator. Our strategy would increase the range of mediator and sensitizer that could be used for a given annihilator molecule unlike previous reports where it needs to be either covalently attached or a charged species.[3] Kinetic modelling supported mediator mediated energy transfer for efficient TTA-UC process, and highlights key differences compared to triplet energy mediation in solid-state.[4]

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# Investigation of the Charge Carrier Dynamics in $MAPbBr_3$ and $MAPbI_3$ Perovskites Using a Near-Field Heterodyne Transient Grating Spectroscopic Technique

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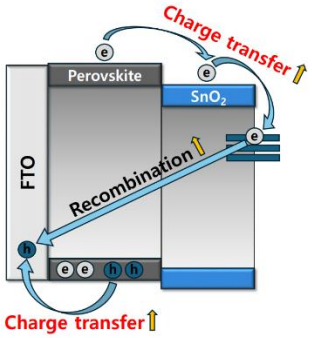


Figure 1. Schematic illustration of charge carrier dynamics in the FTO/Perovskite/$SnO_2$ films.

Organic-inorganic lead halide perovskites (OIHPs) are known for their strong visible light absorption due to their small bandgap and efficient charge transport properties[1]. In addition, OIHPs can exhibit different optical properties and charge carrier dynamics depending on the halide ion that is substituted. Ultrafast spectroscopic technologies have been employed to investigate the photoinduced charge carrier dynamics between the perovskite and transport layer[2]. In this study, we utilize the near-field heterodyne transient grating (NF-HD-TG) spectroscopic method, which offers high sensitivity by amplifying the signal field via constructive interference with a reference field[3]. We explain that, within the perovskite films, a faster recombination between electrons trapped in the electron transport layer ($SnO_2$) and holes migrated from the perovskite to the FTO indicates a greater number of holes transferred to the FTO, thereby implying more charge transfer efficiency in the perovskite (Fig. 1). We fabricated Methyl ammonium lead halide perovskite $MAPbX_3$ (X=I,Br) films as OIHPs material with electron transport layer ($SnO_2$) on a FTO substrate. We then measured NF-HD-TG responses to investigate the recombination of photo-generated electrons trapped at the $SnO_2$ surface with photo-generated holes that migrated to the conductive substrate (FTO) in $MAPbBr_3$ and $MAPbI_3$ perovskites to reveal the difference of charge transfer efficiency in $MAPbBr_3$ and $MAPbI_3$ perovskites. In conclusion, we confirmed the successful fabrication of the films through XRD pattern analysis, and we observed different interfacial binding between perovskites ($MAPbI_3$, $MAPbBr_3$) and $SnO_2$ through XPS analysis. Subsequently, using the NF-HD-TG spectroscopic method, we observed that the recombination in $MAPbBr_3$ is faster than that in $MAPbI_3$, which consequently resulting in a higher charge transfer efficiency in $MAPbBr_3$ compared to $MAPbI_3$. Although $MAPbBr_3$ has a larger band gap than $MAPbI_3$ and is generally less used in solar cells, we observed higher charge transfer efficiency in $MAPbBr_3$ compared to $MAPbI_3$. Therefore, we plan to investigate the optimal condition by adjusting the ratio of I and Br in $MAPbX_3$ (X=I,Br).

**Funding:** G-LAMP Program of the NRF grant (RS-2024-00445180)

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# Influence of linkers between norbornadiene and perylenediimide at the N-position on photoswitching and photochemical properties

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Norbornadiene (NBD) is has been studied for solar thermal energy storage devices for a long time since its photoproduct Quadricyclane (QC) is stable at room temperature and the energy it can store is relatively high[1]. The drawbacks of the NBD-QC-system stems from its poor overlap with the solar spectrum, since its absorption is located within the UV-region[2]. To improve its match with the solar spectrum and the photoswitching many different NBD structures can be found in literature.
A previous work of our group investigated the possibility of triggering the backconversion of QC to NBD through photoexcitation by linking the NBD to perylenediimide (PDI) at a carbon position[3]. To deepen the understanding of the photochemical backconversion of QC to NBD through excitation of PDI, NBD-PDI-systems, which are linked at PDIs N-postion are investigated with stationary and time resolved spectroscopic methods.

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# Pushing the Limits Towards Long-Lived Charge Separation in Ruthenium (II) Phthalocyanine-Subporphyrazine Conjugates

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Solar energy conversion research has increasingly focused on electron donor-acceptor (D-A) assemblies, recognized for their ability to generate long-lived charge-separated states upon light absorption. Porphyrinoids, owing to their versatile optoelectronic characteristics, rapid energy and electron transfer capabilities, and broad absorption spectra, are frequently chosen as components in D-A systems.[1,2] Among these, ruthenium(II) phthalocyanines (RuPcs) stand out due to their ability to afford stable and strongly coordinated assemblies, and efficiency in promoting rapid charge separation and slow charge recombination.[3,4] Subporphyrazines (SubPzs), a class of 14 π-electron porphyrinoids, offer exceptional photophysical properties that can be finely tuned through axial and peripheral functionalization strategies.[5,6] By combining RuPcs and SubPzs, we have developed a series of novel conjugates capable of absorbing light across the visible range of the solar radiation spectrum. Depending on the molecular architecture of the SubPz units, these conjugates demonstrate distinctive photoinduced intramolecular interactions, including *intra*molecular Förster resonance energy transfer (*i*-FRET) and *intra*molecular charge separation (*i*-CS). This study contributes to the fundamental understanding of RuPc-SubPz conjugates and, in turn, paves the way for improved organic photovoltaics and molecular electronics.

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# Function-integrated Cyclometalated Diruthenium Photocatalyst for $CO_2$ Reduction

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A series of dinuclear ruthenium (II) isocyano complexes, $[Ru_2(bbbpy)(CNR)_4(PPh_3)_2]^{2+}$, containing the rolled-over cyclometalating 6,6′-bis(benzimidazolyl)-2,2′-bipyridine (**1**) and its N-methyl derivative (**2**), and phenyl isocyanides of varying electronic properties (**a – b**) have been synthesized (Fig 1). The structures of the compounds have been determined by X-ray crystallography and their photophysical properties have been examined. Both **1** and **2** are found to exhibit similarly structured long-lived emission (Fig 2) peaking at 543 – 558 nm ($\tau$ = 187 ns – 2.25 μs) at room temperature upon photoexcitation ($\lambda_{ex}$ = 430 nm). The compounds are active photocatalysts (PCs) for $CO_2$-to-CO reduction. Light-driven ($\lambda_{ex}$ = 471 nm, LED) $CO_2$ reduction have been performed using **1a** and **2a** respectively in $CO_2$-saturated DMF containing 0.1 M BIH, yielding CO at TON (selectivity) = 104 (93%) and 52 (99%) respectively in the presence of $H_2O$ (0.5 M) and $PPh_3$. On the other hand, higher yields of CO were obtained using **1c** and **2c** (TON = 494 (98%) and 72 (95%) respectively, without added $H_2O$/$PPh_3$.

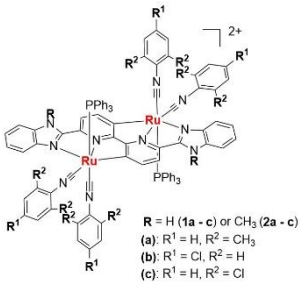


Fig 1. Structure of photocatalysts.

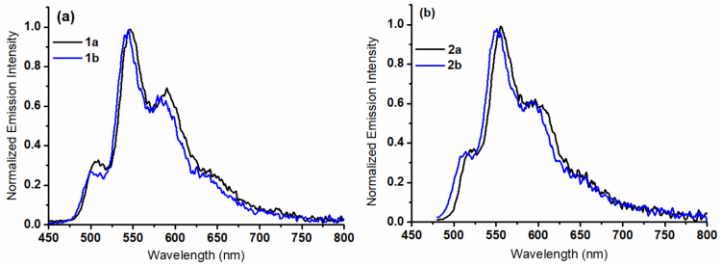


Fig 2. Emission spectra of **1a–b** and **2a–b** in acetonitrile.

**Funding:** Research Grants Council of Hong Kong (projects 18300723 and 18300824)

# Crystalline hydrogen-bonded organic framework for air-tolerant triplet-triplet annihilation upconversion

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Photon upconversion refers to the process of converting lower-energy photons into higher-energy ones. Photon upconversion based on triplet-triplet annihilation (TTA-UC) is increasingly used with the merits of low excitation power density and adjustable broad absorption and emission bands. TTA-UC relies heavily on the migration and collision of the triplet annihilators or triplet excitons, but molecular diffusion is severely hindered in the solid state. However, solid-state upconversion is essential in practical applications.[1-2] In this presentation, we report on developing a crystalline HOF with anthracene-type annihilator as the annihilator component unit. A classic sensitizer, platinum octaethylporphyrin (PtOEP), is introduced to the HOF matrix to obtain the TTA-UC system. The crystalline HOF exhibits superior upconversion performance compared to the disordered powder sample, as the ordered arrangement of DPACOOH molecules facilitates triplet energy migration. Efficient triplet diffusion consequently leads to a 70% increase in the quantum yield and a lower threshold value of 126.0 mW $cm^{-2}$ for crystalline HOF upconversion system. Moreover, the highly dense packing of crystalline HOF provides oxygen shielding, allowing the upconversion system to function as anti-counterfeiting materials at ambient conditions.[3]

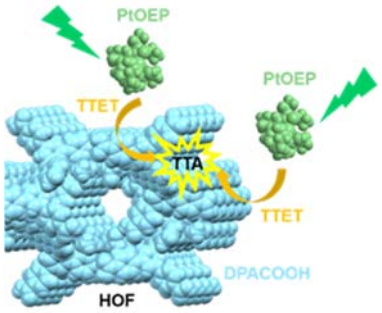


Figure 1. Cartoon illustration of the hydrogen-bonded organic framework developed for triplet-triplet annihilation upconversion

**Funding:** National Natural Science Foundation of China (22273117, 22273110 and 22090012)

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# Impact of semiconducting polymer crystallinity on hydrogen evolution in organic p/n heterojunction nanoparticle photocatalysts

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Nanoparticle photocatalysts based on p/n organic semiconductor heterojunction systems, which are used for the photoactive layer of organic photovoltaics (OPVs), have attracted much attention due to their capability of both efficient charge separation and absorbing visible to near-infrared light.[1,2] We have developed numbers of semiconducting polymers that show wide absorption range covering entire visible or even up to near-IR regions and high external quantum efficiencies of more than 80% in OPVs. Among them, a crystalline polymer **PTNT2T** was found to show a power conversion efficiency of up to 12%, which is among the highest value in fullerene-based OPVs (Fig. 1a).[3] This motivated us to apply **PTNT2T**:$PC_{61}BM$ system to nanoparticle photocatalysts. Here, we report on the photocatalytic hydrogen evolution of **PTNT2T**-based nanoparticles. Furthermore, we investigated impact of the polymer crystallinity in nanoparticles on the hydrogen evolution rate (HER) by comparing nanoparticles using **PTNT2T** having high crystallinity and **PTB7-Th** having low crystallinity (amorphous polymer) (Fig. 1b).

We fabricated nanoparticles of **PTNT2T** and **PTB7-Th** by blending with $PC_{61}BM$ with the weight ratio of 1:4 dispersed in water by using surfactants. Although both polymer nanoparticles showed a similar absorption range, **PTNT2T** showed a more intensified π-π* transition band compared to **PTB7-Th**, implying that **PTNT2T** had higher crystallinity than **PTB7-Th** in nanoparticles. Notably, **PTNT2T**-based nanoparticles showed significantly higher HER than **PTB7-Th**-based nanoparticles (Fig. 1c). In this presentation, we will discuss in detail the difference in the structures and properties as well as photocatalytic activity between these nanoparticles.

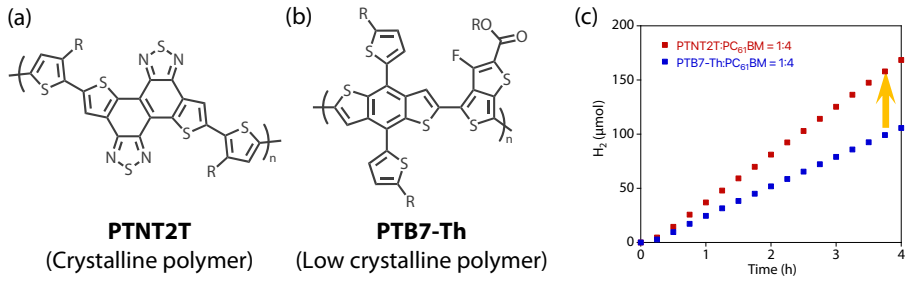


Fig. 1. Chemical structures of (a) crystalline polymer **PTNT2T** and (b) amorphous polymer **PTB7-Th**. (c) $H_2$ evolution rate of nanoparticle photocatalysts based on **PTNT2T**:$PC_{61}BM$ and **PTB7-Th**:$PC_{61}BM$.

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# Just add Salmiakki: Photophysics of $NH_4Cl$-Modified Potassium Poly (Heptazine Imide) for Enhanced Photocatalytic Hydrogen Peroxide Production

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Hydrogen peroxide is a popular antiseptic for wounds, bleaching agent for cleaning and oxidant for water treatment, commonly produced by a complex and expensive process known as the anthraquinone method.[1] Photocatalytic hydrogen peroxide production is a comparatively cheaper, simpler and more sustainable alternative which requires only the illumination of a semiconductor in water with a sacrificial electron donor.[1] For this purpose, graphitic carbon nitrides are stable and cost-effective semiconductors which are good photocatalysts for hydrogen peroxide production, though they usually require structural modifications through the addition of co-monomers and/or salts during their synthesis to improve their production efficiencies.[2] In this study, ammonium chloride (which is coincidentally a popular Finnish confectionary called salmiakki), was incorporated into the synthesis of potassium poly (heptazine imide) to produce a cyano-defect rich (and well-seasoned) photocatalyst, with enhanced photocatalytic hydrogen peroxide production rates. To better understand the mechanism behind this enhanced activity, the photophysics of $NH_4Cl$-modified potassium poly (heptazine imide) were studied in different concentrations glycerin, a sacrificial electron donor, with an unmodified control. Fluorescence spectroscopy results showed the modified samples had quenched fluorescence intensities and reduced fluorescence lifetimes compared to the control. This quenching occurred because of electron trapping at the cyano defects which competed with the normal radiative recombination pathway. Femtosecond transient absorption spectroscopy of the modified samples further demonstrated trapping of the photogenerated carriers at the cyano defects through an increased excited state absorption intensity and lifetime of the $NH_4Cl$-modified potassium poly (heptazine imide), which surpassed the control even after the holes were removed by glycerin.

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# Intramolecular Triplet Diffusion Facilitates Triplet Dissociation in a Pentacene Hexamer

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Triplet dynamics in singlet fission depend strongly on the strength of the electronic coupling.[1,2] Covalent systems in solution offer precise control over such couplings. Nonetheless, efficient free-triplet generation remains elusive in most systems, as the intermediate triplet pair $^1(T_1T_1)$ is prone to triplet-triplet annihilation due to its spatial confinement.[1,2,3] In the solid state, entropically driven triplet diffusion assists in the spatial separation of triplets, resulting in higher yields of free triplets.[4,5] Control over electronic coupling in the solid state is, however, challenging given its sensitivity to molecular packing. We have thus developed a hexameric system consisting of three pentacene dimers, linked via a central subphthalocyanine chromophore, to enable solid-state-like triplet diffusion at the molecular scale. Transient absorption spectroscopy, complemented by theoretical structural optimizations and steady-state spectroscopy, reveals that triplet diffusion is indeed facilitated due to intramolecular cluster formation. The yield of free triplets in the hexamer is increased by a factor of up to 14 compared to the corresponding dimeric reference. Thus, the hexamer establishes crucial design aspects for achieving efficient triplet dissociation in strongly coupled systems by providing avenues for diffusive separation of $^1(T_1T_1)$, while, concomitantly, retaining strong interchromophore coupling without compromising rapid formation of $^1(T_1T_1)$.

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# Ultrafast Insights into Monohybrid CN- via femtosecond-TA and *In-Situ* Gaseous Raman Spectroscopy

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Engineering efficient and photostable photocatalysts for the hydrogen evolution reaction (HER) under visible light remains a significant challenge for conventional g-$C_3N_4$-based composites. Various strategies, including homojunction and heterojunction formation, have been explored to enhance interfacial charge transfer, exciton formation, charge separation, and utilization of electrons and holes for practical applications. Inspired by these approaches, we present an advanced methodology employing femtosecond transient absorption (fs-TA) spectroscopy[1] and in-situ gaseous Raman rotational spectroscopy[2] (Fig.1) to investigate electron transport and product quantification.

We conducted a comparative study of monohybrid photocatalysts synthesized from different g-$C_3N_4$ precursors: Urea/Melamine (UM), Urea/Thiourea (UT), and Thiourea/Melamine (TM) (Fig. 1B). This study aimed to elucidate the structure-activity relationship and develop a robust screening methodology for future photocatalysts. Comprehensive characterization, including XRD, TEM, UV-vis, and photoluminescence spectroscopies, was complemented by fs-TA spectroscopy to probe trap state dynamics and in-situ gaseous rotational Raman spectroscopy (NINGAS Analyzer) for direct, non-invasive quantification of evolved $H_2$. The Pt-loaded UM monohybrid exhibited the highest photocatalytic activity, achieving a hydrogen evolution rate of 1625 µmol $hr^{-1}$ $g^{-1}$, outperforming Pt/UT (1476 µmol $hr^{-1}$ $g^{-1}$) and Pt/TM (901 µmol $hr^{-1}$ $g^{-1}$). Femtosecond-TA measurements revealed a significantly shorter trap state lifetime for Pt/UM (~3.4 ps) compared to Pt/UT (~38.5 ps) and Pt/TM (~23.3 ps), with comparable initial amplitudes, indicating efficient charge carrier trapping and reduced recombination as the primary factors for its superior performance. The trend in photocatalytic activity (Pt/UM > Pt/UT > Pt/TM) was corroborated by in-situ Raman quantification of evolved hydrogen, demonstrating the power of this non-invasive technique for direct activity assessment.

Additionally, we showcase the application of monohybrid materials in creating S-scheme heterojunctions, exemplified by $Bi_4O_5Br_2$ (Fig. 1D)[3]. The ns-ps time-resolved spectroscopy revealed that the mechanism driving the efficiency was vibrational relaxation, quantified by time-resolved spectroscopy in the 15-35ps range. The ultrafast decay, likely due to non-radiative vibrational relaxation, confirmed the enhanced photocatalytic efficiency of $Bi_4O_5Br_2$-40UT, attributed to reduced recombination losses at surface sites. This highlights the potential of monohybrid materials to inspire further research in the field.

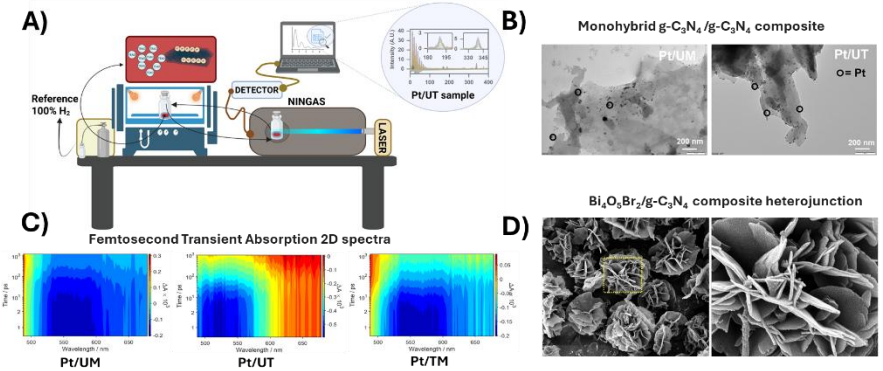


Figure 1. (A) Schematic diagram illustrating the setup for detecting gas samples using NINGAS system, with reference to 100% $H_2$, (B) TEM images of monohybrid composite with Pt/UM and Pt/UT samples, highlighting the presence of platinum (Pt), (C) Femtosecond Transient Absorption 2D spectra for Pt/UM, Pt/UT, and Pt/TM samples, (D) HIM images of the $Bi_4O_5Br_2$/g-$C_3N_4$ heterojunction.

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# *De novo* protein design for efficient solar energy conversion

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Despite significant advances in protein engineering, the fundamental issue regarding artificial photosynthesis to develop the charge separation process, and to obtain precise control over chromophore-protein assemblies, remains a key obstacle. In this way, the research project's motivation for the global challenge of obtaining a renewable energy supply is the design of new photosynthetic proteins. To achieve this, the protein design needs to approach the right distance and angles between the chromophores to tune excitonic coupling and control absorption and fluorescence properties, excited state dynamics, energy transfer, and electron tunneling.[1] Furthermore, the photosynthetic proteins need to perform two fundamental processes: excitation energy transfer and charge separation.[1] *De novo* design is an attractive approach for constructing synthetic proteins with predetermined structures and functions, including the desired protein structure, and the required chromophore-chromophore and chromophore-protein interactions.[2] Our research is focused on the design and modulation of different synthetic proteins, as shown in Fig. 1.a. and 1.b., which could include different α-helices, where the specific position of the histidine chromophore binding site allows the modulation of the chromophore's energy (in our case, Zinc-pheophorbide a). More specifically, here we present six alpha-helices *de novo* protein with 4 binding sites, 2 at the top and 2 at the bottom (Fig. 1.b.). This design allows the formation of chromophore-protein assemblies with 4 chromophores inside the protein, which display an 11 nm red-shift in their absorption maximum compared to the maxima in organic solvent, together with a progressive broadening of the red tail at 700 nm with increasing the number of chromophores inserted (Fig. 1.c.). These observations suggest the stabilization of the chromophore's excited state by the protein, which could also be associated with excitonic interactions due to the dimer formation inside the protein. The presence of excitonic interactions is evidenced by circular dichroism spectroscopy. The absorbance difference signal centered at 669 nm has a partially conservative shape, with both positive and negative components (Fig. 1.d.), which indicates the formation of the excitonically coupled dimers in, at least, a fraction of chromophore-protein assemblies. This result represents a first step towards the design of new solar-energy conversion systems.

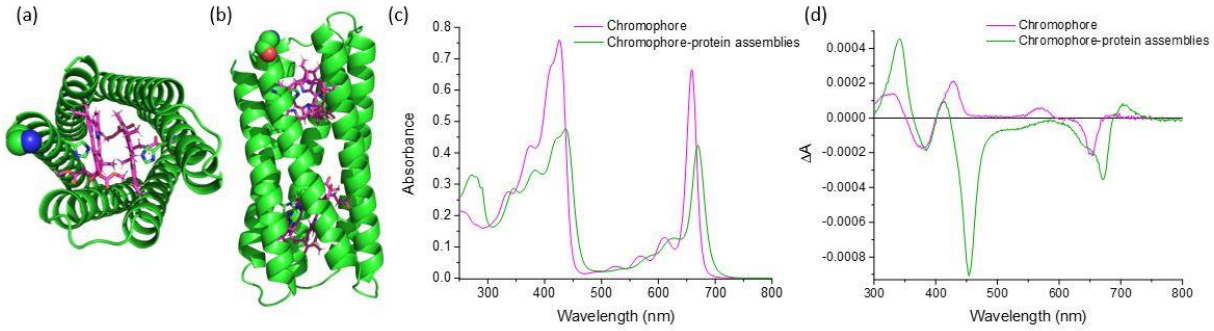


Figure 1. (a) Top view of *de novo* chromophore-protein assembly, only the 2 chromophores bound at the top are shown for clarity. (b) Side view of *de novo* chromophore-protein assembly with 4 chromophores bound. The protein structure shown in a and b have been obtained by AlphaFold 3. The chromophores have been manually inserted into the structure to show their expected position within the protein structure. (c) Absorption spectra of the chromophore in methanol (magenta) and the chromophore-protein assemblies (green) normalized by the chromophore concentration (20 µM), with the assemblies displaying an area difference of 0.90 times that of the chromophore in methanol. (d) Circular dichroism of chromophore-protein assemblies at 20 µM protein concentration.

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**Acknowledgement:** We thank the Spanish Ministerio de Ciencia e Innovación/AEI/EU/PRTR (TED2021-132747A-I00).

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# Unveiling Microscopic Charge Carrier Dynamics of Perovskite Solar Cells in Action

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The performance and stability of solar cells are typically assessed through macroscopic photophysical and electrical measurements. These observed bulk properties result from the convolution of microscopic structural, chemical, and functional properties, which are influenced by defects, carrier transport, and chemical reactions under external stimuli such as light, bias, and ambient conditions. This is especially true for soft and dynamic light-harvesting materials like halide perovskites. Therefore, understanding the functionality of the microstructures in a device, particularly under operational conditions, is crucial for accurately interpreting and enhancing device performance. Conventional techniques such as scanning electron microscopy, and electron/ x-ray-based analytical methods can provide high spatial resolution but are mostly limited to structural characterization. Moreover, these surface-sensitive or invasive techniques often alter the material properties.

To address these challenges, we have implemented a microscale functional imaging method (CLIM) that utilizes photoluminescence fluctuations to reveal contrasts associated with defect dynamics in semiconductor materials. CLIM images correlated with SEM reveal crucial information about the structure-function relationship in the bare thin films. Particularly noteworthy is the large amplitude fluctuation of photoluminescence of these films when incorporated in a solar cell. The local functional regions in a solar cell are much larger as compared to the bare film. Moreover, the fluctuation amplitude and functional regions strongly depend on the device's operational regime. From the statistical analysis of intensity fluctuations, we provide insights into the type of metastable defects responsible for fluctuating non-radiative recombination processes in thin film and operational solar cells.

The insights gained from microscale functional imaging contribute to a deeper understanding of device efficiency, structure, and durability, which are crucial for the rational engineering of the next generation of devices.

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**Acknowledgement:** We thank all authors for their respective contributions.

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# Anodic Potential Shift in Hematite Photoanode Induced by $TiO_2$ Underlayer: Origin and Mitigation

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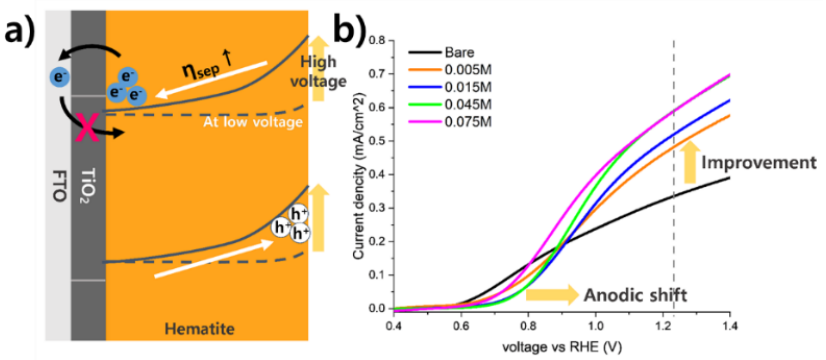


Figure 1. a) Schematic illustration of $TiO_2$/α-$Fe_2O_3$ and b) the J-V curves of bare α-$Fe_2O_3$ (black), 0.005 M $TiO_2$/α-$Fe_2O_3$ (orange), 0.015 M $TiO_2$/α-$Fe_2O_3$ (blue), 0.045 M $TiO_2$/α-$Fe_2O_3$ (green), and 0.075 M $TiO_2$/α-$Fe_2O_3$ (pink) films.

There were many attempts to improve the PEC performance of photoanodes. Among them, depositing a blocking layer between the photoelectrode and the conductive substrate is known to retard the back recombination, in which the long-lived holes trapped at the surface of the photoelectrode are recombined with the photo-generated electrons in the conductive substrate. In this study, we attempted to improve the PEC performance of the hematite (α-$Fe_2O_3$) photoanode by depositing $TiO_2$ as a blocking layer. In fact, when a $TiO_2$ underlayer was induced in α-$Fe_2O_3$ photoanode, the current density was increased, but an unexpected anodic shift of the onset potential was observed. Therefore, we fabricated α-$Fe_2O_3$-based photoanodes with $TiO_2$ underlayer to reveal the origin of the anodic shift.[1] The summary of this study is depicted as Fig.1 (a). Based on the near-field heterodyne transient grating (NF-HD-TG) technique, we confirmed that the $TiO_2$ underlayer played a role in retarding the back-recombination. In addition, through the photoelectrochemical impedance spectra (PEIS), it was revealed that the conductivity is improved when $TiO_2$ layer was deposited. On the other hand, the films with the $TiO_2$ layer showed lower photovoltages and charge separation/transfer efficiencies than the bare α-$Fe_2O_3$ at relatively low applied voltages, which was attributed to the prevention of band bending due to Fermi level pinning in presence of the $TiO_2$ layer. In contrast, at relatively high applied voltages, Fermi level unpinning occurred, enhancing charge separation and transfer efficiencies and thereby improving the overall water splitting performance. Therefore, it was concluded that the anodic potential shift of the onset potential observed in the J-V curve of Fig. 1 (B) can be attributed to the Fermi level pinning by the $TiO_2$ underlayer, but the photocurrent density was enhanced at relatively high applied voltage due to the Fermi level unpinning. In addition, the trap-mediated recombination was accelerated, which resulted in a decrease in the amount of the long-lived holes available for water oxidation, resulting in a decrease in the photocurrent under low applied bias conditions. This was also one of the causes of the anodic shift of the onset potential. To alleviate the anodic shift, we inserted an additional layer. When $NiFe_2O_4$ underlayer was deposited between the FTO substrate and the α-$Fe_2O_3$, it induced the cathodic shift of the onset potential. Thus, by adjusting the thickness of both underlayers, it is probable that we will be able to overcome the above-mentioned problem.

**Funding:** G-LAMP Program of the NRF grant (RS-2024-00445180).

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# Unlocking the Room Temperature Phosphorescence through Halogen Engineering in Carbazole Dimer

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Room-temperature phosphorescence (RTP) in metal-free organic materials offers immense potential for advanced optoelectronic applications. However, the rational design and fine-tuning of RTP properties remain challenging due to the complex correlation between molecular structure and photophysical processes. Herein, we explored the impact of intersystem crossing (ISC), spin-orbit coupling (SOC),[1] and halogen interactions to promote RTP in crystalline brominated carbazole dimer (BrCz-D). In contrast, the unsubstituted analogue, Cz-D exhibits thermally activated delayed fluorescence (TADF) under ambient conditions. Femtosecond transient absorption spectroscopy measurements confirmed the population of triplet manifolds in both dimers. Bromine substitution significantly enhances spin-orbit coupling ($V_{SOC}$ = 66.74 $cm^{-1}$), enabling efficient intersystem crossing (ISC) and robust RTP in BrCz-D. The efficiency of ISC aligns with El-Sayed's rule,[2] which governs the feasibility of ISC between singlet ($S_4$-ππ*) and triplet ($T_{16}$-nπ*) states. Enhanced RTP in crystalline BrCz-D is attributed to unique halogen interactions, including Br···Br, C···Br, and H···Br, within the crystal lattice.[3] Such halogen interactions are negligible in the solution state, accounting for the lack of RTP under ambient conditions (Figure 1). The present work highlights the critical role of SOC and halogen bonding in achieving efficient RTP for designing high-performance organic phosphorescent materials through crystallochemistry.

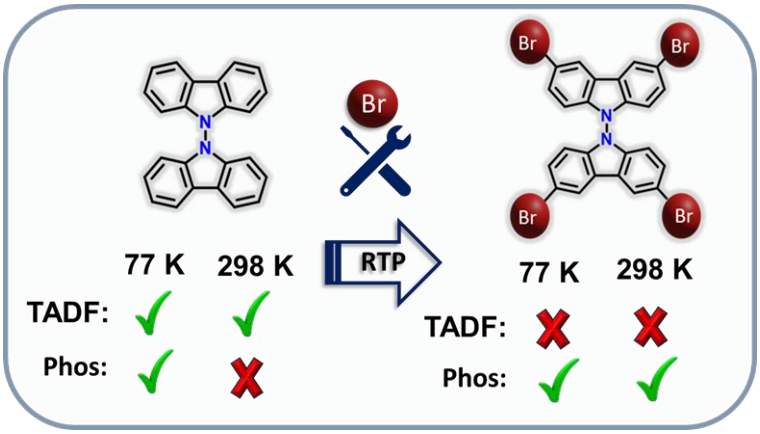


**Figure 1**. The strategic substitution of bromine into the carbazole dimer architecture enables the efficient switching of emission mechanisms from TADF in Cz-D to RTP in BrCz-D.

**Funding**: SERB

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# Interface Engineering between Layered Oxyhalide Photocatalyst and Cocatalyst for Enhancing Water Oxidation

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Loading cocatalysts on photocatalysts is essential to enhance photocatalytic activity; however, the charge transfer from photocatalyst to cocatalyst often governs the overall efficiency of the reactions. Nevertheless, their interface remains elusive and poses challenges for proactive control. The current study addresses the interface engineering to improve the $O_2$ evolution activity of oxyhalide photocatalysts by leveraging the unique band structures. Utilizing an oxyhalide $Bi_4NbO_8Cl$ (Figure 1a) as a model photocatalyst,[1] in which DFT calculations showed electrons and holes tend to accumulate in the fluorite and perovskite layer (Figure 1b), respectively,[2] we combined the exposure of the perovskite layer via acid treatment with the loading of water oxidation cocatalyst Ir species (hereafter denoted as $IrO_2$). This approach resulted in a 17-fold enhancement in the $O_2$ evolution rate compared to unmodified pristine $Bi_4NbO_8Cl$ (Figure 1c). The observed $O_2$ evolution rate was markedly higher than that of the reported oxyhalide photocatalysts, with an apparent quantum yield reaching 16%. Various characterizations, including transient absorption spectroscopy, demonstrated that the significantly enhanced $O_2$ evolution was due to the efficient hole transfer between $Bi_4NbO_8Cl$ and $IrO_2$, resulting from loading $IrO_2$ onto the perovskite layer (the hole accumulation layer) exposed through the acid treatment (Figures 1d and 1e). By employing the surface-modified $Bi_4NbO_8Cl$ as an $O_2$ evolution photocatalyst, interparticle Z-scheme water splitting has been achieved without any electron mediators. This research paves the way for rational control of photocatalyst-cocatalyst interface structures to improve the photocatalytic activities of various materials.

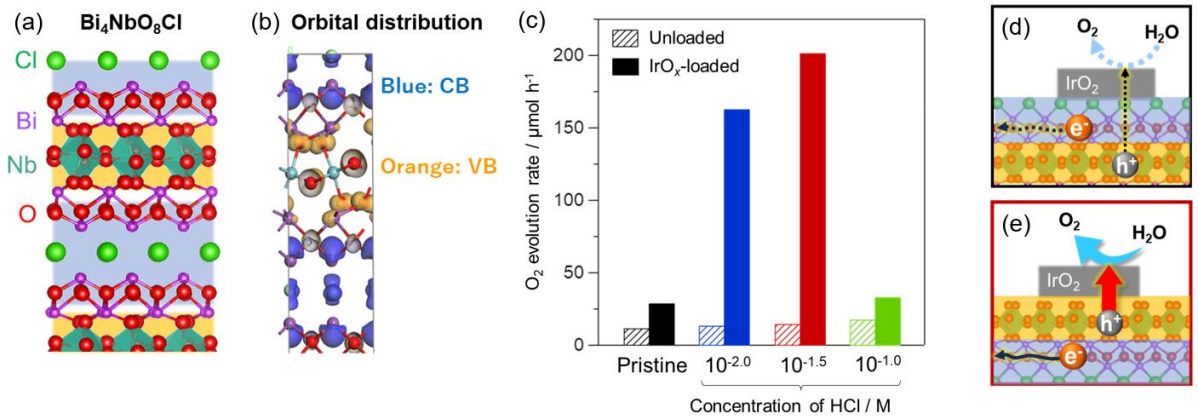


Figure 1. (a) Crystal structure of $Bi_4NbO_8Cl$. (b) Orbital distribution of the lower parts of the conduction band (CB: blue) and the upper parts of the valence band (VB: orange) of $Bi_4NbO_8Cl$ estimated by density functional theory (DFT) calculation. (c) Initial $O_2$ evolution rate of $IrO_2$-loaded (or unloaded) $Bi_4NbO_8Cl$ with acid treatment at different HCl concentrations ([HCl] = $10^{-2}$ – $10^{-1}$ M) in an aqueous $AgNO_3$ solution under visible light irradiation ($\lambda$ > 400 nm). (d, e) Schematic image of $O_2$ evolution over (d) pristine and (e) desirable $Bi_4NbO_8Cl$ loaded with $IrO_2$.

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# Aromatic α-hydroxy Schiff bases for Molecular Solar Thermal Energy Storage applications

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The core of Molecular Solar Thermal Energy Storage (MOST) systems is their active molecular components. The MOST molecules undergo a reversible chemical transformation upon exposure to sunlight. The photochemical path involves a transition of a stable molecule form (**A**) in the ground electronic state to the excited state (**A***) (Figure 1a). Following fast relaxation from the Franck-Condon configuration through the minimum energy conical intersection (MECI) of $S_0/S_1$ directs the reaction back to the ground electronic state, with a change of the molecular geometry and properties induced upon the photon absorption, leading to creation of the metastable form (**B**). Among compounds studied so far for the MOST applications, diazobenzenes and norboradienes play the most important role [1,2]. Here, we would like to propose a different class of systems to be considered as MOST candidates: namely, the α-hydroxy Schiff bases.

The α-hydroxy Schiff bases are known for their high photostability, large Stoke's shifts, and good photoswitching properties [3]: all stemming from the Excited-State Intramolecular Proton Transfer (ESIPT) transformation characteristic for this class of compounds, and all essential for the MOST applications. To examine the hypothesis of their good MOST prospects, here we have selected a few representative α-hydroxy Schiff bases (shown in **Figure 1b**) and studied their properties with use of the quantum-chemical methods. In that regard, we have focused on the energy-storage-relevant properties (energy-per-molecule storage capacity, kinetic stability) and detailed characterization of the mechanism and predicted efficiency of the solar energy harvesting process (photo-reaction potential energy profiles and nonadiabatic molecular dynamics simulations). Our first results indicate promising prospects for employing the α-hydroxy Schiff bases for the solar thermal energy harvesting and storage.

**a)** **b)**

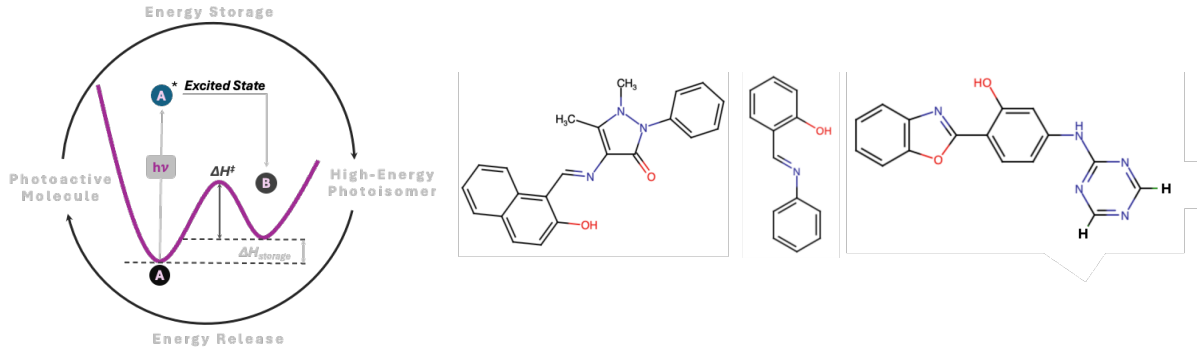


Figure 1. a) A schematic representation of photoreaction cycle in MOST systems. A - ground state isomer, A˚ - excited state of the initial isomer, B - metastable isomer, ΔH; - thermal activation energy of back conversion, and b) Schiff bases under investigation.

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# Enhancing Photocatalytic $O_2$ Evolution over Double-Layered Perovskite Oxyiodide through Flux Synthesis and Surface Modifications

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Sillén–Aurivillius oxyiodides, particularly $Ba_2Bi_3Nb_2O_{11}I$ with double-perovskite layers (Fig. 1a), are promising photocatalysts for visible-light-driven water splitting due to their excellent light absorption and carrier transport properties[1]. However, strategies to improve their photocatalytic performance through advancements in synthesis methods or surface modifications remain limited.

In this study, we report the flux synthesis of $Ba_2Bi_3Nb_2O_{11}I$ and the optimization of cocatalyst loading[2]. Single-phase and plate-like $Ba_2Bi_3Nb_2O_{11}I$ (Fig. 1b) was successfully synthesized using molten alkali iodide salts under appropriate calcination conditions. Among these conditions, the heating rate during synthesis was found to affect crystallinity and carrier lifetime. By enhancing crystallinity and prolonging carrier lifetime (Fig.1c), the optimized flux-synthesized sample exhibited an approximately 12 times higher sacrificial $O_2$ evolution rate than that prepared via the conventional solid-state reaction (SSR). Furthermore, the iron-ruthenium oxide cocatalyst ($(Fe,Ru)O_x$)[3], which was loaded on the oxyiodide under appropriate conditions using suitable precursors, significantly enhanced non-sacrificial $O_2$ evolution from an aqueous $Fe^{3+}$ solution by promoting both water oxidation and $Fe^{3+}$ reduction (Fig. 1d). Finally, Z-scheme water splitting using the optimized $(Fe,Ru)O_x/Ba_2Bi_3Nb_2O_{11}I$ exhibited higher $O_2$ evolution activity efficiency than previously reported the unoptimized sample. This study provides valuable insight into enhancing the $O_2$ evolution activity of oxyiodide photocatalysts for water-splitting applications.

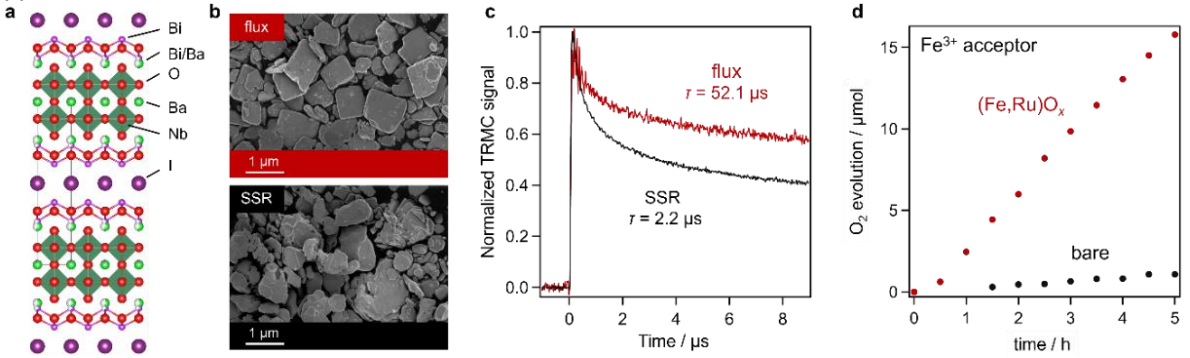


Figure 1. (a) Crystal structure of $Ba_2Bi_3Nb_2O_{11}I$. (b) SEM images of $Ba_2Bi_3Nb_2O_{11}I$ prepared via the flux and SSR methods. (c) Normalized TRMC signals and carrier lifetimes ($\tau$) of the same sample in (b). TRMC signals ($\varphi\sum\mu$) correspond to the product of the charge carrier generation efficiency $\varphi$ and the sum of charge carrier mobilities $\sum\mu$, and the decay profile reflects the carrier lifetime. (d) Time course of photocatalytic $O_2$ evolution over unloaded or $(Fe,Ru)O_x$-loaded $Ba_2Bi_3Nb_2O_{11}I$ samples in $Fe(NO_3)_3$ (aq) under visible light irradiation ($\lambda$ > 400 nm).

**Funding:** JSPS KAKENHI (JP20H00398, JP23H02061, and JP24KJ1470)

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# Fluorinated Nitrogen-rich heterocycle-based hole transport materials for defect passivation in inverted perovskite solar cells

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Energy has been a crucial driver of human progress, yet the soaring demand for energy production is increasingly straining our environment. This pressure has intensified pollution levels and catalyzed significant climate change, igniting urgent calls for alternative renewable energy sources as our natural resources deplete.[1-2] Solar energy offers a robust, sustainable solution to address our escalating energy needs.[3] We have witnessed extraordinary advancements in photovoltaic (PV) technologies in recent decades, ushering in a new era for cleaner and more sustainable energy production. Among these breakthroughs, hybrid organic-inorganic perovskite solar cells (PSCs) stand out as a revolutionary advancement,[4] achieving an impressive overall conversion efficiency of 26.7%.[5] Unlocking the full potential of PSCs requires overcoming intrinsic defects within the perovskite layer, which act as non-radiative recombination centers that undermine device performance.[6] This study introduces an innovative class of non-fluorinated and fluorinated nitrogen-rich heterocyclic molecules (**Cz-Ph**, **Cz-PhF**, **Cz-Py**, and **Cz-PyF**) designed as hole-transporting materials (HTMs). These materials serve a dual purpose: they provide superior charge transport and effectively passivate defects. Incorporating nitrogen atoms in the heterocyclic backbone and the strategic use of fluorine substitutions enhance charge mobility and establish robust bonding with undercoordinated lead ions at the perovskite interface, significantly diminishing deep-level trap states.[7] Comprehensive structural, optical, and electrical characterizations demonstrate remarkable improvements in interfacial compatibility, enhanced hole mobility, and reduced trap-assisted recombination. Devices integrating these HTMs showcase an outstanding power conversion efficiency of up to 22.88% and exceptional operational stability. This study underscores the transformative capabilities of heteroatom-engineered HTMs in overcoming critical challenges that hinder PSC performance. It lays the groundwork for the intelligent design of multifunctional materials, setting the stage for a new generation of photovoltaic technologies that can revolutionize energy production for a sustainable future.

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# Long-Lived Intramolecular Charge Transfer in Persubstituted Perylenediimide

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Photoinduced charge transfer (CT) states play a pivotal role in increasing the power conversion efficiency of molecular systems used in artificial photosynthesis and optronic devices.[1] The absence of intrinsic CT states is one of the main reasons for the poor photoconversion efficiencies of organic chromophores like perylenediimide (PDI). Herein, we explore the excited state dynamics of a persubstituted PDI (AP) with amino groups at the ortho positions and bromine atoms at the bay positions. Due to the influence of bromine atoms and amino groups on the PDI core, nonradiative pathways are accessed on photoexcitation in AP.[2] Femtosecond and nanosecond transient absorption measurements in weakly polar and polar solvents showed the relaxation of the higher singlet excited state in picoseconds time scale, paving the way to an intramolecular charge transfer (ICT) state having a lifetime in the nanoseconds time scale. As the dielectric medium changed from the weakly polar solvent (toluene, ε = 2.38) to a polar solvent (ethyl acetate, ε = 6.02), the lifetime of the solvent stabilized CT state decreased from $\tau$ = 69.1 ± 1.7 ns to $\tau$ = 47.1 ± 0.5 ns, which confirms the solvent dependency of the ICT state. Theoretical investigations employing surface hopping dynamics suggest that the rate of internal conversion ($k_{IC}$ = 1.13 × $10^{11}$ $s^{-1}$) competes with the intersystem crossing ($k_{ISC}$ = 0.85 × $10^{11}$ $s^{-1}$) in AP. Amination on the ortho position induces the CT characteristics to the core of the PDI, as evident from the hole–electron surface analysis of the $S_1$ state. Presented results on persubstituted PDI with long-lived relaxed CT states may improve the designing strategies of organic optoelectronic devices.

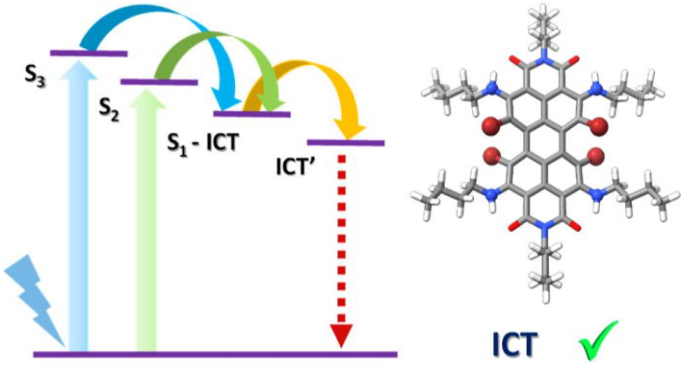


**Figure 1**. A comprehensive investigation into the excited-state dynamics of persubstituted perylenediimide, focusing on its charge transfer states.

**Funding**: MoE- STARS

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# Ruthenium(II) Complexes with Functionalized Phenanthroline Ligands: Synthesis, Structural Characterization

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In the pursuit of efficient molecular systems for solar-to-chemical energy conversion, we report the design, synthesis, and characterization of two novel ruthenium(II) complexes (see Fig.1) incorporating functionalized 1,10-phenanthroline ligands. The ligands were synthesized via Suzuki–Miyaura cross-coupling reactions, enabling precise electronic tuning through strategic aryl substitutions. The resulting Ru(II) complexes were structurally characterized by single-crystal X-ray diffraction (sc-XRD), and further confirmed by NMR spectroscopy, mass spectrometry (MS), and UV–Vis absorption spectroscopy. Photophysical studies reveal strong absorption in the visible region, highlighting their potential as photosensitizers in photocatalytic systems. The combination of synthetic modularity, structural insight, and functional photophysical behavior underlines these Ru(II)-phenanthroline complexes as promising candidates for artificial photosynthesis and solar energy conversion technologies[1-3].

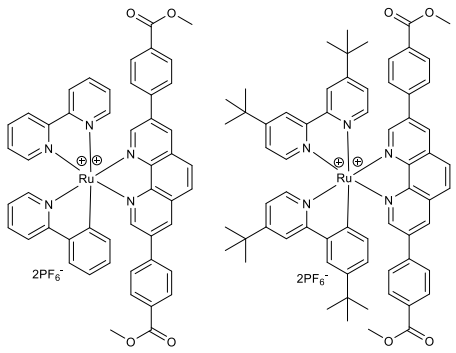


Figure 1. Molecular structures of $[(bpy)_2Ru((mcp)_2phen)](PF_6)_2$ and $[(tbbpy)_2Ru((mcp)_2phen)](PF_6)_2$, $(mcp)_2phen$ = 3,8-bis(4-methoxycarbonylphenyl)phenanthroline

**Funding:** LGFG (Landesgraduiertenförderungsgesetz) scholarship from Ulm University

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# Triplet-Triplet Annihilation Upconversion Mediated Photocatalysis Using Quantum Dots

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Visible-light photocatalysis has been established as a sustainable strategy for chemical transformations. But it operates within the thermodynamic limit set by the maximum energy of visible-light photons. This limits the range of redox potentials accessible through common visible-light active photocatalysts. Therefore, it becomes important to develop novel methodologies that can drive thermodynamically challenging reactions using visible-light. Photon upconversion based on triplet-triplet annihilation (TTA) is one such promising strategy which can convert two lower energy photons to a higher energy photon using an appropriate photosensitizer and annihilator. Upon photoexcitation, the sensitizer transfers its excitation energy to low lying triplet states of the annihilator. Two such triplet excited annihilator molecules can undergo TTA, generating one higher energy singlet excited state. This singlet state formed from the combined energy of two photons can then be utilized for photoredox catalysis.[1] Various photosensitizers have been explored for this purpose with quantum dots (QDs) being the latest candidates. They offer distinct advantages in terms of their strong and tuneable opto-electronic properties and minimal energy loss due to inter-system crossing.[2] In the present study, we have developed a QD-sensitized TTA upconversion (TTA-UC) system for performing a challenging chemical reaction. We have used the environmentally friendly indium phosphide (InP) based quantum dots as sensitizers for a green to blue TTA-UC to carry out a challenging dehalogenation reaction (Fig. 1).[3]

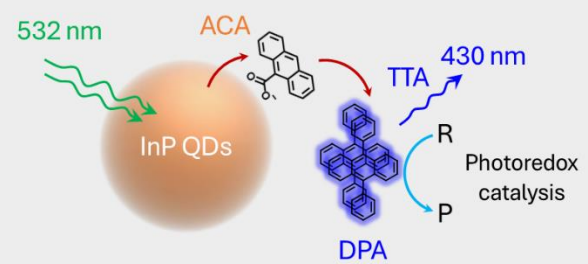


Figure 1. Schematic representation of the QD-sensitized TTA-UC system for photoredox catalysis

**Funding:** DST-SERB India, IISER Pune, PMRF

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# Ultrafast Features of Intermolecular Singlet Fission in Quinoidal Push-Pull Molecules

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Singlet Fission (SF) is a key photophysical process that promises to significantly enhance the efficiency of solar cells by doubling the available triplet yield. Recently, SF has also been studied for applications in quantum information science (QIS) and molecular medicine. [1,2] In recent years, quinoidal derivatives have been found to be ideal candidates for SF owing to their efficient visible light absorption, high photo and air stability and ultrafast SF rates when going from the solution to aggregate phase.[3] In this study, we investigate and compare the SF dynamics of five quinoidal derivatives, each exhibiting varying degrees of charge transfer character due to their asymmetric chemical structures and presence of electron donor substituents. This is achieved by probing the photophysical behavior of the systems by using femtosecond (fs) and nanosecond (ns) transient absorption (TA) in solution, molecular aggregates in water dispersion and thin films to identify the intermolecular activation of SF process. As shown in Figure 1, the fsTA data confirm that the aggregate phase activates SF, since it is observed the presence of the doubly excited state transients, exhibiting a triplet-like spectral shape with lifetimes on the order of picoseconds. Additionally, from those data it was possible to estimate the triplet quantum yield, that exceeds 100% and reaches 200% for some of the systems under investigation.

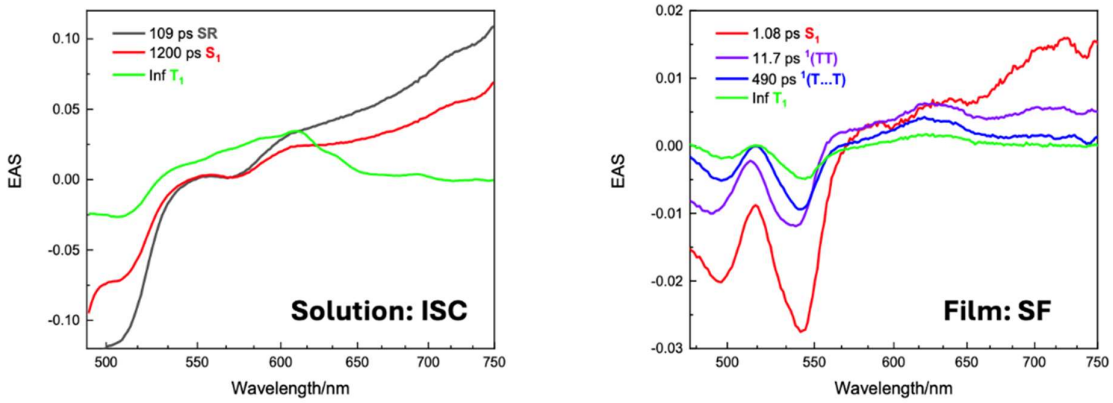


Figure 1. Femtosecond transient absorption EAS (Evolution Associated Spectra) in DMSO solution (a) and thin film (b).

Another powerful tool to investigate the occurrence of singlet fission (SF) is time-resolved Electron Paramagnetic Resonance (TR-EPR) spectroscopy. TR-EPR measurements are currently underway on these systems and may enable the identification and characterization of the $^5$(TT) state. This state is particularly compelling for its potential applications in QIS, as its entangled nature allows it to function as a qubit, opening new frontiers for the applicability of SF.

**Funding:** This work had been funded by the European Union – NextGenerationEU under the Italian Ministry of University and Research (MUR) National Innovation Ecosystem grant ECS00000041 – VITALITY

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# Molecular Basis of Nitric Oxide Sensing by a Blue Fluorescent Protein

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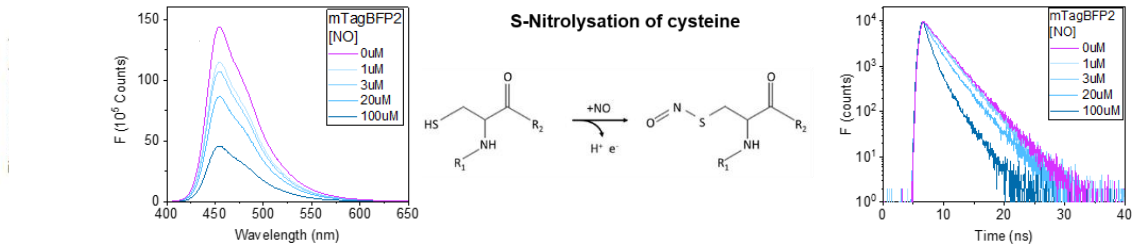
We have examined the response to nitric oxide of fluorescence emission by the blue-emitting fluorescent protein mTagBFP2. To our surprise, upon exposure to micromolar concentrations of nitric oxide, we observed a ca. 70% reduction in fluorescence quantum yield and lifetime. Recovery of fluorescence emission is observed after treatment with Na-dithionite. Experiments on related fluorescent proteins from different families show similar nitric oxide sensitivity of their fluorescence. We correlate the effect with S-nitrosylation of Cys residues. Mutation of cysteine residues in mTagBFP2 removes its nitric oxide sensitivity. Similarly, fluorescent proteins devoid of cysteine residues are insensitive to nitric oxide. In another set of experiments we investigated the NO-transfer to FPs mediated by GSNO. We also show that mTagBFP2 can sense exogenously generated nitric oxide when expressed in a living bacterial or mammalian cells. Theoretical considerations show that excitation energy transfer from the mTagBFP2 chromophore to the CysNO group is a major determinant of the observed fluorescence quenching. We propose mTagBFP2 as the starting point for a new class of genetically encoded nitric oxide sensors based on fluorescence lifetime imaging.

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# Efficient intersystem crossing in donor-Bodipy dyads/triads and photon upconversion application

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Owing to the advantages of low excitation power energy, tunable excitation and emission wavelengths, and high energy conversion efficiency, triplet-triplet annihilation upconversion (TTA UC) has been widely used in photocatalysis, artificial photosynthesis, and solar cells. The development of highly efficient heavy atom free triplet photosensitizers is significant to improve the utilization of solar energy.

Herein, based on the spin-orbit charge transfer intersystem crossing (SOCT ISC) mechanism, Bodipy was chosen as the acceptor unit to construct compact electron donor-acceptor dyads and triads. After fully study on the photophysical properties and excited states processes, we explored the influences of hindrance effects and push-pull electronic effects on the excited states properties and the photophysical processes. These efficient heavy atom free photosensitizers demonstrated excellent performance in visible-to-blue light upconversion.

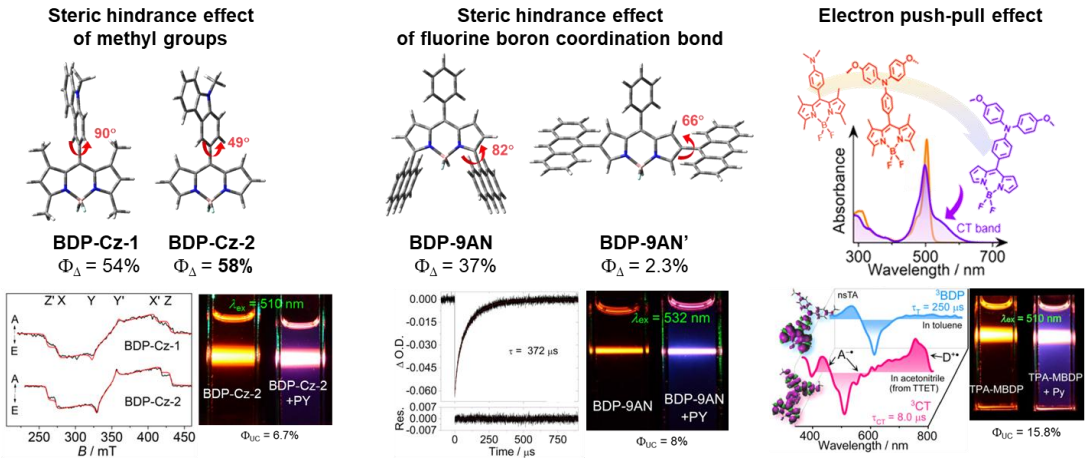


Figure 1. Structures of Bodipy-based dyads/triads, excited states photophysical properties and their upconversion emission by mixing of photosensitizers and perylene.

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**Acknowledgement:** We thank National Key Research and Development Program of China (2023YFE0197600), National Natural Science Foundation of China (22473021, U2001222), and Fundamental Research Funds for the Central Universities for financial support.

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# Spectroscopic Characterization of 2-(2'-pyridyl)-benzimidazole-(water)$_{1,2}$ Complexes Isolated in the Gas Phase

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The solvent interactions with the N-rich biomolecules can help us learn about the innate ability of the chromophores to withstand the photodamage caused by UV radiation.[1] The multi-functional molecules, such as, benzimidazole derivatives, which have a greater number of N-atoms, are known for their exceptional excited state deactivation activities.[2,3] The binding preferences of the solvent on the chromophore can govern the reaction path for the deactivation processes. Here in we present the experimental study of the hydrogen-bonded docking preferences of small solvent molecules on 2-(2′-pyridyl)-benzimidazole (PBI). The PBI–$(H_2O)_{1,2}$ complexes were produced in a supersonically jet-cooled molecular beam and probed using resonant two-photon ionization and laser-induced fluorescence spectroscopy, with multiple isomers confirmed and structural assignment were done using fluorescence-dip infrared spectroscopy and resonant ion-dip infrared spectroscopy. Two distinct isomers of PBI–$H_2O$ and PBI–$(H_2O)_2$ complexes were identified. PBI–$H_2O$-a was found as the most stable structure, with a water molecule forming a hydrogen-bonded bridge between imidazolyl-NH ($N_IH$) and pyridyl-N ($N_P$) at site-a. The site-a isomers exhibit higher $S_1$ state stability compared to the $S_0$ state, resulting in red-shifted $S_0 \rightarrow S_1$ band origin for PBI–$H_2O$-a and a further red-shift for the PBI–$(H_2O)_2$-aa isomers. The NH stretching frequencies of PBI–$H_2O$-a and PBI–$(H_2O)_2$-aa were observed to be red shifted from that of PBI. In contrast, the PBI– $H_2O$ -b isomer, with a hydrogen bond between imidazolyl-N ($N_I$) and pyridyl-CH ($C_PH$) at site-b opposite to site-a, showed a blue-shifted band origin transition, which was confirmed by the similar NH stretching frequency of the isomer as PBI monomer. A unique PBI–$(H_2O)_2$-ab isomer was detected with solvent molecules bound at both sites a and b, displaying a smaller red-shift in the band origin transition than the aa-isomer. But the NH stretching frequency of the ab isomer found more red shifted compared to the other isomer, suggesting stronger H-bond interaction. By investigating the potential landscape of PBI, this study advances our knowledge of spectrum shifts, stabilizing effects, binding preferences of solvent molecules on the chromophore, and their influence on the excited state dynamics in various environments.

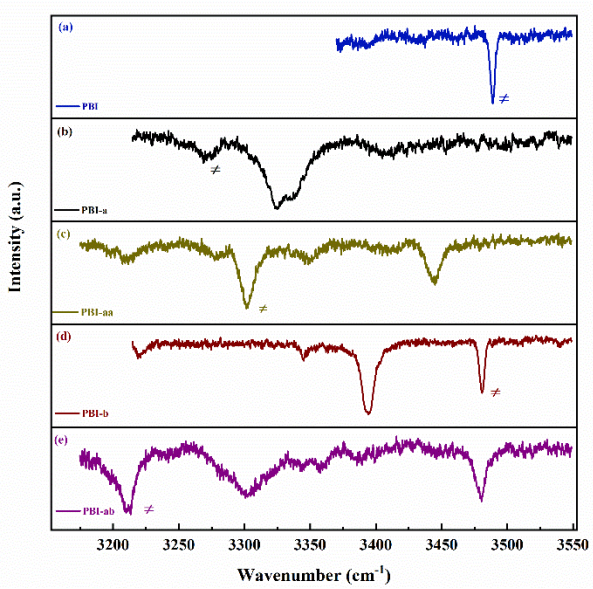


Figure 1. Fluorescence dip infrared spectrum of (a) PBI monomer and ion dip infrared spectra of (b) PBI-$(H_2O)_1$-a, (c) PBI-$(H_2O)_2$-aa, (d) PBI-$(H_2O)_1$-b and (e) PBI-$(H_2O)_2$-ab complexes. (≠ are the NH stretching frequencies of the corresponding systems)

# A novel ultrafast spectroscopic method to determine how and how fast the light-harvesting complexes sense and respond to changes in pH: proof of principle

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In natural environments, plants rely on sunlight for survival, yet the intensity of solar irradiance can fluctuate rapidly. To cope with such variations, plants have evolved mechanisms to protect themselves from potential damage under high light conditions, when excess absorbed energy can lead to severe photooxidative stress. To mitigate this risk, plants employ a rapidly reversible photoprotective process, known as energy-dependent quenching (qE), which dissipates excess excitation energy as heat.[1] qE is triggered by thylakoid lumen acidification during light-saturated photosynthesis, inducing conformational changes in light-harvesting complexes (LHCs) that enable heat dissipation of excess energy.[2] However, these changes occur on ultrafast timescales (≤ µs),[3,4] beyond the resolution of current techniques such as stopped-flow rapid mixing, leaving open the question of how rapidly and through which intermediates LHCs respond to pH.

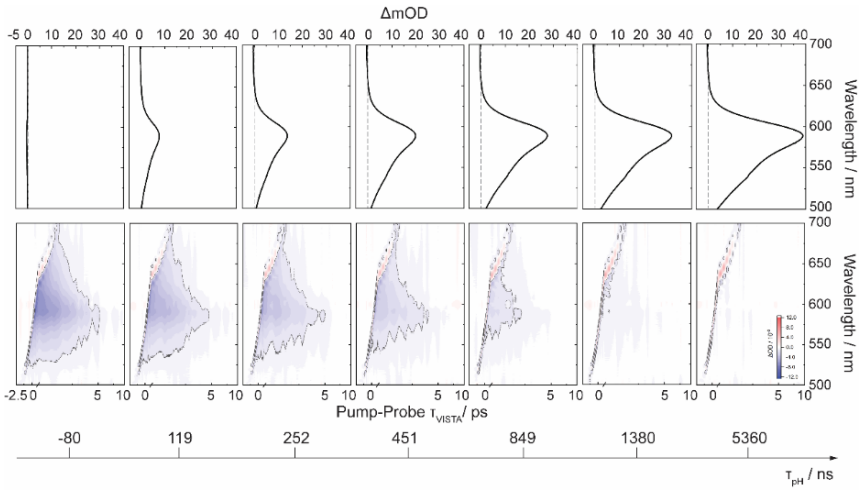


Figure 1. The ground-state (upper panel) and excited-state absorption spectra (bottom panel, averaged every 4 timesteps) with variable pump-probe delay of BCP in the presence of 8mM 2-NBA at selected prepump delay times $\tau_{pH}$ with respect to the pump pulse.

Herein, we present pH-jump Visible Transient Absorption Spectroscopy (pH-VISTA), a novel ultrafast approach combining nonequilibrium pH perturbation with real-time tracking (fs to ms) of excited-state dynamics in photoactive molecules. Using bromocresol purple (BCP) as a pH probe, we demonstrate localized acidification (pH 7 to 4.8) via photoexcitation of 2-nitrobenzaldehyde (2-NBA) as an irreversible photoacid, while simultaneously monitoring excited-state dynamics of BCP. This proof-of-concept establishes pH-VISTA as a powerful tool for studying rapid proton-coupled processes, particularly the initial activation mechanisms of photoprotection in photosynthetic systems.

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# Red Thermally Activated Delayed Fluorescence with nearly zero gap in phenothiazine-naphthalimide derivatives

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Thermally Activated Delayed Fluorescence (TADF) is widely known for its possibility to harvest both singlet and triplet excitons to enhance electroluminescence efficiency in OLED devices without the need to exploit molecules containing heavy metals. Despite the progress with blue and green TADF emitters, achieving highly efficient red-emitting TADF materials with a detailed understanding of their mechanisms remains a challenge [1]. In this study, we explore novel purely organic push-pull compounds bearing naphthalimide (NPI) and phenothiazine (PTZ) as the electron-acceptor (A) and electron-donor (D) groups tuning their molecular design[2], such as varying the number of D-A groups (NPI-PTZ, NPI(3)-PTZ) or extending the conjugation (NPI-Ph-PTZ, NPI(2)-PTZ, PTZ-NPI-Ph-PTZ), to unveil the crucial structural features that lead to red TADF. Femtosecond and nanosecond transient absorption experiments of the compounds in solution revealed ultrafast intramolecular charge transfer and efficient triplet state production. Detailed time-resolved photoluminescence experiments acquiring emission spectra with increasing delay from 7 ns to 20 ms were performed to detect both red prompt and delayed emission, which proved to have lifetimes of hundreds of nanoseconds. Temperature effect measurements, from 5K to 300K, of NPI-PTZ and NPI(3)-PTZ in toluene showed a phosphorescence emission placed in the same spectral region of prompt fluorescence (Fig.1a), indicating a peculiar zero and nearly zero energy difference between the singlet and the triplet excited states. The small $\Delta E_{ST}$ explains why it was possible to detect delayed emission even at very low temperatures, as shown in Fig.1b. While NPI-PTZ and NPI(3)-PTZ are characterized by a low efficient red emission (PLQY=0.002 and 0.009, respectively), the compounds with extended conjugation along the push-pull backbone, which reduces the dihedral angle between the donor and acceptor units, exhibit a more intense emission (PLQY=0.30 and 0.50 for PTZ-NPI-Ph-PTZ and NPI(2)-PTZ, respectively) and red TADF with longer lifetimes due to a larger $\Delta E_{ST}$ (0.2 eV). These results are crucial for deepening the understanding of the relationship between structure and TADF mechanism, contributing to future design of optimized TADF materials for optoelectronic applications.

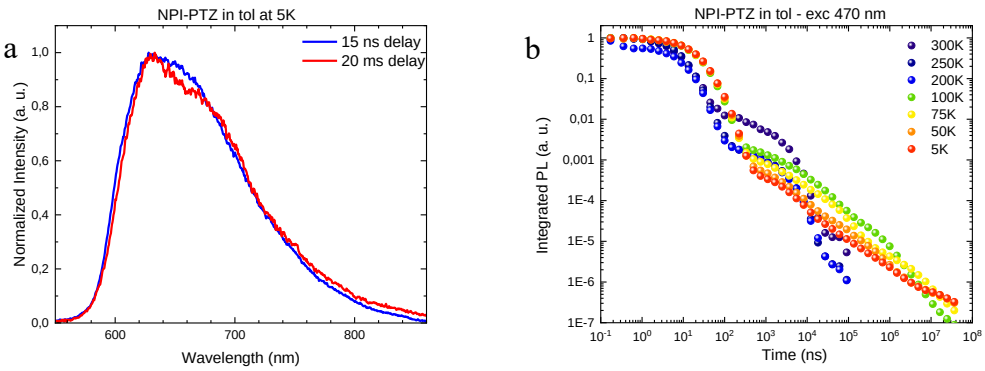


Figure 1. a) Gated emission spectra of NPI-PTZ in toluene at 5K; b) Emission decay kinetics of NPI-PTZ in toluene at different temperatures.

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# Conformational Switching of a Nano-Size Urea-bridged Zn(II)Porphyrin Dimer by External Stimuli

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## Abstract:

For the first time, explicit stabilization of all the three conformers, *viz.* (*cis*,*cis*), (*cis*,*trans*) and (*trans*,*trans*), of a 'nano-sized' highly-flexible urea-bridged Zn(II)porphyrin dimer have been achieved *via* careful manipulations of external stimuli such as solvent dielectrics, temperature, anionic interactions, axial ligation and surface-induced stabilization.[1] The conformers differ widely in their structures, photophysical properties, chemical reactivity with chiral substrates and thus have vast potential applicability.[2,3,4,5] Low temperature promotes the stabilization of (*cis,trans*)-conformer while rise in temperature facilitates flipping to the *(cis,cis)* one. Significantly, exclusive stabilization of the (*trans,trans*)-isomer has been illustrated using acetate anion which facilitates H-bonding with the two amide linkages of the urea spacer. Remarkably, HOPG surface facilitates stabilization of the energetically challenging *(trans,trans*)-conformer via *CH*$\cdots\pi$ and $\pi\cdots\pi$ interactions with the solid surface to the porphyrinic cores. DFT calculations demonstrate that the relative stability of the conformers can be modulated upon slight external perturbations as also observed in the experiment. Several factors contributing towards the conformational landscape for the highly flexible urea-bridged porphyrin dimers have been mapped here.

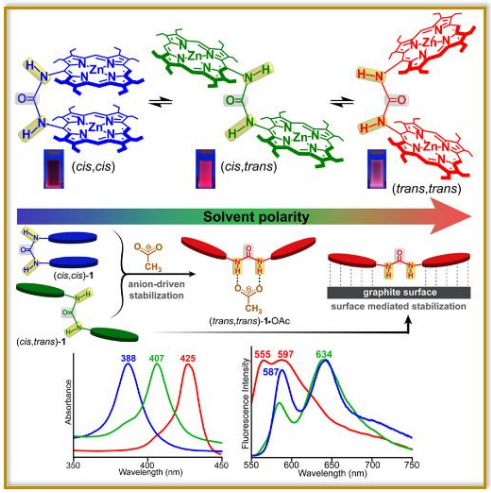


Figure 1. Three possible conformers of a urea-bridged Zn(II)porphyrin dimer and their selective stabilization investigated through advanced spectroscopic methods.

**Funding:** The Science and Engineering Research Board (SERB), India.

**Acknowledgement:** We thank IIT Kanpur for providing all the facilities and support and Prof. Thiruvancheril G. Gopakumar for his help in performing the AFM studies.

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# Fine-tuning the Excited State Dynamics of Ruthenium(II) Polypyridyl Complexes with Benzazole-Substituted 8-Hydroxyquinolines

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A series of structurally related bistridentate heteroleptic Ru(II) polypyridyl complexes: $[Ru^{II}(ttpy)(8\text{-}HQL^{S/N/O})]^{+}$ (**Ru1-Ru3**) were synthesized, where **ttpy** = *p*-tolyl terpyridine and **8-HQL$^{S/N/O}$** are monoanionic N^N^O-donor tridentate ligands (**8-HQL$^{X}$**), derived from 8-hydroxyquinoline (8-HQ), viz. **8-HQL$^{S}$** = 2-(2'-benzothiazole)-8-hydroxyquinoline, **8-HQL$^{N}$ =**2-(2'-benzimidazole)-8-hydroxyquinoline, **8-HQL$^{O}$** = 2-(2'-benzoxazole)-8-hydroxyquinoline. The electronic structure of these rigid ligands was systematically tuned by varying the non-coordinating heteroatom (S, NH, O) in the five-membered heterocyclic ring, impacting the electronic properties, redox potentials, excited state lifetimes deactivation pathways and photophysical behavior of the corresponding Ru(II) complexes.[1,2,3,4,5] Given their reasonable excited state lifetime and $^{1}O_2$ generation ability, these heteroleptic Ru(II) complexes demonstrated potential as photocatalysts for oxidation of organic substrates.[6,7,8]

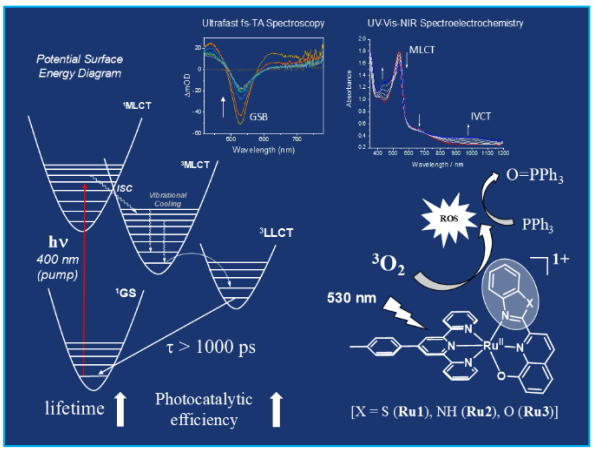


**Figure 1.** Systematic variation in five membered ring heterocycle of 8-hydroxyquinoline ligand backbone impacting on the overall excited state lifetime and dynamics of the heteroleptic bis(tridentate)Ru(II)-polypyridyl complexes.

**Funding:** Science and Engineering Research Board (SERB) (CRG/2021/000527), India.

**Acknowledgement:** We thank IIT Kanpur for infrastructures and providing High Performance Computing (HPC-2013) facility for the DFT calculations and we also acknowledge Dr. V. S. Mothika from IIT Kanpur for his help with UV-vis-NIR Spectroelectrochemistry experiments.

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# Ground-State Structure and Excited-State Dynamics of a Donor-Acceptor Complex with Two Charge-Transfer Bands

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Electron donor-acceptor complexes (DACs) are increasingly used in many light-based applications such as molecular electronics[1] or photoredox catalysis[2]. Surprisingly, although DACs have been known for more than 70 years[3], little is known about their structure in liquids.

Here, we investigate the excited-state dynamics of the D = anisole / A = tetracyanoethylene DAC in different solvents at room temperature. This DAC exhibits two charge transfer (CT) absorption bands that are usually explained by invoking two distinct π-stacked isomers[4,5] of the complex, suggesting the possibility of photoselection of either isomer. Transient absorption spectroscopy upon excitation at either band maximum, however, reveals that the ensuing excited-state dynamics are largely independent of the initially excited CT transition. Moreover, the pure ground-state bleach dynamics, extracted from polarized transient absorption measurements, show no holeburning effect and remain independent of the excitation wavelength. Molecular dynamics simulations explain these findings and suggest that a broad ensemble of DAC structures contributes equally to both transitions, challenging the commonly accepted view.

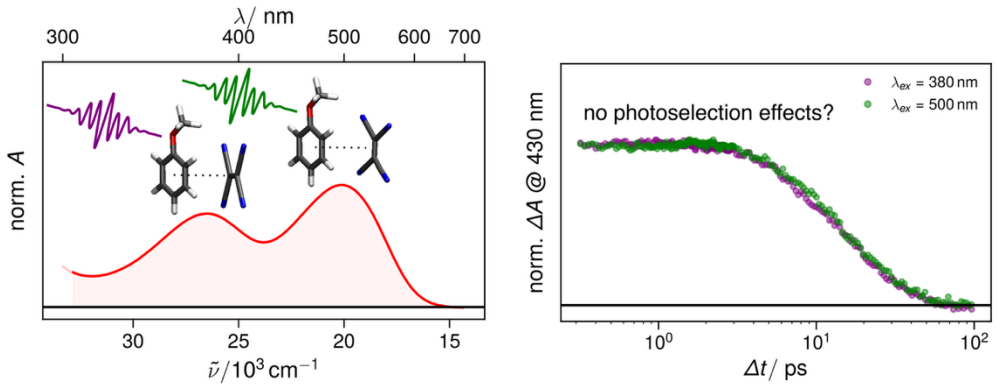


Figure 1. *Left:* Absorption spectrum of the anisole-tetracyanoethylene DAC in paraffin oil together with the structures of the two main isomers that are commonly believed to be at the origin of the two CT bands. *Right:* Dynamics of the transient absorption signal upon excitation at the band maximum of either CT band.

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# The spatial distribution of triplet state wave function in molecules with large π–conjugated systems

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The spatial distribution of the triplet excited state wave function is an important research topic in photochemistry.[1] Regulating the delocalization of the triplet state wave function within π-conjugated frameworks is essential for optimizing the performance of materials in applications such as photovoltaics, photocatalysis, and molecular electronics. Nevertheless, directly extracting information about the spatial distribution of the triplet state using steady-state and transient absorption/emission optical spectra is challenging. In this regard, time-resolved electron paramagnetic resonance (TREPR) spectroscopy offers significant advantages. It can provide detailed insights into the population dynamics of triplet states, as well as the distances between spin-correlated electrons. This is achieved by analyzing the magnitude and sign of the zero-field splitting (ZFS) *D* and *E* parameters, along with the orientation of the ZFS axis.

We selected a series of Bodipy dimers with acetylene or butadiyne bridges, which exhibit either symmetrical or asymmetric molecular structures, to study the spin delocalization of the triplet states. The triplet spatial distribution of these dimers was analyzed using the TREPR spectrum at a low temperature of 77 K.[2] Through the simulation of TREPR spectra, we discovered that the ZFS parameters |*D*| and |*E*| of the dimers are similar to those of the Bodipy monomer. Consequently, we conclude that the triplet state wavefunctions are highly localized on a single Bodipy unit in both symmetrical and asymmetric dimers. This finding aligns with *ab* initio computations, which reveal that the delocalized triplet state is destabilized by 12–14 kcal mol$^{-1}$ compared to its localized counterpart. This contrasts with the previously reported triplet distribution in porphyrin dimer systems, indicating that there is no universal principle governing the regulation of triplet state spatial distribution. The investigation of Bodipy dimers not only offers new insights into the excited state properties of organic chromophores but also holds significance for fundamental photochemistry research and the development of organic optoelectronic materials.

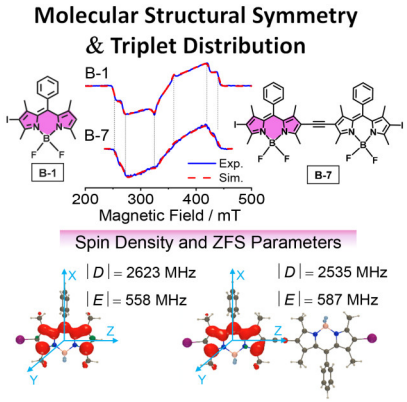


Figure 1. Molecular structures, TREPR spectra, ZFS parameters and electron spin density surface of Bodipy monomer and dimer

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# Assignment of Transient States in Copper(I) Complexes by Femtosecond Near Infrared Spectroscopy

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Copper(I) complexes are emerging as potential alternatives to iridium- and platinum-based emitters in OLED technologies. Contrary to iridium and platinum, copper is earth abundant, resulting in ecological and economic advantages[1]. Achieving efficient luminescence requires ligands with high oscillator strengths. Here, we investigate the complex [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]-(dibenzoylmethanoate)copper(I) (**1**), featuring the strongly absorbing dibenzoylmethanoate ($DBM^-$) ligand. While $DBM^-$ itself exhibits a high oscillator strength, its fluorescence quantum yield is extremely low ($\Phi \approx 10^{-5}$), likely due to excited-state isomerization[2]. Complexation with Cu(I) was expected to inhibit this process and enhance emission, yet the resulting complex still shows extremely weak photoluminescence.

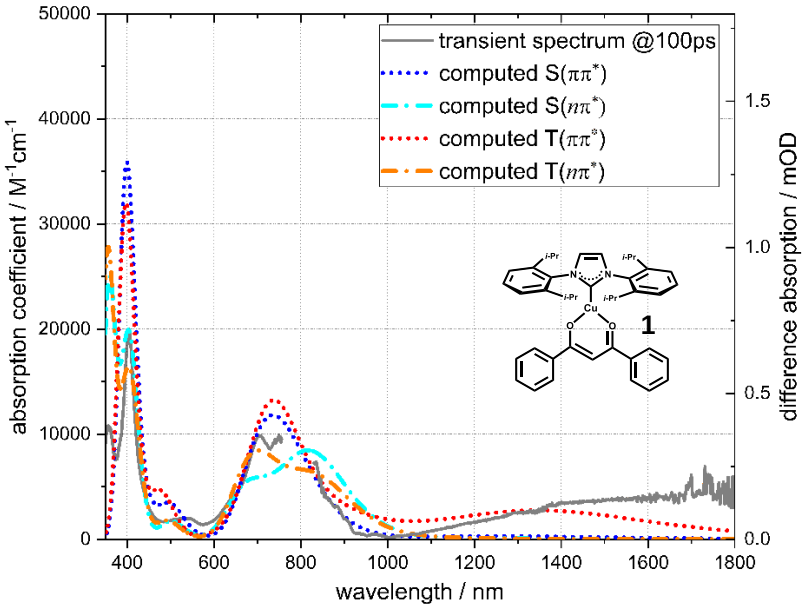


Figure 1: UV/Vis and NIR transient absorption data in comparison to computed spectra for the respective excited states

Femtosecond transient absorption spectroscopy reveals that the complex - the free $DBM^-$ ligand has a lifetime of <10 ps - exhibits excited states with lifetimes on the nanosecond timescale (~1 ns). These states can be detected using conventional UV/Vis probing. However, their nature remains ambiguous due to limited spectral coverage (see Fig.1). By extending the probe window into the near infrared (NIR) region, we access additional low-energy transitions between excited states that are inaccessible in the UV/Vis range. The NIR signatures together with quantum chemical computation allow an assignment – in this case to a state of $^3\pi\pi^*$ character. The combination of femtosecond NIR spectroscopy and theoretical modeling thus provides crucial insight into non-radiative deactivation in these complexes.

**Funding:** GRK 2482 MOD ISC (grant 396890929)

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# Probing Excited-State Dynamics in TiO2 and TiO2/rGO Hybrids via Transient Absorption

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Transient absorption (TA) spectroscopy, also referred to as flash photolysis, is a powerful pump-probe technique for investigating excited-state dynamics, including singlet/triplet absorption and charge carrier lifetimes in a wide range of materials.

In this study, we explore the excited-state behaviour of $TiO_2$ and reduced graphene oxide (rGO)-modified $TiO_2$ hybrids using the Edinburgh Instruments LP980 Spectrometer. This versatile system enables both spectral (220 nm to 2.5 µm) and kinetic (nanoseconds to seconds) measurements by integrating an ICCD camera and a photomultiplier tube (PMT). The ICCD detector provides TA spectra in very short acquisition times, avoiding sample photodegradation.

Representative data will be presented, showcasing both spectral and time-resolved TA profiles of $TiO_2$ and $TiO_2$/rGO hybrids. These measurements provide valuable insight into how rGO incorporation influences charge carrier dynamics in $TiO_2$-based systems.

# The BOLD project: Applying organic chemistry and photochemistry to particle physics by means of Barium tagging

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The neutrinoless double $\beta$ decay ($\beta\beta0\nu$) of $^{136}Xe$ produces a $^{136}Ba^{2+}$ cation alongside a distinctive electronic energy profile. Correlating these two signatures is a promising approach to demonstrating that the neutrino is a Majorana fermion, providing insights into the matter-antimatter asymmetry of the early universe.[1] The BOLD (Barium atOm Light Detection) project aims to develop fluorescent chemosensors capable of selectively trapping $Ba^{2+}$ ions, generating a virtually background-free signal on a dry solid-gas interface.[2,3,4]

As an appealing example of multidisciplinary chemistry, this communication covers the journey from designing and characterizing the physicochemical properties of several generations of sensors in solution to an extensive study on their covalent anchorage to suitable surfaces and the submicrometric detection of the signal using state-of-the-art microscopy techniques (Fig. 1).

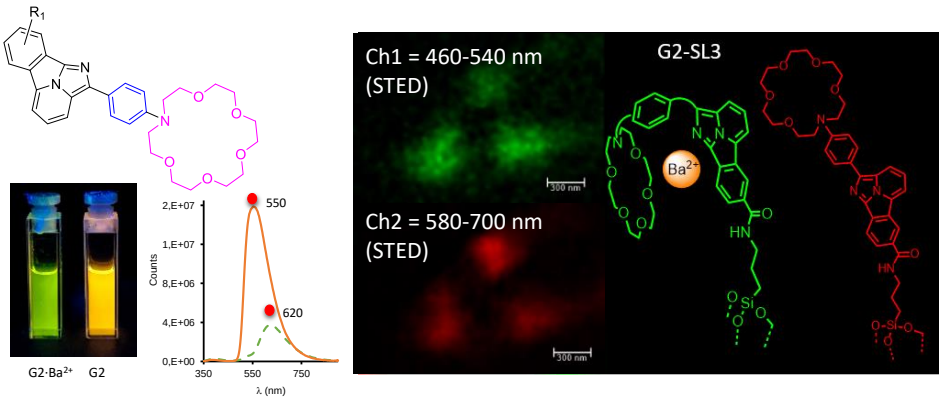


Figure 1. In-solution and on-surface behavior of a second generation (G2) fluorescent bicolor indicator.

**Funding:** Basque Government (IT-1553-22); MICINN (PID2023-151549-NB-I00) and European Commission (ERC-2020-SyG-951281).

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# Photoinduced cleavage of triarylmethane crosslinked polymers with a photoacid

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Responsive polymers are triggering interest and research efforts from the scientific community owing to their potential as smart materials for their auto-diagnostic and self-healing properties, as actuators in robotics and as prospective recyclable polymers. In this context, light-responsive polymers can be triggered remotely and with high time and space resolution, enabling applications in high-value chains. A light-responsive polymer undergoes, when irradiated, a significant structural modification such that optical stimulation significantly changes mechanical, adhesive or solubility properties of the polymeric material.

Herein we present a light-responsive polymer – a PDMA polymer crosslinked with a triarylmethane crosslinker[1] – and demonstrate the possibility to tune the mechanical properties of this thermoset polymer using light. In particular, we describe the use of a photoacid[2] (PAH) to activate the reversible protonation of the crosslinking moieties. This novel strategy leads to sudden de-crosslinking of the polymeric material as shown schematically in Fig. 1.

The photochemical cycle, the protonation, the decrosslinking processes and the recovery kinetics are investigated via photochemical time-resolved methods, combined with photo-rheological experiments. We demonstrate partial-to-complete de-crosslinking of the thermoset material upon irradiation, enabling fine tuning of the mechanical properties and opening to recycling possibilities for thermoset polymers.

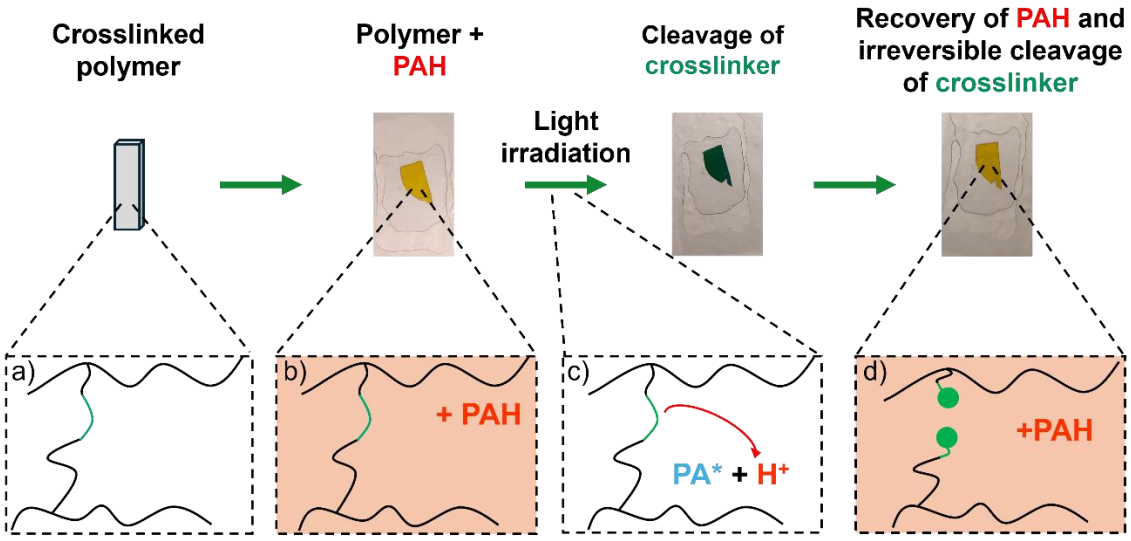


Figure1: Mechanism of cleavage of crosslinked thermoset polymer with photoacid (PAH): a) crosslinked thermoset polymer, b) crosslinked thermoset polymer with PAH, c) light irradiation leads the PAH to release free protons that interact with the crosslinker moiety, d) the photoacid comes back to its initial protonated form and the crosslinker is cleaved.

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# Integrating deployment of bio-waste based complex-nanosystem' photo-active modulable behavior in colloidal aqueous solution

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The Nature is a continuum mixture of evolving reactions occur on functionally upgrading systems, that induce unfolding, restructuring and condensation process following multiple pathways under shaping conditions.[1] Taking advantage from current human knowledge about Nature' chemical paths, it's possible to use mild optimum conditions for the development of sustainable material with photo-active modulable behavior starting from carbon waste.[2] The convergence between top-down and bottom-up methodology applied to bio-polymers, molecules and atomic elements – which are a naturally available carbon resource inside coffee factory waste - shows smart promising ways for the implementation of bio-waste based complex-nano-systems. The resulting aqueous solution of carbon nanoparticles (CNPs) appears like a multicomponent integrant network, enabling of chemical and physical cooperative effects inside colloidal components.[3]
A deep investigation integrating techniques such as morphologic approaches (atomic force microscopy and scanning electron microscopy), spectroscopic methods (steady state and time-resolved absorption and emission spectra), electrochemistry and chemistry tools, proves to be useful for the deployment of the characteristic complexity linked to multicomponent nature of the obtained bio-waste based nanostructures. Moreover, the synergistic optical effects, features of the needed investigation CNPs world, appear like a correlation with their double face as donor/acceptor or reductant/oxidant agents, becoming potential platform for a dynamic cooperant interaction among the multicomponent' parts, over then for an environment interaction response.[4,5] One of main aims is take advantage from the whole of the multicomponent carbon-nanosystem' characteristic complexity - by the codification, the tune and at list the application - in a light input-output device for photoinduced process and technologies.[6]

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# Elucidating the UV-Induced Response of Dual Stimuli-Responsive pNIPAM Microgels Functionalized with Photolabile Protected Amines

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Microgels are three-dimensional, crosslinked polymeric networks that swell in suitable solvents and exhibit remarkable responsiveness to external stimuli such as temperature, pH, and light. Their versatile properties have spurred significant interest across a broad range of technological applications.[1] In this study, we investigate dual stimuli-responsive microgels based on poly(*N*-isopropylacrylamide) (pNIPAM). Beyond the intrinsic thermoresponsiveness of pNIPAM, we incorporated a photolabile protected polymerizable amine into the microgel. We used o-nitroveratryloxycarbonyl (NVOC) as photocleavable protecting group for the amine.[2] Upon UV irradiation, NVOC is cleaved, thus liberating the amine functionality and inducing notable changes to the microgels, including an increase in hydrodynamic radius.[3] We monitored the deprotection process by online UV–Vis spectroscopy, examining both the free monomer and the microgel-integrated protected amine. Future work will focus on elucidating the kinetics of the deprotection reaction, identifying potential side reactions, and investigating the resulting structural modifications within the microgel network.

**Funding:** RWTH Aachen University

**Acknowledgement:** We would like to thank Kristofer Weinberg and Celina Kollmann for their valuable assistance with the experimental work. We also gratefully acknowledge Filip Vukelic for his support in establishing the analysis routine for online UV–Vis spectroscopy.

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# Bio-Inspired Chromophore-Protein Complexes as Color Converting Layers of LEDs

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Solid-State Lighting Devices as Light-Emitting Diodes (LEDs) have emerged strategically as a way for energy saving.[1] To obtain different color outputs, LEDs are usually combined with Color Converting Layers (CCLs), which are typically based on toxic components as rare-earth elements. On this regard, biogenic matrices have emerged to mitigate the use of noxious components, towards greener alternatives that employ low-energy input methods to deposit devices' layers, with materials that are biodegradable at the end of their life cycle, and are biocompatible for wearable devices applications.[2] A primary source of inspiration for biogenic matrices comes from the photosynthetic machinery of plants and algae, a system composed of pigment-protein complexes with different functions. The proteins play a major role in regulating pigments' electronic states, with the intention of maximizing the utilization of sunlight, and avoiding emission quenching. The *de novo* design of proteins allows the production of artificial protein scaffolds capable of performing similar functions, providing versatile mimetics for the possibility of hosting and modulating the electronic structure of synthetic chromophores. We make use of this principle in protein maquettes containing four-α-helices connected via random coils, where the amino acid sequences result in water soluble structures with hydrophobic cores.[3] Due to the maquettes' robust structures, it was possible to precisely decorate them with a chlorophyll analogue, Zn-pheophorbide-a (ZnPa, Figure 1). In our design, ZnPa is connected to histidine residues placed inside the maquettes' hydrophobic core, resulting in a chromophore-protein complex with a wide absorption cross-section covering a large portion of the visible spectrum. Upon ZnPa binding, its emission efficiency increases 50%, which also ended up narrowing the emission spectrum in comparison to ZnPa free in buffer solution. These features are boosted when dispersing the chromophore-protein complex in a polymer matrix to fabricate the CCLs, with the complex depicting deep-red emission. The protein maquette incremented the photo and thermostability to ZnPa, with a CCL of 60% larger EQE. Thus, our research contributes to pave the way for custom made artificial photosynthetic systems to act as CCLs of Solid-State Lighting devices due to the maquettes' superior structuring in an eco-friendly approach that allows the tunning of electronic states similarly to natural proteins of photosynthetic complexes.

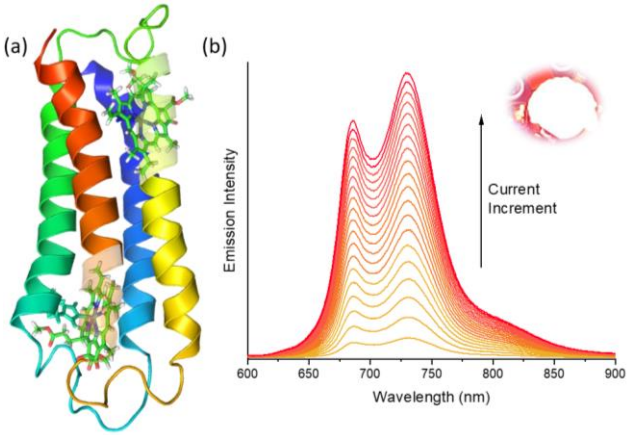


Figure 1. (a) *De novo* chromophore-protein complex and (b) its CCL emission spectrum pumped by an UV-LED. The inset picture shows an operating device.

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**Acknowledgement:** We thank the funding from the European Research Council under the European Union's Horizon 2020 Research and Innovation Programme.

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# Photochemistry of chiral porphyrin assemblies on thin ferromagnetic films

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In recent years, magnetic inorganic-organic hybrids have become a hot topic in the scientific community, partly due to the discovery of the CISS effect.[1] The chiral-induced spin selectivity (CISS) effect observed in organic layers opens up the possibility of utilizing molecular compounds in systems dedicated to the storage, transfer[2] and analysis of information via electron spin. These properties may be harnessed in molecular spintronics applications. In this study, we focused on investigating, using spectroscopic techniques, how the magnetization of Co/Ni ferromagnetic layers (FM), capped with a thin gold (Au) layer, affects the properties of porphyrin molecules adsorbed on their surface (Fig 1A). The porphyrins selected for this study were 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrins with attached polypeptide chains in the form of L and D enantiomers. Through adsorption from solution onto prepared solid samples coated with a ferromagnetic (FM) layer, self-assembled monolayers (SAMs) were formed on the surface. These organic-inorganic hybrid systems were analyzed using both steady-state and time-resolved optical spectroscopy. Importantly, the spectroscopic properties of porphyrins in solution were compared with those in the form of self-assembled monolayers, allowing us to identify changes induced by surface adsorption and interaction with the FM/Au substrate. Although the enantiomeric porphyrins exhibited identical properties in solution, femtosecond transient absorption measurements of the solid samples revealed differences in bleach decay rates that depend on the magnetization of the FM layer (Fig. 1A). These differences were not observed in samples without the ferromagnetic layer indicating a molecular-level interaction between the chiral system and the FM layer.

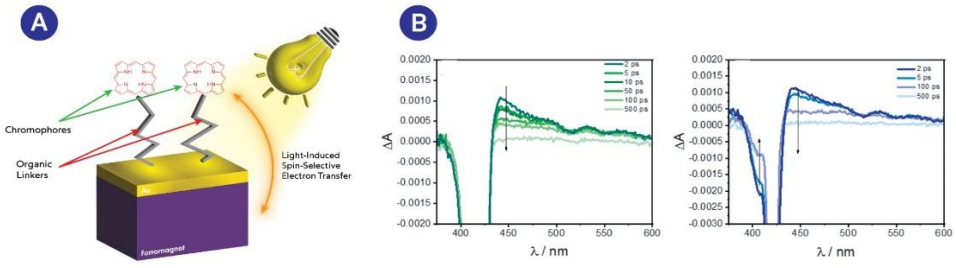


Figure 1. (A) Schematic representation of the FM/chiral self-assembled monolayer system. (B) Transient absorption spectra of FM/organic samples under a modulated magnetic field.

**Funding:** This research was financially supported by the National Science Centre (project no. 2020/39/I/ST5/00597) and the German Research Foundation (DFG, Deutsche Forschungsgemeinschaft, project no. 464974971)

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# Synthesis and optoelectronic properties of original bicarbazole-based π-conjugated helical chiral structures

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Organic open-shell molecules have attracted a lot of attentions in materials science for their potential in new generations of optoelectronics.[1] The stability of such compounds however remains a main aspect of their limitations and research has focused on a peculiar class of open-shell systems showing a SOMO-HOMO inversion (SHI).[2] The SHI has been the source of numerous theoretical and experimental studies to understand the origin and the consequences of these specific molecular orbitals.[3] In this context, our group described the synthesis and characterization of a series of carbazole-based chiral open-shell systems comprising persistent helical diradical cations with configurational stability (Fig. 1a).[4] It was also shown that the helical π-conjugated helped to stabilize the monoradicals while creating intense CP-light absorption in the near-infrared region (Fig. 1b).

These results were encouraging to design new chiral open-shell systems to further investigate even more persistent organic radicals and the organic spins' interactions. We present herein the synthesis of original helical carbazole-based systems with various N-functionalization, with a focus on triarylamine conjugated compounds (Fig. 1c), to explore organic polyradical systems and their stability. Optical and electrochemical characterizations of these new systems as well as the latest results on the characterization of the open-shell state are discussed.

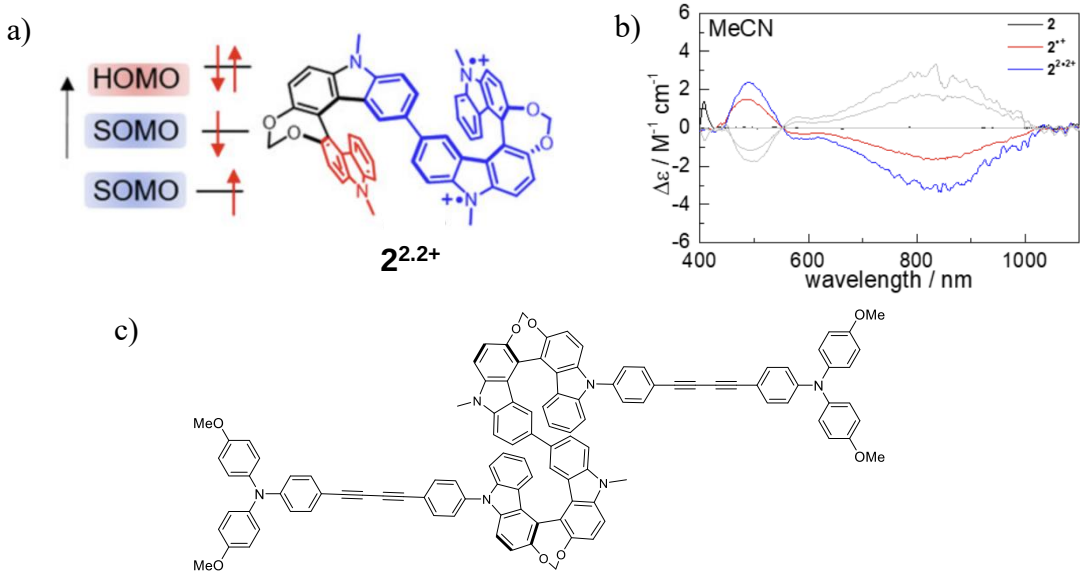


Figure 1. a) SOMO-HOMO inversion in a configurationally stable carbazole-based helical open-shell system, b) ECD spectra of monoradical (red), and diradical (blue) in acetonitrile of compound **2**, c) Example of an original triarylamine conjugated helical carbazole-based system presented in this work.

**Funding:** ERC SHIFUMI, Grant agreement ID: 101041516

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# Photofunctional Behavior and Tunability of Molecular Solids under Mechanical Stimuli

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Mechanical stimuli such as shearing, compression, and fracturing can alter molecular arrangements in the solid state. These changes in intra- and intermolecular conformations lead to modifications in electronic properties, including absorption, excitation, and emission. Particularly, mechanically induced spontaneous light emission without a light source (mechanoluminescence, ML) and mechanically induced changes in emission color under photoexcitation (mechanochromic luminescence, MCL) have attracted significant attention for the development of smart materials capable of converting mechanical signals into photophysical outputs. Such materials find applications across diverse fields, including strain and pressure sensing, structural monitoring, data encryption, healthcare technologies, and anti-counterfeiting systems [1–5]. However, the underlying mechanisms and key factors—whether chemical or physical—governing such responsivity remain poorly understood.

In this study, we investigate the mechanical responsiveness of fluorophores composed of organic molecules and/or lanthanide(III) ions. Their responsiveness is characterized by the relative intensity of ML or wavelength shifts observed in MCL. Since the ML and MCL behavior of molecular solids cannot be easily rationalized based solely on crystal structures or conventional photophysical parameters, we introduce an additional perspective by conducting nanomechanical testing (nanoindentation), enabling quantitative evaluation of deformation and fracture behavior. Our results reveal clear correlations among photophysical, structural, and mechanical parameters across different classes of compounds—for example, between fracture generation probability and ML activity, or between material softness and the recoverability of MCL.

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**Acknowledgement:** We gratefully acknowledge Dr. Shiro Funahashi (National Institute for Materials Science, Japan) for single crystal X-ray analyses.

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# Tuning phosphorescence through molecular rigidity: role of intramolecular hydrogen bonding in *trans*-bis(iminopyrazolato)platinum(II) complexes

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Non-covalent interactions, including π–π stacking and hydrogen bonding, critically modulate the emission properties of luminescent compounds.[1] Intramolecular hydrogen bonding, in particular, has been extensively studied in organic fluorophores, however, in transition-metal complexes, its relationship with emission efficiency remains poorly understood. To gain mechanistic insight into this phenomenon, we designed a series of *trans*-bis(iminopyrazolato)platinum(II) complexes (**1**), in which an intramolecular hydrogen bond is formed between the nitrogen atom of one *N*-alkylpyrazolato ligand and the *α*-position C–H bond of the opposite ligand. By systematically investigating this series of complexes with different H-bonding strengths, we observed a remarkable progressive increase in the quantum efficiencies, directly correlated with the strength of the hydrogen bond. Theoretical calculations revealed that stronger hydrogen bonding enhances molecular rigidity in the triplet excited state, effectively suppressing structural torsion and thereby reducing non-radiative decay pathways.

A series of *trans*-bis(iminopyrazolato)platinum(II) complexes (**1a**–**1e**) was synthesized, featuring various *N*-substituents, including polymethylene chains (**1a**: C10, **1b**: C12), as well as pentyl, isopropyl, and trifluoroethyl groups, with $CH_\alpha\cdots N$ distances ranging from 2.674 Å to 2.314 Å (Fig. 1a). Interestingly, their emission intensity in 2-MeTHF at 298 K increases progressively from **1a** to **1e**, with $\Phi_{298K}$ rising from 0.04 to 0.72 (Fig. 1b), while their quantum yields at 77 K remain similarly high ($\Phi_{77K}$ = 0.64–0.72), suggesting that the emission efficiency is primarily governed by thermally activated non-radiative decay processes.

To elucidate the mechanism, DFT calculations were performed to optimize the ground state ($S_0$), the triplet excited state ($T_1$), and the minimum energy crossing point (MECP), which corresponds to the intersection of the $S_0$ and $T_1$ potential energy surfaces (Fig. 1c,d). The effect of structural variations on the energy of the MECP, which is associated with thermally activated non-radiative decay pathways, was systematically investigated. All complexes exhibited planar structures in both the $S_0$ and $T_1$ states; however, at the MECP geometry, a distinct torsional distortion between the imine group and the C–$H_\alpha$ moiety emerged. For **1a**, which exhibits the weakest hydrogen bonding and negligible emission, the $T_1$ and MECP energies were calculated as 51.8 and 58.3 kcal/mol ($\Delta E$ = 6.5 kcal/mol), while for **1e**, featuring the strongest hydrogen bonding and the highest emission efficiency, the $T_1$ energy remained similar at 53.0 kcal/mol, but the MECP energy increased markedly to 75.5 kcal/mol ($\Delta E$ = 22.5 kcal/mol), thus indicating a significantly higher barrier for non-radiative decay in the latter. These findings provide important mechanistic insights into how intramolecular hydrogen bonding enhances the emission intensity of phosphorescent transition-metal complexes.

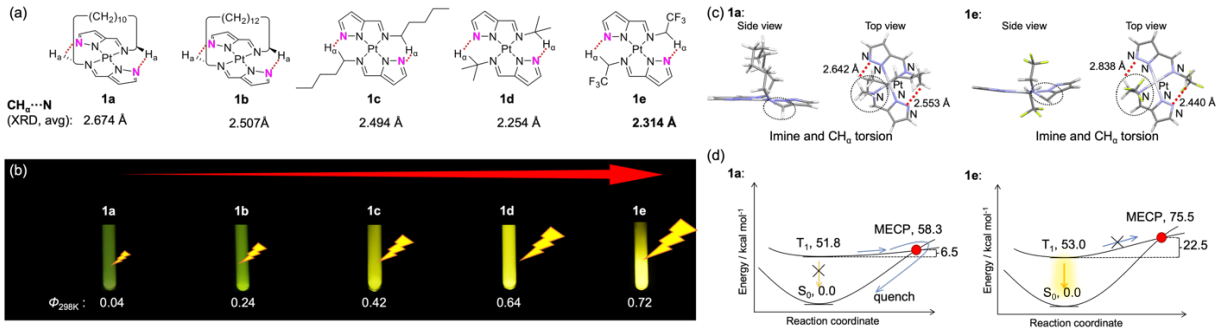


Figure 1. a) Chemical structures and average XRD distance of $CH_\alpha\cdots N$ for **1a**–**1e**, b) photographs of **1a**–**1e** in 2-MeTHF ($1.0\times10^{-4}$ M) under UV irradiation, c) Molecular structure of MECP for **1a** and **1e**. d) Schematic representation of energies of $S_0$, $T_1$ and MECP for **1a** and **1e**.

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# Photoactive stimuli-responsive flexible Lewis pair oligomers

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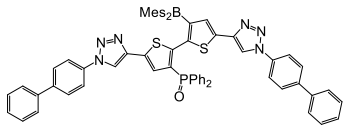
Flexible Lewis pairs (FlexLPs) are systems that encompass phosphine oxide Lewis bases and dimesitylboranes Lewis acids attached to a bithiophene scaffold, which can switch between an “open” unbound Lewis pair and a “closed” bound Lewis adduct depending on the hydrogen bond-donating (HBD) strength of the solvent[1,2]. These chromophores are of interest for application in bioimaging and chemical sensing. Incorporating these species into polymers allows modulation of the electronic properties of the material by switching FlexLP moiety in the backbone, resulting in absorption and emission changes. We report here an approach using click chemistry towards FlexLP containing polymers. A model compound (Fig. 1) has been prepared to optimize the synthetic conditions needed for oligomer and polymer preparation, and the photophysical behavior of this compound (Fig. 2) and the corresponding oligomers under varying stimuli will be discussed.




**6**

Figure 1. Structure of triazole linked biphenyl-FlexLP complexes **6**.

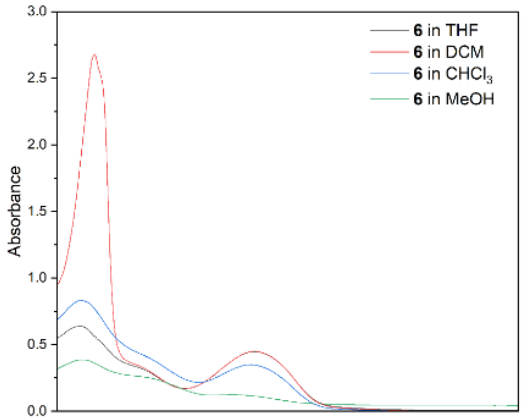



Figure 2. UV-vis spectra of compound **6** in various solvents.

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# Ligand Effects on Photothermal Properties of Atomically Precise $Au_{25}$ Nanoclusters

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Non-invasive photothermal therapy (PTT) has emerged as a promising therapeutic method for the treatment of cancer, where real-time temperature monitoring is crucial to make the therapeutic procedure more effective and potential.[1] This promotes the design and development of photothermal agents with accurate temperature control and excellent photothermal conversion.[2] Here, we investigate how the efficiency of light-to-heat conversion can be modulated by changing the surface ligands of thiolated gold nanoclusters (Au NCs; $Au_{25}(SR)_{18}$). Furthermore, the developed nanoheaters show excellent temperature sensing based on fluorescence lifetime. Atomically precise $Au_{25}(SR)_{18}$ NCs (SR = 4-mercapto benzoic acid (pMBA), glutathione (SG), N-acetyl-cysteine (AcCys), captopril (Capt)) were synthesized and fully characterized by high resolution mass spectrometry as well as fluorescence and absorption spectroscopy. The photothermal effect of the NCs was evaluated using a thermal infrared imager (FLIR) to record the temperature change of the aqueous solution of NCs at different concentrations under 808 nm laser irradiation (2 W $cm^{-2}$, 15 min). The value of photothermal conversion efficiency (η) was calculated using Roper model.[3] Lifetime-based nanothermometry was measured using a home-built time-resolved fluorescence setup, where the samples were excited with picosecond laser at an excitation wavelength of 450 nm. $Au_{25}(SR)_{18}$ NCs showed quite pronounced characteristic absorption peaks at 450 and 670 nm, and of particular interest is the remarkable absorption in the 800-900 nm range, which makes them suitable for near-infrared excitation in PTT. The temperature of the $Au_{25}(Capt)_{18}$ solution with a concentration of 0.11 mM rapidly increased to 50 °C within 15 minutes during irradiation with 808 nm continuous laser, and the photothermal conversion efficiency (η) was calculated to be 41.13%. To show the effect of ligands on photothermal efficiency, the temperature changes under the same conditions were compared, and it was found that the light-to-heat conversion efficiency was in the order Capt> AcCys> SG> pMBA (Fig. 1A). In addition, the temperature detection based on lifetime was also found to follow a similar trend, showing the highest sensitivity of 1.46% $K^{-1}$ for $Au_{25}(Capt)_{18}$ (Fig. 1B). These results show that the pulsed or continuous excitation mode allows separate activation of the nanothermometry and heating functionalities.

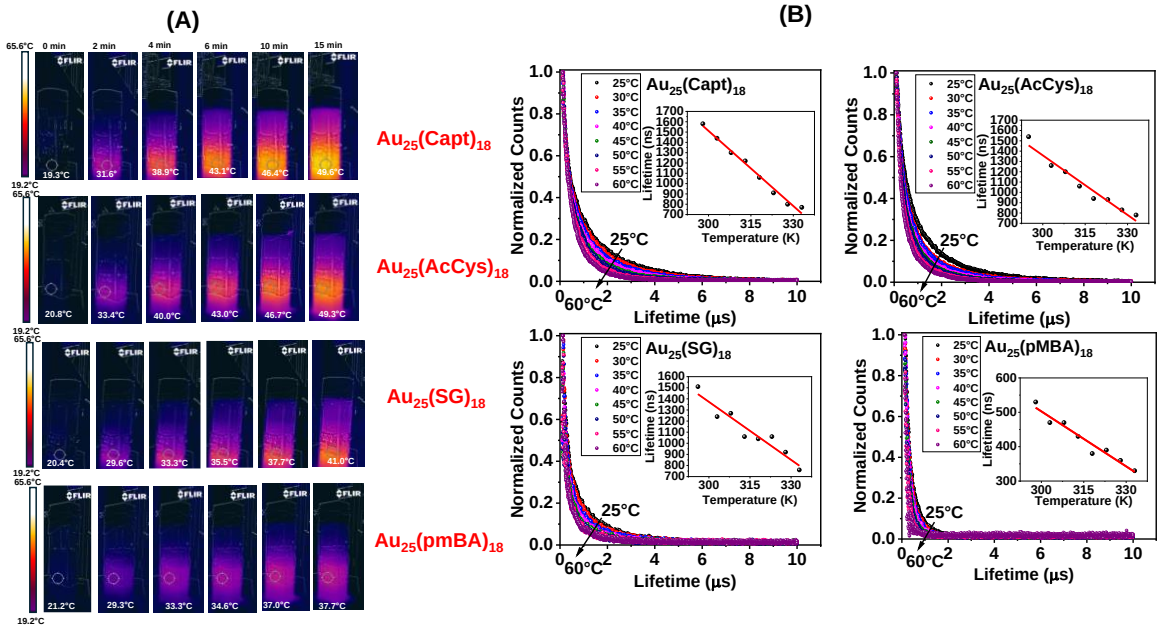


Figure 1. (A) Photothermal effect and (B) luminescence lifetime nanothermometry in $Au_{25}(Capt)_{18}$ , $Au_{25}(AcCys)_{18}$ , $Au_{25}(SG)_{18}$ and $Au_{25}(pMBA)_{18}$ NCs.

# The effect of HOMO-FRET on the donor-acceptor FRET efficiency in thin films

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Optimizing the Förster resonance energy transfer (FRET) efficiency in organic thin films is crucial for numerous photovoltaic applications. In devices like hyperfluorescent OLEDs the aim is to maximize FRET (TADF sensitizer to terminal emitter) efficiency whereas for solid-state triplet-triplet annihilation upconversion (TTAUC), there are FRET channels that need to be both maximized (annihilator to singlet sink) and minimized (Back transfer from annihilator to sensitizer). [1,2] Even though FRET has been extensively studied in biological and solution environments, amorphous solid-state samples are largely underexplored. Unlike the one-on-one donor-acceptor interactions in dilute solution, in the solid-state there are multiple donor-acceptor interactions, over a range of interchromophoric distances, contributing to the overall efficiency.

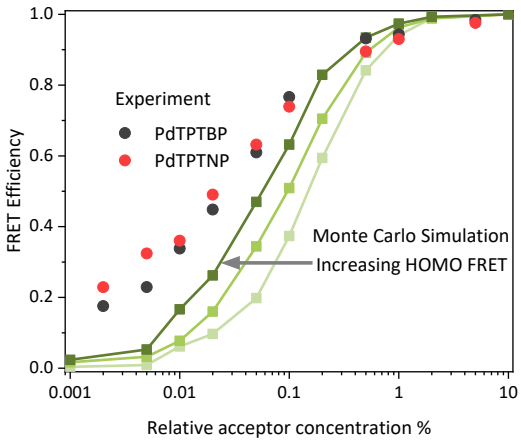


Figure 1. FRET efficiency as a function of relative acceptor concentration. Black and red circles represent FRET efficiency calculated from quantum yield measurements of for BODIPY thin films doped with PdTPTBP and PdTPTNP acceptors respectively. Green squares correspond to the FRET efficiency of Monte Carlo simulations with same Förster distance between donor and acceptor but increasing singlet exciton diffusion within donor.

Here we study FRET efficiency as a function of dopant acceptor concentration in spin coated thin films of donor chromophores. We use a BODIPY-derivative, designed to form glassy films with minimal morphological imperfections, as the donor matrix and two different porphyrin-based acceptors to experimentally follow the FRET efficiency as a function of acceptor concentration. Monte Carlo simulations, which previously have shown to accurately model exciton diffusion, was used to model the effect of homo and hetero FRET. [3.4] Our combined experimental and modelling studies indicate that the exciton diffusion within the donor singlet excited state manifold, assumed to be dominated by HOMO FRET, plays a crucial role in determining the overall donor-acceptor FRET efficiency.

**Funding:** This project has received funding from the European Union's Horizon 2023 research and innovation programme under the Marie Skłodowska Curie grant agreement No 101152418.

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# Fluorescent sensor for monitoring pH in cementitious materials

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The long-term performance and mechanical integrity of cementitious materials are closely tied to the complex physicochemical reactions that begin with hydration and continue throughout the material's lifespan. Hydration refers to the series of chemical reactions that occur when the anhydrous mineral phases of cement come into contact with water, producing hydrates that gradually form the hardened cement paste [1 As this process unfolds, a highly alkaline pore solution develops and remains confined within the microstructure. This trapped solution plays a pivotal role in the material's chemical evolution and aging behavior. In the case of Portland cement, the pH of the pore solution typically ranges from 12.45 to 13.5 at 20 °C. However, as the material ages, a gradual decline in pH is commonly observed. This phenomenon poses a significant risk for reinforced concrete structures: when the pH falls below 11.2, the protective passivation layer on steel reinforcement can break down, triggering corrosion and compromising the structural performance [2]. Despite the importance of monitoring pH, existing standard methods for measuring it in concrete are destructive and thus unsuitable for continuous or in-situ assessment [3]. In this context, the development of new optical sensors capable of measuring the pH of cementitious materials is of great interest.

In the present work, we describe the development of molecular fluorescent probes and their incorporation into optodes for pH measurement in alkaline media [4-6]. The suitability of the optode for real cementitious materials has been proven by pH measurements during the early hydration phase of a "low-pH" cement paste, with an accuracy of ±0.1 pH units and a fast response time of about 100 seconds. Then, it has been extended to the monitoring of the dynamic diffusion of "aggressive" water through cementitious samples with encouraging results according to the nature of the probe. Also a ratiometric sensor has been developed for long term monitoring of OH- migration in cementitious materials (7]

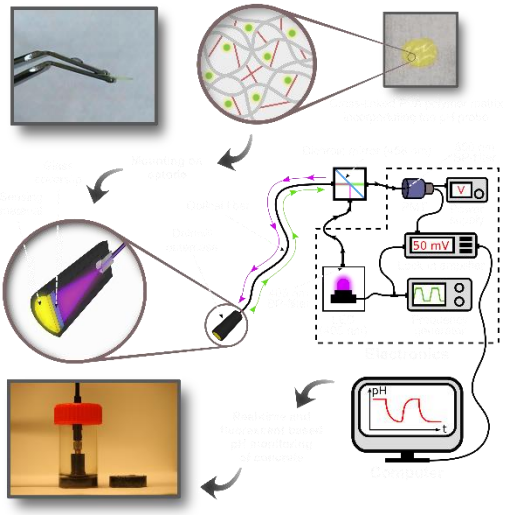


Figure 1 : Principle of the fluorescent sensor

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# $Au_{25}$ atomically precise nanoclusters: on the way to elucidate a complex photophysics

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Metal nanoclusters (NCs) with ultra-small sizes (metallic cores smaller than 2 nm in diameter) offer an exceptional platform for investigating structure–property correlations at the atomic level, owing to their monodisperse size and well-defined structures. To date, more than 100 nanocluster species—ranging from mono-metallic (Au or Ag) to bi- and tri-metallic alloy clusters—have been structurally characterized [1]. Among them, $Au_{25}(SR)_{18}$ (where SR = PET, 2-phenylethanethiol) stands out as one of the most extensively studied, typically existing in three oxidation states (−1, 0, and +1).

Despite the significant interest in these systems, systematic photophysical studies and detailed analyses remain limited. Previous investigations often suffered from incomplete spectral data collection, especially in the near-infrared region, due to the restricted spectral coverage of common commercial fluorometers. Moreover, excited-state dynamics have frequently been oversimplified, partly because of insufficient sensitivity of typical experimental setups in this spectral range [2]. Addressing these gaps, this work aims at providing a comprehensive understanding of the photophysical properties of $[Au_{25}(PET)_{18}]^-$ and $[Au_{25}(PET)_{18}]^0$.

To achieve this, we recorded absorption and fluorescence spectra (steady-state and time-resolved) by exciting the samples at different energies. Unlike its anionic "closed-shell" counterpart, the neutral NC displayed several deviations from conventional molecular photophysics. These include discrepancies between the absorption and luminescence excitation spectra, violation of Kasha's rule—evident from the strong dependence of emission spectra and lifetimes on excitation energy—and clearly multi- or non-monoexponential behavior in the nanosecond to microsecond emission decays. Time-resolved analyses probably suggest that a continuous distribution of decay times best describes the observed dynamics. Our findings are discussed in the context of previous experimental studies on similar nanocluster systems [3,4].

**Funding:** Swiss National Science Foundation (209554)

**Acknowledgement:** We would like to thank Jiangtao Zhao for synthesizing all the samples (Bürgi's group).

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# Morphological and electronic control of interfacial charge transfer in 2D transition metal dichalcogenides

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We describe herein the preparation of transition metal dichalcogenides (TMDs)–phthalocyanine nanohybrids, and the investigation of their photophysical properties. Zinc phthalocyanines (Pcs) 0–5 are presented as charge transfer building blocks of variable electrochemical strengths. The obtained nanohybrids $MoS_2$/0-5 and $WS_2$/0-5 were fully characterized (Raman, steady-state and pump-probe transient absorption spectroscopy) as both, dispersions[1] and nanosheet networks[2], and studied in terms of electron donor–acceptor interactions in the ground and excited states. In this context, newly formed charge transfer states were identified in the ground state and analyzed within the Mulliken-Hush formalism[3]. Charge separated states were identified upon photo excitation, interestingly the direction of the charge separation is determined by the alignment of the molecular orbitals and the band structure of the TMD.

**Funding:** DFG project RTG-2861 Planar Carbon Lattices

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# All-Carbon Mixed Valency: Thiele's, Chichibabin's, and Müller's Radical Cations

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Mixed valence (MV) compounds with their intervalence charge-transfer (IVCT) bands bear a great treasure of application potentials in the area of optoelectronics[1], molecular conductors, like molecular wires[2] and switches[3], and quantum computing[4] due to their tunability and customizable electronic coupling. MV Compounds with N, S, or B redox centers have been widely explored, but their all-carbon congeners remain elusive.[5-6] Hence, MV species, **1**, **2**, and **3**, obtained through oxidation of Thiele's[7], Chichibabin's[8-9] and Müller's[10] hydrocarbon diradicals, are given herein (Fig. 1a). All redox-processes between the neutral and cationic redox states of the MV species are reversible as proved by cyclic voltammogram measurements. The near-infrared (NIR) IVCT bands and unpronounced solvent-dependent absorption shifts indicate their delocalized electron characters (Fig. 1b, 1c). Hush analysis[11] reveals that all three radicals qualify as valence-trapped Class II MV compounds. The electronic coupling values $V$, decreasing from 1625 $cm^{-1}$ in **1** to 726 $cm^{-1}$ in **3**, indicate increasing localization of the redox centers as the π-bridge lengthens.

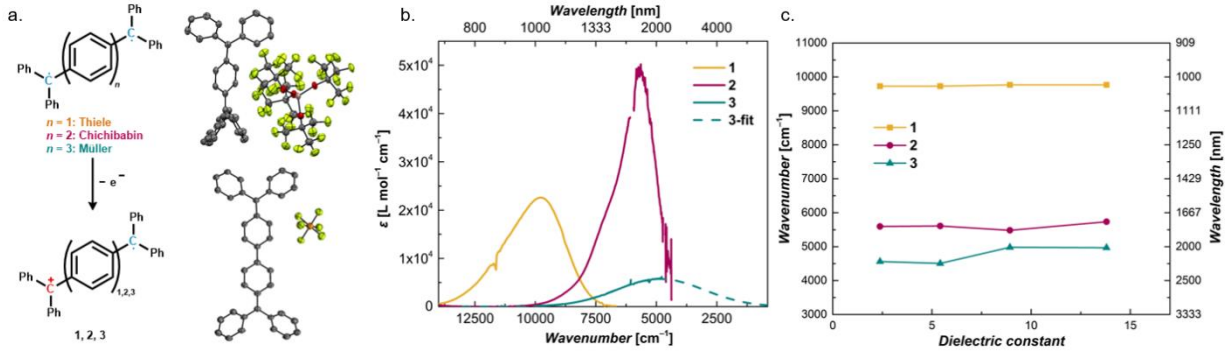


**Figure 1.** a) All-carbon cationic radicals **1**, **2**, and **3** of Thiele's, Chichibabin's and Müller's diradicals and solid structures of **1** and **2**; b) IVCT absorption bands of **1**, **2**, and **3** in *o*DFB; c) *Wavenumber–dielectric constant–wavelength* plot of IVCT absorption bands of **1**, **2**, and **3**.

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# Efficient Blue to UV Up-Conversion through Energy Transfer between $Pr^{3+}$ and $Gd^{3+}$

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The search for UV-up-conversion materials is of great scientific and technological interest due to the wide range of applications and potential to increase efficiency in various optoelectronic devices. Studies have shown that inorganic wide band gap materials based on Gadolinium can achieve UV/Vis-up-conversion under near-infrared (NIR) excitation.[1] In addition, the use of $Gd^{3+}$ in conjunction with other dopants such as $Pr^{3+}$ has been shown to lead to efficient photon conversion and intense UV-B emission around 311 nm, branding these materials also as potential candidates for applications such as photochemistry and biomedicine.[2] Up-conversion from the blue spectral range has a significantly higher quantum yield than up-conversion processes using NIR radiation.[3] It is therefore important to re-examine the efficiency and adjustability of up-conversion from the blue spectral range in more detail.

In this study, the converter materials were synthesized using solid-state synthesis and examined with regard to their optical properties. Particular attention was paid to the up-conversion (Fig. 1) and the underlaying energy transfer between $Pr^{3+}$ and $Gd^{3+}$.

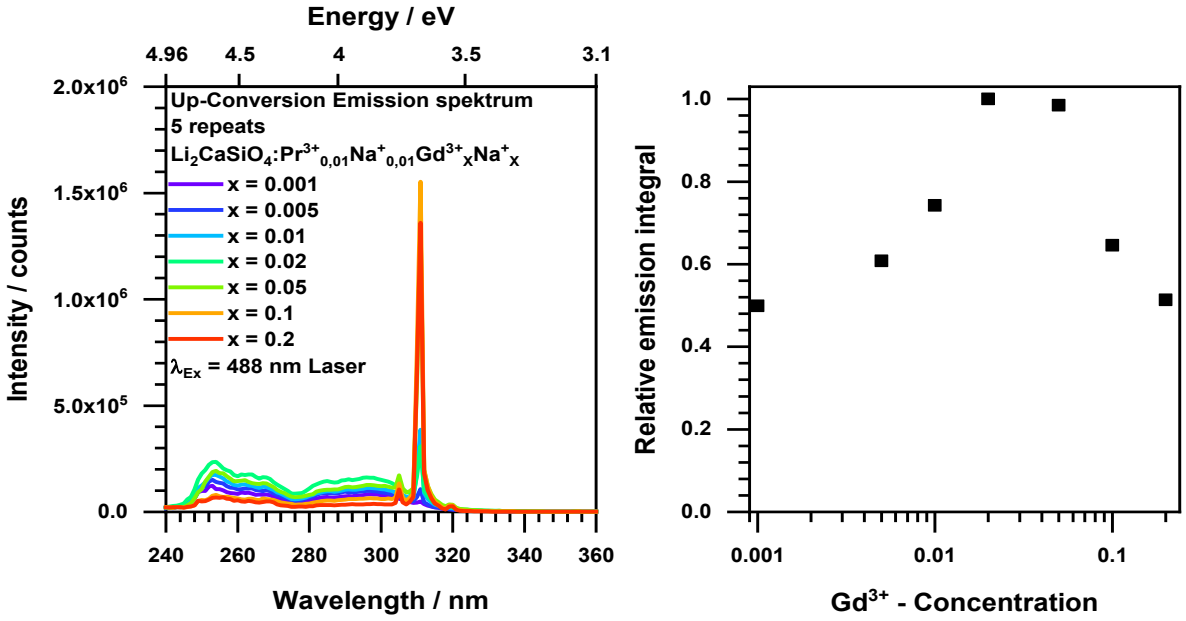


***Figure 1:*** Up-conversion emission spectra of $Li_2CaSiO_4$ doped with $Pr^{3+}$, with $Gd^{3+}$. All materials are also doped by $Na^+$ for the sake of charge compensation. Spectra were recorded upon excitation of 488 nm Laser (75 mW).

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# Axially chiral NIR emitters

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Axially chiral indolenine-based dyes, such as squaraines and merocyanines, have been shown to exhibit a high electronic circular dichroism (ECD) signal with Δε up to approximately 1500 $M^{-1}$ $cm^{-1}$.[1] In this context, flexible dimeric chromophores whose mutual orientation is susceptible to the environment have been synthesised. These dyes have in common a prochiral subunit consisting of two 3,3-dimethylindole derivatives connected at the 4-position. The small steric impact of the methyl groups enables rotation around the bond upon heating, allowing the molecule to take on different conformers. In a chiral environment, the environment can bias the axial chirality of the emitter towards one of the enantiomers. (Fig. 1). The chromophoric units can further be polymerised via azide-alkyne Huisgen reactions. The impact of the chromophore arrangements on the absorption, emission and ECD was investigated.

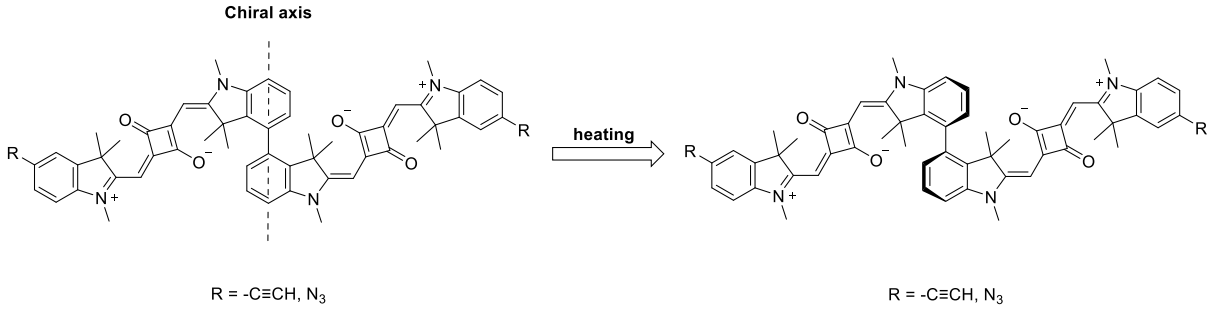


Figure 1. Structural representation of a prochiral squaraine dye that takes on a chiral structure as result of the surrounding environment.

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# Organic Long-Persistent Luminescence Enhanced by Charge-Transfer States in Donor–Acceptor Molecules

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Organic long-persistent luminescent (OLPL) materials are fully organic systems that can emit light for seconds and even hours after the excitation light ceases.[1,2,3] They are usually based on mixtures of electron-donating and electron-accepting molecules, where the mechanism of delayed luminescence strongly relies on photoinduced charge separation and emissive charge recombination. Upon irradiation, an electron can be transferred from a donor molecule to an acceptor and can further diffuse, forming a charge-separated state that stores part of the absorbed energy (Fig. 1a). Therefore, the more separated charges are formed, the more energy can be preserved in the system, the brighter and longer-lasting delayed emission can be achieved. However, in most reported OLPL systems, the charge separation process remains relatively inefficient and unexplored, which limits the brightness and lifetime of delayed emission and restricts the range of practical applications.

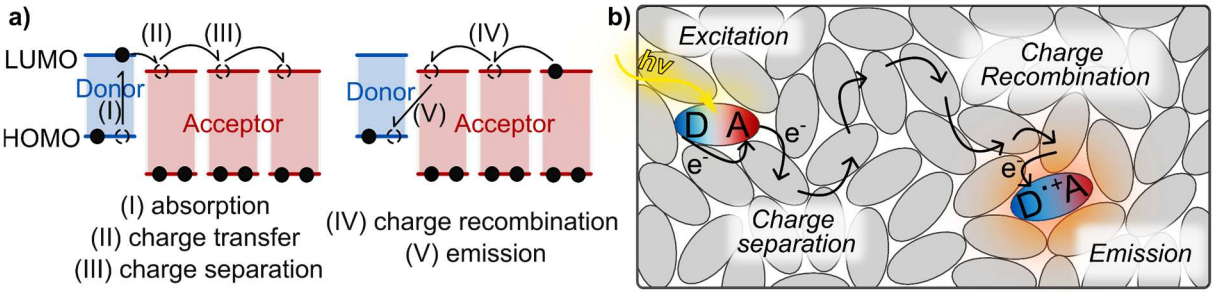


Figure 1. a) The mechanism of long-persistent luminescence in a classic OLPL system, where a donor is doped into an electron-accepting host. b) A schematic representation of the processes occurring in an OLPL system composed of donor–acceptor dopants dispersed within a host. Gray ellipses represent host molecules, while the colored ones represent donor–acceptor dopant molecules. Upon excitation, an intramolecular charge-transfer state is formed within the dopant, followed by electron transfer to the host material. Subsequent charge separation occurs through charge diffusion, eventually leading to recombination and resulting in delayed luminescence.

The aim of this research is to improve the efficiency of the charge-separation process in OLPL materials. We focused on combined donor–acceptor structures, as the excitation of these molecules causes an intramolecular charge shift, which is expected to facilitate intermolecular charge transfer and support more efficient charge separation (Fig. 1b). We selected several widely used organic emissive molecules, including acridinium-based photoredox catalysts and commonly used donor–acceptor dyes. A series of OLPL films was prepared by doping these dyes into semiconductor hosts with varying electronic properties (donor, acceptor, and bipolar) to evaluate their OLPL performance. Preliminary results indicate that OLPL films made by mixing donor–acceptor dopants into bipolar hosts show better performance compared to purely donor or acceptor environments. A more detailed discussion of these findings will be presented on the poster.

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# Electrochemical and fluorescence dual-mode detection of norepinephrine with a portable smartphone assay by nitrogen-doped $Ti_3C_2$ MXene quantum dots

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Next-generation 2D materials, including transition metal carbides and nitrides (MXenes), have gained significant interest due to their exceptional physicochemical properties. In this study, we developed nitrogen-doped MXene quantum dots (N-MQDs) with high fluorescence using a simple and time-efficient microwave-assisted method. The N-MQDs were employed as dual probes for electrochemical and fluorescence detection of the neurotransmitter norepinephrine (NE, 0.1 to 500 μM). The sensing mechanism based on Förster resonance energy transfer (FRET) from the N-MQDs results in fluorescence quenching at 400 nm and exhibits a new emission peak at 500 nm, accompanied by color changes. In the electrochemical reaction, the conversion of NE to NE quinone formation. Fluorescence and electrochemical measurements in human serum samples showed limits of detection of 40 nM and 33 nM, respectively. We developed a smartphone-integrated sensor array for point-of-care diagnostics to monitor intensity changes, with relative red/green/blue (RGB) values measured across different NE concentrations. [1] This synthesized fluorescent probe is a promising tool for NE detection in biofluids, exhibiting high selectivity for NE and potential for early diagnosis of neurological disorders [1,2].

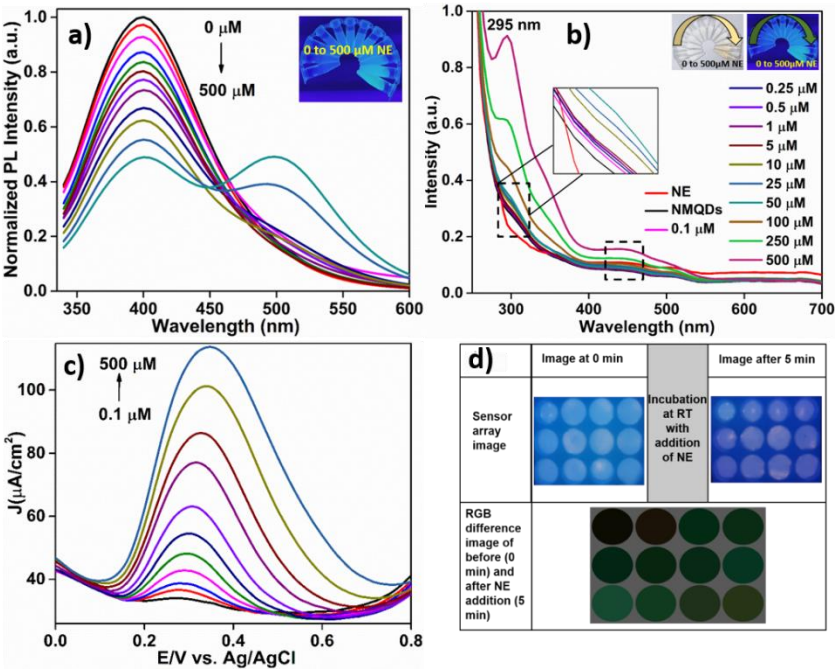


Figure 1. (a) PL spectrum of N-MQDs with different concentrations of NE from 0 to 500 μM (inset: N-MQDs with different concentrations of NE from 0 to 500 μM samples under 365 nm UV-light), (b) The UV-visible spectrum of NE, N-MQDs, and N-MQDs with different concentrations of NE from 0.1 to 500 μM, (c) DPV analysis using an N-MQDs modified GCE with different concentrations of NE from 0.1 to 500 μM, (d) RGB difference image of N-MQDs with different concentrations of NE (0 to 500 μM) analysis by a smartphone-based color sensor array under UV light.

**Acknowledgements:** This research was supported by the Basic Science Research Program through the National Research Foundation (2021R1A6A1A03038996) and project BK21 FOUR (202007880005).

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# Photophysical properties of indium-doped zinc oxide nanocrystals

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Degenerate semiconductor nanocrystals (NCs), where the Fermi level resides within the conduction band due to heavy doping, maintain their n-type characteristics even under oxygen-rich conditions, thus emerging as promising candidates for applications such as transparent solar cells and smart windows[1]. Among these, indium-doped zinc oxide (IZO) NCs have attracted attention owing to their low cost, low toxicity, and potential applications in photocatalysis. Although the understanding and control of carrier dynamics are critical for enhancing photocatalytic performance, investigations into carrier behaviors following ultraviolet-induced interband transitions remain elusive. In this study, we synthesized IZO NCs with varying indium doping levels and investigated their carrier dynamics using transient absorption spectroscopy.

IZO NCs with varying indium doping concentrations were synthesized following a previously reported method[2]. Oleic acids were used as surface ligands for the IZO NCs. Upon excitation at 347 nm in chloroform, a broad absorption band associated with photoexcited carriers was observed across the visible region immediately after the excitation and persisted on the nanosecond timescale (Fig. 1a). Notably, a fast decay component on tens of picosecond timescales became more pronounced with increasing indium concentration (Indium concentration is described relative to the zinc concentration). It is implied that the fast decay component originates from hole trapping by oxygen defects. This result is supported by previous studies that reported that $In^{3+}$ increased oxygen vacancies[3].

We further examined excitation intensity dependence for IZO NCs with 9% indium doping (Fig. 1b). An increase in the fast decay component within 20 ps with higher excitation fluence indicated the presence of biexciton Auger recombination. These results are consistent with intensity-dependent carrier relaxation mechanisms[4].

Carrier dynamics of IZO NCs are summarized in Fig. 1c. We revealed that indium doping significantly modulates carrier recombination processes in IZO NCs. The details are shown in the presentation.

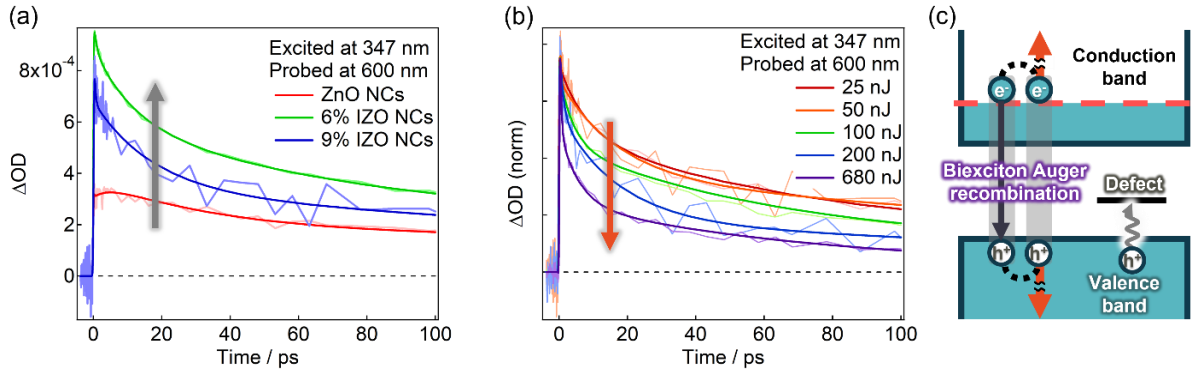


Figure 1. Transient absorption dynamics at 600 nm of ZnO and IZO NCs in chloroform excited at 347 nm; (a) Indium doping dependence, (b) Excitation intensity dependence in IZO NCs (In/Zn = 9 mol%). (c) Energy diagram of IZO NCs.

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# Studying Thermochemiluminescence through rational design and nanoparticle integration

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Thermochemiluminescence (TCL), the thermally triggered emission of light from unstable precursors like 1,2-dioxetanes, is a promising strategy for developing reagentless - and thus potentially much simpler - bioanalytical detection systems [1]. Acridine-containing 1,2-dioxetanes offer advantages over traditional adamantyl analogues, including lower decomposition temperatures and intrinsically higher emission efficiencies [2]. We have investigated the synthesis, characterization, and application of novel acridine-based 1,2-dioxetanes, focusing on modulating their properties through structural modifications and nano-encapsulation. We explored the impact of substituents on the acridine core, comparing an unsubstituted and substituted derivative, revealing enhanced fluorescence quantum yields for the acridone emitter. The critical oxygenation step for the dioxetane ring formation from olefin precursors was thoroughly studied employing a photooxigenation reaction based on the formation of singlet oxygen through the use of a photosensitizer (Figure 1) [3]. TCL kinetics were evaluated by heating and monitoring emission decay on samples deposited on a substrate using CCD/EMCCD detectors. Furthermore, the dioxetanes were successfully nano-encapsulated and preliminary TCL experiments on doped NPs demonstrated detectable emission at low concentrations and highlighted the potential benefits of the nanoparticle environment. The possibility of covalent functionalization of NPs is currently being studied, expanding the potential utility of these probes. These findings demonstrate that a strategic design provides effective routes based on acridine-containing 1,2-dioxetanes to design sensitive and efficient TCL probes for advanced detection applications.

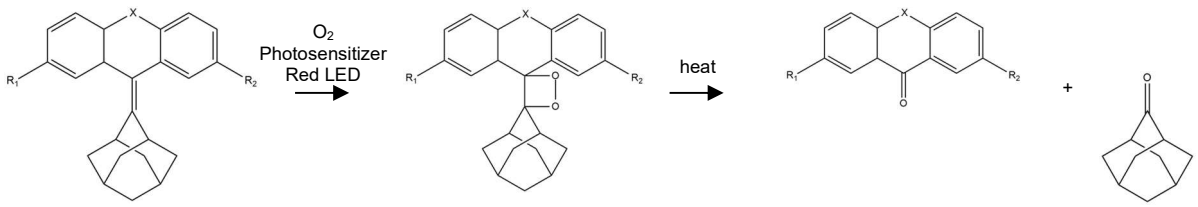


*Figure 1* Photooxygenation reaction of adamantane-containing tricyclic aromatic olefins and thermally induced fragmentation.

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# Stabilizing Diketopyrrolopyrrole Radical Cations Through Carbazoles: Substitution Pattern vs. Spin-Delocalization

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The synthesis of organic radicals continues to garner significant interest due to their fascinating optical, electronic, and magnetic properties. Moreover, the growing demand for chemically stable organic radicals is driven by the rapid expansion of the market for electronic devices utilizing organic semiconductors.[1] In this context, the development of multifaceted approaches for designing stable organic radicals is of great importance. In this work, we introduce a strategy for generating stable radical cations of diketopyrrolopyrroles (DPP) by modulating the substitution pattern of the electron-donating carbazole substituent. Using electronic, spin resonance, and vibrational spectroscopies, supported by density functional theory, we carefully investigated the electronic structures and chemical stability of the DPP radical cations. Our findings demonstrate that the position of electron-rich heteroatoms and the presence of Clar's aromatic sextets in donor moieties play a pivotal role in enhancing the chemical stability of DPP radical cations.

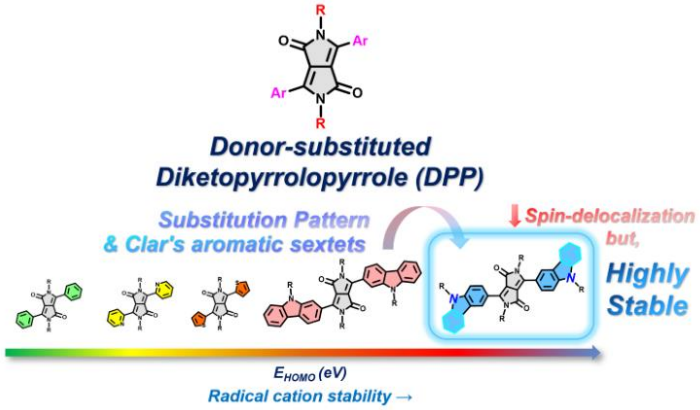


Figure 1. Electron-deficient DPP was employed as an acceptor, and increasing the electron-donating strength of substituents enhanced the stability of the radical cation. Notably, carbazole substitution yielded exceptionally stable radical cations. Intriguingly, despite reduced spin delocalization upon substitution at the 3,6-position, the radical cation exhibited significantly enhanced stability. These results suggest that, beyond delocalization, additional structural factors must be considered when designing molecules for stable radical cation formation.

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**Acknowledgement:** S.D. thanks Council of Scientific & Industrial Research (CSIR), India, for Senior Research Fellowship and Indian Institute of Science (IISc) Bangalore for the financial assistance. S.D. and S.P. would like to acknowledge Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR) for providing a facility for MALDI measurements. S.D. and S.P. would like to acknowledge NMR Research Centre, IISc (NRC), for providing NMR facility. R.K.C.B would like to acknowledge the Department of Science and Technology (DST), India, for the DST_INSPIRE Faculty Fellow award (IFA20-CH-341). S.P. thanks Science and Engineering Research Board for funding the project through the IRHPA grant IPA/2020/000033. W.K. and J. O. were supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (RS-2023-00210400 for W. K.; RS-2024-00343229 and RS-2024-00404760 for J. O.). The DFT calculations were supported by the National Institute of Supercomputing and Network (NISN)/Korea Institute of Science and Technology Information (KISTI) with needed supercomputing resources, including technical support (KSC-2023-CRE-0419).

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# Enhancing Self-Assembly Complexity via Ligand Exchange in Luminescent Pt(II) Complexes

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**Abstract**

Over the past four decades, coordination-driven self-assembly has emerged as a powerful strategy for constructing discrete nanoscale architectures by exploiting the predictable interactions between metal ions and purposefully designed organic ligands.[1] Grounded in the principles of coordination chemistry, this approach enables the spontaneous formation of well-defined, thermodynamically stable structures, guided by the coordination preferences of metal centers and the geometric characteristics of the ligands.[2] In this study, we exploit dynamic coordination chemistry and metal–metal interactions to develop a series of luminescent Platinum(II) complexes. These incorporate a well-established N^N^N terdentate chromophoric ligand alongside a range of pyridine- and imidazole-based ancillary ligands, as exemplified by complexes 1 and 2 in Fig. 1. Our results show that these complexes undergo dynamic ligand exchange in solution at room temperature. Notably, pyridine and benzimidazole derivatives are readily and preferentially displaced by imidazole-based ligands, such as 1-methylimidazole. This selective exchange induces the formation of a metastable kinetic phase—a gel—that arises exclusively through in situ ligand substitution.

Real-time fluorescence microscopy reveals two distinct pathways for dynamic ligand exchange: one proceeds via the dissolution of preformed aggregates (Fig. 1i), while the other takes place within intact supramolecular structures (Fig. 1ii), which undergo transformation while preserving their original morphology. Overall, our findings highlight the critical role of imidazole ligands in driving structural reorganization and demonstrate new possibilities for the design of adaptive, stimuli-responsive soft materials through reversible coordination chemistry.

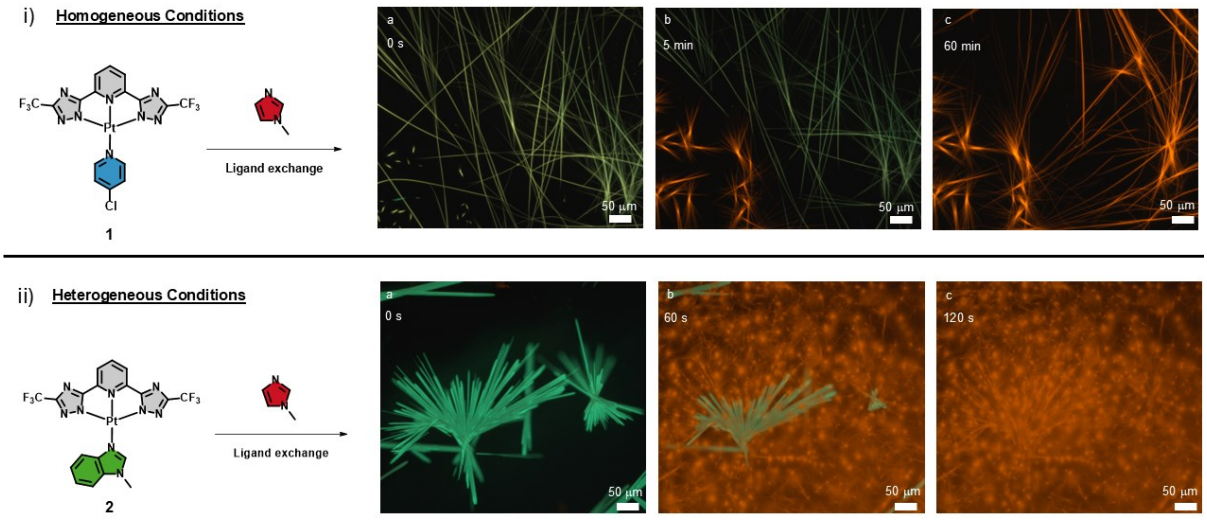


Figure 1. i) Ligand exchange reaction of complex **1** with 1-methylimidazole under homogeneous conditions through molecularly dissolved state. ii) Ligand exchange reaction of complex **2** with 1-methylimidazole under heterogeneous conditions through a template effect.

**Funding:** FARE framework (Prot. R20S3XECXT).

**Acknowledgement:** The authors are grateful for the support from the project AIEPhotoCat founded by MIUR under FARE framework (Prot. R20S3XECXT).

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# Encapsulation of silver nanoclusters to increase their luminescent properties

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DNA-stabilized silver nanoclusters (DNA-AgNCs) are atomically precise systems with sizes between 1 and 2 nm. DNA-AgNCs exhibit remarkable potential in several applications such as sensing, imaging, and therapeutics, thanks to their unique photophysical properties, which are easily tunable across the Vis-NIR spectrum by changing the DNA sequence. [1-4] These properties are also strongly dependent on the media: a disadvantage of these luminophores lies in their poor handling in solution with different values of temperature, pH and ionic strength. [6] Therefore, with this work, we propose an innovative strategy to enhance the stability of the DNA-AgNCs' optical properties.

The encapsulation in transparent polyacrylamide gel was performed to mitigate the sensitivity of the DNA-AgNCs towards their environment, thereby enhancing their practical applicability. The gel is obtained through radical polymerization of an acrylamide/bis-acrylamide precursor in an aqueous buffer. The DNA-AgNC sample was added a few minutes after the beginning of the polymerization to minimize the damage induced by radicals. Our results confirm the success of this approach, since the absorption band remains stable, showing no significant changes even after several weeks and the luminescence quantum yield and decay time increased from 0.32 to 0.46 and from 2.5 ns to 3.4 ns, respectively, resulting in enhanced long-lasting emission properties. [5]

In conclusion, DNA-stabilized silver nanoclusters encapsulated in polyacrylamide gel exhibit improved spectroscopic features and stability, representing a substantial advancement in the field of nanomaterials and paving the way for future innovations in nanocluster applications.

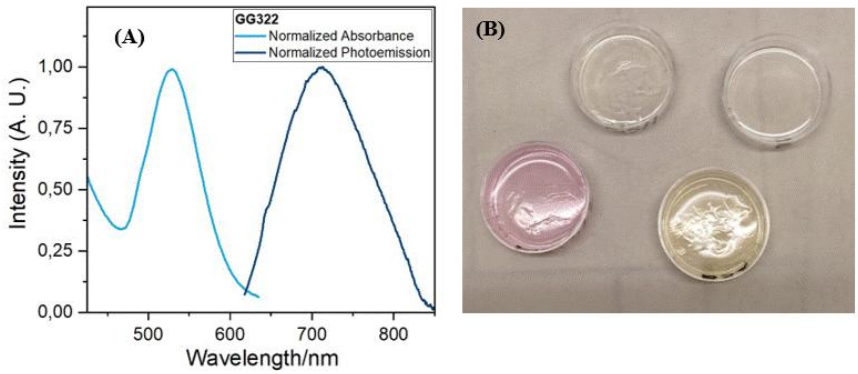


Figure 1. A) Normalized absorption and photoemission of the DNA-AgNC in polyacryilamide gel, B) Palette of some DNA- and glutathione-stabilized silver nanoclusters in polyacrylamide gel.

**Funding:** National Research Agency (12354) (Arial 9)

**Acknowledgement:** We thank all the contributors for using this template and allow a nice and coherent presentation of the conference papers. (Arial 9)

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# Exciton dynamics in CdTe quantum dot superlattices with minibands

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Semiconductor quantum dots (QDs) have attracted attention because their electronic states can be controlled by modifying their size. Much research has been conducted on the fabrication of QDs and their optical properties [1-3]. Recently, quantum interactions between QDs, which are caused by the proximity and periodic alignment of QDs, have been actively studied. The main interactions between QDs are the long-range dipole-dipole interaction [4-6] and the short-range quantum resonance [7,8]. Long-range energy transfer (ET) is caused by the dipole-dipole interaction, where the ET rate is inversely proportional to the sixth power of the distance between the centers of QDs [4]. In contrast, the quantum resonance is caused by the short-range delocalization of wave functions between QDs, where the energy of the extended state varies exponentially with the distance between the surfaces of the QDs [7]. In QD superlattices (QDSLs) with QDs regularly arranged within approximately 2 nm of each other, quantum resonance enables miniband formation with electronic states extending throughout the array [7-9], analogous to band formation in bulk crystals. Therefore, it is of great scientific interest to understand the physical properties of QDSLs as artificial and new kind of crystals where QDs behave like artificial atoms. The formation and physical properties of QD assemblies have been investigated experimentally and theoretically [9,10]. From an application point of view, QD assemblies can be used to improve the conversion efficiency of solar cells [11-13].

Research on the optical properties of QD assemblies have focused mostly on photoluminescence (PL) properties, and observed optical phenomena have been attributed to long-range ET rather than short-range quantum resonance [4-6]. This is because the long chain ligands attached to QD surfaces make it difficult for them to get very close to each other [8] and have inhibited the quantum resonance. QD assemblies with QDs in close proximity have been fabricated by replacing long chain ligands with short ligands, and studies on the coupling of electronic states in these assemblies have mostly been conducted from the viewpoint of optical absorption and charge transport properties [14,15]. PL inhibition due to ligand exchange has limited studies on PL properties. Elucidating PL dynamics in QDSLs with observed quantum resonance requires investigation of both absorption and PL spectra and their temperature dependence. However, there has been no systematic study of those characteristics.

We have successfully fabricated three-dimensional isotropic CdTe QDSLs with periodic arrangements of CdTe QDs coated with a short ligand, *N*-acetyl-*L*-cysteine (NAC), by utilizing the chemical bonds between NACs [8]. The formation of the minibands was then evaluated by studying the detection energy dependence of the PL excitation (PLE) spectra and the excitation energy dependence of the PL spectra [8]. In this study, we further investigate the temperature dependence of the optical absorption and PL spectra as well as the PL decay profiles of CdTe QDSLs in order to elucidate their optical properties. In particular, we show that the PL dynamics of CdTe QDSLs with minibands can be understood by taking into account both the extended- and localized-exciton states.

**Acknowledgement:** D.K. acknowledges financial support from JSPS KAKENHI, Grant No. 20H02549, 24K01277, and 24K21196.

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# Photophysics of Platinum(II) Flexible Lewis Pairs Compounds

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Stimuli-responsive luminescent compounds have attracted considerable attention due to their capability to change emission color under different external stimuli such as solvent, temperature and light. We have developed a series of bithiophene-based flexible Lewis Pairs (FlexLPs) which consists of a dimesitylboron Lewis acid and a diphenylphosphine Lewis base. They show changes in emission color through an equilibrium between the unbound open form and closed Lewis adduct, which can be controlled by the hydrogen-bond donating strength of the solvent[1] We have also prepared FlexLPs functionalized with platinum(II) terpyridine complexes and demonstrate that the charge-transfer (CT) energies of the complexes can be tuned by controlling the equilibrium between the open and closed form.[2]

Herein we show a series of mono-/bi-metallic platinum(II) phosphine or bipyridine complexes with FlexLP ligands. Spectroscopic and computational methods were used to elucidate the ground-state and excited-state photophysics of the platinum(II) complexes. The results demonstrate that the conformation of the FlexLP ligands has a strong influence on the photophysical properties such as the absorption and emission energy, triplet excited-state lifetime of the complexes.[3,4]

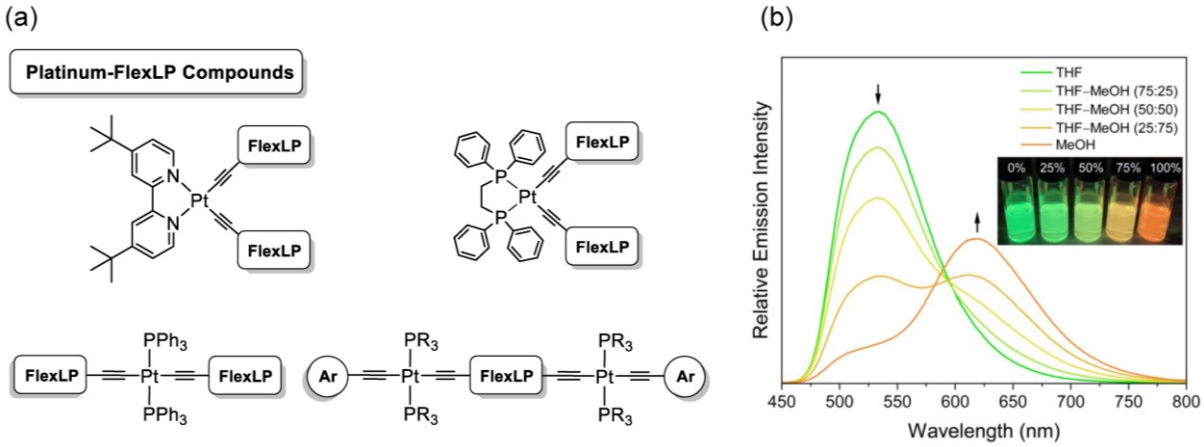


Figure 1. (a) Structures of the platinum(II) FlexLP compounds and (b) an example of the emission spectrum of a platinum-FlexLP compound.

**Funding:** Natural Sciences and Engineering Research Council of Canada (NSERC)

**Acknowledgement:** We would like to acknowledge the Laboratory for Advanced Spectroscopy and Imaging Research (LASIR) for facilities access.

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# In Vivo Optogenetics Based on Heavy Metal-Free Photon Upconversion Nanoparticles

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Photon upconversion (UC) from red or near-infrared (NIR) light to blue light (<500 nm) has significant promise for biological applications such as optogenetics. Our group previously demonstrated the first NIR-driven in vitro optogenetic system using a triplet–triplet annihilation-based upconversion (TTA-UC) hydrogel capable of converting NIR light to blue light.[1] However, the use of heavy-metal osmium ions in the sensitizer shows biocompatibility challenges, limiting its application in vivo. The realization of in vivo optogenetics using heavy metal-free TTA-UC materials has the potential to mitigate biocompatibility issues and expand the toolbox of photochemists and neuroscientists.

In this work, we present the first example of in vivo optogenetics enabled by biocompatible, heavy metal-free TTA-UC nanoparticles (Fig 1).[2] We developed a novel organic thermally activated delayed fluorescence (TADF) sensitizer—a boron difluoride curcuminoid derivative modified with a bromo group—that facilitates efficient intersystem crossing to the excited triplet state, markedly enhancing the TTA-UC efficiency. TTA-UC nanoparticles composed of biocompatible surfactants and an oil solvent exhibit water dispersibility and remarkable oxygen tolerance. When combined with genome engineering techniques utilizing a blue light-responsive, photoactivatable Cre-recombinase,[3] the TTA-UC nanoparticles induce EGFP expression in neurons in vivo.

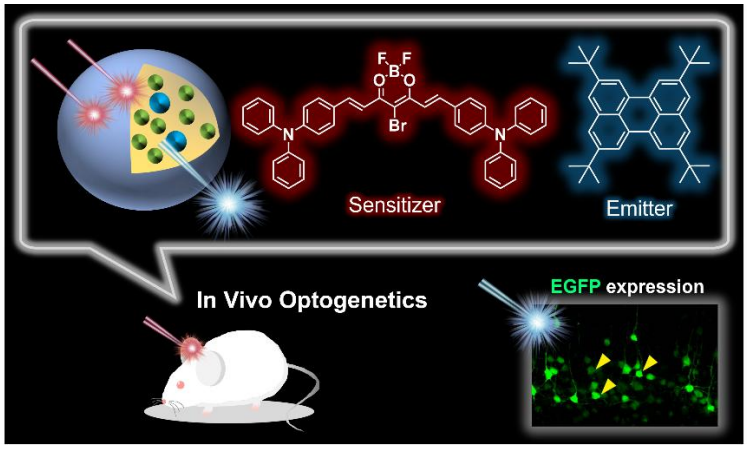


Figure 1. In vivo optogenetics using nanoparticles showing near-infrared/red-to-blue TTA-UC.

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**Acknowledgement:** We thank Dr. Moritoshi Sato for generously providing PA-Cre plasmid.

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# Boosting the Stability and Optoelectronic Performance of $CsPbI_3$ Nanocrystals for the Design of Advanced Red-Emitting LEDs

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Light-emitting diodes (LEDs) are widely used in modern technology, with organic LEDs (OLEDs) and quantum dot LEDs (QLEDs) among the most common types. However, both materials cannot meet all the criteria for an ideal LED, as OLEDs suffer from a low maximum brightness and limited color purity, while QLEDs exhibit slow response times.[1] Perovskite-based LEDs (PeLEDs) are a promising alternative, which offer high color purity, tunable bandgap and high photoluminescence quantum yield (PLQY). Despite these advantages, their practical application is hindered by material degradation caused by defects and ion migration, leading to loss of their desirable optoelectronic properties.[2] Improving the stability of the perovskite material is therefore crucial to realize high-performance PeLED devices.

In the case of $CsPbI_3$, ion migration and defects lead to degradation of the optically active black phase to the non-active yellow phase, losing all desired properties. A first approach to stabilize $CsPbI_3$ is to work within the size-confined region, which applies to $CsPbI_3$ nanocrystals. A second approach involves introducing strain into the crystal lattice through atomic substitution, which can enhance phase stability.[3]

In my poster, I will focus on the synthesis and stabilization of $CsPbI_3$ nanocrystals for LEDs. The hot injection method is optimized to produce small, monodisperse nanocrystals with high color purity and PLQY. The stability of the $CsPbI_3$ nanocrystals is further improved through atomic substitution using $LaI_3$ as a dopant. $La^{3+}$ was selected as dopant based on its proven ability to enhance the efficiency of $CsPb(Br/Cl)_3$ nanocrystals, however, the knowledge on its effect on $CsPbI_3$ remains limited.[4] The stability is assessed using photoluminescence (PL) and PLQY measurements, where a decline in values indicates the formation of the yellow, non-emissive phase. This degradation is also visually evident, as after 60 days, the doped sample retains its active black phase, while the undoped sample is fully degraded, as illustrated in Fig. 1.

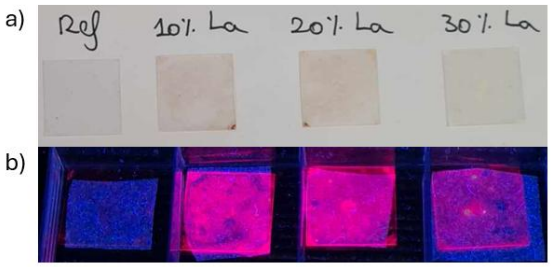


Figure 1. Photographs of La-doped $CsPbI_3$ samples compared to the pristine (Ref) $CsPbI_3$ sample: a) under ambient light and b) under UV-light. While the undoped sample has degraded to the yellow phase, the doped samples show enhanced stability.

**Funding:** KU Leuven Internal Funds (C14/23/090)

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# Targeted therapy at the speed of light

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About 20 million new cases of cancer were diagnosed in 2022, with an estimated increase up to 35 million cases anually in 2035.[1] With an increased demand for new therapies, new challenges need to be overcome. To improve low efficacy and reduce side-effects of chemotherapeutic agents, polymeric nanoparticles can passively target tumor cells and release drugs upon an endogenous trigger, e.g. the presence of reducing agents such as glutathione (GSH) or upon exogenous triggers such as light.[2] The main advantage in using photocleavable groups in polymers for drug delivery applications is the temporal and spatial control that is gained over the release.

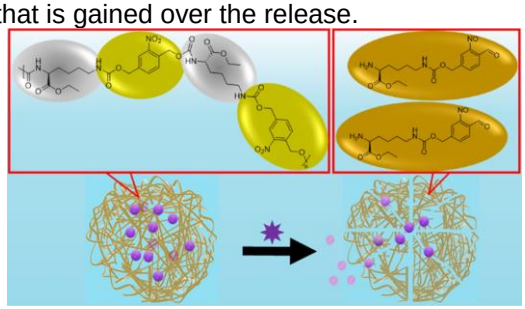

Figure 1. Nanoparticles made of ONB based polyurethanes can be degraded by UV irradiation to release their cargo

Photoresponsive groups can be included in the back-bone or the side-chain and their cleavage can either trigger immediate disruption of the back-bone or induce self-immolative processes that lead to the degradation of the polymer. One example is the use of ONB-groups that has been proven to be an effective trigger in both the disruption of the polymer-backbone as well as a light-degradable photo protection group for self-immolative polymers. New polyurethanes including 6-nitropiperonal based ONB-esters were synthesized and fully characterised by NMR spectroscopy, GPC and DSC analysis.[3] The irradiation and subsequent degradation of the polymers was followed by UV-Vis spectrometry and GPC. A backbone cleavable PU showed a decrease of molecular weight by more than 70% after only 30 s of irradiation while the side-chain cleavable polymer showed slower mass loss of more than 40% after 240 s of irradiation. Nanoparticles that were formulated from bioinspired lysine-based ONB copolymers showed a decrease in count rate of 60% after irradiation for 5 min and were shown to have an excellent biocompatibility.[4] Loaded cargo (nile red) was shown to be released within 15 s from microparticles to prove usability as drug delivery systems. Another example of light-degradable self-immolative polymers are polydisulfides based on dithiothreitol which carry a 2-mercaptopyridine end-group. They can be depolymerized within seconds at wavelengths below 400 nm. It was also shown that nanoparticles formulated from this self-immolative polydisulfide were shown degrade upon irradiation. The use of p-hydroxyphenacyl protection groups does not only add light responsivity above 400 nm to polymeric drug carriers, but also allows traceability of nanoparticles via fluorescence.

**Funding:** Deutsche Forschungsgemeinschaft (397670170).

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# Antimicrobial textiles based on photocrosslinked poly(ethylene-*co*-acrylic acid)

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**Abstract**

We recently developed dual-functional photocrosslinkable polymers that are both antimicrobial and antiviral and can be used to treat fabrics and other surfaces.[1] These materials are based on aminopropylmethylsiloxane dimethylsiloxane copolymers (PDMS-$NH_2$) with attached photosensitizers and have both passive and photosensitized functionality. It is of interest to expand the classes of polymers which can be used in this approach, here a modified poly (ethylene-co-acrylic acid) (PEAA) will be described as an organic analog of PDMS-$NH_2$.[2] Modified PEAAs with 3 different lengths of side chains are synthesized to study the effect of varying side chain length on polymer photooxidative cross-linking and antimicrobial activity (Fig. 1). Materials with longer side chains show elimination of *E. coli* and *MRSA* by contact lysis which is enhanced under irradiation with green light.

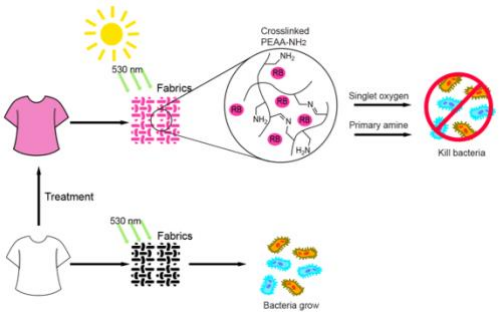


Figure 1. Schematic illustration of the antimicrobial mechanism of photocrosslinked PEAA-$NH_2$ coated fabrics. Upon treatment, the PEAA-$NH_2$ coating incorporates Rose Bengal (RB) and crosslinks under light exposure. Under 530 nm illumination, the RB-functionalized fabrics generate singlet oxygen, which, along with the primary amine groups, effectively kills bacteria. In contrast, untreated fabrics allow bacterial growth.

**Funding:** Natural Sciences and Engineering Research Council (NSERC).

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# From mechanosensitive to locked: environment-induced structural diversity in dendronized anthracene nanofibers

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Supramolecular stacking governs the optical and mechanical properties of self-assembled luminescent materials. Here, we report two distinct nanofiber assemblies of dendron-functionalized 9,10-bis(phenylethynyl)anthracene, controlled solely by environmental humidity and solvent quality.[1] Under ambient conditions, a green-emitting nanofiber ($\lambda_{em}$ ~ 500 nm) forms through planar π-π stacking and J-aggregation. Atomic force microscopy (AFM)-assisted mechanical perturbations reveal that fiber deformation (especially transverse pressure) significantly alters the emission spectra and fluorescence lifetimes, indicative of structural flexibility and mechano-responsive luminescence.

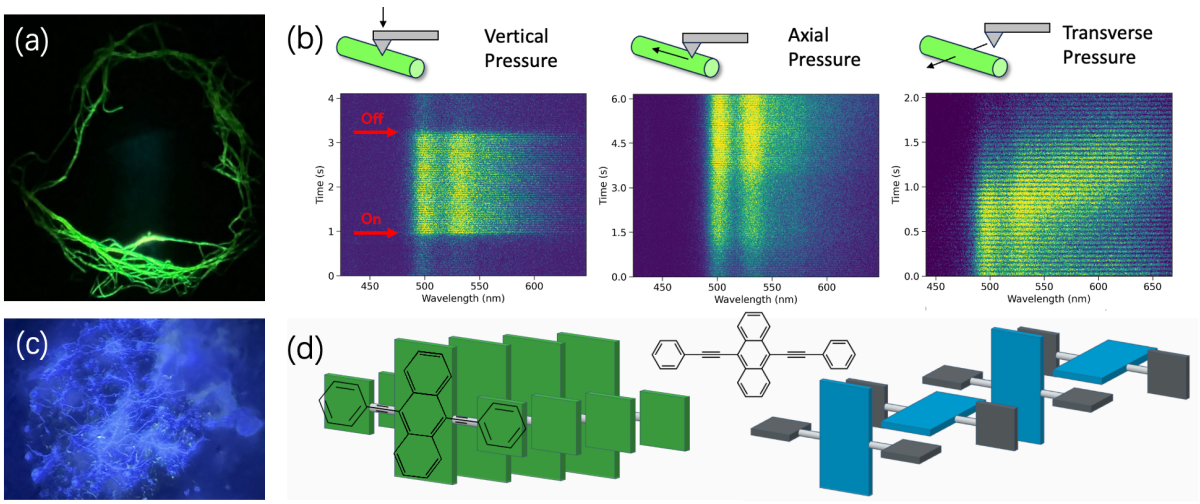


Figure 1.(a) Green-emitting nanofibers; (b) Emission changes of green nanofibers under different AFM-applied pressures; (c) Blue-emitting nanofibers; (d) Schematic models of emissive core packing in green and blue nanofibers.

In contrast, under low humidity (< 50%) with $MgSO_4$-dried solvents, we obtained a remarkably stable blue-emitting nanofiber ($\lambda_{em}$ ~ 405 nm). Its emission resembles the anthracene core with slight red-shift, suggesting twisted, non-coplanar conformations. Molecular dynamics simulations (GROMACS, vacuum conditions) revealed small clusters adopting metastable orthogonal interlocks, indicating that such local motifs, although rare, can form spontaneously and exhibit notable stability throughout the simulation window (~0.9 ns). Experimentally, the blue nanofiber maintains both its morphology and emission spectra even after one-year ambient exposure. Polarization-dependent fluorescence[2] and exciton diffusion measurements further confirm this rigid, uniform packing, showing exciton diffusion reduced by a factor of 3 compared to the green nanofibers.

Our results highlight how subtle environmental control can drive distinct supramolecular architectures, yielding nanofibers with either responsive luminescence (green, flexible) or extraordinary stability (blue, interlocked). These findings offer new design strategies for supramolecular materials with tunable optical properties and enhanced structural robustness.

**Funding:** The research is funded by the JSPS KAKENHI grant number 24K01449 and the JSPS KAKENHI grant number 23H04875 in Grant-in-Aid for Transformative Research Areas 'Materials Science of Meso-Hierarchy'.

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# Modification of Tetrapyrrolic Photosensitizers as a Strategy to Enhance Photodynamic Therapy Efficiency

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Photodynamic therapy (PDT) is a modern therapeutic approach that integrates principles of chemistry, physics, and biomedical sciences. It employs light-sensitive compounds, known as photosensitizers (PSs), which absorb light, typically in the visible or near-infrared (NIR) range, and subsequently transition to an excited triplet state, from which they generate reactive oxygen species (ROS). These ROS induce oxidative stress within the tumor microenvironment (TME), ultimately leading to cancer cell destruction, vascular occlusion, and activation of the immune response [1].

The efficacy of PDT relies, among other factors, on the efficient population of long-lived triplet states. To enhance this, structural modifications to photosensitizers are introduced, such as the presence of fluorine atoms which exhibit higher spin-orbit coupling constants compared to carbon and the coordination of heavy metal ions (e.g., $Zn^{2+}$, $Pd^{2+}$) to the tetrapyrrolic core. Moreover, reducing the porphyrin macrocycle to a bacteriochlorin core results in the emergence of an intense absorption band in the NIR region, which is particularly beneficial for *in vivo* applications. Together, these two straightforward modifications—metal ion coordination and macrocycle reduction—significantly influence the physicochemical properties and therapeutic performance of tetrapyrrolic compounds in PDT [2].

In this study, a series of tetrapyrrolic photosensitizers was systematically evaluated for their light absorption efficiency, photostability, triplet state lifetimes, ROS generation capacity, and lipophilicity (assessed via n-octanol/PBS partition coefficients). *In vitro* experiments included assessments of dark cytotoxicity, cellular uptake kinetics in cancer cells, and photodynamic efficacy. Preliminary *in vivo* studies demonstrated that a selected bacteriochlorin derivative exhibits high stability, preferential accumulation in tumor tissue, and robust therapeutic effectiveness. The findings provide a comprehensive characterization of the investigated compounds and underscore their potential for further development toward targeted anticancer therapies.

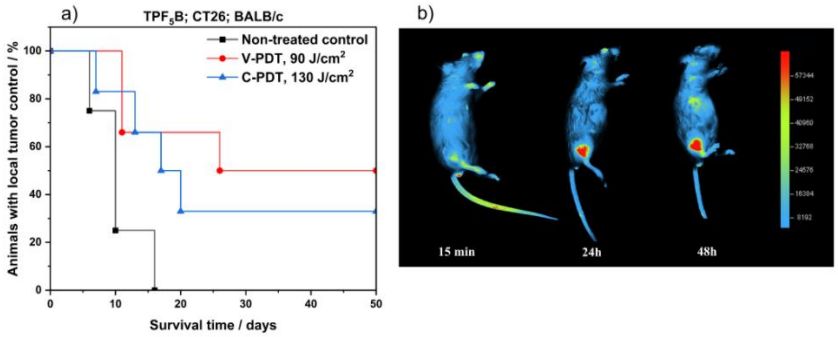


Figure. 1 (a) Antitumor efficacy of $TPF_5B$ formulated in Pluronic P123 micelles against CT26 tumors in the BALB/c mouse model, evaluated at DLI = 15 min (V-PDT) and DLI = 24 h (C-PDT). (b) Whole-body fluorescence imaging of BALB/c mice bearing CT26 tumors in the right leg, captured at 15 minutes, 24 hours, and 48 hours following intravenous administration of 1.5 mg/kg $TPF_5B$-P123.

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# Fluorescent coumarins for the photoinduced activation of Artemisinin – *A photopharmacological approach*

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Artemisinin **1** (ART) is a natural product which has shifted the paradigms to combat malaria, and its derivatives remain the lead compounds to treat it.[1,2] The combination of physiological tolerability and high potency make ART a good candidate for non-malarial applications, and its anticancer activity has captured a great deal of attention and puts forth continuing research.[3] There is consensus that, under physiological conditions, ART is activated by Fe(II) via single electron transfer (SET) to the endoperoxide bond, generating reactive oxygen radicals. These radicals undergo distinct rearrangements depending on the initial Fe(II) coordination site, ultimately forming three major 'decomposition' products which indicate an activation via the pharmacologically relevant intermediates (Figure 1). Recent investigations, particularly during the last couple of years[4], uncovered a novel approach to activate ART upon a remote and precise trigger – by light. This novel photopharmacological strategy unfolds new perspectives and is based on the conjugation of ART with chromophores capable of activating the pharmacophore in the desired fashion, presumably via energy transfer. In current investigations, fluorescent coumarins are successfully employed as chromophores whose photophysical characteristics can be fine-tuned by distinct structural changes paving the way for the activation of ART by light in the visible and perhaps longer wavelength visible region (Figure 1).

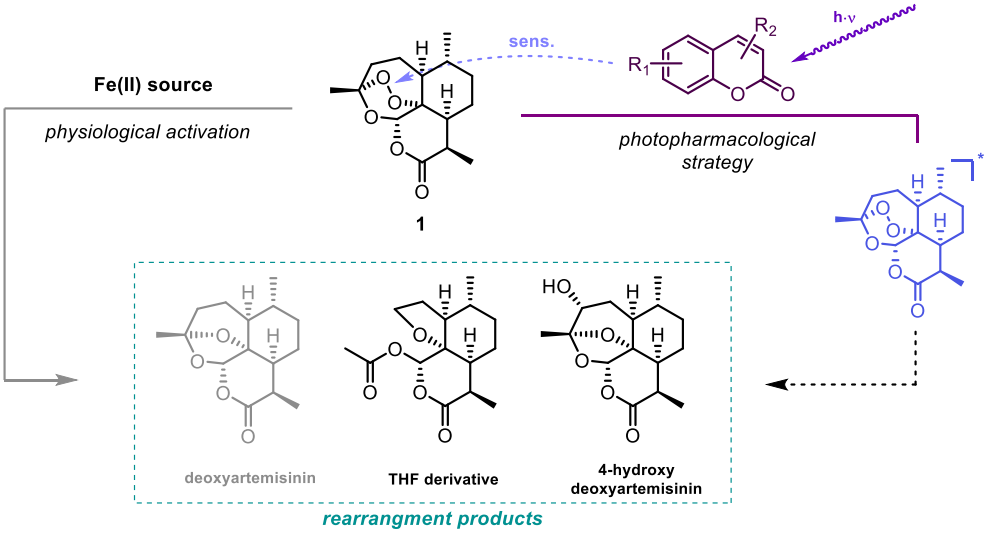


Figure 1. Novel photopharmacological strategy using fluorescent coumarin derivatives (absorption-, emission and potential depending on the 3-,6-, and 7-substituents) to activate Artemisinin **1** which rearranges to shown products (deoxyartemisinin is not detected by the light-induced rearrangement).

Besides their versatile photophysical applications, coumarins have drawn substantial attention owing to their pharmacological properties, not least because of their anticancer activities.[5] Thus, conjugation with ART would not only allow for the remote, precise and desired regulation of ART in cancer therapy but might further lead to a synergistic effect of the merged drugs. The dual functionality of coumarin derivatives and the ease of suitably manipulating their absorption and emission behaviour in addition to their excellent fluorescence in water will eventually lead towards novel ART-coumarin hybrids for photopharmacological applications.

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# Chalcone Derivatives for β-gal and Aminopeptidase N Detection

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Chalcones are a class of chemicals with a variety of uses. They are easy to synthesize, have several modification sites, exhibit strong biocompatibility, and are highly sensitive to environmental stimuli. In aqueous conditions, chalcone derivatives often emit weak fluorescence signals. However, because their structures contain several reactive functional groups, they can easily form complexes with biomacromolecules such as proteins, resulting in strong fluorescence signals. In addition, strong fluorescence in aqueous conditions can be achieved by developing chalcone derivatives with excited-state intramolecular proton transfer (ESIPT) and aggregation-induced emission (AIE) properties. Chalcone derivatives are thus commonly used for the fluorescence sensing of biomolecules. Herein, we designed and synthesized two chalcone derivatives (Fig. 1), Ala-OMN[1] and gal-HCA[2], to detect β-galactosidase (β-gal) and Aminopeptidase N (APN). Ala-OMN undergoes alanine group hydrolyzation, releases OMN in the presence of APN and thus exhibits significant green fluorescence with BSA in phosphate-buffered saline (PBS). β-Galactosidase (β-gal) can catalyze the cleavage of gal-HCA, releasing HCA with ESIPT and AIE properties. As a result, there is a significant redshift of fluorescence from 532 nm to 615 nm. These probes demonstrate high sensitivity, precise recognition ability, and bioimaging capabilities, presenting promising tools for enzyme activity assays and disease diagnostics.

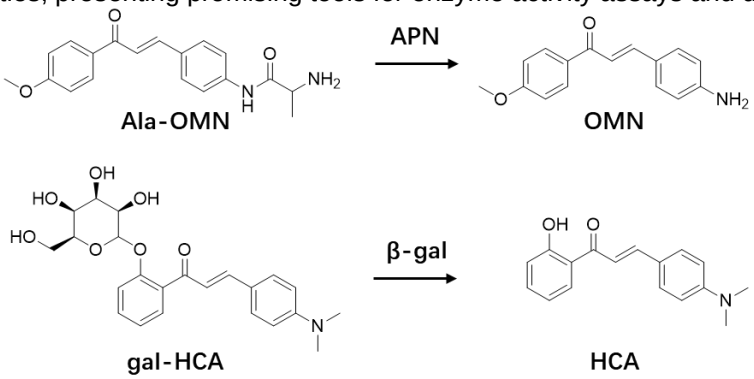


Figure 1. Schematic of the Reaction Mechanism of Ala-OMN and gal-HCA

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**Acknowledgement:** Thank all the collaborators and students who participated in this work and the funding support.

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# Fluorescent Organic Nanoparticles: A Bright Nanotool for Early Detection in Biological Systems

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Fluorescent Organic Nanoparticles (FONs) have emerged as promising materials for biosensing applications compared to their inorganic counterparts due to their structural variability, lower toxicity, biodegradable potential, good photostability, and easy cellular uptake.[1,2] Previous studies by M. Pan showed the potential of FONs with a BODIPY in the hydrophobic core and a hydrophilic shell for their versatility and early bacterial growth detection.[3] In this study, we focused on the photophysical properties of FONs comprising a green BODIPY within the core of the nanoparticles (tilted G-FNPs, figure 1)[4], emitting at 543 nm. By attaching a pH sensing fluorophore (dubbed "Ruby")[5], which is an ON-OFF fluorophore based on the pH of its environment, with SPAAC click chemistry, we studied the ratiometric properties in various pH buffers, resulting in a pKa of 5.3 ± 0.2. Furthermore, we applied these FON to the determination of pH in the presence of different types of cells.

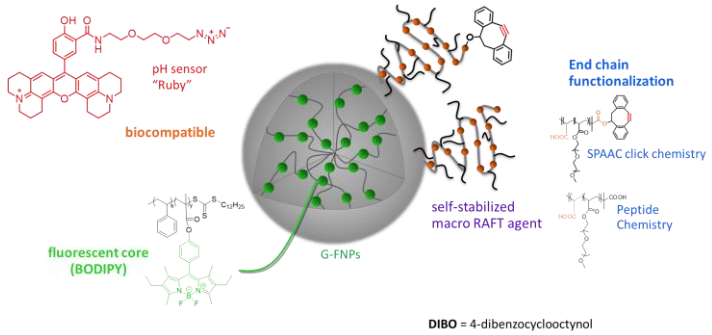


*Figure 1: The G-FNPs design, containing the green BODIPY fluorophore within the core and functional groups on the shell for surface functionalization, alongside the pH sensor "Ruby".*

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**Acknowledgement**: This research project is thanks to the 2MIB doctoral school at Université Paris-Saclay as well as CNRS. I also wish to thank my supervisors and the biological technician for their help.

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# Development of a mitochondria-targeted fluorogenic probe for monitoring LDE reactivity during ferroptosis.

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**Abstract:**
Lipid-derived electrophiles (LDEs) are a group of reactive products formed during cell membrane degradation[1]. While low concentrations of these compounds play an essential role in cellular signaling pathways, increased levels are associated with several pathological states. While LDE formation occurs in all cell compartments, these species react differently within cellular organelles. Particular interest in this regard is placed on mitochondria as a primary lipid-derived Reactive Oxygen Species (ROS) source and, consequently, a significant site of LDE generation. However, investigations on the key aspects of mitochondria LDE generation and reactivity have yet to be conducted[1,2,3].
Despite several developed approaches to investigate molecular targets of LDEs, the detailed mechanistic roles of LDE reactivity and trafficking in these pathological states have only recently been examined[1,3]. Previously, our group has utilized fluorescence microscopy to study the cellular reactivity of LDEs and their influence on cell death pathways[4]. In particular, the reported fluorogenic LDE analog AcroB, a BODIPY chromophore bearing an electrophilic LDE warhead, allowed for *in vivo* observation of LDE trafficking. AcroB reacts with glutathione, a cellular nucleophile, allowing observation of adduct trafficking. Inspired by these results, a late-stage functionalization of the AcroB scaffold was performed by inserting an asymmetrical mitochondria-specific targeting moiety.

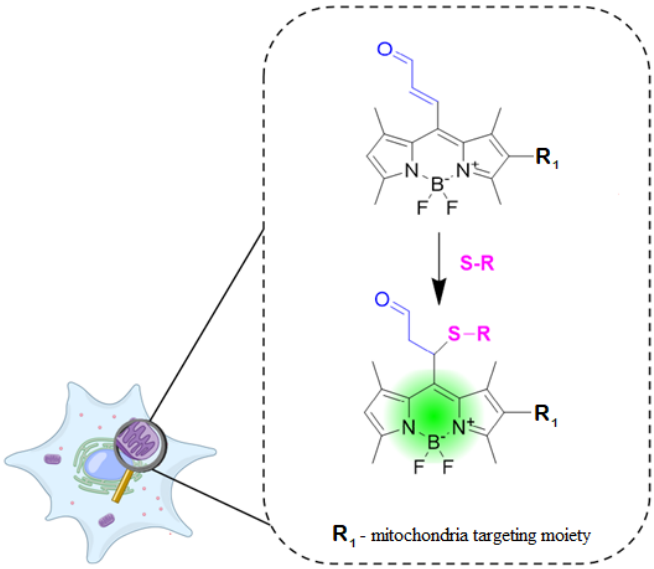


Figure 1. Structure and the proposed reactivity mechanism of the MitoAcroB probe.

This mitochondria-specific LDE reporter can reveal organelle-specific LDE formation and reactivity. In my presentation, I will describe the probe preparation, photophysical studies, and, ultimately, live cell imaging studies in various physiological conditions.

**Acknowledgments:** D.H. and L.X. are grateful to the Fonds de Recherche du Québec–Nature et Technologies for postgraduate scholarships. G.C. is grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Canadian Foundation for Innovation for funding.

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# Tumor-Targeted Exosome-based Heavy Atom-Free Nano-sensitizer for effective Sono-Photodynamic Therapy of Solid Tumors

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Fluorescence image-guided photodynamic therapy holds great promise for non-invasive and precise treatment of deep-seated tumors. However, the limited tissue penetration depth of light restricts its efficacy, promoting the use of sono-photodynamic therapy (SPDT) with near-infrared (NIR) fluorescence as a complementary modality[1,2]. Still, the development of effective nanosensitizer for NIR fluorescence image-guided SPDT remains a significant challenge due to low reactive oxygen species (ROS) generation efficiency, poor photostability, and lack of cancer specificity.

In this study, a novel heavy atom-free nanosensitizer is synthesized, exhibiting strong NIR fluorescence, high ROS generation efficiency and enhanced aqueous stability. By introducing a bulky, electron-rich group, 4-(1,2,2-triphenylvinyl)-1,1,'-biphenyl(TPE), at the meso-position of IR820 backbone, the resulting IR820-TPE nanosensitizer generates ROS through both type I and type II photochemical pathways upon exposure to an 808 nm laser and ultrasound, improving the sono-photodynamic effect of IR820.To enhance the intracellular delivery and tumor-targeting capability of IR820-TPE, biotin-conjugated exosomes(B-Exo) are employed as natural nanocarriers. In vitro studies highlight the exceptional therapeutic performance of IR820-TPE-loaded B-Exo (IR820-TPE@B-Exo) in synergistic SPDT effect in breast cancer cell. In vivo studies revealed that, following intravenous injection, IR820-TPE@B-Exo exhibited high tumor accumulation and sustained fluorescence signals for up to 24 hours. Moreover, it demonstrated effective antitumor efficacy via SPDT while maintaining excellent biocompatibility. These findings highlight IR820-TPE@B-Exo as a promising sono-phototheranostic agent for safe, targeted cancer therapy offering a potential strategy to overcome the limitations of conventional therapeutic modalities[3].

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**Acknowledgement:** Thanks to all the contributors to this work.

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# Spectroscopic insights into photophysical properties and interactions of m-THPC with Pluronic P123

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This study focuses on the characterization of the *m*-THPC (temoporfin) system in a Pluronic P123 matrix as a potential photosensitizer delivery platform for photodynamic therapy (PDT)[1–4]. Due to its high hydrophobicity, *m*-THPC exhibits limited solubility in aqueous environments[5], which poses a significant barrier to its clinical applications. In highly aqueous systems, *m*-THPC is also prone to aggregation, which leads to a loss of its capability to generate singlet oxygen—an essential reactive species for effective PDT. To improve its bioavailability and control over drug distribution, the non-ionic block copolymer Pluronic P123 was employed, enabling the encapsulation of the photosensitizer within micellar structures. Spectroscopic analyses (steady-state and time-resolved absorption and emission)) and dynamic light scattering (DLS) confirmed the successful formation of micelles and the presence of *m*-THPC within their cores. The spectroscopic data indicated that the photophysical properties of *m*-THPC, characteristic of its monomeric form, were preserved after encapsulation. The results suggest that Pluronic P123 may serve as an effective carrier for temoporfin delivery, preventing aggregation, ensuring its stability and activity in aqueous media, thereby opening new possibilities for the development of more selective and efficient photodynamic therapies.

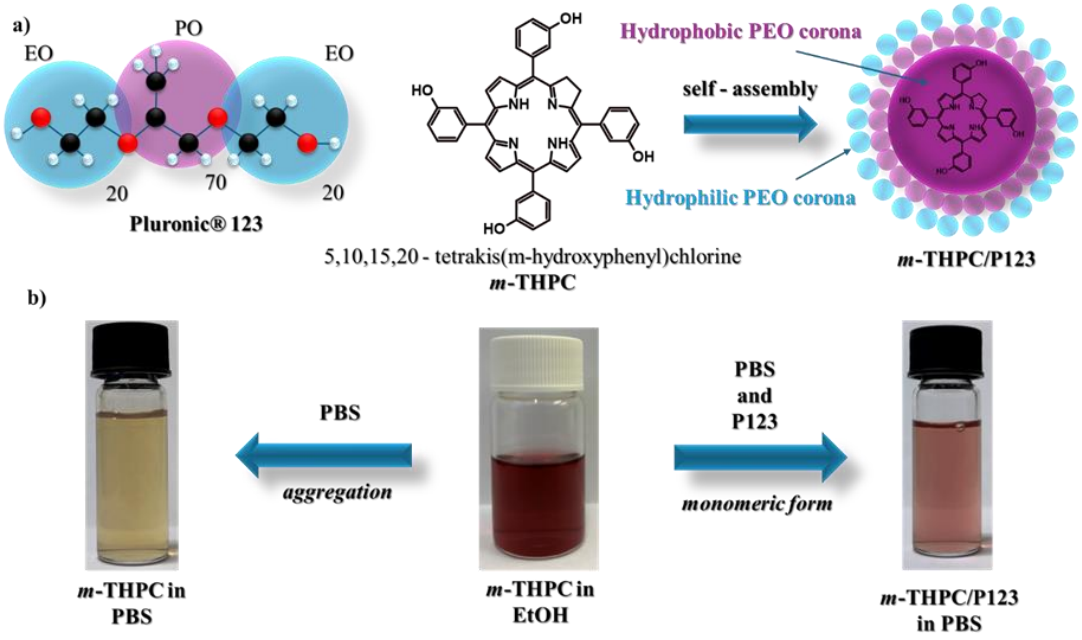


Figure 1. The structure of the block copolymer Pluronic P123 and the encapsulation mechanism of the hydrophobic m-THPC molecule within the micelle core. The lower part shows photos of the samples: *m*-THPC in EtOH, PBS solution of Pluronic P123, and the *m*-THPC/P123 system in PBS, demonstrating enhanced solubility of *m*-THPC due to micelle formation.

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# Time-resolved fluorescence NADH signals as a tool to investigate the adaptative capacity of cell-lines towards changes in available metabolic substrates

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Autofluorescence microscopy has been revolutionary as a new biomedical analysis technique. FLIM (Fluorescence Lifetime Imaging Microscopy) is an imaging technique that allows the study of cellular metabolism from images generated with endogenous fluorescence signals. Thus, the relation of free to protein-bound NADH (nicotinamide-adenine dinucleotide in its reduced state) can be quantified with measurements of fluorescence lifetimes and fluorescence intensity, parameters characteristic of a given metabolic state. Here, a higher proportion of free NADH indicates a metabolic shift towards glycolysis, whereas an increase in the proportion of protein-bound NADH indicates a state which favors the oxidative phosphorylation pathway. Fibroblasts were used as biological samples for this study, which were subjected to stress and metabolic inhibition to characterize the metabolism and adaptive capacity of this cell line. The type of adaptation generated to these conditions could serve as a diagnostic of healthy cells or cells with a mitochondrial disease. It has found that this cell line can successfully adapt to a galactose-rich medium by not significantly decreasing their percentage of free NADH (an indicator of the glycolytic pathway). Fibroblasts in pyruvate-rich medium did not have the same adaptation as this percentage was decreased by almost 8%.

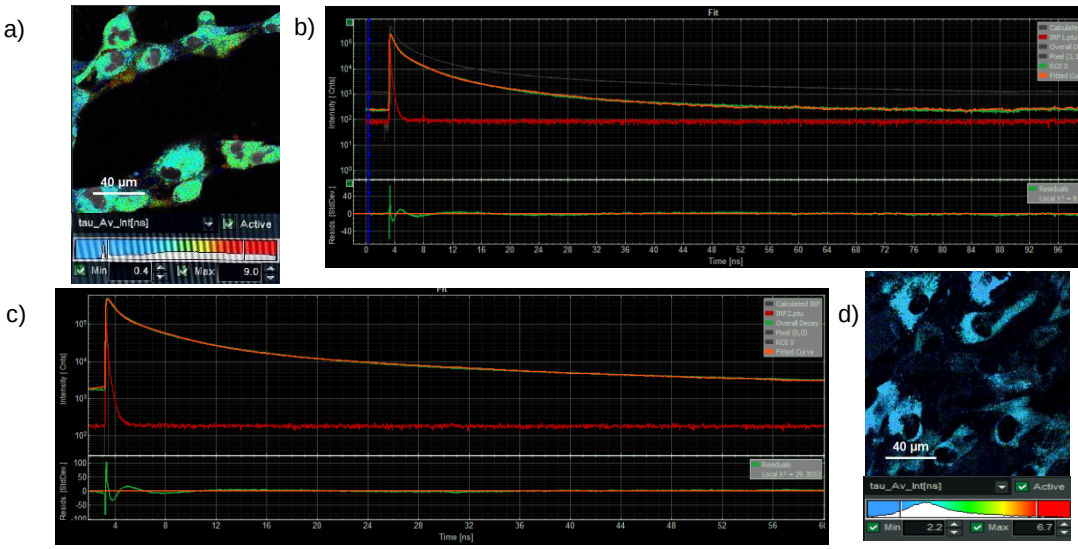


Figure 1. a) FLIM image of cells in HG medium. b) Exponential decay for fluorescence lifetime of NADH free and protein-bound of cells in HG medium. c) Exponential decay for fluorescence lifetime of NADH free and protein-bound of cells in Pyr medium. d) FLIM image of cells in Pyr medium.

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# Control Of The Optical Absorption Properties Of Nanovectors For Photoacoustic Imaging (CAP-PHOTOAC)

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Photoacoustics (PA) is an emerging technology that turns light waves into sound waves. The sound waves emitted by optically absorbing structures through the PA effect find use in several applications, one of which is the non-invasive, high-resolution imaging of biological tissues[1]. Currently, the research community is developing dyes ever more stable with high photoacoustic generation efficiency. Bodipy-based dyes are frequently employed as PA contrast agents because of their high absorption coefficient, tunable absorption maximum, and photostability[2]. In recent years, our research group has produced a novel Bodipy-based chromophore that, when conjugated to a lactide chain and grafted onto a PEGylated nanoparticle (NP), shows remarkable absorption properties and biocompatibility, features that make it an excellent platform for tissue-level PA imaging as well as drug delivery[3]. Building on that success, this project aims to enhance its precision and specificity by bringing that imaging capability to the cellular level. One way to achieve this is to use a probe that is pH responsive and shows different photophysical properties whether it is exposed to a more acidic environment, such as the organelles within a cell (e.g. Lysosomes). In this study, the goal is to develop a stimulus-responsive PA agent by synthetizing and characterizing a pH-sensitive molecule using the Bodipy scaffold. So far, our work has produced two Bodipy molecules, equipped with a clickable handle and a *3-nitro-4-phenol* group, whose phenol-phenolate interconversion provides the capacity of responding to pH changes in the cellular environment[4]. The pH-sensitive Bodipys are conjugated to PLA-PEG and formulated into pH sensitive PLA-PEG NPs. The NPs are characterized and their performances evaluated with the goal of selecting the most promising dye to create a multifunctional nanovector.

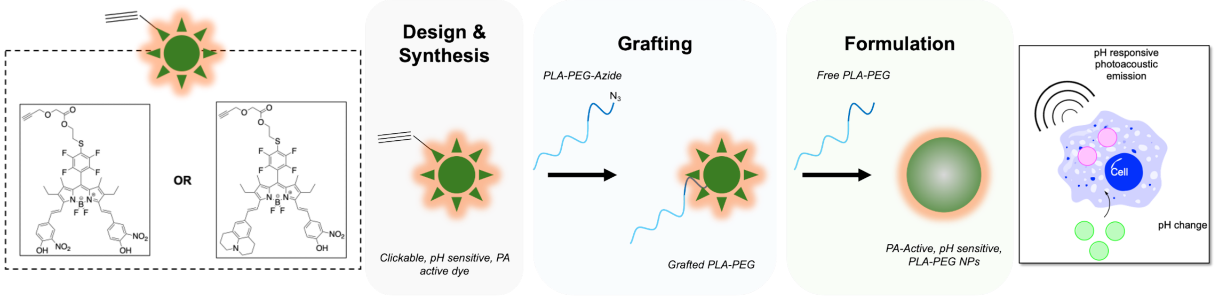


**Figure 1.** Graphical Abstract.

**Funding:** This project has received funding by the French National Research Agency under the program ANR-21-CE09-0024-01

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# Photoreaction vs. Electron Transfer: Time-Resolved Spectroscopy on Amotosalen and Mixed DNA Oligomers

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Psoralens are naturally occurring photosensitizers that protect plants from various harmful microorganisms such as viruses, bacteria and fungi [1]. They are also widely used in dermatology and cancer therapy because of their targeted DNA-damaging properties. The mode of action entails two consecutive steps: First, a psoralen reversibly intercalates between the base pairs (bp) of the helical DNA regions. Secondly, UVA illumination leads to an irreversible photoreaction, during which the excited psoralen is covalently bound to a thymine base (T). If a second photon is absorbed, interstrand crosslinks (ICL) can be formed with an additional T on the opposite strand. Both the monoadduct and the ICL disrupt DNA replication and cell proliferation. Pioneering work by our group showed that photoexcited psoralens are quenched by a reductive electron transfer (PET) involving guanine bases in direct vicinity [2]. Further mechanistic studies unraveled the formation of the monofunctional photoproduct on the µs-time-scale involving an intermediate biradical species [3].

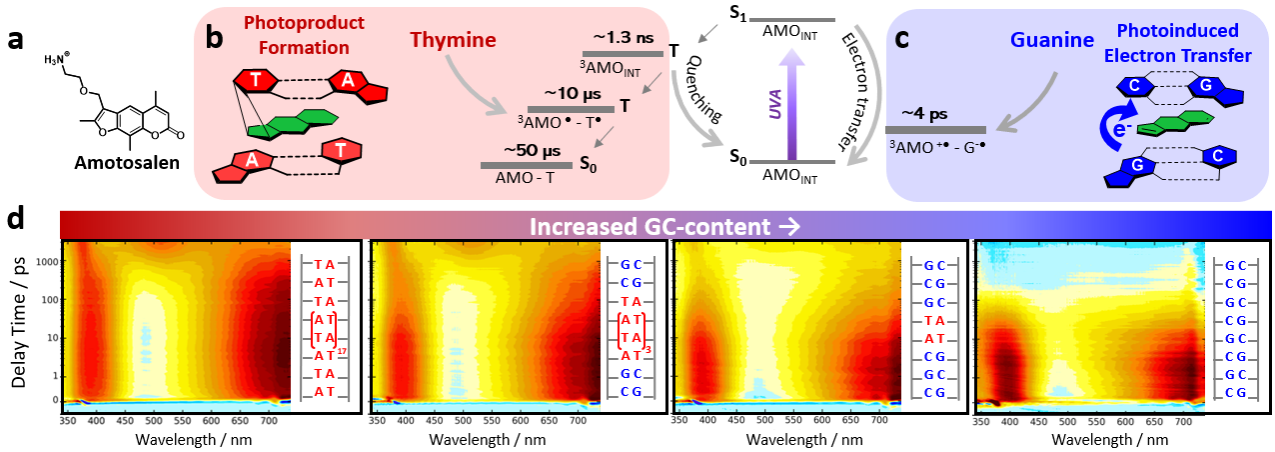


Figure 1. a) Structure of amotosalen (AMO). b) Photoaddition of AMO to thymine (T). c) Photoinduced electron transfer (PET) from guanine (G) to AMO (blue). d) Femtosecond transient absorption measurements of AMO intercalated into different DNA oligomers.

Here, the interaction of the synthetic psoralen derivative amotosalen (AMO), which is used for the decontamination of blood products, is studied intercalated into different DNA oligomers [4]. AMO, unlike other psoralens studied, intercalates with greater affinity into synthetic DNA strands containing only adenine-thymine (AT) bp than into strands containing only guanine-cytosine (GC) bp [5]. It is, therefore, a suitable molecule to investigate a possible long-range, DNA-mediated PET as seen, e.g., in the works by Lewis et al. [6]. Femtosecond-transient absorption measurements on AMO in “mixed” DNA sequences, containing all DNA bps, show the characteristic signatures of the PET and the photoproduct formation. The time constants for the PET process range between 15-20 ps and coincide with the local PET in GC-only-intercalates. Steady-state spectroscopy measurements prove photoproduct formation in DNA containing only one AT-intercalation site, further supporting the absence of a long-range, DNA-mediated PET.

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# (Time-Resolved) Spectroscopy on the Interaction of Novel Angelicins with DNA

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Angelicins (angular structures, Fig. 1a) and psoralens (linear ones) belong to the naturally occurring furocoumarins. They are found in various plants, fruits, and vegetables, acting as phytoalexins in plant defense mechanisms against microbial pathogens. In clinical medicine, psoralens are eponymous for PUVA (psoralen + UV-A irradiation) therapy, which is widely used for treating autoimmune skin disorders. Recently, angelicins have garnered attention in biological research[1], as they show two promising properties compared to psoralens: After reversible intercalation between DNA bases, psoralens only photoreact with thymine (T) bases and "suffer" from a picosecond photoinduced electron transfer (PET) with guanine (G)[2]. This is a disadvantage, as only photoadducts lead to apoptosis or necrosis of the affected cells. Contrary to that, angelicins may form photoadducts with T *and* cytosine (C) bases (Fig. 1b, c)[3]. Unlike psoralens, angelicins are postulated not to form interstrand-cross-links within DNA after photoexcitation due to their angular structure. This ability to form only monoadducts is associated with significantly reduced phototoxic side effects[4]. Heretofore, angelicins have not been studied spectroscopically in detail.

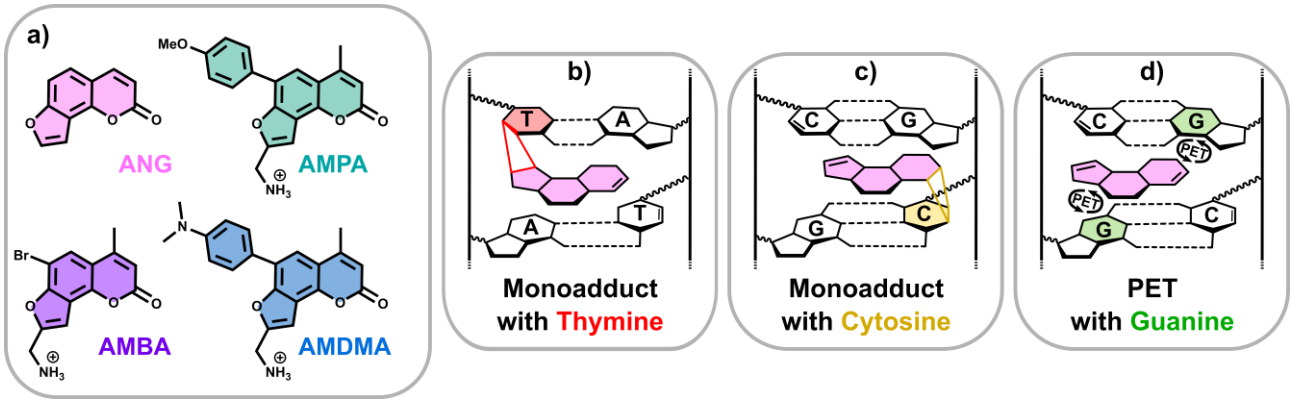


Figure 1. Investigated angelicins (a) and their potential interaction with different DNA bases (b-d).

Based on our extensive investigations on the molecular mechanisms of psoralens with synthetic DNA[2,5,6], first results on angelicin (ANG) and novel derivatives (AMBA, AMPA, AMDMA) are presented here. The parent structure ANG does not seem to be a suitable candidate due to its poor water solubility and low intercalation ability. The decorated derivatives, shown in Fig. 1a, perform better in these aspects. However, preliminary time-resolved measurements on AMBA indicate characteristic patterns of PET[2] in the presence of G (Fig. 1d)[7], which has not yet been reported in the literature for angelicins. The other two derivatives, which are more electron-rich and PET should not be feasible energetically, are currently under investigation.

**Funding:** This work was funded by the Deutsche Forschungsgemeinschaft, grant number GI 349/6-2, and by the Jürgen Manchot Stiftung (scholarship for M. P. R.).

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# Modified Zn(II) and Pt(II) Sulfonyl Phthalocyanines for Photodynamic and Theranostic Applications

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Photodynamic therapy (PDT) is a minimally invasive therapeutic strategy used treat cancer [1] and other conditions, such as age-related macular degeneration (AMD) and localized infections [2]. It involves the combination of $O_2$, light, and a photosensitizer to generate reactive oxygen species (ROS) that are toxic to cancer cells. PDT works through a variety of mechanisms, including damage to tumor blood vessels, direct killing of cancer cells, induction of localized inflammation, and long-term enhancement of the immune system. The generation of ROS occurs through two mechanisms: Type I, in which the photosensitizer reacts with an organic molecule to produce reactive oxygen species, and Type II, in which energy is transferred from the photosensitizer to $O_2$, generating singlet oxygen. The cytotoxic action of ROS results from their reactivity with biomolecules in proximity to their site of generation. Due to their high reactivity and short lifetime, PDT is limited to regions where ROS are produced. An ideal photosensitizer should exhibit chemical purity, a known and stable composition, light absorption in the range of 630-850 nm, a long triplet lifetime, and high quantum yield for ROS generation [3].

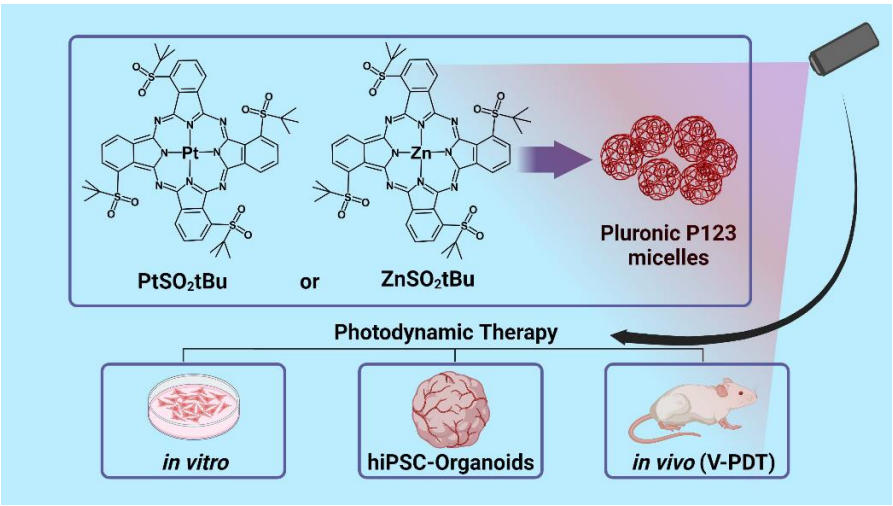


Figure 1. Schematic of PDT in vitro, organoids and mouse model using phthalocyanines as PS.

Phthalocyanines represent a promising group of second-generation photosensitizers that absorb light in the red region of the spectrum, allowing better tissue penetration [4]. However, their aggregation and solubility in aqueous solutions pose challenges, which have been addressed through the synthesis of phthalocyanines with sulfonic acid substituents and diamagnetic metal ions ($ZnSO_2tBu$ and $PtSO_2tBu$). $PtSO_2tBu$ exhibited high singlet oxygen generation efficiency ($\Phi_\Delta$ = 0.87–0.99), while $ZnSO_2tBu$ generated both singlet oxygen ($\Phi_\Delta$ = 0.45–0.48) and additional ROS. Their incorporation into Pluronic-based micelles enhanced serum albumin interactions, cellular uptake, and phototoxicity. Preclinical studies in CT26 tumor-bearing mice demonstrated potent anti-cancer effects: vascular-targeted PDT resulted in tumor eradication in 84% of $ZnSO_2tBu$- and 100% of $PtSO_2tBu$-treated mice, with no recurrence observed [5].

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# Illuminating Artemisinin: A Photochemical Approach to Unlock Its Pharmacological Potential Beyond Malaria

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Artemisinin is a natural compound containing an unusual 1,2,4-trioxane endo-peroxide. This endo-peroxide provides the unique and important pharmacological potential of Artemisinin with the treatment of malaria being its main application. In this context, the mode of action of Artemisinin proceeds via an activating reductive homolytic cleavage of the peroxide through biologically available Fe(II)-ions. This initiates a radical cascade with several reactive oxygen species (ROS) and carbon-centered radicals. These intermediates act as alkylating agents and initiators of oxidative stress within the malaria pathogen, resulting in the death of the malaria-causing parasite through irreparable DNA damage.[1,2]

In the light of the concept of photopharmacology, we investigate a new approach to transfer this unique mode of action onto other types of diseases, e.g. cancer therapy. We found that the homolytic peroxide-cleavage can be photochemically initiated via irradiation of triplet-sensitizers or new singlet-emitters.[3] Herein, we report the synthesis and comprehensive photophysical characterization of new xanthone- and acridone-based activators as well as molecular dyads composed of these activators and Artemisinin. We found a highly solvent-dependent fluorescence behavior concomitant with the attenuation of fluorescence in the presence of Artemisinin which we assign to an energy transfer from the excited activator onto the peroxide-motif. Additional irradiation experiments indicate a decomposition process similar to the above-mentioned Fe(II)-induced activation of Artemisinin.

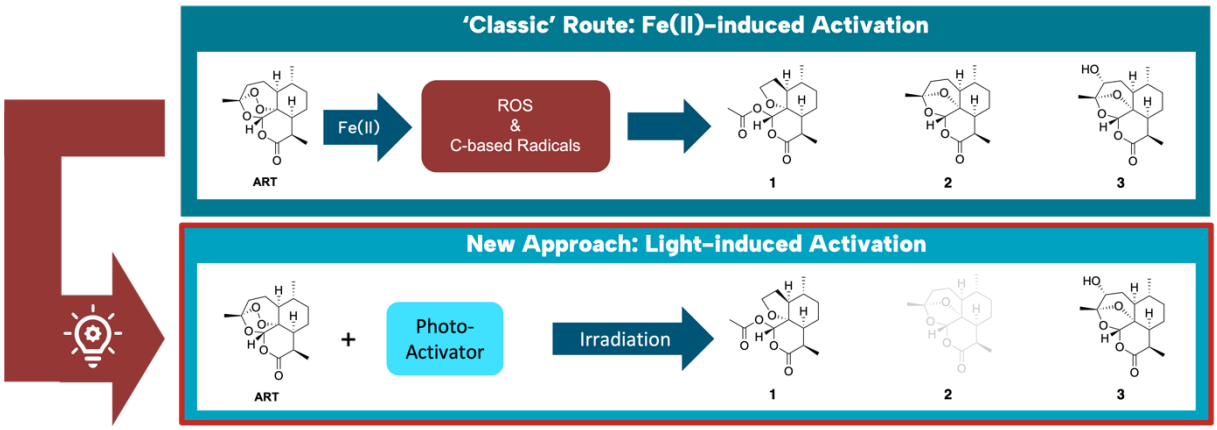


Figure 1. General concept of the Photoactivation of Artemisinin (**ART**). Irradiation with a suitable photo-activator leads to the same rearrangement products **1** and **3** as the known Fe(II)-induced route indication a similar reaction pathway.

These investigations provide an insight on the light-induced activation of Artemisinin which unlocks the possibility of transferring Artemisinin's pharmacological potential onto other diseases while ensuring selective on-site activation as well as complete independence from the usually required Fe(II)-sources.

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# Comparison of *cis* and *trans* cyclometalated Palladium photosensitizers on the photophysics and supramolecular self-assembly

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*Cis* and *trans* configurations are researched extensively for cyclometalated Platinum(II) complexes, including the effect on electron transitions, [1] photophysics, [2] crystallization, [3] etc. Previously, a series of cyclometalated palladium(II) complexes were researched as carrier-free nano photosensitizers(PSs) for photodynamic therapy (PDT), in which the cyclometalated N^C^C^N Pd photosensitizer (Fig.1a **PdL**) show efficient cellular uptake and green light PDT.[4] Due to the planar structure and close distance in dimer, the Pd···Pd interaction and pi-pi stacking overcome the Pauli repulsion. More importantly, metallophilic interaction induces red shift of absorption in dimer. Thus, this research focuses on *trans* form of similar cyclometalated C^N^C^N Pd complexes to figure out the effect of *trans* form on photophysics for both monomer and dimer.

As Fig.1 shows, there are "trans/open" (**Pd(CNCN)-2**) and "trans/close" (**Pd(CNCN)-1**) Pd complexes compared with the "cis/open" (**PdL**). **Pd(CNCN)-1** forms nanospheres and nanocrystals in cell culture medium (Fig.1b), which is different from **PdL**, which only forms nanospheres. Similar to **PdL**, **Pd(CNCN)-1** aggregates also show red shift of absorption compared with the monomer (Fig.1b). The DFT calculation for the dimer elucidates that the Pd-Pd distance in **Pd(CNCN)-1** dimer (3.458 Å), which proves the possibility of metallophilic interaction (Fig.1a). Besides, DFT calculation suggests that 26% of the metallophilic interaction and 74% of the pi-pi stacking are in **Pd(CNCN)-1** dimer. The electron transition difference in the three complexes will also be researched.

For PDT *in vitro*, **Pd(CNCN)-1** nanoaggregates is proven to have a PDT effect on skin cancer cells. The photoindex (PI) is 7.0 under blue light (454 nm, 1.7 J/cm$^2$) and 4.4 under green light (520 nm, 26 J/cm$^2$), respectively (Fig.1c). A better blue light PDT result because the main absorbance is at 467 nm (Ɛ = 6599 M$^{-1}$ cm$^{-1}$). However, the green light PDT effect of **Pd(CNCN)-1** is lower than that of PdL (PI 72, 520 nm, 13 J/cm$^2$). Different light doses will be adjusted, and the PDT effect of **Pd(CNCN)-2** will be researched.

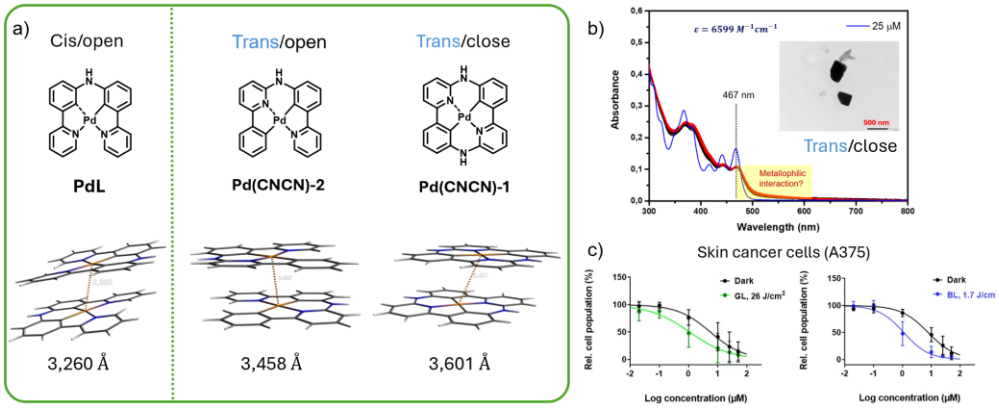


Figure 1. a) The molecular structures and corresponding dimer structures calculated by dispersion-corrected DFT (ADF/DFT/PBE0/TZP/COSMO (Methanol)). b) The absorption spectrum of **Pd(CNCN)-1** monomer in DMSO (25μm) and aggregates formation (25μm, 1% DMSO/OptiMEM(+)2.5%FCS) monitored in 12h. c) The dose-responsive curve of **Pd(CNCN)-1** for skin cancer cell (A375) under green light (520 nm, 26.0 J/cm$^2$) and blue light (454 nm, 1.7 J/cm$^2$), respectively.

**Acknowledgement:** China Scholarship Council (CSC)

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# Enhancing Antitumor Immunity with Bacteriochlorin-Based Photodynamic Therapy and Immune Checkpoint Inhibition

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Photodynamic therapy (PDT) is an emerging, minimally invasive therapeutic modality that leverages the synergistic action of three individually non-toxic components: a photosensitizer (PS), visible or near-infrared (NIR) light, and molecular oxygen. Upon activation, this combination leads to the generation of reactive oxygen species (ROS), which cause direct cytotoxicity and destruction of the primary tumor mass. Beyond its local effects, PDT also plays a pivotal role in modulating the immune system, offering systemic protection against distant metastases and positioning PDT as a promising strategy within the broader field of cancer immunotherapy [1]. Recent studies have demonstrated that PDT can induce immunogenic cell death (ICD), a highly desirable form of cell death that promotes the maturation of dendritic cells and the establishment of a long-lasting antitumor immune memory [2].

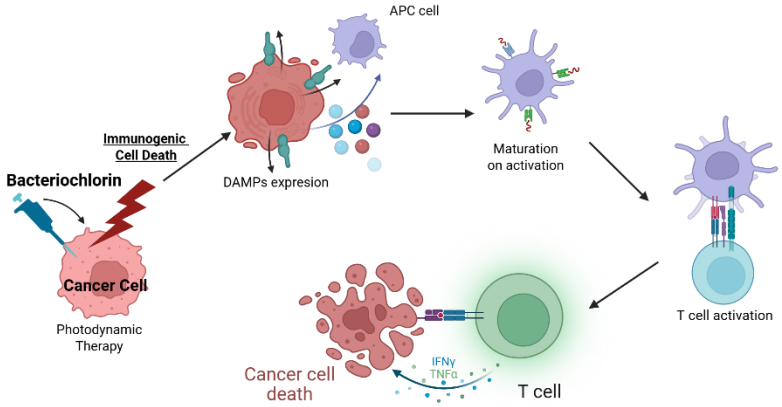


Figure 1. Induction of immunogenic cell death leading to T cell activation by bacteriochlorin-based photodynamic therapy.

Notably, the efficacy of ICD induction appears to be influenced by the subcellular localization of the photosensitizer, which in turn affects the activation and function of antigen-presenting cells (APCs), including macrophages (Figure 1). Moreover, the type of photosensitizer and its formulation, such as encapsulation within micelles, can significantly modulate the extent and quality of the immune response elicited. Despite these advances, tumors can evade immune surveillance by upregulating immune checkpoint proteins such as programmed death-ligand 1 (PD-L1), suppressing T cell-mediated antitumor activity. To overcome this limitation, combining PDT with immune checkpoint blockade therapies, specifically, antibodies targeting PD-1 or PD-L1, has emerged as a promising approach to enhance therapeutic efficacy. This combinatorial strategy has the potential not only to improve tumor eradication but also to establish a robust, systemic antitumor immunity capable of preventing disease recurrence.

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# Intracellular oxygen sensing based on time-resolved emission measurements using phosphorescent Ir(III) complexes

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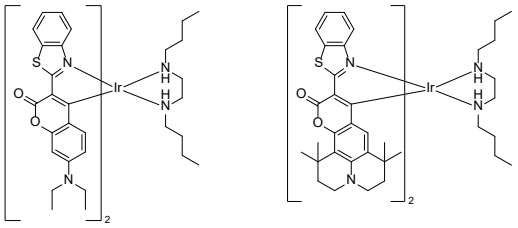
Molecular oxygen ($O_2$) plays an indispensable role as a terminal electron acceptor in the electron transport chain in mitochondria. Acute or chronic $O_2$ deprivation (hypoxia) in organisms results in various diseases, and the elucidation of the pathogenic mechanism of hypoxia-related diseases and various cellular responses to hypoxia is an urgent issue. Optical $O_2$ imaging methods using phosphorescent probes have opened up techniques for noninvasive imaging of the intracellular and tissue $O_2$ status, and $O_2$-sensitive probes play a key role in the development of this approach. We expect that phosphorescent Ir(III) complexes can serve as new $O_2$-sensing probes for intracellular and intravascular $O_2$ imaging in vivo [1-3]. Emission lifetime measurements using a phosphorescent $O_2$ probe is an innovative technique for elucidating the behavior of oxygen in living cells and tissues. In this study, we designed and synthesized cationic Ir(III) complexes, C6-BA and C545T-BA (Fig. 1), that exhibits long-lived phosphorescence in the red wavelength region and enables intracellular $O_2$ sensing and imaging using lifetime-based measurements.

C6-BA and C545T-BA showed strong absorption bands with maxima at around 482 nm and 498 nm in the visible region (400 – 550 nm) and with large molar absorption coefficients. The emission maxima of C6-BA and C545T-BA were observed at 594 nm and 622 nm, respectively, indicating that the introduction of the julolidine moiety causes a bathochromic shift of the emission spectrum of C545-BA, similar to the results obtained from the absorption spectrum measurements. These emission spectra are attributed to phosphorescence because the emission intensities significantly decrease under the presence of dissolved $O_2$.

We investigated whether the change of the $O_2$ partial pressure ($pO_2$) in living cells due to cellular respiration could be tracked by monitoring the phosphorescence lifetime of C6-BA and C545-BA using a microplate reader. Here, we used carbonyl cyanide *p*-(trifluoromethoxy)phenylhydrazone (FCCP) to alter $O_2$ status of living cells. Control cells showed a gradual increase in lifetime of C6-BA and C545T-BA over time, indicating that intracellular $pO_2$ decrease due to normal respiration of cells. In contrast, FCCP-treated cells showed a quick increase in their lifetime of both probes over time with increasing FCCP concentration, i.e., a decrease sharply to less than 20 mmHg (FCCP: 2 μM) by increased $O_2$ consumption due to activated cellular respiration. These results demonstrate that the intracellular $pO_2$ depending on the cellular metabolism can be evaluated from time-resolved intensity measurements using the microplate reader in combination with C6-BA and C545T-BA as $O_2$ probes.



C545T-BA

Fig. 1. Chemical structures of C6-BA and C545T-BA.

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# Turning nitroarenes into photocatalysts for energy transfer: triplet energies and beyond

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Energy transfer (EnT) catalysis enables the selective population of triplet states without direct photoexcitation of the substrate, eliminating one of the major roadblocks in photochemistry: that the reacting molecule must be photoactive at the irradiation wavelength. This also allows the use of lower-energy light sources, leading to higher selectivities towards the desired photoproduct. Traditionally, the selection of adequate photocatalysts has been based exclusively on their corresponding triplet energies, which must be higher, or at least identical, to that of the substrate[1,2].

Here we will show that this procedure is not general for any kind of photocatalyst, and that complex screening methods must be developed. We focused our attention on nitroarenes, which our research group has been using in recent years for several photochemical transformations[3-5]. A combination of computational and experimental studies shows that other parameters such as the electronic configuration of the triplet state (nπ* or ππ*), the excited-state lifetime, or even the excited-state (anti)aromaticity can play a greater role in determining the reactivity of a given nitroarene towards EnT. Our results demonstrate the necessity to redefine the requirements for an optimal photocatalyst: showing a large triplet energy is no longer enough.

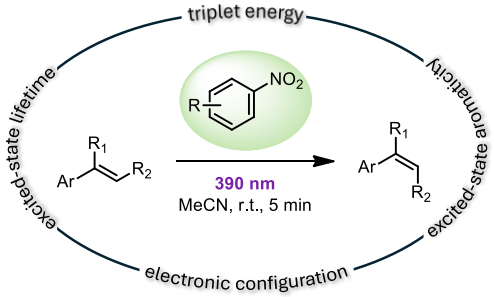


Figure 1. The nitroarene-catalyzed *E*-to-*Z* photoisomerization of olefins is governed by several photophysical properties of the catalyst, not just its triplet energy.

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# Single-Molecule Spectroscopy of the Excited-State Proton Transfer

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Experimental investigations in chemistry are typically performed in bulk, leading to ensemble averaging of the resulting chemical or physical properties. Single-molecule spectroscopy applied to chemical reactions can therefore provide insight into the reaction mechanism by revealing competing reaction pathways and/or microheterogeneities in the sample that remain hidden in ensemble studies.[1,2]

Here we present our investigations on the reaction mechanism of the excited-state proton transfer (ESPT) using single-molecule fluorescence microscopy. Excitation of a so-called photoacid leads to an increase in acidity, which favours the release of a proton on the adiabatic excited-state energy surface. The subsequent proton migration affects the electronic structure of the photoacid and thus the fluorescence wavelength of various intermediates along the reaction path (Fig. 1). After emission, reprotonation takes place on the ground-state potential energy surface.[3,4] Due to its cyclic nature, the reaction can be probed repeatedly until photobleaching occurs, making it particularly suitable for investigation by single-molecule spectroscopy. By embedding highly fluorescent and photostable photoacid molecules[5] in a solid phosphine oxide matrix, ESPT can be studied using total internal reflection fluorescence microscopy. A transmission grating in front of the sCMOS camera[6] is used to record emission spectra of individual photoacid-phosphine oxide complexes. Deconvolution of the obtained spectra yields the fractions of the different intermediates, revealing an extremely heterogeneous environment in the matrix (Fig. 1b) which is not covered by ensemble studies.[7] These heterogeneities serve as an excerpt of the microenvironments that are ubiquitous in chemical reaction dynamics.

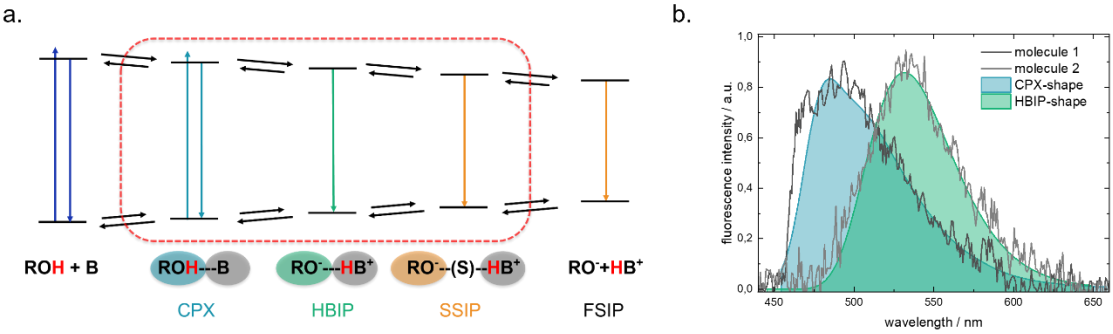


Figure 1. a) Eigen-Weller model describing the reaction mechanism of the ESPT with CPX: hydrogen-bonded complex, HBIP: hydrogen-bonded ion pair, SSIP: solvent-separated ion pair and FSIP: fully separated ion pair and b) emission spectra of single photoacid molecules in a phosphine oxide matrix.

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**Acknowledgement:** We thank Alexander Grandjean, Luis Pérez-Lustres, Stephan Götzinger and Vojislav Krstic for helpful discussions.

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# Enhancing the Efficiency of Flavin Photoreduction Inside Enzymes for Application in Biocatalytic Halogenation

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The application of photochemistry in the context of biocatalysis has gained considerable interest over the last years.[1] Flavoenzymes are of particular interest because photochemistry of the flavin cofactor can be used for cofactor regeneration in catalysis. We implemented the photochemistry of enzyme-bound flavin in flavin-dependent halogenases using blue light in the presence of the external electron donor EDTA.[2] Limiting to the application is the low quantum yield caused by ultrafast deactivation of the excited state by nearby tryptophan residues (Fig. 1a). By mutation of tryptophan to phenylalanine in the flavin binding site, the efficiency of the photoreduction of oxidized flavin to the flavin neutral radical and further to the fully reduced state could be increased by 20%.[3] To investigate the mechanism of photoreduction, nanosecond time-resolved UV-vis difference spectroscopy was applied. From these difference spectra, the concentration of reaction intermediates was deduced by fitting with reference spectra of all species involved (Fig. 1b). A kinetic reaction model was applied to simulate the conversion. We found that after excitation by the laser pulse, the triplet excited state of flavin in the wild-type enzyme reacts with EDTA to the flavin anion radical within 500 nanoseconds. In the mutant, the concentration of photoinduced flavin anion radical is drastically increased and the lifetime is enhanced. This increase is the result of a larger tryptophan-to-flavin distance disfavoring the recombination reaction of the radical pair. Accordingly, the mutant is opening up a second productive pathway with the protein for photoreduction of flavin from the singlet excited state in addition to the reaction from the triplet excited state with the external reducing agent. By using these insights into the mechanism of photoreduction, the efficiency of photocatalysis will be further increased by exploiting the additional protein-based pathway.

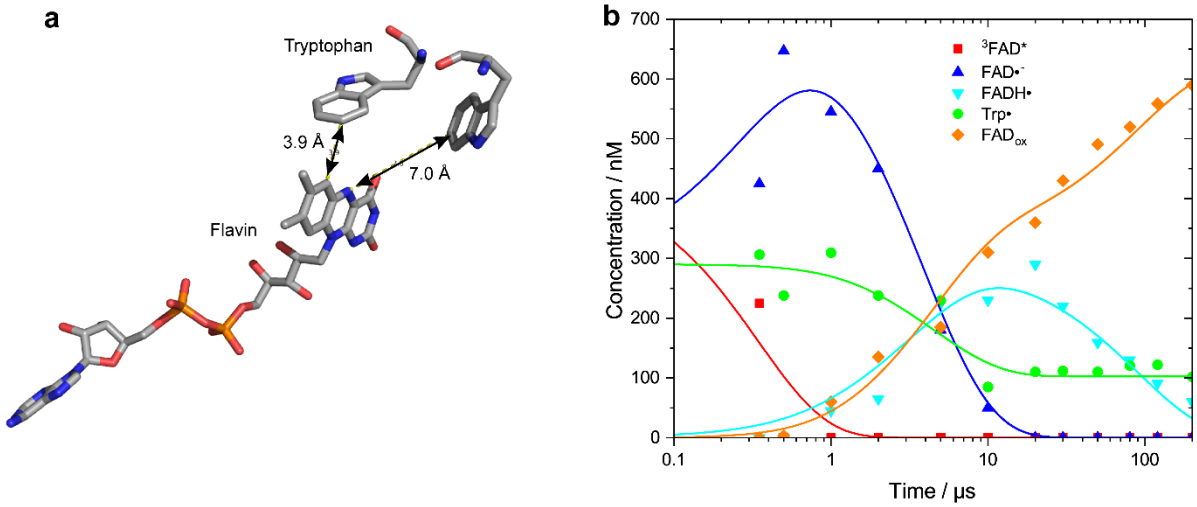


Figure 1. Investigation of the mechanism of artificial light-driven biocatalysis in halogenases. (a) Structure of flavin cofactor bound in the binding-site of the halogenase with two tryptophan residues as potential reaction partners for excited flavin. (b) Concentration profiles of intermediates of the photoreaction of flavin derived from the UV-vis difference spectra with a kinetic reaction model.

**Funding:** Deutsche Forschungsgemeinschaft (KO3580/8-1)

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# H-Tunneling Rotamerization in Glycine Imine

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As the number of atoms in molecules increases, conformational analysis of even simple compounds becomes increasingly challenging. Therefore, spectroscopic methods that produce high-resolution spectra with clearly distinguishable conformers are essential. Matrix isolation technique combined with tunable infrared lasers, has made conformational changes more accessible via narrow-band near-infrared (NIR) irradiation. It was successfully applied for studies of high-energy conformers of amino acids[1,2], carboxylic acids[3] and alcohols[4]. In this study, we investigate the NIR light-induced generation of a higher-energy conformer of glycine imine, the simplest imino acid, and its subsequent hydrogen tunneling CO-bond rotamerization in various cryogenic matrix environments, including solid argon (Ar), para-hydrogen (*p*-$H_2$), and dinitrogen ($N_2$).[5]

Using a narrow-band OPO laser, we selectively excite the OH overtone vibration at 6483.0 $cm^{-1}$ (1542.8 nm), leading to the controlled formation of the *anti*-(*Z,E*) conformer of glycine imine from its more stable *anti*-(*E,E*) conformer (Fig. 1). This process demonstrates the effectiveness of vibrational excitation in triggering conformational rearrangements, enabling the production of high-energy species that would otherwise be impossible to isolate. After formation, the *anti*-(*Z,E*) conformer undergoes spontaneous H-tunneling rotamerization back to the lower-energy *anti*-(*E,E*) conformer in the dark.

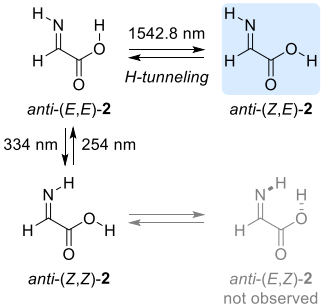


Figure 1. Conformational switching of glycine imine conformers by UV and NIR light as well as H-tunneling CO-bond rotamerization in the *anti*-(*Z,E*) conformer (top right).

The tunneling half-life of this process is highly dependent on the matrix environment, emphasizing the role of intermolecular interactions in modulating quantum mechanical effects. In solid argon, the half-life is approximately 5 hours, while in *p*-$H_2$ and $N_2$ matrices, it extends significantly to around 18 hours. The unexpectedly long half-life in *p*-$H_2$ suggests a stabilizing interaction, likely due to the formation of a dinitrogen complex, as $N_2$ is a byproduct of the initial photolysis process. This observation aligns with previous studies, in which dinitrogen complexation has been shown to stabilize high-energy conformers and slowing down tunneling processes[1]. Additionally, experiments with the deuterated carboxyl group in glycine imine support the tunneling mechanism because it completely inhibits the tunneling process.

These findings underscore the power of NIR irradiation as a precise tool for manipulating molecular conformations at cryogenic temperatures. The ability to selectively generate and study high-energy conformers provides valuable insights into the interplay between vibrational excitation and quantum tunneling, with implications for astrochemistry, spectroscopy, and reaction dynamics in extreme environments.

**Funding:** This work was supported by the Fonds der Chemischen Industrie and funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) as part of the Emmy-Noether program (DFG project 530220027) and under Germany's Excellence Strategy − EXC-2033−390677874 - RESOLV.National Research Agency

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# Fluorescent water-sensitive probes for dynamic polymer wetting

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In order to assess and map the reversible (de)hydration dynamics in thermally-switchable layers such as poly(di(ethylene glycol) methyl ether methacrylate) (PDEGMA), the tailor-made reporter fluorescent dyes for monitoring of water content or of the general media polarity are required. A combination of specifically labelled polymer layer and the time-resolved fluorescence microscopy was examined as a promising approach for the direct detection of water in the vicinity of the polymer chains. The wetting of the PDEGMA layer was mimicked by aqueous THF and MeCN solutions.

With the direct water sensor, β-carboline phenol derivative bCar3OH, which might acted as a photoacid in the excited state, the fluorescence quantum yield ($\varphi$) and decay time ($\tau$) decreased drastically in the presence of water in THF (Fig 1a) as well as in MeCN (Fig 1b). The nonlinear character of the Stern-Volmer plot for the lifetime $\tau_0/\tau$ ratio indicated complex dynamic fluorescence quenching pathway in THF (Fig 1a). The ratio $\varphi_0/\varphi$ decreased stronger with water than $\tau_0/\tau$ showing that a static fluorescence quenching also takes place. The ground state complex formation of bCar3OH with water ($K$ = 0.3 $M^{-1}$) led to a moderate blue shift of the absorption maximum of 390 $cm^{-1}$.

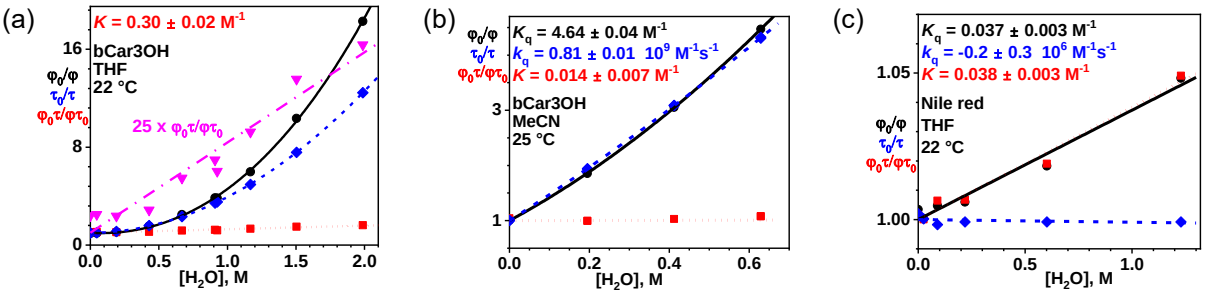


Fig. 1. Stern-Volmer plots for fluorescence quenching of β-carboline bCar3OH (a,b) and Nile red (c) by water in THF (a, c) and MeCN (b) at 22 °C.

With a general media polarity sensor, Nile red (NR), no marked fluorescence quenching of NR by water occurred, but the NR fluorescence band shifted substantially to the red in aqueous THF. The $\tau$ value remained practically unchanged in the presence of water, whereas $\varphi$ slightly decreased. Both absorption and fluorescence spectra are shifted to the red for respectively 220 and 630 $cm^{-1}$ at water concentration of 1.23 M.

The mechanisms of fluorescent water sensing in organic solvent was shown to be different for bCar3OH (simple in MeCN and complex in THF dynamic fluorescence quenching) and for NR (red shift of absorption and fluorescence bands).

The fluorescence spectra of NR indicated that PDEGMA had a moderate polarity that lay in the range between that of ethyl acetate and acetone. The fluorescence of NR in PDEGMA decayed double exponentially with a major long-lived (4.6 ns) and a minor short-lived (2.1 ns) component. The PDEGMA brushes are hydrated below 32°C and are dehydrated above this temperature. When the temperature varies from 20 to 50°C, strong de-swelling of PDEGMA (swelling ratio from 3 at 25°C to 1.5 at 50°C) was accompanied with a substantial reduction (from 0.22 to 0.12) of the contribution of the short-lived decay component of NR fluorescence decay.

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# Unraveling biological magnetoreception by modulating cryptochrome photochemistry

**Christopher Einholz[1], Johannes Ruhnke[1], Jonas Diez[1], Stefan Weber[1] and Erik Schleicher[1]**

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The interaction between magnetic fields and chemical systems varies widely with field strength and system characteristics. Notably, even weak magnetic fields can influence chemical systems in non-equilibrium states via the Radical Pair Mechanism (RPM), currently the predominant model for animal magnetoreception via Cryptochromes (Crys). Despite two decades of experimental research, we lack precise understanding of both the molecular principles and signal transduction pathways involved[1]. This knowledge gap can partially be attributed to the absence of systematic investigations into the Magnetic Field Effect (MFE) across various magnetically sensitive Crys. In this talk, I will first introduce the fundamental concepts of the RPM and its derived MFEs. Following this foundation, I will present in-depth systematic analyses of magnetic sensitivity across several representatives of the Photolyase-Cryptochrome Superfamily (PCSF). The obtained results will be discussed within the framework of the RPM and classical physical principles, offering new insights into this fascinating phenomenon.

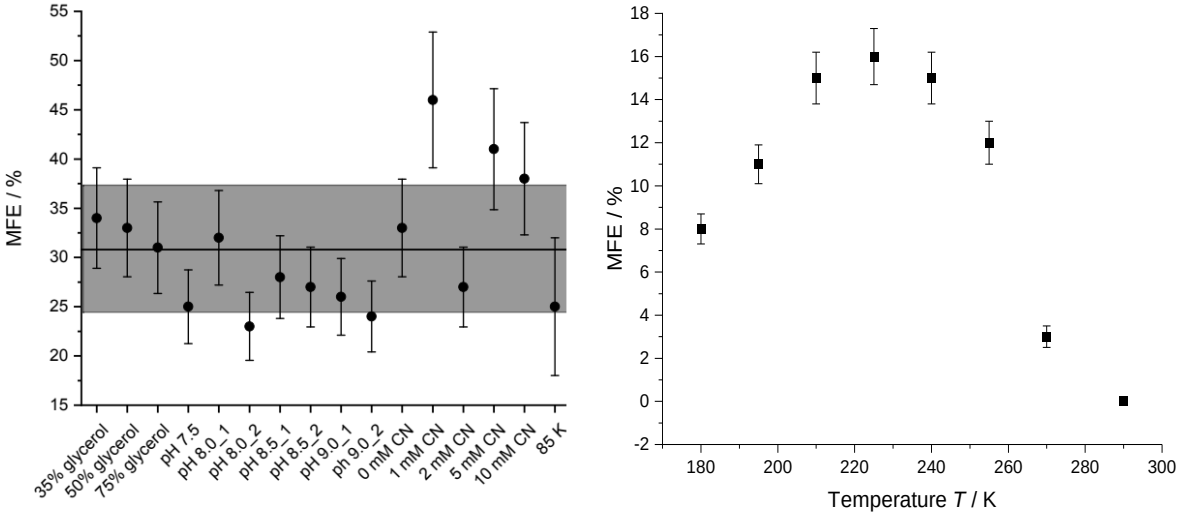


Figure 1. MFE measurements of *Dm*Cry W394F under varied experimental conditions (left side) and *Ec*PL E109A at varied temperatures yet steady buffer conditions (right side).

The ability to modulate flavin photochemistry with magnetic fields in various systems has recently gained significant attention with the advent of quantum-based fluorescent magnetosensors and the rising interest in flavin photocatalysis[3,4]. Our systematic investigation provides crucial insights that will not only enable optimization of experimental techniques, but also facilitate the rational design of more sensitive magnetosensors and efficient photocatalysts. These advances have potential applications spanning from biophysics to quantum sensing technologies, establishing a foundation for novel approaches in fields where precise magnetic field detection and control are paramount.

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**Acknowledgments**: The authors are indebted to Christine Disch and Patricia Stehle for assistance with large-scale protein production for spectroscopic investigations.

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# Mechanistic Insight into the Photocatalytic Deoxygenation of N–O Bonds Using [Re(CO)$_3$bpyCl] Photocatalyst

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The development of selective new methods for the deoxygenation of N–O bonds is critical for reducing harmful nitrogen oxide (especially $N_2O$) emissions and synthesizing nitrogen-containing heterocycles, important in pharmaceutical and fine chemical industries. Traditional deoxygenating methods have been relying on hazardous reagents, and often display poor selectivity and low atom economy. A specificity of N–O bonds is that they can spread over a wide range of redox potentials: from +1.77 to -1.04 V vs. SHE for N2O and pyridine N-oxide respectively. New photocatalytic methods have however recently been developed [1,2] that enable the selective deoxygenation of both substrates.
In this study, we investigate the key mechanistic steps of the photocatalytic deoxygenation of nitrous oxide ($N_2O$), a significant greenhouse gas, and pyridine N-oxide (PNO), an important intermediate in pharmaceutical synthesis, using rhenium(I) tricarbonyl bipyridine complex, [ReI(bpy)(CO)$_3$Cl] (Re-Cl), in the presence of a sacrificial electron donor (DIPEA). Optimization of the reaction conditions revealed that the addition of water (3 M) enhances catalytic efficiency, particularly for PNO reduction, suggesting a crucial role of proton availability in facilitating N–O bond cleavage.

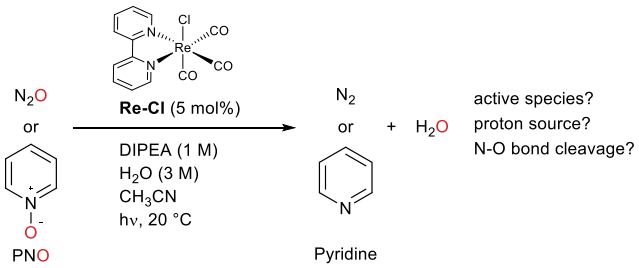


Figure 1. Nitrous oxide ($N_2O$) and pyridine *N*-oxide (PNO) photocatalytic deoxygenation using rhenium tricarbonyl bipyridine complexes (**Re-Cl**) as catalyst and diisopropylethylamine (DIPEA) as sacrificial electron donor.

Through a combination of techniques such as nanosecond transient absorption spectroscopy, NMR, infrared spectroscopy, and density functional theory (DFT) calculations, we elucidate the mechanism of this photocatalytic transformation.[3] The reaction is initiated by photoexcitation of the Re-Cl complex, followed by reductive quenching by DIPEA, generating the singly reduced species (1ERS), which serves as the catalytically active species. The deoxygenation mechanism proceeds via proton-assisted N–O bond cleavage, forming a metal-hydroxo intermediate. The rate-limiting step is identified as the electron transfer to the substrate. The presence of water facilitates proton transfers and ligand exchanges during PNO photodeoxygenation but has no significant impact on $N_2O$ reduction

**Funding:** National Research Agency (ANR), PRC Grant no ANR-22-CE07-0028

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# *Ab initio* photochemical reaction modeling of the relaxation of $S_1$ photoexcited azobenzene to the ground state using RRK theory

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Simulation of the time-evolution of photoexcited electronic states using quantum chemistry is generally associated with high computational costs. This is a consequence of the underlying electronic structure theory in interplay with approximated dynamics. For a statistically significant result multiple trajectories need to be considered further increasing the computational cost. Moreover, the analysis of the data from dynamics simulations requires refined techniques and can be cumbersome.

In ground state chemistry, an alternative approach for simulating reaction dynamics is the via microkinetic modeling. In such models, critical points on the potential energy surface (PES) are used to determine kinetical parameters for elementary reaction steps. These can then be used in a kinetic model to determine the overall time-evolution, which provides an intuitive interpretation and a direct conversion to reaction formulas. We are interested to transfer this approach to photochemical reactions. The model is based on the Rice-Rampsberger-Kassel theory[1] and adapted for systems with an initial excess energy.

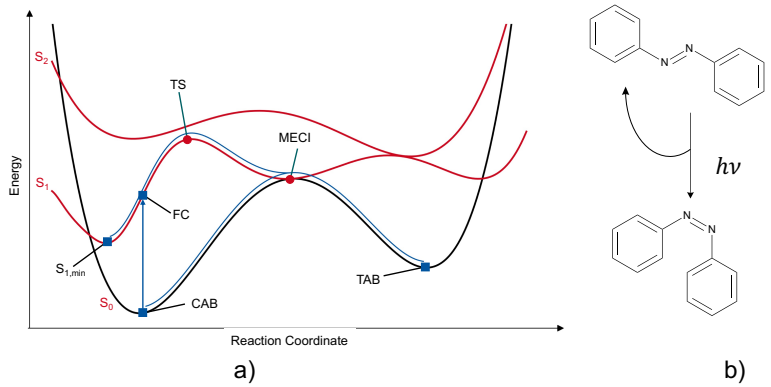


Figure 1. a) Schematic overview of the PES of azobenzene. Possible transition routes are given in blue. b) Photochemical reaction of CAB to TAB or a relaxation to CAB.

To study applicability, a test system is necessary. Cis-azobenzene (CAB) can undergo a photoisomerization to trans-azobenzene (TAB) when being excited to the $S_1$ state. To achieve this, different routes are possible. The excited CAB can surpass a transition state (TS) to arrive at a minimum energy conical intersection (MECI) from which relaxation to either CAB or TAB can take place. Likewise, a non-reactive MECI can be reached that, directly, yields back the ground state CAB. In this work, the relaxation of the $S_1$ state to the ground state considering these different pathways of the azobenzene is investigated with a kinetic model. For comparison, *ab initio* multiple spawning simulations with the same electronic structure theory was used.[2] We report a relaxation on the same time scale as the AIMS simulation and a comparable ratio of the relaxation routes. Additionally, same similar ground state ratio of TAB and CAB could be achieved.

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# $^{15}$N-labeling of Donor-Acceptor-Dyads for Investigations of the Magnetic Field Dependent Spin Interconversion

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In an external magnetic field, the triplet levels of charge-separated states are split up due to the *Zeeman* effect, leading to field dependent spin-interconversion and recombination rates (figure 1A). One main driving force behind the spin interconversion in these systems is the hyperfine interaction between radical electrons and the nuclei.[1, 2]

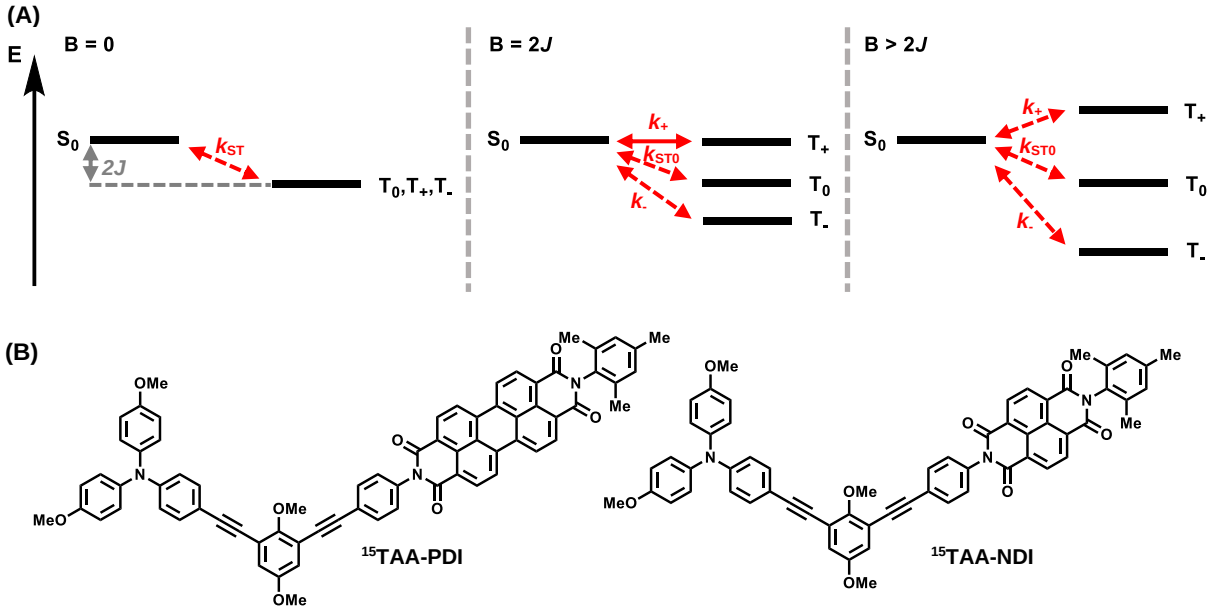


Figure 1. Magnetic field dependency of spin interconversion resulting from *Zeeman*-splitting in an external magnetic field **(A)** and investigated $^{15}$N-labeled compounds **(B)**.

Therefore, the $^{14}$N isotope in the triarylamine donor of literature known dyads was replaced by the $^{15}$N isotope to study the resulting effects on spin interconversion (figure 1B) .[3, 4] This was achieved by transient spectroscopy experiments in a tunable external magnetic field, followed by rate fitting to simulate the experimental data to gain insights into the spin dynamics.

**Funding:** This work was funded by the Deutsche Forschungsgemeinschaft (La 991/20-1)

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# Effect of the Substitution Groups On the Excited-state Dynamics of Oxindole-based Photoswiches Revealed by Ultrafast Spectroscopies

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The E-Z photo-isomerization of a C=C bond is the central mechanism present in a variety of nature-inspired synthetic photo-switches and photo-motors currently under development [1]. Using the example of oxindole-based photo-switches, we recently demonstrated that the quantum yield of switching ($\Phi_{ISO}$) could be modified by adding electron-donating groups to the chromophore [2]. In a follow-up investigation, we aim to discover how these substitution groups influence the excited-state dynamics, ultimately revealing the causality between chemical modification and photo-switching behavior, paving the way for a unified theoretical guide for designing molecular photo-switches. We present four variants of oxindole-based switches, differing in the substitution group (-$NO_2$, -$CF_3$, -H and -OH) at the para position of the benzene ring (Figure 1 a). Their $\Phi_{ISO}$ increases with the electron-donating strength ($\sigma_p$ value). Transient absorption (TAS) and femtosecond fluorescence upconversion (FLUPS) experiments were conducted. No correlation was found between $\sigma_p$ and kinetics, whereas in a similar study on another C=C bond based photoswitch, such correlation was well established [3]. However, the substitution groups have induced significant changes in the excited state lifetimes, notably the variants with –H and with –$CF_3$ groups experiencing a much slower decay (Figure 1 b). The quantitative analysis revealed that in addition to the sub 2 ps fluorescence lifetimes, a new distinct fluorescence lifetime up to 30 ps has appeared in the variants with –H and with -$CF_3$. This indicates that substitutions can not only alter the energy gap between $S_0$ and $S_1$, but also create a new local minimum on the potential energy surface before the conical intersection. In previous studies, such a local minimum, featured by red-shifted weak emission, has been referred to as 'phantom state' [3]. Our current work aims at exploring the tunability of this phantom state and its role in photoswitch design.

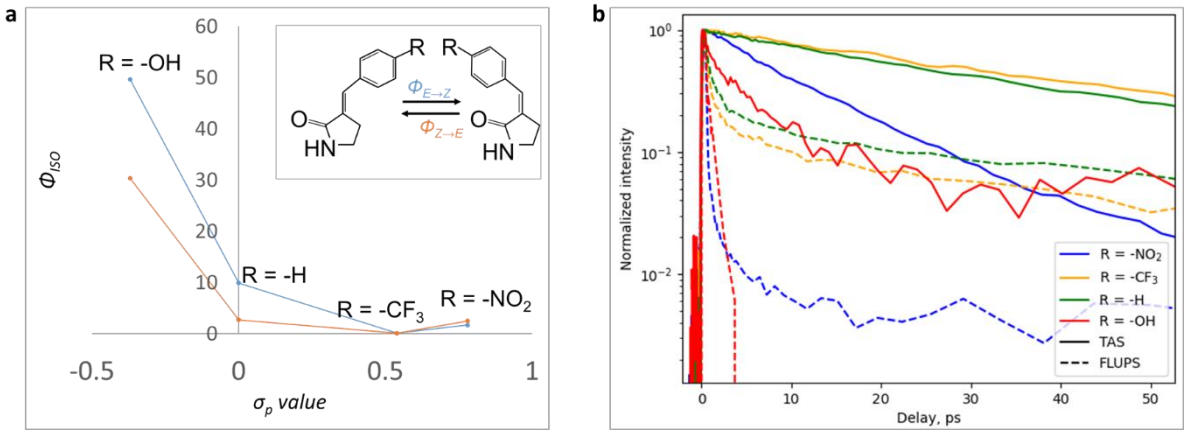


Figure 1. a. Four oxindole-based photoswitches and their $\Phi_{ISO}$; b. Kinetic traces of the excited-state decay taken at the maximum signal wavelength from TAS and FLUPS experiments.

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# Magnetic field dependent fluorescence in donor-acceptor-dyads

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Thermally activated delayed fluorescence in donor-acceptor-compounds can be used to construct highly efficient OLEDs.[1] By increasing the distance between both moieties electron transfer towards long lived charge separated states can be achieved, giving rise to a magnetic field dependent delayed fluorescence after endothermic charge recombination.[2] The excited state dynamics were studied by stationary and transient (fs to ns) spectroscopic experiments in the presence and absence of an external magnetic field to investigate the underlying electron transfer processes.

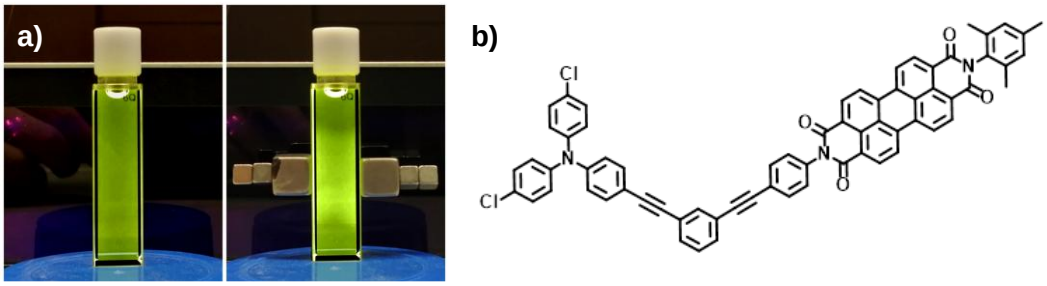


Figure 1. a) Increased fluorescence after application of an external magnetic field (right) caused by several small permanent magnets and fluorescence without an external magnetic field (left) and b) molecular structure of the investigated compound.

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**Acknowledgement:** -

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# Excimer of 1-Methylnaphthalene Originates in Ground State Dimer

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Excimers have been a subject of interest for over 60 years, as they are believed to play a key role in photophysical processes such as singlet fission and triplet–triplet annihilation. Here, we revisit the excimer of 1-methylnaphthalene (1-MeNp) across a range of temperatures (77–350 K) and phases[1]. Fluorescence measurements allow us to distinguish between the crystalline, glassy, and liquid phases (Fig. 1). Furthermore, we elucidate the mechanism of excimer formation for 1-MeNp in neat liquid and concentrated solutions by combining UV–VIS absorption and fluorescence spectroscopy, NMR, femtosecond transient absorption and Raman scattering. We provide unambiguous evidence that the widely accepted mechanism of excimer formation—originally proposed by Kasper and Förster[2] for pyrene—is invalid in the case of 1-MeNp. Instead, we show that a ground-state dimer serves as the precursor to the excimer. While such behavior was previously proposed for pure benzene[3], our study presents the first reported case of this mechanism occurring in solution.

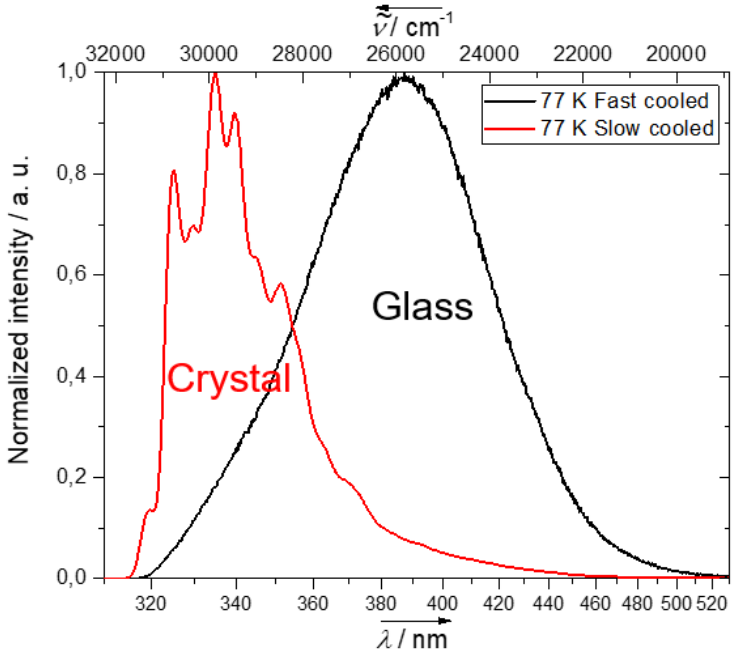


Figure 1. The normalized fluorescence emission spectra ($\lambda_{exc}$ = 274 nm) of crystals formed by slow cooling (red) and glass resulting from fast cooling in methane (black) of 1-MeNp.

**Funding**: ELIUPM4-85, GA25-15358S

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# Photochemical reactions of oxazolones – Insights in the reaction mechanism

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Photochemical intra- and intermolecular electron and hydrogen transfer lead to unusual products using a green chemistry method of organic synthesis.[1,2] Such reactions play an important role in the organic synthesis as they generate heterocycles with a high degree of molecular complexity and diversity which makes them interesting for application to the synthesis of biologically active compounds.

Physicochemical investigations provide a profound understanding of such processes. Our recent research in this domain deals with photo-induced intramolecular hydrogen transfer in oxazolones possessing an imine function (Figure1).[3] Acetale or thioacetale functions on the side chain are hydrogen atom donors. The excitation of the oxazolone to the triplet state occurs by direct light absorption followed by intersystem crossing. Triplet diradical intermediates are formed by hydrogen atom transfer (HAT) from the acetale to the nitrogen atom. We are particularly interested in the regioselectivity of these reactions. After intersystem crossing in the diradical intermediates, the final products are obtained. A (C-C)- or a (C-N)-bond is formed. The regioselectivity is determined in the last step by the intersystem crossing mode [4] and the structure of the singlet state. The rate of the decarboxylation depend on the substitution pattern. The reaction has also been performed using continuous flow conditions.[5]

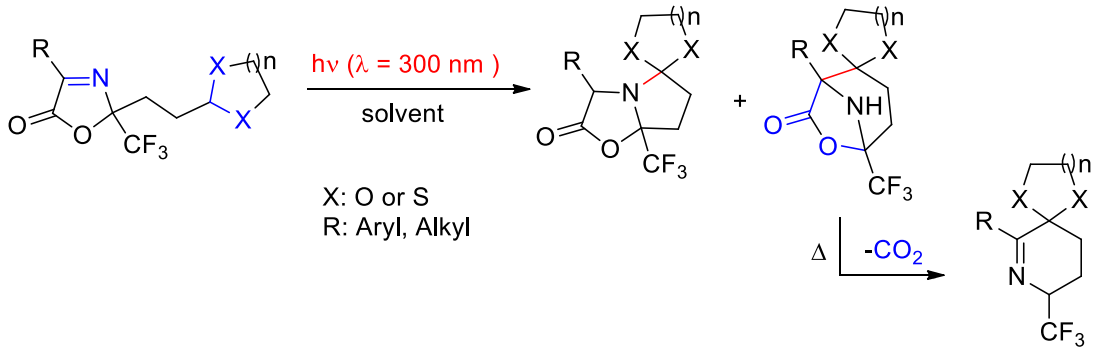


Figure 1. Intramolecular reactions of oxazolones involving photo-chemically induced hydrogen atom transfer.

**Funding:** Agence national de la Recherche **(**ANR, Projet IMPHOCHEM, ANR-18-CE07-0026-02)

**References:**

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# Light in the Garratt–Braverman/[1,5]-H Shift of Ene-diallenes

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Organic chemists have been using computational chemistry to explain experimental results and gain a better understanding of reaction mechanisms for decades. With the wide range of theories and computational methods available, we tend to start with those that we are most familiar with and easily fall into the trap of picking the computational results that fit the experimental ones. For example, while transition state theory (TST) has been widely used to estimate reaction rates and product ratios, it is not sufficient for some reactions, such as the hydroboration of alkenes, where experimentally observed Markovnikov product ratio is higher compared to the TST prediction.[1,2] These reactions are often labeled as nonstatistical reactions. The failure of TST serves as a warning of the potential pitfalls of the conventional free energy diagram. As a team of synthetic and computational chemists, in this presentation, we revisit a reported nonstatistical reaction, Garratt-Braverman (GB)/[1,5]-H shift of ene-diallenes leading to *Z*/*E* alkenes[3] using combine experimental and computational approaches (Fig. 1). Unexpected reaction under UV light was observed experimentally and the photoreaction pass way was examined by computational method. We explain how to use modern and freely available computational chemistry tools to guide experiments design during the synthesis process, rather than merely serving as complementary data for finished experimental studies.

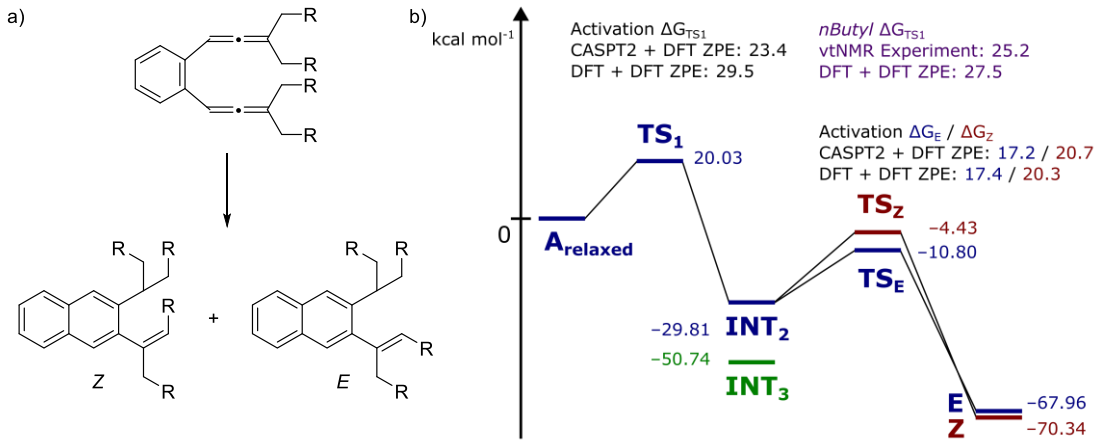


Figure 1. a) General scheme of GB/[1,5]-H shift of ene-diallenes; b) CASPT2 ground state electronic energies of key structures on the DFT reaction path.

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# Janus-Type Photophysics of Rotational Isomers in a Diphenylanthracene Dimer

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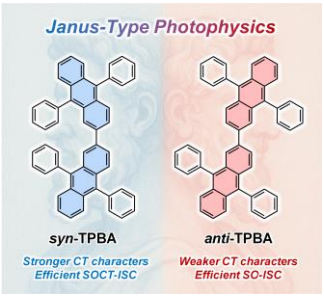


Figure 1. **TPBA** demonstrates Janus-type photophysics of rotational isomers, highlighting different types of exciton coupling, charge transfer characteristics, and triplet formation mechanisms.

Interchromophore interactions in organic semiconductors play a pivotal role in manipulating photophysical processes. Molecular dimers, as simple models for these interactions, enable controlled studies of electronic coupling through linker and connectivity variations. However, their structural flexibility introduces conformational isomers with comparable energies[1,2], leading to diverse exciton couplings due to distinct transition dipole interactions[3,4]. Here, we report the Janus-type photophysics of rotational isomers in a directly linked diphenylanthracene dimer, 9,9'10,10'-tetraphenyl-2,2'-bianthracene (**TPBA**). The ***syn***- and ***anti***-**TPBA** isomers exhibit contrasting electronic properties. Quantum mechanical calculations reveal opposing short-range charge transfer (CT) couplings. Excitation-wavelength-dependent spectroscopy shows stronger CT in ***syn***-**TPBA** and enhanced radiative behavior in ***anti***-**TPBA**. Additionally, transient electron paramagnetic resonance (trEPR) and transient absorption spectroscopy reveal distinct triplet exciton spin polarization patterns, highlighting different triplet formation pathways. Overall, our findings underscore the profound influence of conformational isomerism on the photophysical landscape of organic molecular systems.

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# The Addition of Photoexcited Nitroarenes to Alkenes traced by Femtosecond Spectroscopy

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The addition of photoexcited nitroarenes to alkenes has recently gathered considerable attention in organic synthesis. It was initially applied to the oxidative cleavage of alkenes [1,2] as an alternative to ozonolysis but has also been used to access a plethora of other, valuable compound classes.[3-5] Mechanistic details on the initial photoaddition are however heretofore unknown. Here, femtosecond UV/VIS and IR absorption spectroscopy together with quantum chemical computations are used to investigate the kinetics and intermediates for an exemplary pair of nitroarene (4-cyanonitrobenzene (4CNNB)) and alkene (cyclooctene (cyO)). The triplet state of 4CNNB is shown to be quenched by cyO with a bimolecular rate constant of $6 \cdot 10^9$ $M^{-1}$ $s^{-1}$. Quenching goes along with the formation of a transient species persisting for ca. 1 ns. Femtosecond IR spectroscopy gives strong evidence for the triplet biradical character of this intermediate (for structure see Fig. 1).[1,2] It is shown, that only 10% of the quenching events result in product formation while the rest reform the starting material, thus severely diminishing the energetic efficiency. We attribute the loss channel either to triplet energy transfer to the alkene or to an unproductive decay of the biradical intermediate.

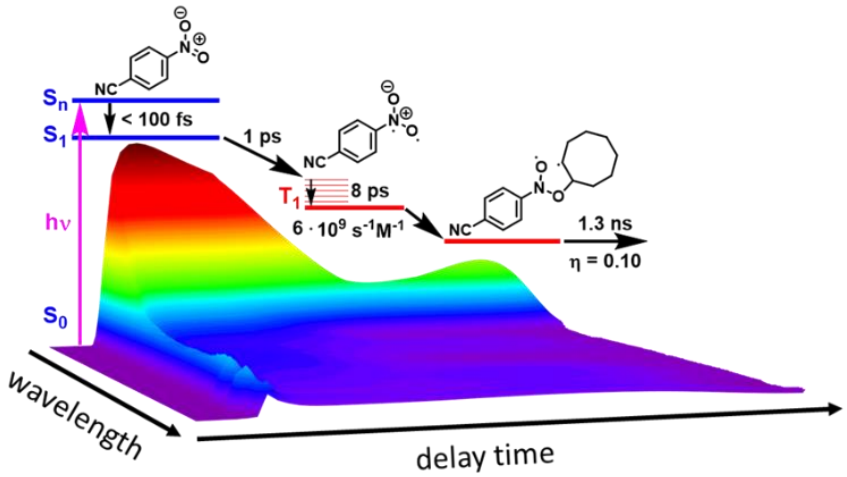


Figure 1. Femtosecond UV/VIS absorption and kinetic scheme of the processes and intermediates involved in the addition of photoexcited 4CNNB to cyclooctene in MeCN.

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# Photo-induced electron transfer in [FeFe] hydrogenases studied by multiscale time resolved infrared spectroscopy

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Hydrogenases are metalloenzymes catalyzing the reversible cleavage of $H_2$, which is of interest for its potential utilization as a clean and sustainable fuel. IR spectroscopy proved to be a powerful technique for investigating all redox-structural states of hydrogenases, due to the presence IR-active and structurally sensitive bond-stretching vibrations of CO and $CN^-$ ligands at their active sites.[1] [FeFe] hydrogenases form the most efficient subclass of hydrogenases, but despite extensive research, their catalytic mechanism is not fully understood. One of the key limitations is that studying elementary catalytic steps in real time and under representative conditions is experimentally challenging, due to fast reaction steps and processes over multiple timescales.

In the current study, we have employed $UV_{pump}$-$IR_{probe}$ spectroscopy with a multi-probe pulse delay scheme that allows covering picosecond to millisecond timescales in a single timer-resolved (TR) experiment.[2] This way, we could follow reaction steps of hydrogenases over all relevant timescales. As a model system, we have utilized the [FeFe] hydrogenase from *Desulfovibrio desulfuricans* (*Dd*HydAB) in its inactive $CN^-$-inhibited state, $H_{trans}$-like. Although not belonging to the catalytic cycle, $H_{trans}$-like is an interesting target due to its oxygen stability and potential light sensitivity.[3] Furthermore, its structural and spectral features are still not fully resolved, which creates additional motivation for its investigation. During the experiment, the light-triggered transformation of $H_{trans}$-like was initiated with a UV pump pulse, and a sequence of IR probe pulses was used to record the structural changes of the enzyme. As a result, the previously unknown photochemical formation of the one-electron reduced state, $H_{inact}$-like, was observed on the picosecond timescale. This process, which is reversible on the nanosecond timescale, is notable for involving light-driven electron transfer beyond the H-cluster active site of the enzyme. While reminiscent of a recently reported process in [NiFe] hydrogenases,[4] the current study represents the first investigation of light-driven electron transfer in a metalloenzyme in real time and at ambient temperature, to the best of our knowledge. Besides the photo process, picosecond-timescale vibrational dynamics was studied, which among others provides additional insights into the structure of the $H_{trans}$-like state. In particular, two unresolved vibrational modes were distinguished by different vibrational lifetimes, thereby laying a foundation for their assignment and structural interpretation. Complementary analyses of vibrational dynamics of other states of [FeFe] hydrogenases have yielded similar insights. Overall, the study demonstrates the variety of photophysical and photochemical processes in [FeFe] hydrogenases and the advantages of applying multiscale time-resolved methods for investigating single catalytic steps.

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# Illuminating Single- and Multi-Branched Donor–Acceptor Systems with Multidimensional Spectroscopies: Intrinsic Asymmetry, Torsional Disorder and their Redox Dependence

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We are investigating Donor–Acceptor (D–A) and Donor–Acceptor–Donor (D–A–D) systems linked via acetylene bridges. Starting from fluorenone acceptor-based D–A–D systems,[1] we focus on the corresponding single-branched D–A counterparts with 4-N$R_2$-phenyl donor units, studying the influence of the alkyl chain length on the excited-state dynamics and spectral properties. In a second step, we expand the scope of D–A molecules by introducing different donor chromophores with intrinsic asymmetry, whilst completing the survey by varying the acceptor core (Figure 1).

Using time-resolved infrared spectroscopy (TRIR) as well as transient electronic absorption spectroscopy (TA), we explore the surprisingly complex behaviour of single-branched D–A systems in the excited state, as a function of both solvent polarity and the identities of donor and acceptor. This approach helps us to understand the role of the involved moieties, whilst comparing the results with those obtained for the symmetric D–A–D molecules, where symmetry breaking takes place.

The presence of the acetylene bridges leads to a wide distribution of dihedral angles between the donor and acceptor planes in the ground state. In the excited state, however, the rotational barrier is significantly increased.[2] In the phenyl-substituted molecules, rotation around the C-C bond produces a symmetric modulation of the conjugation of the system, whilst in the novel naphthyl-substituted molecules this modulation is asymmetric. This in turn gives rise to increased differences in both the electronic absorption spectra and the observed dynamics as a function of the D–A torsion angle (θ). Transient two-dimensional infrared (t2DIR) spectroscopy is uniquely suited to study this phenomenon, in combination with excitation wavelength dependence studies.

Furthermore, we explore the effects of electrochemically reducing or oxidising suitable D–A and D–A–D molecules. These spectroelectrochemical (SEC) investigations allow us to determine the influence of single-electron transfer upon the excited state behaviour, as well as its potential to induce or inhibit symmetry breaking in both ground and excited states in case of the D–A–D systems—akin to inorganic mixed-valence complexes.

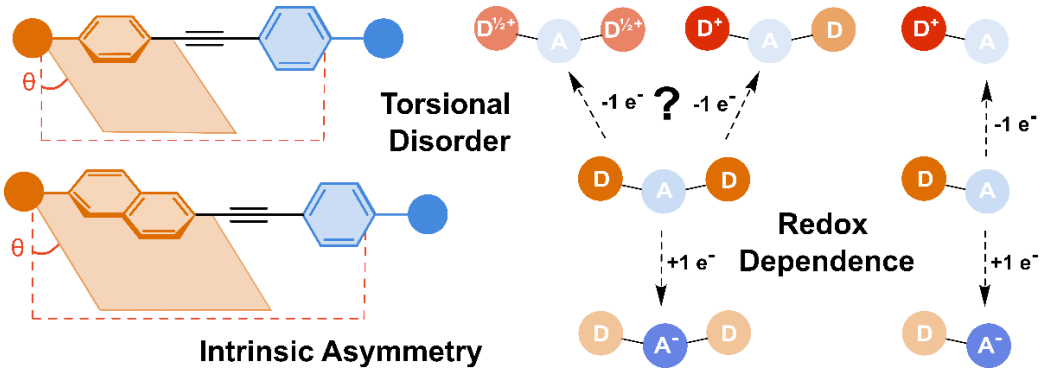


Figure 1. Intrinsic Asymmetry and Torsional Disorder of Single- and Multi-Branched Donor–Acceptor Systems and their Redox Dependence.

**Funding:** Swiss National Science Foundation, Ambizione grant PZ00P2-216249.

**Acknowledgement:** We warmly thank Prof. Dr. Eric Vauthey for hosting our research group and for helpful discussions.

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# Early Time Photophysics of Atomically Precise Gold Nanoclusters

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Atomically precise metal nanoclusters (NCs) have molecule-like behavior instead of metal-like. [1] They even emit luminescence although showing several uncommon properties: excitation dependent emission, ns-µs long luminescence decay and non-Kasha emission. The scarcity of detailed studies and accurate analysis of the measurement data has been the driving force for this research work. We intend to find an accurate description of the states involved in this exotic behavior.

Transient absorption data with sub-picosecond time resolution, collected under different conditions show that the early dynamics of the Ncs after electronic excitation are much faster than what can be observed by slower means. Moreover, the initially excited Franck-Condon state vanishes in less than 20 ps.

In view of these observations, a hypothesis about the photophysical behavior of NCs will be presented.

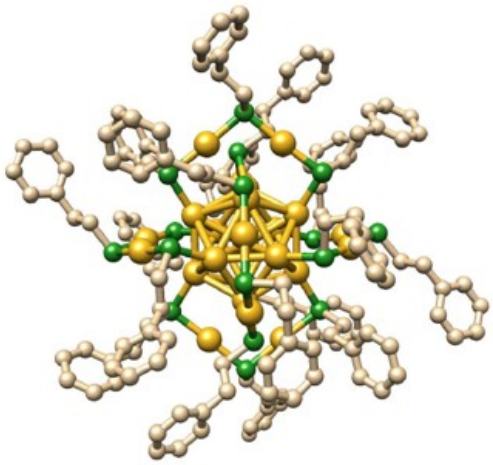

Figure 1. $Au_{25}$(2-phenylethanethiol)$_{18}$
Au: gold, S: green, C: beige.

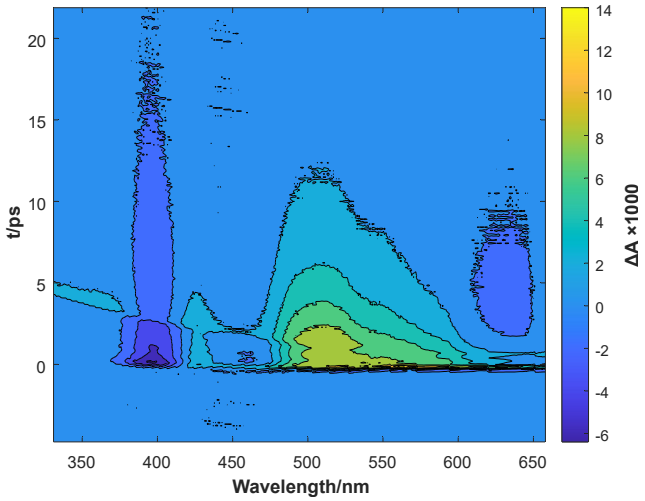


Figure 2. $Au_{25}(PET)_{18}$ in dichloromethane:
TA data with excitation wavelength 690nm

**Funding**: Financial support by Narodowe Centrum Nauki, grant OPUS LAP 22 2021/43/I/ST4/01411.

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# Towards Understanding the Mechanism of Magnetoluminescence in Triarylmethyl-Based Diradicals

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Interest in luminescent stable radicals has been growing steadily due to their unique electronic configurations and long-lived excited states. The emissive properties of open-shell molecules can be finely tuned through deliberate molecular design strategies[1,2]. Recently, the ability to modulate luminescence using magnetic fields—known as magnetoluminescence—has garnered significant attention, as it paves the way for advancements in high-resolution optical imaging and future quantum information technologies [3]. A notable example is a diradical composed of two luminescent (2-chloro-3-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical units connected by a 5,6,8,9-tetrahydro-7-phenyldibenz[c,h]acridine (THDBA) linker (see Figure 1). This system represents the first organic radical-based material where magnetoluminescence emerges intrinsically at the molecular level [4], likely due to the formation of excimer-like excited states. In this study, we present the results of time-dependent density functional theory (TDDFT) and correlated wavefunction method calculations performed to elucidate the electronic structure of the emissive states of the diradical and its components (monoradical and isolated radical). Our findings offer valuable insights into the mechanisms underpinning magnetoluminescence in diradical systems, providing a stronger foundation for future developments in this field.

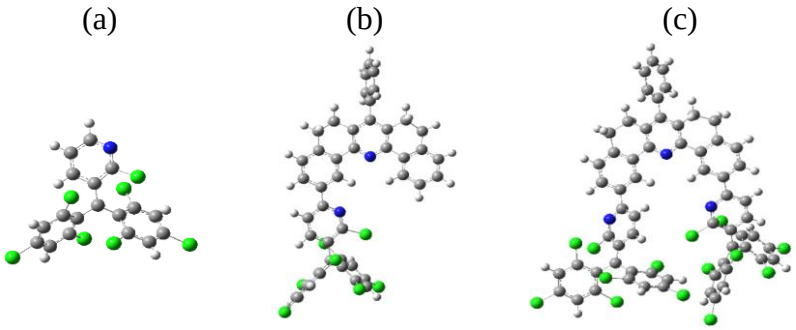


Figure 1. Derivatives of Triarylmethyl-Based Diradicals. (a) isolated radical, (b) monoradical, (c) diradical.

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# Ultrafast Charge Transfer Dynamics in Excited-state Donor-acceptor Benzylideneaniline

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Imine-based molecular systems have served as promising semi-conductive materials for applications in light-emitting diodes and photovoltaics. Benzylideneaniline, an imine-based molecular system, acts as a bioisostere of diarylethylenes such as stilbene and resveratrol, and plays a crucial role in pharmaceutical and biological applications. However, excited-state dynamics of benzylideneanilines is less explored.[1,2] In this context, we investigated 4'-(Dimethylamino)benzylidene-4-nitroaniline (DMABNA), an imine-based donor-acceptor system, to unravel the excited-state dynamics. Here, we explored excited-state charge transfer dynamics and associated structural dynamics in various solvent environments through femtosecond transient absorption (fs-TA) and femtosecond fluorescence spectroscopic methods. The fs-TA measurements revealed distinct spectral and temporal features from cyclohexane (CHX) to acetonitrile (MeCN) indicating that DMABNA essentially undergoes significant configurational changes in the excited state, leading to intramolecular charge transfer (ICT), particularly in polar environments. The fs-Fluorescence measurements reveal ultrashort lifetime (a few ps) of fluorescence across all the solvents indicating an effective non-radiative relaxation in the excited electronic state. These studies are corroborated by the computational analysis through DFT and TDDFT methods, wherein we predicted that DMABNA undergoes significant structural changes in the excited state (S1) for varying solvent polarity and viscosity. Such excited state molecular activity can play a significant role in the context of photo-initiated applications.[3] The schematic representation of the potential energy profiles of DMABNA in non-polar and polar solvents is shown in Fig 1.

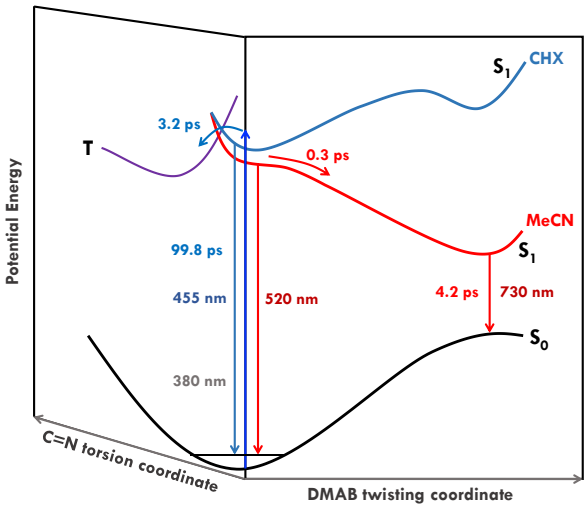


Figure 1. Schematic potential energy diagram of the excited state dynamics of DMABNA in CHX and MeCN.

**Funding:** CRG grant (CRG/2020/000321) of the Science and Engineering Research Board (SERB), India.

**Acknowledgement:** We sincerely acknowledge Dr. Y. Adithya Lakshmanna for his guidance and support throughout this work. We are grateful to IISER Thiruvananthapuram for the fellowship support and for providing access to all research facilities.

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# An unexpected way to boost Type I photoinitiator reactivity: singlet-singlet energy transfer

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Introduction of a fluorophore in an acrylate polymerizable resin containing a Type I phosphine oxide photoinitiator resulted in an unexpected and significant increase in the photopolymerization kinetics. RT-FTIR measurements revealed high rates of polymerization for this system, under low irradiance (1 mW/cm$^2$, 365 nm). For low fluorophore concentrations, a three-fold increase in the reactivity of the photoinitiating system was reached. Fluorescence study showed that the specific interaction between the two components occurred from the singlet excited state of the fluorophore, and was attributed to a Förster resonance energy transfer (FRET). The photosensitizer, having excellent absorption properties, thus opens a new pathway of excitation of the photoinitiator. Using the Förster resonant energy transfer model, the efficiency of this new excitation channel was calculated, allowing to model the increase in initiating radicals upon addition of the fluorophore in the polymerizable resin. This latter quantity was then successfully correlated to the experimental maximal rates of polymerization. This approach opens new possibilities for the maximization of photoinitiating systems efficiency.

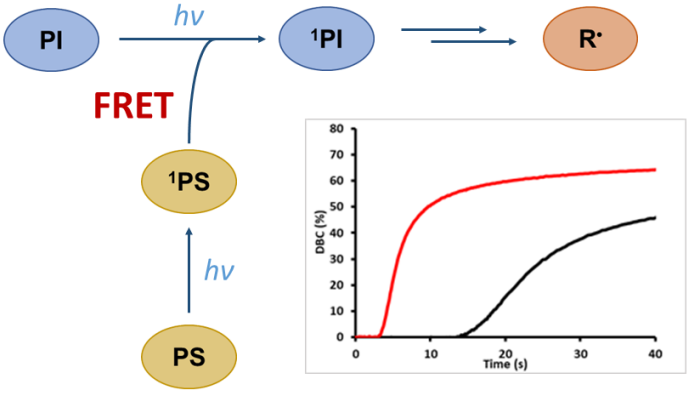


Figure 1. Mechanism of photosensitization relying on a Förster resonance energy transfer (FRET), resulting in an increase of the kinetics of polymerization.

**Funding:** Région Grand-Est (Photosafe).

# Substituent Effects on the Photochemistry of Sulfoxide-Bridged Anthracenes

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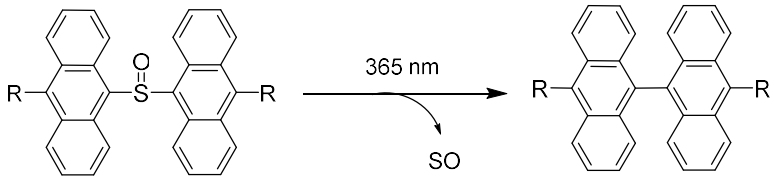
Fluorescent dyes with complex and tunable photochemical behavior are of growing interest for anti-counterfeiting applications. Sulfoxide-bridged anthracene dimers are known to undergo rapid light-induced photoconversion via SO extrusion to yield 9,9'-bianthracenes.[1,2] In this study, we explore how structural modifications at the 10, 10'-positions, specifically electron-donating and electron-withdrawing groups, as well as extended conjugation through oligothiophene chains (Fig. 1), affect the photochemical and photophysical properties of dianthryl sulfoxides.

A series of dianthryl sulfoxide derivatives were synthesized and characterized using $^1$H NMR, IR, UV-Vis absorption, and emission spectroscopy. The photophysical and photochemical properties were analyzed by evaluating the absorption and emission profiles, photoluminescence quantum yield (PLQY) and the relative rates of photoconversion. While substituents did not exhibit a clear correlation between electronic effects and photochemical efficiency, extended conjugation led to red-shifted emission, varying SO extrusion rates, and emission intensities.

These findings demonstrate how targeted molecular modifications can be used to tune the performance of the photoresponsive system, contributing to the design of customizable organic materials for optoelectronic and anti-counterfeiting technologies.




R= H, F, Br, Cl, $CH_3$, $OCH_3$, $NO_2$, CN

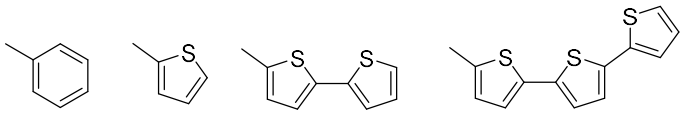



Figure 1. Structure of dianthryl sulfoxide and the photoextrusion reaction under UV light.

**Funding:** Natural Sciences and Engineering Research Council of Canada

**Acknowledgement:** We thank Dr. Saeid Kamal at the Laboratory for Advanced Spectroscopy and Imaging Research (LASIR) for his help with PL lifetime measurements and access to photophysical instrumentations.

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# Structural Dynamics of Photo-functional Metal Complexes Studied by Time-resolved XAFS

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A detailed understanding of photoexcitation-induced changes in electronic states and associated structural changes is important for the design of the next generation of photo-functional materials. In this study, time-resolved XAFS measurements using synchrotron radiation were performed to investigate the electronic states and molecular structures of metal complexes in the photo-excited states in detail. The target metal complexes are known to exhibit ultrafast and large changes in physical properties upon photoexcitation due to the strong correlation between anisotropic localized orbital electrons and molecular structure. The purpose of this study is to clarify the origin of these phenomena and to obtain guidelines for the development of new materials.

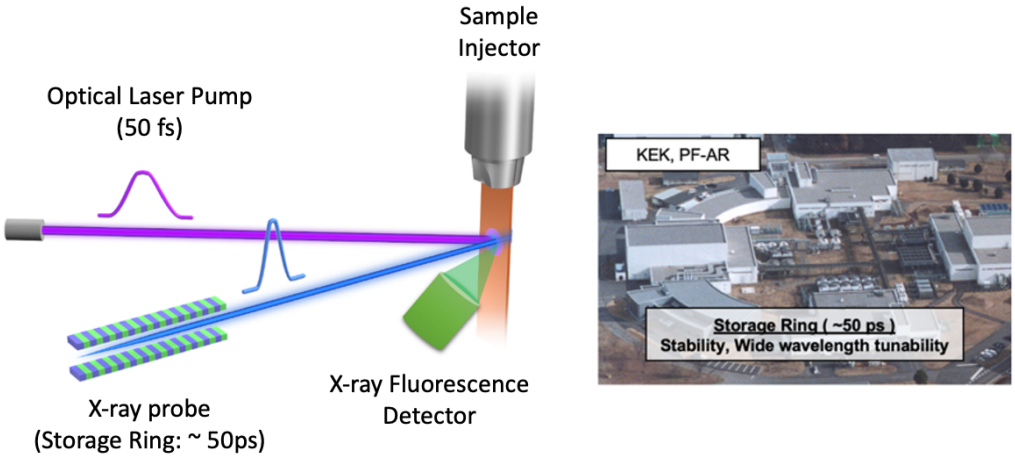


Figure 1. Schematic of time-resolved XAFS measurement using synchrotron radiation X-rays

Synchrotron radiation, which can provide hard X-rays with a wide energy range and high frequency, is a very suitable light source for time-resolved XAFS because the high signal-to-noise ratio for weak transient signals can be obtained by detecting photo modulation components with high frequency [1-4]. In this study, metal complex molecules in solution were excited by a high repetition rate laser pulse of 400 kHz, and their photo modulation components were measured. As a result, we succeeded in visualizing transient electronic state changes from spectral changes in the XANES region and molecular structures of excited states at the atomic level from vibrational modulations in the EXAFS region. In the talk, this photoreaction process will be explained in detail.

**Funding:** JST-CREST (JPMJCR20R2), JSPS (21H04974)

**Acknowledgement:** Time-resolved XAFS experiments were performed with the approval of the Photon Factory Program Advisory Committee (Proposal No. 2024G101)

**References:**

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# Photoinduced Electron Transfer in Bilirubin Model - Oxygen Complex

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This study was motivated by an ongoing collaboration with the research group of Prof. Klán at Masaryk University (Brno), which is aimed at elucidating the details of bilirubin photochemistry. In this context, I investigated the photoinduced electron transfer from the excited state of a bilirubin model compound, tetramethyldipyrrinone, to molecular oxygen. Although this step is proposed as the initiating event in bilirubin's photooxidation pathway, direct mechanistic evidence remains scarce.[1] I explored the reaction by calculating the binding energy of oxygen to tetramethyldipyrrinone and mapping the potential energy surfaces using a range of methods, including time-dependent and constrained density functional theory, multireference approaches, and semiempirical techniques. I also implemented and applied nonadiabatic dynamics with Landau–Zener surface hopping algorithm in combination with time-dependent density functional theory. The results provided strong evidence for electron transfer, with a located crossing between the excited state of tetramethyldipyrrinone and the electron-transfer state, and electron transfer occurring in about half of the simulated trajectories on a femtosecond timescale, indicating that the process is both feasible and ultrafast.

Funding: Czech Science Foundation (23-07066S and 24-11466S)

**References:**

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# Breaking Kasha's rule to unlock higher excited state reactivity in photoredox catalysis

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Kasha's rule has long shaped our understanding of excited-state reactivity by dictating that photochemical reactions occur only from the lowest electronically excited state. This constraint stems from the ultrafast relaxation of higher excited states, which prevents productive reactivity, particularly because diffusion-based bimolecular processes typically require excited-state lifetimes on the nanosecond timescale (Figure 1a). Together, these limitations have, until now, restricted the design of photochemical mechanisms, the scope of reactions, and the design of photocatalysts.[1]

We challenge this foundational principle by demonstrating, using time-resolved laser spectroscopy, that the 4,4"-dicyano-*p*-terphenyl radical anion can undergo photoinduced electron transfer directly from a higher-energy excited state, facilitating reactivity that is inaccessible from the lowest excited state (Figure 1b). The radical-π interaction enables pre-association with the substrate,[2] and careful driving-force optimization is critical for overcoming the kinetic barrier to sub-nanosecond electron transfer. This enables bimolecular anti-Kasha reactivity for the first time, offering a novel pathway for photoredox catalysis.[3]

Extending this strategy to Fe(II) chromophores, we addressed the fundamental challenge that ultrafast deactivation to lower-lying metal-centered (MC) states typically quenches the photoactive metal-to-ligand charge transfer (MLCT) states. Through a novel ligand design for first-row transition metal complexes, we developed Fe(II) pyridinium complexes with a 3 ps MLCT excited state lifetime before decaying to the $^3$MC excited state. To exploit this short-lived excited state for productive photochemistry, substrate pre-association is essential. We employed micellar solutions with an anionic surface to localize the hydrophobic dicationic Fe(II) chromophore within the micelle (Figure 1c). The negatively charged surface simultaneously attracts the hydrophilic dicationic methyl viologen, a classical electron acceptor, bringing both species into proximity. This pre-association enables ultrafast photoinduced electron transfer directly from the higher-lying MLCT state.[4]

This advance establishes a general and broadly applicable framework for bypassing one of the most fundamental principles of photochemistry, Kasha's rule, and opens new possibilities in photoredox catalysis and photocatalyst design by rethinking the energetic and kinetic landscape.

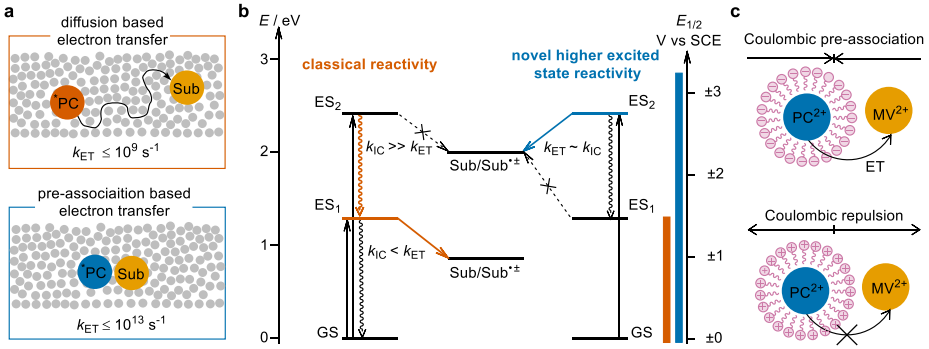


Figure 1. a) Diffusion-controlled versus pre-association-based electron transfer (ET) kinetics. b) Energy diagrams showing classical Kasha reactivity (orange), where internal conversion ($k_{IC}$) to the lowest excited state ($ES_1$) suppresses higher-state reactivity ($ES_2$), and anti-Kasha reactivity (blue), where pre-association enables competitive ET from higher excited states. c) Pre-association-driven photoinduced ET using micellar supramolecular structures.

**Funding:** Swiss National Science Foundation (P500PN_225730).

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# The Mechanistic Process of Catalyst Degradation on RuPt-Based Photochemical Molecular Devices: From Theoretical Perspective

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In recent years, mimicking natural photosynthesis through artificial photocatalysis has become a major research focus, with the ultimate goal of reducing fossil fuel use by efficiently harnessing solar energy[1]. To scale up molecular photocatalysis from laboratory experiments to industrial applications, addressing the instability of catalysts during light-driven operations is crucial[1]. Since many noble metal-based catalytic centers (such as Pt and Pd) tend to form nanoparticles during (photo)catalysis, shifting the process from homogeneous to heterogeneous, understanding the factors that influence nanoparticle formation is critical[2]. One important factor is the selection of bridging ligands. This study, therefore, aims to explore the degradation mechanism of platinum catalysts in Photochemical Molecular Devices (PMD). We will investigate the degradation of halogen ligands in $[(tbbpy)_2Ru(p(ph)p)PtX_2]$ (X = Cl and I)[3] using a combination of density functional theory (DFT) and time-dependent density functional theory (TD-DFT). Understanding this mechanism from a theoretical perspective could provide a foundation for selecting bridging ligands that prevent nanoparticle formation in photocatalytic processes.

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# In-situ measurement cell integrated into photocatalytic setup for automated exploration of photocatalytic reactions

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Photocatalytic water splitting is a promising approach for sustainable hydrogen production. Nevertheless, progress towards applicable systems is hindered by challenging reproducibility of photocatalytic experiments and limited access to data that provides mechanistic insight. To develop more efficient systems, a systematic, reproducible and data-driven exploration of the chemical space is needed.

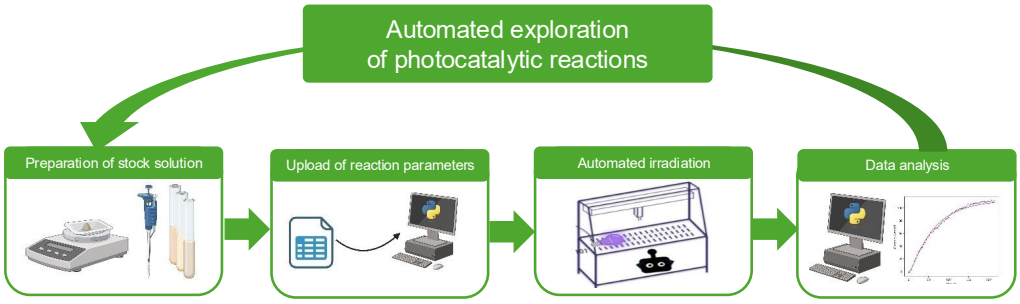


Figure 1. General workflow for the automated process to conduct photocatalytic oxygen evolution experiments.

In this contribution, we present an automated process for the systematic investigation of photocatalytic oxygen evolution reactions. The system integrates liquid handling, light source control, *in-situ* oxygen sensing, and automated kinetic data evaluation using a Python-based framework, requiring minimal user intervention (see workflow shown in Fig. 1). To develop the process, $[Ru(bpy)_3]^{2+}$ was chosen as a photosensitizer and simultaneously catalyst precursor for photocatalytic water oxidation.[1] Using this benchmark system, the automated process was used to measure the effect of different reaction parameters (pH, irradiance, catalyst concentration, and sacrificial oxidant concentration) on the rate of oxygen evolution. The results show that the automated process allows for performing highly reproducible experiments, obtaining for each experiment full time-concentration curves with a high time resolution (seconds). The automated screening of reaction parameters allowed both for the reproduction of previously observed reactivity trends (e.g. optimal catalyst concentration) and the identification of novel patterns, such as an unexpected optimal performance at pH 10. This work illustrates how the combination of *in-situ* kinetic measurements and automation unlocks a data-driven exploration of the chemical space. Furthermore, it lays the foundation for closed-loop optimization of photocatalytic reactions.

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# Investigation of Iridium(III) Complexes for Organic Photocatalysis *via* Triplet-Triplet Energy Transfer

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Visible-light-mediated photocatalysis offers a novel/powerful/valuable method in the synthesis of organic molecules *via* triplet-triplet energy transfer (TTEnT).[1] By investigation of iridium(III) complexes developed by screening methodologies these TTEnT reactions showed remarkable reactions towards photo-induced processes.[2] Detailed mechanistic analysis gave insight into the photocatalytic processes. These were investigated in detail using advanced spectroscopic methods like transient absorption spectroscopy. Furthermore, gained knowledge was used to create tunable, next-generation catalysts that improved the catalytic processes opening a new approach towards synthesis of efficient photosensitizer as well as their application regarding organic synthesis.

**Acknowledgement:** We thank all the contributors.

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# Phenothiazine Sulfoxides as Active Photocatalysts for the Synthesis of γ-Lactones

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*N*-substituted phenothiazines are widely recognized as highly effective organic photoredox catalysts due to their strong reducing properties.[2,3] Recently, their radical cations have also been examined as photocatalysts for oxidations.[4,5] In contrast, phenothiazine sulfoxides—easily formed via oxidation—have remained largely unexplored in photocatalysis. Here, we report the discovery and application of *N*-phenylphenothiazine sulfoxide as a novel photocatalyst for the reductive activation of cyclic malonyl peroxides, enabling the direct synthesis of complex γ-lactones from simple olefins. Comprehensive mechanistic studies were conducted to elucidate the in situ formation of the active catalyst from *N*-phenothiazine via its radical cation as well as the overall photocatalytic mechanism. Our approach employed a combination of time-resolved spectroscopy, transient UV–vis absorption spectroscopy, spectroelectrochemistry, cyclic voltammetry, isotopic labeling, radical trapping, NMR spectroscopy, and DFT calculations. The synthetic utility of this protocol was demonstrated through a broad substrate scope, providing efficient access to biologically relevant spirocyclic γ-lactones.

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# Intersystem Crossing in Nitroaromatics Through a $^1(\pi\pi^*)$ to a Twisted $^3(\pi\,\pi^*)$ Mechanism

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Substituted polyaromatic compounds are considered to typically exhibit intersystem crossing (ISC) pathways mediated by a spin-orbit coupling between $S_1(\pi\pi^*)$ and $T_2(n\pi^*)$ states. Such process would follow the regular El-Sayed Rules. However, certain compounds, such as nitro and carbonylic polyaromatics, deviate from this pathway and instead can possess strong couplings between a singlet $^1(\pi\pi^*)$ and a twisted $^3(\pi\pi^*)$ isoenergetic triplet state,[1] where the $(n\pi^*)$ triplets lie at significantly higher energies. As we show here, this pattern implies that the photophysics of some nitroaromatics including, nitropyrenes have significant solvent dependencies since the $^1(\pi\pi^*)$ singlet is highly sensitive to the dipolar environment and can de-couple from the receiver $^3(\pi\pi^*)$ state in polar environments. We also show that for cases where the $^1(\pi\pi^*)$ and the twisted $^3(\pi\pi^*)$ state are decoupled, the ISC channel still occurs through the same $^3(\pi\pi^*)$ state but involving a thermally activated process where the activation energies are consistent with the singlet-receiver triplet gap estimated from excited state calculations.[2] In Figure 1A, we demonstrate this effect showing that the solvent-dependent $S_1$ lifetimes for 4-nitropyrene follow the pattern of an activated process.

With respect to the afore-mentioned geometric effects, the twisting distortion of the $NO_2$ group (Fig. 1B) tilts its $\pi\pi^*$ orbitals away from the aromatic plane, creating a pathway for efficient spin-orbit coupling despite the $\pi\pi^*$ nature of both states. This behavior extends El-Sayed's rules, demonstrating that rapid intersystem crossing can occur even without $n\pi^*$ intermediates, provided the $\pi\pi^*$ triplet states adopt geometries that break planarity and enable out-of-plane spin-orbit interactions.

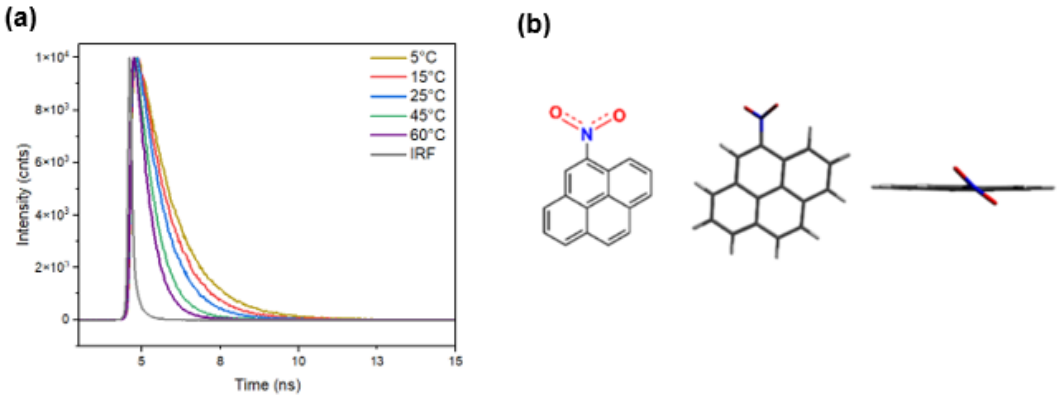


Figure 1. (a) Fluorescence decay profile of 4-nitropyrene in a polar environment at variable temperature. (b) Molecular structure of 4-nitropyrene. [2]

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# Ultrafast Excited-state Dynamics of 4-Hydroxychalcone: Role of Intramolecular Charge Transfer and Photoacidity

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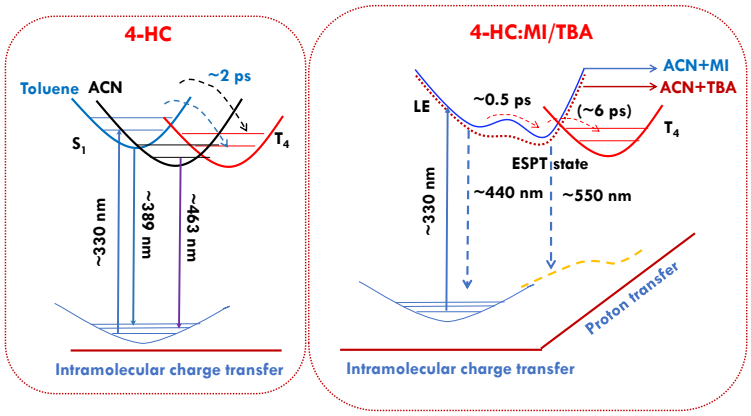
Diarylketones such as benzophenones, oxybenzones, chalcones and their derivatives exhibit promising applications as UV filters/sunscreen agents due to their effective absorption in the UV region and dissipation through non-radiative pathways.[1,2] However, elucidation of underlying photoreactive mechanism is non-trivial due to the ultrafast lifetimes of transient species, involvement of non-adiabatic curve crossings among the potential surfaces, etc. In this context, we investigate the excited-state photoreaction dynamics of 4-hydroxychalcone (4-HC) under various environments through femtosecond–transient absorption (fs–TA), nanosecond–transient absorption (ns–TA), and femtosecond–fluorescence upconversion (fs–FL) measurements. Steady-state fluorescence measurements of 4-HC in presence of 1-methylimidazole (MI)/tert-butylamine (TBA) exhibit dual band emission. The fs-TA measurements of 4-HC in presence of MI/TBA exhibit distinct spectral and associated lifetimes as compared to 4-HC alone indicating a significant interaction of the hydroxyl proton with bases and influencing the reaction dynamics. The 4-HC:MI/TBA adduct undergoes excited-state intermolecular proton transfer within a time scale of ~500 fs and subsequently relaxes back to the ground state through long–lived triplet state. The experimental observations of excited–state reaction dynamics of 4–HC in presence of MI/TBA bases have been well corroborated with the computational analysis.




Scheme: Schematic representation of the excited-state dynamics of 4-HC and 4-HC:MI/TBA adducts upon photoexcitation.

**Funding:** YAL acknowledges the financial support of this work through the CRG grant (CRG/2020/000321) of SERB.

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# Ultrafast Bond Cleavage in Diorganyl Bis(pyridyl)imino Isoindolide Aluminum Complexes

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Photochemical processes are of great relevance in nature and synthetic chemistry.[1,2] An understanding of the elementary steps is of crucial importance in order to optimize photoreactions in a targeted manner or to find yet unknown reactivity. Therefore, the present work contributes to a deeper understanding of the photochemistry of main group complexes in general and diorganyl bis(pyridylimino) isoindolide (BPI) aluminum complexes in particular.[3,4] This interdisciplinary work combines the synthesis of BPI complexes with femtosecond transient absorption spectroscopy and quantum chemical calculations in order to correlate the decisive ultrafast processes with stationary properties. It is shown, that an initial charge transfer is the first relevant step after photoexcitation, which determines the fate of the molecule and thus the outcome of the reaction. Triggered by this charge transfer an elongation of one aluminum carbon bond takes place and the molecular wavepacket evolves on the $S_1$ potential energy surface to a region of conical intersections. Here a channel branching occurs and the molecule either relaxes back to the ground state or undergoes an ultrafast E-C bond cleavage, opening the vivid field of radical reactivity. The nature of the diorganyl substituents has a huge impact of the branching ratio and thus enables a tuning of the complexes. This understanding paves the way for the systematic development of main group photocatalysts or photoinitiators, which are currently investigated in our groups.

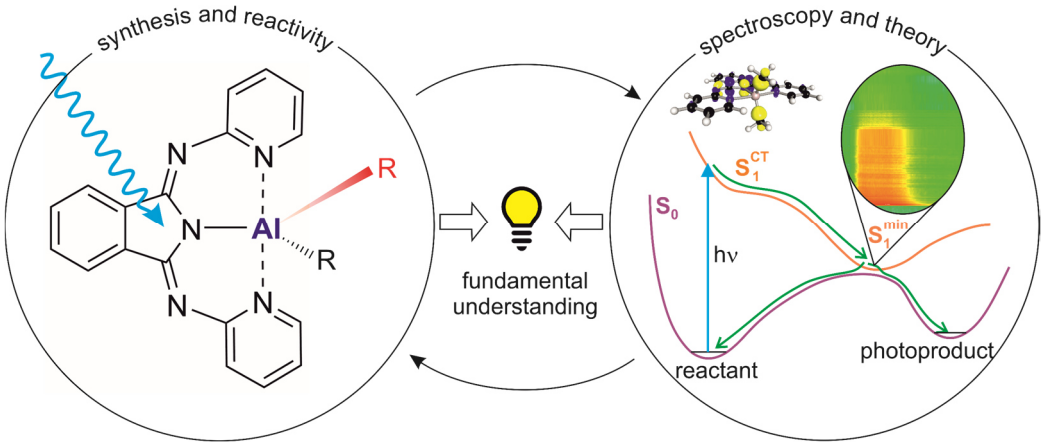


Figure 1. Left: Studied complexes in this work, which undergo photoinduced bond cleavage. Right: Schematic description of the potential energy surface of the studied complexes.

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# Computational Investigation of Relaxation Pathways in Organic Donor-Functionalized Doublet Emitters

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In recent years, organic radicals have received great attention for their potential application as optoelectronic devices like organic light-emitting diodes (OLEDs). Different from conventional dyes, the key design principle of open-shell emitters is that they are not limited to 25% of bright singlet excitons, but that they can reach internal quantum efficiencies of up to 100%, because a restriction by spin-statistics is circumvented. A very prominent class for this type of application are donor-functionalized radicals based on tris(2,4,6-trichlorophenyl)methyl (TTM). These molecules provide relatively stable neutral radicals in solution and can thus be studied and employed most efficiently. A successful example of a donor-functionalized TTM radical employs a carbazole unit as donor (TTM-Cz) and excellent photoluminescence quantum yields (PLQYs) of ~90% were reported depending on the used solvent.[1] In contrast, unfunctionalized TTM exhibits poor PLQYs of only 2%.[2] The key difference between these two compounds (TTM-Cz, TTM) is that the donor—acceptor (DA) alignment leads to the energetically lowest excited doublet state ($D_1$) to show clear charge transfer (CT) characteristics, while the $D_1$ in TTM is a symmetry-forbidden locally excited (LE) state. The convincing attributes of various DA radical emitters known in literature to date[3] make a thorough understanding of their photophysical properties indispensable.

The present contribution deals with the quantum chemical investigation of a series of donor-functionalized radical emitters that are derivatives of TTM-Cz and related compounds. As a joint project between experimental and theoretical research groups, comparisons between experimental and theoretical spectroscopy are drawn to understand the validity of different theoretical approaches. Time-dependent density functional theory[6] and $\Delta$SCF[7] calculations are employed to assess radiative (fluorescence) as well as nonradiative (internal conversion) processes in these molecules. In addition to unimolecular nonradiative relaxation channels from the $D_1$ excited state minimum to the electronic ground state $D_0$, we explore whether additional relaxation channels may become accessible in solution.

**Funding:** DFG, German Research Foundation – Project number 500226157

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# Breaking Energy Barriers: Red Light ConPET Photoredox Catalysis

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The advancement of photoredox catalysis into the red and near-infrared (NIR) region represents a transformative leap toward more sustainable and selective chemical synthesis.[1] Traditional photoredox approaches, limited to ultraviolet and visible light, face significant limitations in reaction scope, energy efficiency, and penetration depth. A fundamental challenge in extending photochemical transformations to red and NIR wavelengths lies in the lower photon energy (≤2.0 eV), which is often insufficient to activate many organic substrates. A red-light photon at 640 nm provides only 1.9 eV which is typically below the activation threshold for demanding molecular transformations. However, the advent of multiphoton activation strategies has redefined the energetic landscape of photochemistry. Among these, the *Consecutive Photoinduced Electron Transfer (ConPET**)*** mechanism presents a emerging multiphoton strategy[2], enabling the accumulation of multiple low-energy photons to drive high-energy transformations.[3–6] By sequentially harnessing two or more low-energy photons, *ConPET* overcomes the thermodynamic constraints associated with long-wavelength excitation, offering an innovative pathway for red and NIR light-driven chemical synthesis. This presentation will highlight a red light based *ConPET* approach for the reductive activation of inert organic molecules such as aryl halides. The presentation will reveal rational design principles behind catalytic system, mechanistic insights supported by comprehensive spectroscopic studies, and synthetic utility of newly developed red light *ConPET* process.

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# Iron-Catalysed LMCT Activation of Alcohol Derivatives for Sustainable Radical Alkylation

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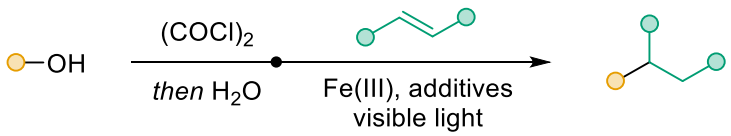
The ability to construct C(sp³)–C(sp³) bonds is important as it provides a valuable strategy for building complexity in pharmaceuticals, agrochemicals, and other fine chemicals from readily available feedstocks.[1] Photoredox strategies for generating alkyl radicals from alcohol derivatives have opened new avenues in C–C bond formation, with enormous libraries of alcohols available, but they often rely on precious-metal catalysts. For example, Overman and MacMillan demonstrated that caesium oxalate esters derived from tertiary alcohols undergo visible-light-induced decarboxylation using an iridium photocatalyst.[2] MacMillan and Dong later used N-heterocyclic carbene salts to activate alcohols for metallaphotoredox deoxygenative arylation using an iridium photocatalyst again.[3] Doyle and Rovis used iridium to generate benzyl radicals from alcohols via phosphoranyl intermediates.[4] While effective, these methods pose sustainability challenges due to the high cost, scarcity, and environmental impact of Ir and Ru.[5]

Here we describe a new method using simple, Earth-abundant iron salts and visible-light-induced ligand-to-metal charge transfer (LMCT) to activate hydrogen oxalate esters derived from a wide range of alcohol substrates. Upon LMCT excitation, these complexes fragment cleanly to form alkyl radicals, which then undergo C–C bond formation via addition to alkenes under mild, redox-neutral conditions. This precious-metal-free protocol offers a sustainable and operationally simple alternative for radical generation, expanding the synthetic utility of alcohols while minimising environmental and economic costs.

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# Visible-Light Photocatalysis with Iron(II) Pyridine–NHC Complexes in Radical and Cationic Photopolymerizations

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ABSTRACT : First-row transition metals have recently emerged as promising candidates for sustainable photocatalysis in photopolymerization and 3D printing technologies.[1–3] Iron(II) complexes are particularly attractive due to their earth abundance, low toxicity, and rich redox chemistry.[2] In this study, two novel organoiron(II) complexes, FeC1 and FeC2, bearing bidentate pyridine–NHC ligands, were synthesized by reacting $FeCl_2$ in tetrahydrofuran (THF) with a two-fold excess of PyImes($PF_6$) or PyIPh($PF_6$) in the presence of KOtBu. Both complexes were fully characterized by spectroscopic techniques, cyclic voltammetry, and mass spectrometry. For both iron complexes, the absorption spectra are in the range of 200-500 nm, and they present emission from 300-405 nm. Also, the reactivity of the iron complexes with the addtivies, Iod and EDB have been evaluated in the quenching experiments with low $K_{SV}$ values for both complexes. Despite a low lifetime (ps) for the complexes, their photocatalytic activity was evaluated in both free radical photopolymerization (FRP) and cationic photopolymerization (CP) processes under different visible light sources (395, 405, 455, and 532 nm) under air in thick samples (1.8 mm). Both exhibited excellent performance in the FRP of ethoxylated trimethylolpropane triacrylate (TMPETA) under, LED@405, LED@455, and diode laser@532 nm, using di-tert-butyl-diphenyl iodonium hexafluorophosphate (Iod) and ethyl dimethylaminobenzoate (EDB) as co-initiators. For FeC2 the highest conversion values were achieved 89% of conversion in 100s at LED@405nm. In addition, FeC2 also catalyzed the CP of EPOX and GE60 monomers under LED@395, laser@405 nm irradiation. The underlying CP/FRP mechanism was further investigated using fluorescence spectroscopy, cyclic voltammetry, and steady-state photolysis.

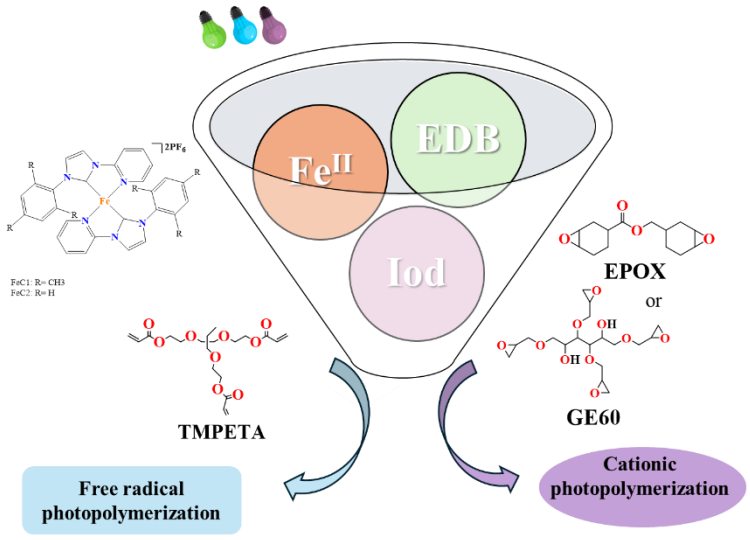


Figure 1. Representative scheme for the FRP and CP in the presence of $Fe^{II}$/Iod/EDB.

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# Harnessing LMCT in Fe-Photocatalyzed Chlorooxygenation of Alkenes: A Gateway to Access Orthogonally Functionalized Synthetic Intermediates

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The simultaneous introduction of two distinct functional groups across a carbon–carbon double bond in a single step has gained significant interest in modern synthetic organic chemistry. Such unsymmetrical difunctionalization of alkenes is increasingly recognized as a powerful strategy for rapidly enhancing molecular complexity and providing valuable synthetic intermediates.[1] Alkenes, being low-cost and readily available, serve as ideal substrates for these transformations.[2] Recent advances have demonstrated that halogen radicals (X·) can be efficiently generated via ligand-to-metal charge transfer (LMCT)-mediated homolysis of Fe–X bonds.[3] These electrophilic halogen radicals readily add across the carbon–carbon double bonds of alkenes, forming carbon-centered radicals that are subsequently trapped by oxygen-centered aminoxyl radicals, leading to the formation of 1,2-difunctionalized chloro-oxygenated products (Figure 1a). This methodology exhibits a broad substrate scope, accommodating a wide range of vinyl arenes, unactivated alkenes, and Michael acceptors. The resulting adducts serve as versatile synthetic intermediates, readily undergoing further transformations either through simple bimolecular nucleophilic substitution ($S_N2$) reaction at the chlorine-bearing carbon center or through photoredox reactivity targeting the carbon–oxygen bond (Figure 1b). These downstream modifications significantly expand the accessible chemical space, offering new opportunities for the construction of complex molecular architectures. In addition, detailed mechanistic studies involving reaction kinetics, electrochemical analysis, EPR spectroscopy, UV-vis absorption and HRMS studies are currently underway to further elucidate the reaction pathway.

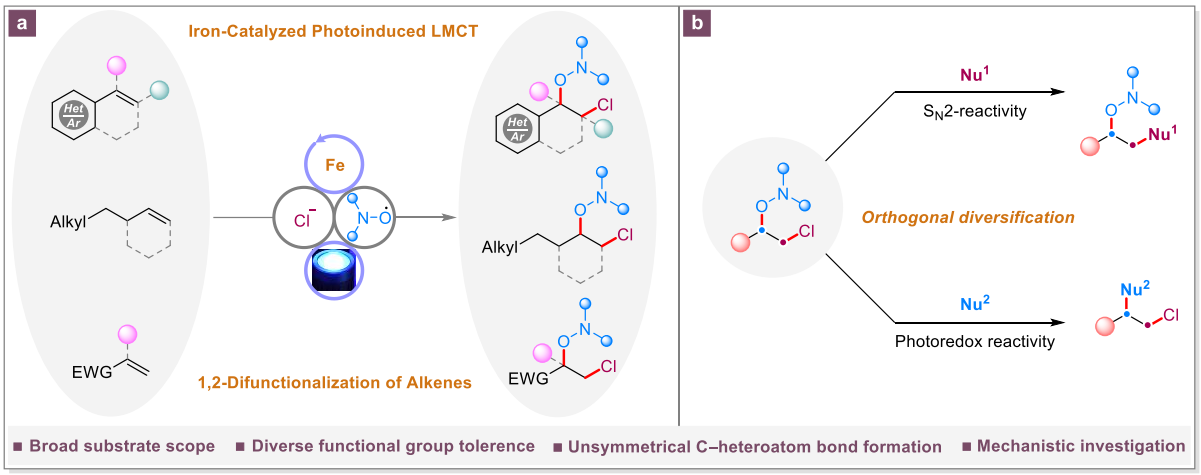


Figure 1. Iron-photocatalyzed LMCT-mediated hetero-difunctionalization of alkenes to generate versatile synthetic intermediates.

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**Acknowledgement:** We thank all the staff of the NMR department, mass spectrometry department, and X-ray diffraction service for their support.

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# Highly Selective Photocatalytic Conversion of C1 to C2+ Hydrocarbons, $H_2$ Evolution, and Photodegradation of CV Dye Using SbSI and SbSeI as Catalysts

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The use of photocatalysts to turn carbon dioxide into high value-added fuels and chemicals can meet key strategic and sustainable development goals. There are many reports in the literature about Antimony-Chalcohalides (SbAX, A = S, Se, Te; X = Cl, Br, I) and mixed metal Antimony-Chalcohalides (MSbAX, A = S, Se, Te; M(II) =Sn Pb, Ba, M(I) = Ag, MA, Cs) is used in solar cells, and its energy gap is between 0.47-3.03 eV, covering the entire visible light and part of the infrared light [1-3]. Antimony sulfoiodide (SbSI) and antimony selenoiodide (SbSeI) are widely used in electronic materials, however, its application in C1 ($CO_2$, $CaCO_3$, $NaHCO_3$, HCOOH, HCHO, $CH_3OH$) reduction has not been explored. The experimental results confirmed that SbAI (A = S, Se) could be successfully synthesized by hydrothermal method with selenourea (or thiourea), antimony trichloride, and ammonium iodide added to 1M HCl aqueous solution. By changing the temperature and time to synthesize a variety of photocatalysts and the best catalyst composite graphitic carbon nitride (g-$C_3N_4$), C1 was further reduced to $CH_4$ and other hydrocarbons (C2+) and crystal violet (CV) photocatalytic degradation dye, and the catalytic effect of the various photocatalysts were explore. The research results showed that the yield of $CO_2$ reduction to $CH_4$ was 121.1 and 204.5 ppm under the reaction of SbSI and SbSeI. The findings significantly advance the photocatalytic conversion of $CO_2$ into C2+ hydrocarbons compounds, which are crucial in the chemical and energy industries. The SbSI and SbSeI, which have a remarkable selectivity to hydrocarbons (52% $CH_4$, 48% C2+), was optimized to achieve the optimum progressive selective conversion from C1 to $CH_4$ and finally to C2+ hydrocarbons, respectively. Besides, SbSI and SbSeI also had an excellent effect in degrading CV, and its degradation rate appeared k = 0.1679 and 0.0563 $h^{-1}$.

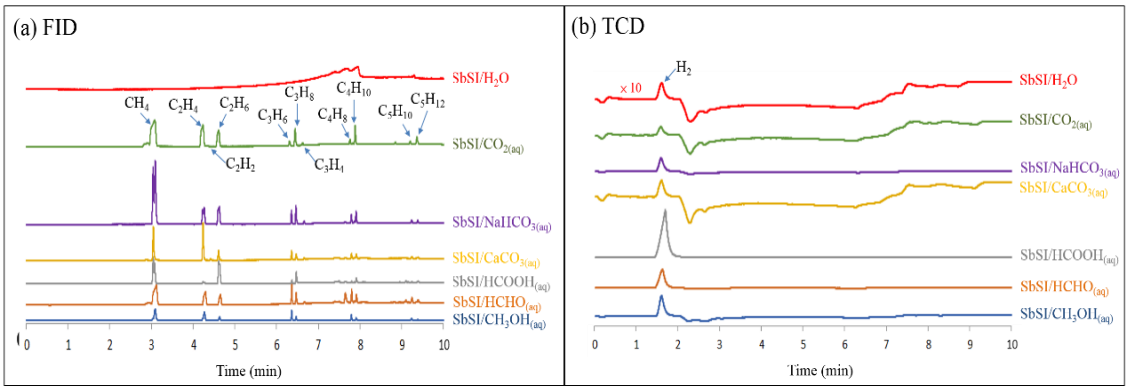


**Figure 1.** Photocatalytic reduction shows that the product is separated and identified by (a) GC-FID and (b) GC-TCD. SbSI is dispersed in water, $CO_{2\ (aq)}$, $NaHCO_{3\ (aq)}$, $CaCO_{3(aq)}$, $HCOOH_{\ (aq)}$, $HCHO_{\ (aq)}$, and $CH_3OH_{\ (aq)}$ aqueous solutions for photocatalytic reaction.

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# Controlling Cage Escape Yields of Transition Metal Complexes in Photoinduced Electron Transfer Processes

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Light-induced chemical reactions that proceed via electron or energy transfer mechanisms are employed in several research fields ranging from solar fuel production[1] to organic synthesis.[2] Photoredox reactions involve a photosensitizer (PS) and an electron donor/acceptor quencher (Q), thus resulting in a reductive or an oxidative quenching of the PS, respectively. The accepted mechanism associated with these reactions (schematically shown in Fig. 1) can be summarized as follows: (i) the formation of a "solvent cage" subsequent to the interaction between the photo-excited photosensitizer (PS*) and the quencher, also called encounter complex; (ii) the electron transfer leading to the corresponding charge-separated products, which are known as geminate radical pair ({$PS^-$, $Q^+$}); (iii) the cage escape process, i.e., the separation of the geminate radical pair ({$PS^-$}, {$Q^+$}).[3] Unfortunately, cage escape yields ($\Phi_{CE}$) can be significantly less than unity, as reactants trapped inside the solvent cage can undergo an (unwanted) charge recombination with a rate constant $k_{CR}$ that competes with the cage escape one ($k_{CE}$), thus lowering $\Phi_{CE}$. The present work focuses on the study of $\Phi_{CE}$ associated with the reductive quenching of closed-shell metal complexes photosensitizers, specifically $[Ru(bpy)_3]^{2+}$, $[Ru((CF)_2bpy)_3]^{2+}$, $[Os((CF)_2bpy)_3]^{2+}$ and $[Ir((dFCF3)ppy)_2(dtb)]^+$, with tri-p-tolylamine (TTA) as a quencher, in different polarity solvents. Among the investigated complexes, the largest cage escape yields (0.67-1) were recorded for the Ir(III) complex, while yields dropped to values around 0.65 for both Ru(II) photosensitizers and to values around 0.38 for the Os(II) photosensitizer. [4] Our first attempt to rationalize this trend was based on the determination of the nature of charge transfer excited states and the spin associated with these relevant states by exploiting DFT and TD-DFT frameworks. As a next step, we will take advantage of QM-MM calculations and MD simulations to further investigate other key aspects influencing $\Phi_{CE}$ such as the effect of the polarity of the solvent by including both purely electrostatic and polarization effects, as well as the consequence of using bulky counterions (*e.g.*, $BaRF^-$) that could dramatically reduce the efficiency of the charge transport inside the geminate radical pair.

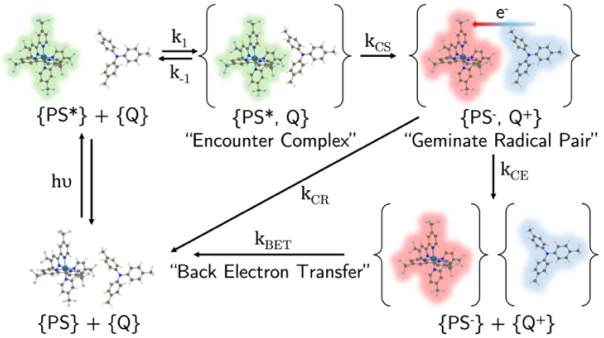


Figure 1. Photophysical scheme describing the electron transfer reaction between a photosensitizer (PS) and a quencher (Q) induced by light absorption (a reductive quenching mechanism is shown).

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**Acknowledgement:** This research used resources from the Consortium des Equipments de Calcul Intensif (CECI) and Tier-1 supercomputer of the Walloon Region.

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# Visible-Light Mediated Synthesis of Substituted Furanones

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Over the last decades, photochemistry has established itself as a valuable and versatile tool complementary to thermally driven chemistry, enabling transformations previously unattainable through traditional methods via more sustainable processes.[1,2] The research presented here is focused on the photocatalytic oxidation of 3-bromo-2,5-dihydrofuran derivatives (**1**) towards 3(*2H*)-furanones (**2**) and 4-bromo-3(*2H*)-furanones (**3**), depicted in Fig. 1a).

The reaction is performed by irradiation with visible light utilizing aerial oxygen as the oxidant together with an acridinium-based photocatalyst at room temperature. Depending on the solvent, either the furanone scaffold **2** (in acetone) or the brominated furanone scaffold **3** (in acetonitrile), allowing for further functionalization through coupling reactions, is obtained. These scaffolds enable access to different natural products and pharmaceutical targets containing a furanone motive. Fig. 1b) shows two examples of these target structures; bullatenone (**4**), traditionally used as ulcer treatment, insect repellant and sunscreen,[3] and Polmacoxib (**5**), an NSAID approved for use against osteoarthritis in South Korea.[4]

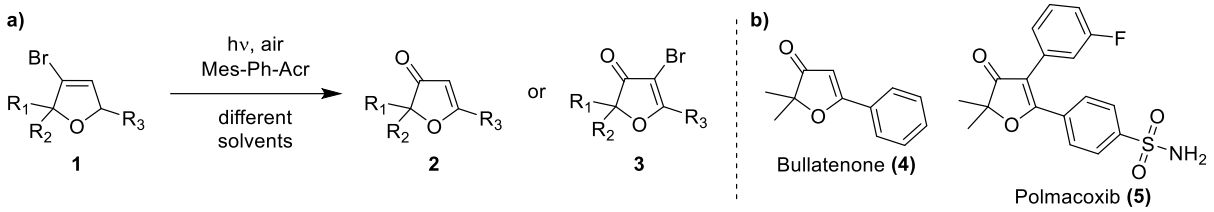


Figure 1: a) Photooxidation investigated in this research. b) natural products and pharmaceutical targets

A working protocol for the two photooxidations was established and the substrate scope of both reactions were probed, focusing on position 2 ($R_1$, $R_2$) and 5 ($R_3$). Mechanistic studies regarding the formation of furanone **2** were performed utilizing kinetic measurements on selected substrates, Hammett analysis, exclusion experiments, electrochemical measurements and intermediate trapping. Isotope labeling experiments were conducted, to measure kinetic isotope effects of deuterated substrates and effects as well as to follow selected atom movements during the reaction. Computational studies were performed to evaluate the energetic characteristics of reaction intermediates. Bullatenone **4** could already be isolated with excellent yield, investigation of the reaction mechanism forming furanone scaffold **3** and further functionalization is the focus of ongoing research to also obtain Polmacoxib **5**.

The demonstrated photocatalytic oxidation presents an easy way to access the two different furanone scaffolds **2** and **3**. These scaffolds are part of many different natural products and valuable synthetic intermediates of pharmaceutical compounds. Understanding these photooxidations in detail is of great value, as they potentially enable access to functionalized bioactive compounds through more sustainable processes.

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# Photoredox-catalysed cross-coupling reactions with halogenated amino acids

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Peptides are, due to their wide array of biological functions, important compounds in chemical research, for example in the context of drug development. One particular downside is that natural peptides are labile towards degradation leading to short *in-vivo* lifetimes, which makes chemical modification, particularly through cyclisation or the incorporation of naturally non-occurring motifs, often necessary.[1]

With the growing popularity of photoredox catalysis in organic chemistry, we aim at establishing reaction conditions for peptide cyclization using halogenated amino acids and dual photoredox/transition metal catalysis. This could offer a complimentary approach to traditional cyclization methods, as the C-terminal amino acid can be used as the reaction partner, while also introducing a non-peptidic bond.

Figure 1. Schematic representation of the investigated reactions between bromotryptophan and various natural amino acids. Iodophenylalanine was also investigated as a halogenated amino acid.

We started this approach by investigating the reactions between two amino acids with bromotryptophan and iodophenylalanine as the halogenated reaction partners (compare Fig. 1) and adapting the conditions described in the literature[2] in order to meet the substrate requirements. In regard to the coupling partner special emphasis was placed on the avoidance of stereoisomer formation, which is often described for radical reactions.[2] A first approach involved the use of amino acids, where the newly formed bond would not introduce a stereocenter into the compound. Afterwards, stereoselective approaches utilizing chiral ligands on the cross coupling catalyst[3] were investigated to further broaden the scope of possible amino acid coupling partners.

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# Tri-oxo-triangulene: a new versatile photocatalyst of highly selective photoredox systems.

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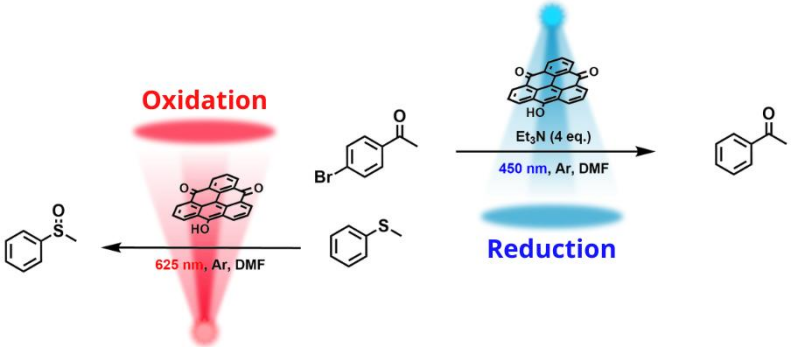
Triangulenes[1] are open shell polyaromatic hydrocarbons. Their highly conjugated and flat scaffold favors the formation of stable radicals. They are promising compounds in various fields such as spintronics, electrochemistry, organic semiconductors and photocatalysis. However, despite their promising properties, their long and difficult synthesis does not encourage practical applications.

Our work introduces photocatalytic systems based on tri-oxo-triangulene (TOT). This triangulene can be synthesized on gram-scale in four steps and with limited number of purifications steps[2]. We demonstrate that the TOT can be used as a powerful photocatalyst to perform substrate reduction but also oxidation. We prove that we can fully control the outcomes in a complex mixture. Through the dehalogenation of a challenging substrate, the 4-bromoacetophenone and the oxidation of thioanisole to sulfoxide, we showcase a sequential photoredox system with high selectivity.

These examples are the gateway to a new type of photocatalyst and bring back to light triangulenes as promising candidates for practical photocatalytic applications but also expand the knowledge about the triangulene-light interactions and more efficient photocatalytic redox systems.

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# Mechanistic Investigation and Optimisation of the Photocatalytic Production of Hydrogen Peroxide

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Photocatalysis utilises solar radiation as an abundant energy source, operates under mild reaction conditions and offers alternative reaction pathways. Among other methods like electrochemistry, photocatalysis can address the ever-increasing demand for environmentally friendly processes that strive to achieve high energy and atomic efficiency and use sustainable raw materials.[1]

We present the photocatalytic production of hydrogen peroxide ($H_2O_2$) from water and oxygen as an alternative for the energy-intensive anthraquinone process. In addition to its well-known applications as an oxidation agent, for disinfection, bleaching and water treatment, $H_2O_2$ is a promising candidate for energy storage. It can be transported in aqueous media and electrical energy can be generated at the desired location using a $H_2O_2$ fuel cell, producing only water and oxygen.[2,3]

As heterogeneous photocatalysts nitrogen-containing carbon networks such as covalent triazine frameworks (CTF)[4] were applied. In addition to the classical characterisation of heterogeneous catalysts regarding their stability, structure and surface properties, it is essential to possess a comprehensive understanding of the optoelectrical properties of the photocatalysts. The characteristic band gap energy and the flat-band potential can be determined using the Tauc method[5] and Mott-Schottky analysis[6], respectively. Furthermore, electrochemical impedance spectroscopy[7] and chronoamperometry[8] provide insightful information about the behaviour of these materials under light irradiation. For a better comparability of the photocatalytic reactions, the PhotoFlexys reactor platform is applied ensuring a reproducible and homogeneous 360° irradiation of the reaction solution.[9]

To investigate the mechanism of the photocatalytic production of $H_2O_2$ in more detail, reactions were carried out under inert and various oxygen-containing atmospheres while measuring the $O_2$ concentration in the aqueous reaction solution. Radical scavenging experiments were performed to identify the reactive oxygen species involved. In addition, the reaction has been investigated in terms of mixing, reactor type and shape as well as the influence of additives such as alcohols. Under UV light (50 W $m^{-2}$) promising activities of up to 3.9 mmol$H_2O_2$ $g_{CTF}^{-1}$ $h^{-1}$ were achieved with CTF-1,4-phenyl in demineralised water.

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# Near-UV driven photocatalytic defluorination of PFAS by ZnO nanocrystals

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Perfluoroalkyl substances (PFASs) such as perfluorooctanesulfonic acid (PFOS) have been widely used in industrial materials. However, their high stability causes environmental persistence and waste issues. Recently, we successfully decomposed PFASs by visible light irradiation of CdS nanocrystals (NCs)[1]. However, cadmium leaching poses another significant environmental concern. This study demonstrates that zinc oxide (ZnO) NCs, which have low toxicity, can decompose PFOS into fluoride ions ($F^-$) under 365-nm LED irradiation. While ZnO is generally effective at driving oxidation reactions, our study revealed that PFOS decomposition proceeds predominantly via reduction reactions mediated by highly excited electrons generated through the stepwise multiphoton absorption (Fig. 1a).

The defluorination efficiency after 3-hour LED irradiation (767 mW/cm²) increased with decreasing NC diameter ($D$) with a particularly sharp rise as $D$ decreased from 15 to 7 nm (blue part in Fig. 1b). Furthermore, defluorination efficiency showed a nonlinear dependence on light intensity for NCs with $D$ = 17 nm (Fig. 1c). These results suggest that nonlinear optical processes such as Auger recombination contribute to photodecomposition. On the other hand, for smaller NCs ($D$ = 5.2 nm), defluorination efficiency exhibited a linear dependence on excitation intensity. This suggests that the rate-determining step of photodecomposition is not Auger recombination because Auger recombination is already rapid in small NCs. This inference is further supported by the plateauing of defluorination efficiency as $D$ decreases from 7 to 5.2 nm (orange part in Fig. 1b).

From an industrial application standpoint, complete defluorination of PFASs—including all reaction intermediates—is essential. In this study, the defluorination efficiency of PFOS using ZnO NCs reached 92% within 24 h, suggesting that comprehensive decomposition, encompassing short-chain PFASs intermediates, was achieved. Therefore, this work is expected to contribute to the development of practical PFASs remediation systems.

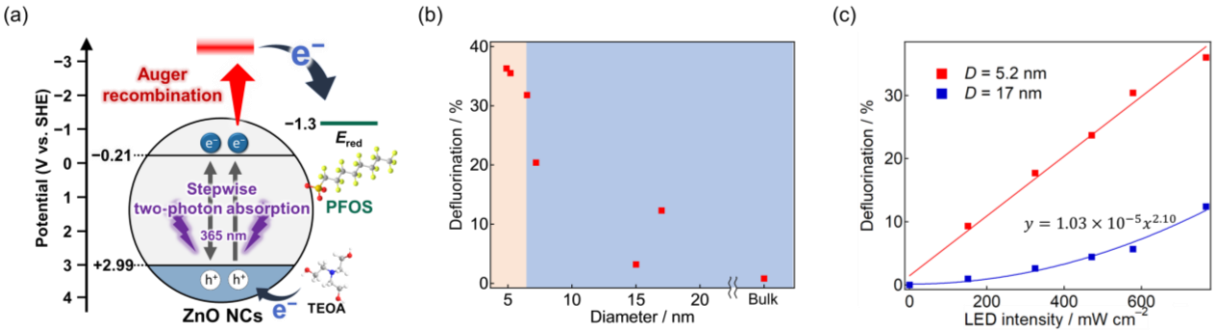


Figure 1. a) PFOS decomposition mechanism using ZnO NCs via Auger recombination. Dependence of the defluorination efficiency on b) diameter of ZnO NCs and c) light intensity.

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# Enhancing Visible-Light Driven Photocatalytic Hydrogen Evolution through Organic Conjugates Integrated with Graphitic Carbon Nitride

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**Abstract**

Green hydrogen production via photocatalytic water splitting has drawn significant attention, leading to the development of various photoactive materials.[1] Among them, metal-free graphitic carbon nitride (*CN*) is notable for its low cost, ease of synthesis and stability. However, its efficiency is limited by poor visible light absorption (up to 450 nm) and rapid charge recombination. Sensitizing *CN* with organic conjugates has emerged as an effective strategy to extend light absorption and enhance photocatalytic performance.[2] In this regard, we synthesized different organic conjugates, including naphthalene monoanhydride (**Np**), perylene monoimide diester (**PMDE**) (Fig.1a) [3] and donor–acceptor (D–A) conjugates based on carbazole (D) and benzothiadiazole (A), namely **CBP** and **CBCN** that exhibit strong intramolecular charge transfer (ICT) characteristics (Fig.1b) [4] Following comprehensive photophysical and electrochemical characterization of these conjugates, their composites with *CN* were prepared. These conjugates exhibited favorable optical and electronic properties and feature polyaromatic skeletons with functional groups (e.g., anhydride, formaldehyde and cyanoacrylic acid) that facilitate π–π interactions with polymeric *CN* or enable covalent bonding with surface–$NH_2$ groups. **Np/*CN*(c)** and **PMDE/*CN*(c)** composites were synthesized via *in-situ* calcination (c), while **Np/*CN*(a)** and **PMDE/*CN*(a)** were obtained through *ex-situ* physical adsorption (a). *In-situ* **Np/*CN*(c)** and **PMDE/*CN*(c)** composites demonstrated significantly enhanced hydrogen evolution rates (HER) of 1069 and 705 μmol $h^{-1}$ $g^{-1}$, respectively, compared to *ex-situ* **Np/*CN*(a)** and **PMDE/*CN*(a)** composites, which exhibited HER values of 465 and 252 μmol $h^{-1}$ $g^{-1}$, respectively. All photocatalytic reactions were conducted under visible light irradiation (400 W Xe lamp with a 420 nm cut-on filter), using triethanolamine (TEOA) as a sacrificial electron donor (SED) and Pt as a co-catalyst. These results represent improvements of 10-, 7-, 4.8-, and 2.5-fold, respectively, compared to bulk *CN*. Additionally, **Np/*CN*(c)** composite showed notable apparent quantum efficiency (AQE) values of 5.1%, 2.14% and 0.65% under irradiation at 400 nm, 450 nm and 500 nm, respectively.

Furthermore, D–A conjugate composites **CBP/*CN*** and **CBCN/*CN*** were prepared using the same *ex-situ* physical adsorption method. Among these, **CBCN/*CN*** composite achieved a significantly higher HER of 3211 μmol $h^{-1}$ $g^{-1}$ compared to 1003 μmol $h^{-1}$ $g^{-1}$ for **CBP/*CN***, again using TEOA as SED and Pt as co-catalyst. These HER values represent 32- and 10-fold enhancements over bulk *CN*, respectively. The **CBCN/*CN*** composite also exhibited impressive AQE values of 11.3%, 4.68% and 2.04% under irradiation at 400 nm, 450 nm and 500 nm, respectively.

The enhanced photocatalytic performance observed in all the composite systems, as compared to

# Advanced metal-free photocatalytic strategies for on-resin and in-solution synthesis of peptidomimetics

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This project aims to investigate advanced strategies for the synthesis of peptidomimetics, molecules designed to mimic the properties of natural peptides while incorporating a non-natural backbone. These structural modifications improve affinity and metabolic stability, with potential applications in nanomaterials [1]. In contrast to conventional methodologies, which necessitate the prior synthesis of amino acids before their incorporation into peptide sequences, our photocatalytic approach enables the direct formation of non-coded amino acids within the peptide structure, facilitated by the formation of the Cα-CO bond.

In this study, we explored a metal-free photoredox-catalyzed strategy utilizing 4CzIPN as an organic photocatalyst (PC) to access the α-amino amide scaffold[2]. Aldimines and 4-amido Hantzsch ester (HE) derivatives were employed as radical precursors, leading to the formation of a new C–C bond, with pyridine (HP) as a by-product (Fig. 1.). 4CzIPN, a donor-acceptor cyanoarene widely applied in photoredox catalysis[3], is readily synthesized on a large scale from inexpensive starting materials. Additionally, it exhibits bench stability and lower toxicity compared to Ru- and Ir-based PCs.

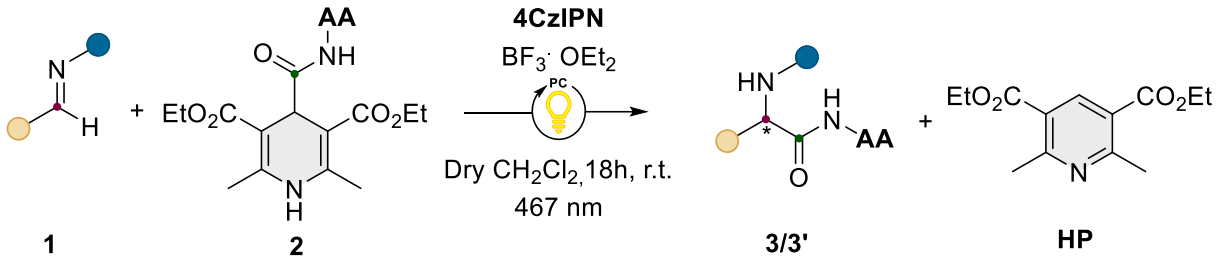


Figure 1. In situ generation of ultrashort peptidomimetics.

This approach has been successfully implemented in solid-phase peptide synthesis, enabling the production of peptides with varying lengths and secondary structures. These results confirm the efficiency of this protocol, even in sterically demanding environments.

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# Supramolecular control of selectivity in photocatalytic C-H bond functionalisation

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C–H bonds are ubiquitous in organic compounds—from polymers to drugs, resins, and cosmetics—and represent an exceptional opportunity for diversification, enabling the synthesis of derivatives with novel properties.Light-promoted hydrogen atom transfer (HAT) has emerged as a powerful strategy for the photocatalytic activation of otherwise unreactive $sp^3$ C–H bonds. However, despite extensive efforts, the direct site-selective cleavage of unactivated C–H bonds remains a major unresolved challenge in organic chemistry.[1]

Enzymes catalyse chemical transformations with exquisite selectivity by leveraging secondary catalyst–substrate interactions. Inspired by this, synthetic chemists have developed “supramolecular catalysts” that use engineered, reversible interactions to direct reactions at specific positions within a molecule.[2,3]

Here, we present our studies on the design and synthesis of a new supramolecular photocatalytic platform for the site-selective functionalisation of C–H bonds, based on a recognition-driven, photoinduced HAT reaction (Figure 1).

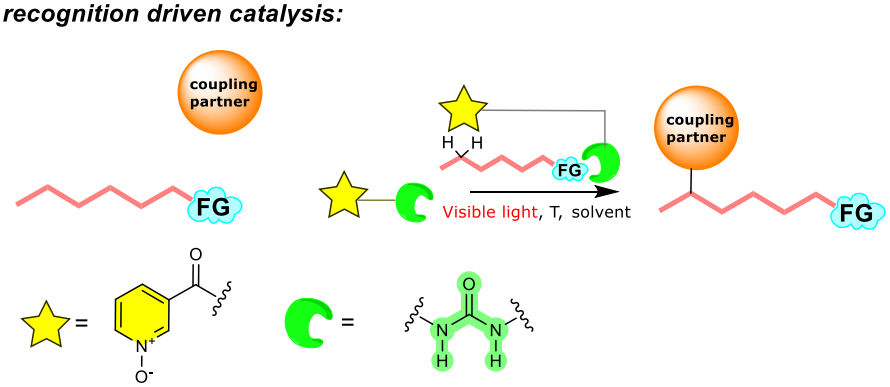


Figure 1. The supramolecular platform is designed to guide the HAT reaction to a specific position on the aliphatic chain through secondary interactions between the catalyst and substrate.

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# Polypeptoid Micellar Photocatalysts for Visible-Light-Driven Arene Cyanation in Water

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Micellar catalysis offers a promising and more sustainable approach for organic transformations in aqueous media.[1,2] However, its application in photoredox transformations faces several interconnected challenges, including limited light penetration, instability of micellar structures, poor solubility and diffusion of reactants, and catalyst deactivation in aqueous environments.[3–6] Hereby, we report the use of polypeptoid-based block copolymer micelles, composed of poly(*N*-methyl glycine)-*block*-poly(*N*-n-propyl glycine) (PMG-*b*-PPG), to support visible-light-driven arene cyanation in aqueous media and address some of the challenges mentioned above (**Figure 1**).

The bioinspired micelles were formed in water in the presence of 3,6-di-*tert*-butyl-9-mesityl-10-phenylacridinium tetrafluoroborate (Mes-Acr-Ph$^+$), encapsulating the acridinium-based photocatalyst (PMG-*b*-PPG/Mes-Acr-Ph$^+$) (**Figure 1, A-B)**. Dynamic light scattering (DLS) measurements reveal nanostructures with hydrodynamic radii around 20 nm, while cryogenic transmission electron microscopy (cryo-TEM) confirms the formation of well-defined spherical micelles. Photocatalytically active PMG-*b*-PPG/Mes-Acr-Ph$^+$ micellar nanostructures (**Figure 1, B)** were tested for arene cyanation, and our results demonstrate the selective C–H cyanation of both electron-rich and electron-deficient arenes under mild, pH-neutral, and fully aqueous conditions (**Figure 1, C**). The nanoconfined environment enhances catalyst solubility, stabilizes reactive intermediates, and improves overall catalytic efficiency. Furthermore, the system exhibits good structural integrity and recyclability, as shown by recycling experiments. This work establishes a robust supramolecular platform for advancing photoredox transformations in water, addressing key limitations of conventional micellar systems through the design of chemically stable, tunable polypeptoid assemblies.

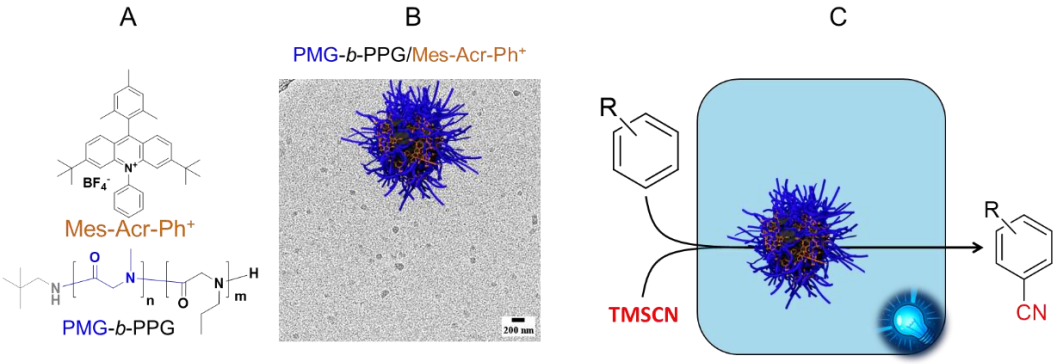


**Figure 1.** (A): Structural depiction of poly(*N*-methyl glycine)-*block*-poly(*N*-n-propyl glycine) (PMG-*b*-PPG) and 3,6-di-*tert*-butyl-9-mesityl-10-phenylacridinium tetrafluoroborate (Mes-Acr-Ph$^+$); (B) Cryo-TEM micrographs of PMG-*b*-PPG micelles loaded by Mes-Acr-Ph$^+$; (C) Schematic of the cyanation reaction of arenes by micelles under light irradiation ($\lambda_{max}$ = 450 nm) in water.

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**Acknowledgement:** The authors gratefully acknowledge the University of Potsdam for providing infrastructure and research facilities. Valuable discussions along with hosting by Prof. Dr. Helmut Schlaad, are also sincerely appreciated.

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# Conjugated polymers with a built-in metal complex catalyst for visible-light-driven $CO_2$ reduction

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Reductive conversion of $CO_2$ into energy-added molecules has been an important subject in various fields including materials chemistry, catalysis, electrochemistry, and photochemistry, from viewpoints of both decreasing $CO_2$ concentration and gaining energy and carbon resources. Among the various methods and schemes proposed, visible-light-driven $CO_2$ reduction in combination with water oxidation, one of the representative models of artificial photosynthesis, is an attractive solution because it enables abundant water and inexhaustible solar energy to be used to produce value-added chemicals. Molecular metal complexes and semiconductors are promising candidates for photocatalysts that can reduce $CO_2$ to CO, formate, formaldehyde, or other hydrocarbons. Although both molecular metal complexes and semiconductors have strengths and weaknesses, their weaknesses (low oxidation ability and low selectivity for reduction reactions) can be overcome via the construction of a suitable molecule/semiconductor hybrid material. However, facilitating electron transfer at the molecule/semiconductor junction while suppressing unfavorable back electron transfer events is challenging.

Recently, organic conjugated polymers have emerged as new candidates for photocatalyst materials. The organic polymers not only exhibit semiconducting properties due to the extended p-conjugation but also have the molecular designability. Metal-based catalytic sites are frequently required to selectively reduce $CO_2$. Hence, the design principle, that maximizes the synergy between the conjugated skeleton and catalyst moiety, is strongly desired for achieving efficient photocatalytic $CO_2$ reduction. Herein, we show strong impacts of excited charge distribution in conjugated polymer photocatalysts with a site-selectively incorporated Ru(II) complex catalyst, which are elucidated by a combination of ultrafast spectroscopy and theoretical calculation, on their photocatalytic activity for $CO_2$ reduction.[1-3]

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# $[Cr(tpPO)_2]^{3+}$ – a highly photooxidizing and photostable photoredox catalyst

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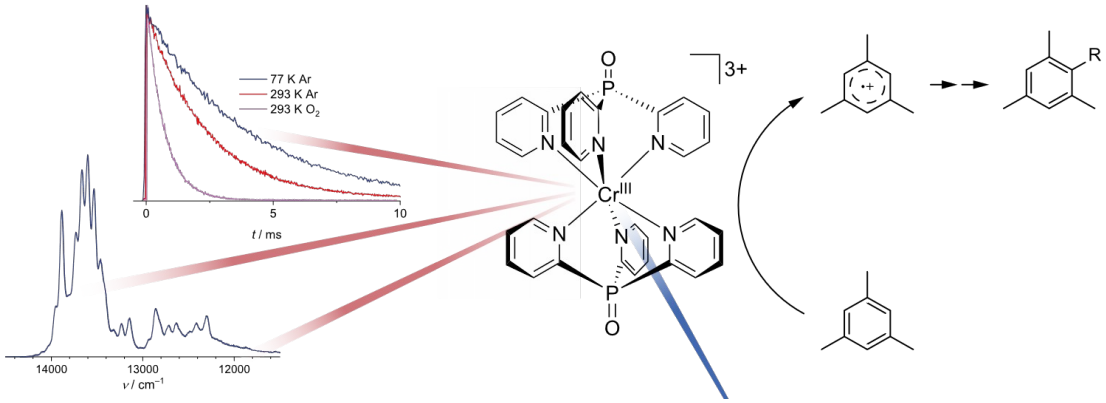
Due to their high excited state lifetimes up to milliseconds[1,2] and high excited state reduction potentials,[3–5] chromium(III) polypyridines have been shown to be versatile photoredox catalysts for reactions initiated by reductive quenching.[3–7]
In this work we present the synthesis, structure and comprehensive characterization of $[Cr(tpPO)_2]^{3+}$ (tpPO = tris(2-pyridyl)phosphane oxide). This complex is a highly photooxidizing chromium(III) spin-flip emitter with a tripodal trispyridyl ligand. The photophysical properties of the complex were determined by absorption spectroscopy as well as steady-state and time-resolved emission spectroscopy at ambient temperature and 77 K. Redox properties were measured using cyclic voltammetry.
We report the use of $[Cr(tpPO)_2]^{3+}$ as a photoredox catalyst. The outstanding combination of photophysical and redox properties of the complex permit the photoredox catalysis of reactions that have previously only been performed with 9-mesitylacridinium salts, a class of organic photoredox catalysts currently used in most challenging oxidative photoredox reactions (Fig. 1).[8,9]

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# Photoredox-Assisted Nickel-Catalyzed Cross-Couplings Facilitated by Brønsted Acid

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**Abstract**

Transition metal-catalyzed cross-coupling reactions are an indispensable tool in modern organic synthesis, enabling the rapid construction of molecular complexity. Traditionally, palladium has been the metal of choice for these transformations. Over the last decade, the field has advanced with the development of metallaphotoredox reactions, substantially expanding the toolkit available to synthetic chemists[1]. A common feature of the most well-known metal-catalyzed cross-couplings to date involves the use of bases, with only a few exceptions reported[2]. Recently, we introduced Adaptive Dynamic Homogeneous Catalysis (AD-HoC), which relies on the formation of catalytic species assemblies[3,4,5]. Among other reactions, the AD-HoC-based C($sp^2$)-S cross-coupling stands out due to its unique reaction conditions, which diverge from the conventional norms of traditional cross-couplings: the protocol does not require bases, ligands, or additives.

We report a novel transition metal-catalyzed thioetherification cross-coupling protocol, which, to the best of our knowledge, is the first to be facilitated by a mineral acid[6]. In contrast to conventional methods, our approach enables the efficient synthesis of thioethers using substoichiometric amounts of mineral acid. The protocol is readily scalable and compatible with continuous flow, achieving productivities of up to several hundred grams per hour in select cases. NMR kinetic studies indicate that, in the absence of acid, the reaction exhibits autocatalytic behavior and an induction period, both of which are suppressed upon acid addition, leading to accelerated reaction rates. Furthermore, the method enables the direct synthesis of thiophenols from $H_2S$ gas and demonstrates excellent functional group tolerance under acidic conditions, including *in situ* protection of basic moieties *via* protonation.

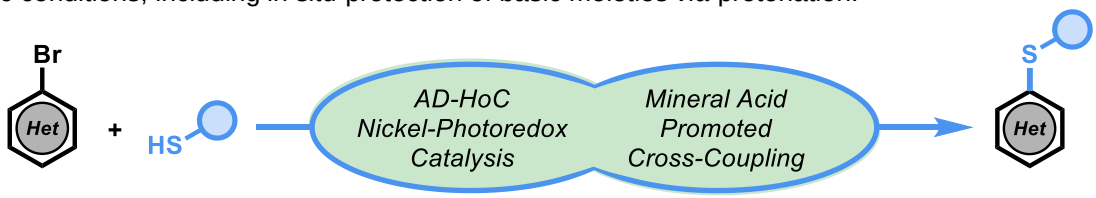


Figure 1. Mineral acid-promoted C($sp^2$)-S cross-coupling reactions with nickel and visible light.

In summary, we have developed, to the best of our knowledge, the first mineral acid-promoted transition metal-catalyzed cross-coupling reaction protocol. The method opens new avenues for synthetic chemists, enabling cross-couplings with previously challenging substrates.

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# Influence of cobalt precursors on the photocatalytic activity of $Nb_2O_5$-based composites for $CO_2$ reduction

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The photoreduction of carbon dioxide ($CO_2$) using UV-vis activated catalysts has emerged as a promising route for converting $CO_2$ into value-added compounds.[1,2] In this study, pure niobium oxide ($Nb_2O_5$) was synthesized, and $Nb_2O_5$/Co composites were developed using different cobalt precursors (nitrate, acetate, and sulfate), aiming to evaluate their performance in the photoreduction of $CO_2$ in aqueous media. $Nb_2O_5$ was obtained by precipitation from ammonium niobium oxalate, and the composites were prepared via impregnation followed by reduction with $NaBH_4$. The materials were characterized by XRD, FTIR, DRS, BET, SEM-EDS, XPS, and AAS. XRD patterns indicated that all materials exhibited an amorphous structure, with evidence of $Co_3O_4$ phase formation in the $Nb_2O_5$/Co-N and $Nb_2O_5$/Co-S composites. FTIR spectra revealed characteristic Nb–O and Co–O vibrational bands, confirming the formation of the composite structures. XPS analysis identified cobalt in multiple oxidation states ($Co^{2+}$, $Co^{3+}$, and $Co^0$), with metallic Co signals observed in the $Nb_2O_5$/Co-N and $Nb_2O_5$/Co-S samples. The $Nb_2O_5$/Co-S sample also showed features attributed to $NbO_2$, suggesting partial reduction of $Nb_2O_5$. Surface area measurements (BET) revealed values of 17, 20, 67, and 30 $m^2 \cdot g^{-1}$ for $Nb_2O_5$, $Nb_2O_5$/Co-A, $Nb_2O_5$/Co-N, and $Nb_2O_5$/Co-S, respectively, highlighting the influence of the cobalt precursor on material texturing. Photocatalytic activity was evaluated under UV irradiation in aqueous media. Pure $Nb_2O_5$ exhibited high CO production (2163.58 $\mu mol \cdot g^{-1}$), while the Co-modified composites demonstrated enhanced selectivity for $CH_4$ and $H_2$ formation. Among them, $Nb_2O_5$/Co-N achieved the best performance, producing 47.44 $\mu mol \cdot g^{-1}$ of CO, 3.50 $\mu mol \cdot g^{-1}$ of $CH_4$, and 1.95 $\mu mol \cdot g^{-1}$ of $H_2$. The $Nb_2O_5$/Co-A and $Nb_2O_5$/Co-S composites also exhibited photocatalytic activity, although at lower levels. These results demonstrate that the nature of the cobalt precursor significantly influences the structural, electronic, and catalytic properties of the materials, thereby affecting the efficiency and selectivity of $CO_2$ photoreduction.

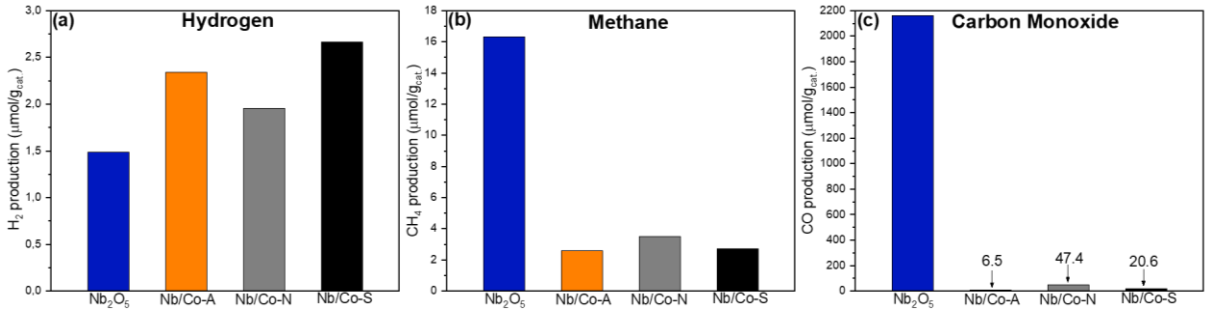


**Figure 1.** Production of $H_2$ (a), $CH_4$ (b), and CO (c) during the $CO_2$ photoreduction process under UV irradiation with 12 h of reaction.

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**Acknowledgement:** The authors acknowledge the support from Embrapa Instrumentação and the Brazilian National Nanotechnology Laboratory (LNNano) for the access to facilities and technical assistance.

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# HIGHLY EFFICIENT TRIPLET PHOTOSENSITIZERS BASED ON BORON-CENTERED DYES

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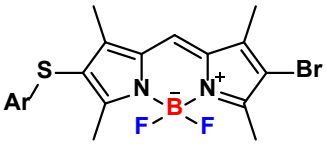
Photosensitizers (PSs), an outstanding entity category in both life science and material science, are compounds that can be readily activated by UV or visible light to convert light energy into chemical energy, permitting the formation of species like reactive oxygen species (ROS) and radicals. Thus, triplet PSs have attracted much attention in recent years, due to the significance of these kinds of compounds in fundamental photochemistry studies and applications in photocatalysis, photodynamic therapy (PDT) and triplet–triplet-annihilation upconversion (TTA-UC). In this context, PSs are currently a hot research subject of intense research.[1]

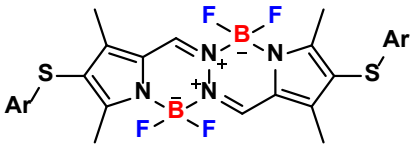
The role of the triplet PSs in photoinduced processes is to harvest the excitation light energy, then populate the long-lived triplet excited state of PSs via intersystem crossing (ISC), and finally drive the subsequent electron transfer or energy transfer. In the triplet energy transfer, the triplet PSs acts as triplet energy donor. Considering the intermolecular diffusion feature of the energy transfer processes involved in the above applications, there are at least two requirements for the PSs, i.e., strong visible light-harvesting ability and long excited state lifetime. A long-excited state lifetime is critical to improve the intermolecular energy transfer efficiency.

Within the realm of PSs, the expansion of BODIPY-based and BOPHY-based PSs has rapidly progressed over the past few decades, thanks to developments in modern synthetic chemistry.[2] Nevertheless, this progression has encountered several issues, such as poor water solubility, aggregation-induced fluorescence quenching, photobleaching, low cell permeability, and limited photocatalytic activity and efficacy. Therefore, diverse strategies for structural modification are essential to improve functional performance and achieve outstanding optical and electronic properties.

Herein, new asymmetric BODIPY dyes were successfully synthesized and fully characterized. They presented excellent optical characteristics such as absorption and ISC quantum yield, making triplet excited states capable of transferring their energy to an acceptor.[3]




On the other hand, a family of symmetric BOPHY dyes with arylsulfenyl groups at the 2 and 7 position onto the main core were also synthesized and fully characterized.[4] The molecular structures were supported by X-Ray diffraction (XRD) technique. The photophysical properties were studied in detail, including spectroscopic measurements, as well as laser flash photolysis investigations. These dyes were found to be suitable triplet photosensitizers in bimolecular systems for TTA-UC. Furthermore, not only direct, but also indirect experiments revealed that they properly acted as photosensitizers for singlet oxygen generation, making them potential candidates to be applied in biological investigations.




**Funding**: Spanish Government (PID2023-148367OB-I00, PID2022-1381890NB-I00, PRE2020-093783) and Valencian Regional Government (CIGRIS/2022/027).

**Acknowledgement:** We thank Prof. Diego Sampedro, Dr. Alejandro Cortés-Villena, Prof. Raquel E. Galián and Prof. Julia Pérez-Prieto for their contribution in these studies.

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# Entatic State Model Systems in Photochemistry

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The entatic state has been a useful tool in bioinorganic for the past 60 years where it explains the heightened reaction rates of copper electron transfer proteins. Central to the entatic state is the increase of reactivity by energizing the reactant and/or product sides of a reaction by employing steric strain and ligand-metal misfit. Work by our group as well as the Hadt group showed that the entatic state can also serve to increase intersystem crossing rates and $^3$MLCT lifetimes of tetracoordinate copper photosensitizers.[1, 2] This opens up the possibility of transferring thermal electron transfer systems into the area photoredox chemistry.

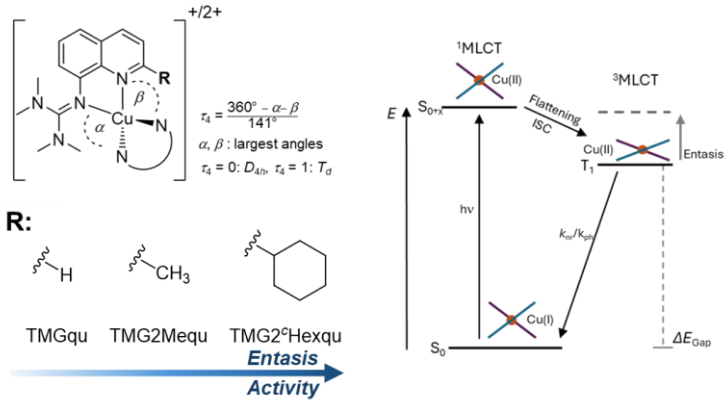


Figure 1: Left: The studied copper guanidine quinoline model systems Right: The effect of entasis on the triplet state geometry and energy.

The oral presentation is intended to insights into our current research concerned with classifying and understanding the photophysical and photochemical properties of copper guanidine quinoline complexes. These systems are known as model systems for the entatic state and serve to improve the understanding of entasis in coordination compounds.[3] To gauge their photochemical properties, we employed pump-probe XAS, DFT and the standard repertoire of cyclic voltammetry, UV/Vis spectroscopy and fluorescence emission spectroscopy. The data show that increasing rigidity of the copper systems serve to increase the triplet lifetimes and result in favorable kinetics for reduction and oxidation events of both the ground state and excited states. Finally, the systems were tested as photoredox catalysts in photocatalyzed ATRA reactions where they show varying efficacy with the degree of entasis present.

The results show to deepen the understanding of the entatic state in photochemistry and further demonstrate that copper guanidine quinoline systems, despite being designed for different purposes, can serve as photosensitizers.

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**Acknowledgement:** We thank the Regional Computing Center of the University of Cologne (RRZK) for providing computing time on the DFG-funded High Performance Computing (HPC) system CHEOPS as well as support.

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# Photoredox O-ATRP of Styrene via Molecular Design of Imidazole-based Organic TADF Photocatalysts

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**Abstract:**

Controlled radical polymerization has revolutionized polymer synthesis, allowing chemists to precisely tailor polymer topology to achieve desirable properties. Among these methods, atom-transfer radical polymerization (ATRP) has become a cornerstone for constructing complex polymers due to its versatility and efficiency.[1] However, the reliance on transition-metal catalysts presents a significant challenge, as residual metal contaminants can limit its widespread application in fields such as biomedicine, cosmetics, and electronics. In line with the emergence of photocatalysis in organic synthesis, organocatalyzed photoredox ATRP (O-ATRP) has emerged as a powerful metal-free alternative to Cu-based ATRP, offering a minimal catalyst loadings.[2] Despite recent advances, the range of polymerizable monomers remains constrained by the reduction potential of available photocatalysts, with styrene posing a particular challenge due to its susceptibility to back electron transfer. Here, we present a series of imidazole-based,[3] purely organic thermally activated delayed fluorescence (TADF) photocatalysts with diverse molecular designs, including heteroatom incorporation, structural constraints, and π-extension, enabling the polymerization of a broader range of monomers, including styrene. Overall, these materials show promise as state-of-the-art photocatalysts, featuring a molecular design that integrates sulfur and structural constraints. This design results in a high reduction potential, long-lived excited states, and strong molar absorptivity in the visible range, enabling the synthesis of polymers with low dispersity in near-quantitative yields.

**Funding:** Natural Sciences and Engineering Research Council of Canada.

**Acknowledgement:** I would like to my sincere gratitude to Zachary M. Hudson for invaluable guidance and support and UBC for departmental and central facilities.

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# Photophysical Properties of Tunable Co(III) Photosensitizers with Phenothiazine-based Ligands

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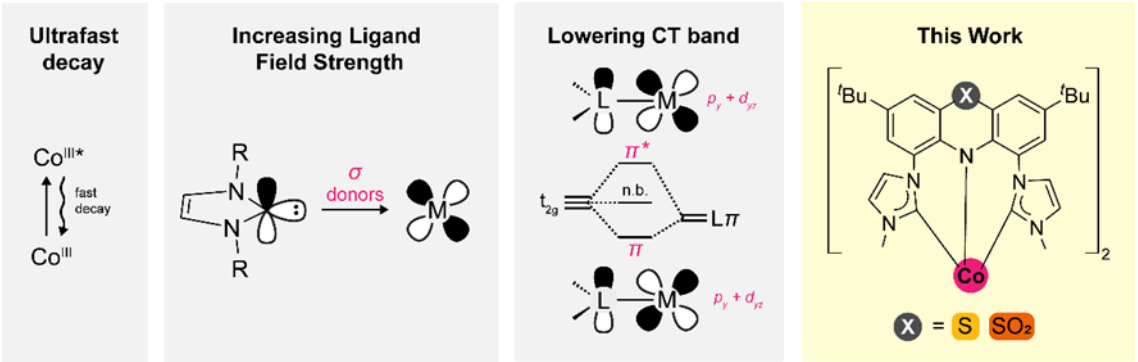
Complexes containing 1st row metals often show low efficiency in converting light to other forms of chemical energy due to ultrafast decay. Recent studies have shown that increasing the ligand field strength with strong σ-donating cyclometallated carbene ligands and lowering the photoactive charge transfer (CT) can increase the decay lifetimes of Fe(II) and Co(III).[1–3] Despite significant advances, these complexes continue to be largely uncompetitive in most photochemical applications and exhibit limited tunability.

Here, we show how sulfur-bridged ligands can tune the structural and photophysical properties in Co(III) photosensitizers. We use a tridentate chelated ligand based on phenothiazine combining two σ-donating NHC units and a central amido π-donor. The sulfur-bridge increases the bite angle compared with the carbazole-based Co(III) photosensitizer, favoring the formation of the *facial* isomer. [4] The electron density at the metal center is modulated by the oxidation state of sulfur, thus dictating the excited state dynamics and excited state character. The presence of the phenothiazine is beneficial to engage photoinduced electron transfer of methyl viologen. These findings demonstrate that the photophysical properties of Co(III) complexes can be modulated by the oxidation state of sulfur to achieve different photoactivities.




**Funding:** Natural Sciences and Engineering Research Council of Canada (NSERC)

**Acknowledgement:** We thank the Laboratory for Advanced Spectroscopy and Imaging Research (LASIR) for facility access.

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# UVA-light induced photocatalytic defluorination of perfluoroalkyl substances by silver-loaded titanium dioxide

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Perfluoroalkyl substances (PFASs) possess exceptional thermal stability, chemical resistance, electrical insulation, and surface activity, which have led to their widespread use across various industrial applications. However, the strong carbon-fluorine (C–F) bonds within these compounds confer extreme environmental persistence and bioaccumulative potential, posing significant ecological and health concerns. Accordingly, the development of degradation strategies under mild conditions is essential for realizing a sustainable fluorine cycle.

Previously, we reported that cadmium sulfide nanocrystals (CdS NCs) in combination with continuous irradiation with a 405 nm LED can efficiently degrade PFASs into fluoride ions.[1] The degradation mechanism involves nonlinear photochemical processes via multiphoton absorption by CdS NCs and photoinduced detachment of organic ligands. Despite its effectiveness, this approach suffers from key limitations, including the release of toxic cadmium ions and the requirement for relatively high-intensity light sources.

In this study, we aimed to develop a more environmentally benign method for PFAS's degradation by employing low-toxicity materials. We selected silver-loaded titanium dioxide ($Ag/TiO_2$) as the photocatalyst, due to its excellent chemical stability, low toxicity, and low cost. Electrons in the valence band of $TiO_2$ are excited to the conduction band by UV irradiation, and these photoexcited electrons can subsequently transfer to the supported silver nanoparticles. This electron transfer is expected to contribute to improved charge separation under UV light, thereby enhancing photocatalytic efficiency.

Using $Ag/TiO_2$ under irradiation of a 365 nm LED, we achieved an efficient degradation of perfluorooctanesulfonic acid (PFOS, Fig. 1a), one of the most chemically persistent PFASs. $Ag/TiO_2$ was prepared by impregnation of Ag on $TiO_2$. The concentration of Ag was maintained at 1 wt-% of $Ag/TiO_2$. The synthesized 1 wt-% $Ag/TiO_2$ exhibited a structure in which face-centered cubic Ag NCs with an average diameter of ~5 nm were loaded on anatase-phase $TiO_2$ powders with particle sizes below 44 μm, as observed by transmission electron microscopy. In the experiments, triethanolamine (TEOA) was used as a hole scavenger to further promote the reaction.

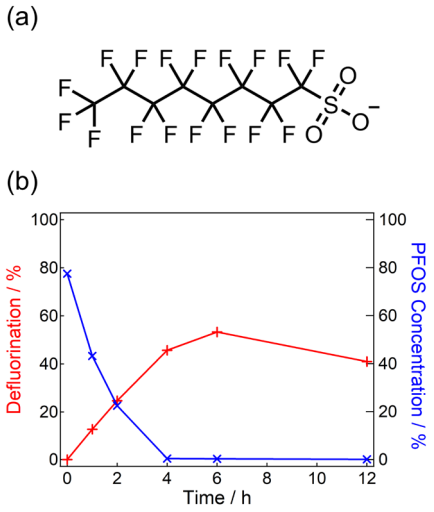


Figure 1. a) Molecular structure of perfluorooctanesulfonate b) PFOS degradation under 365 nm UV light irradiation (760 mW, 0.76 W/cm$^2$) using $Ag/TiO_2$.

In a typical defluorination experiment, 0.60 mg of PFOS potassium salt, 5.0 mg of $Ag/TiO_2$, and 18 mg of TEOA were suspended in 1.0 mL of deionized water. After 4 hours of 365 nm UV-light irradiation, 99% of PFOS was degraded, and approximately 46% of its 17 C–F bonds were cleaved (Fig. 1b). These results highlight the potential of the $Ag/TiO_2$/LED system as a practical and sustainable technology for PFAS remediation. Detailed mechanistic insights will be discussed in the presentation.

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# Visible light-driven hydrogen production by hydrated electrons in aqueous solutions using a single-molecule catalyst

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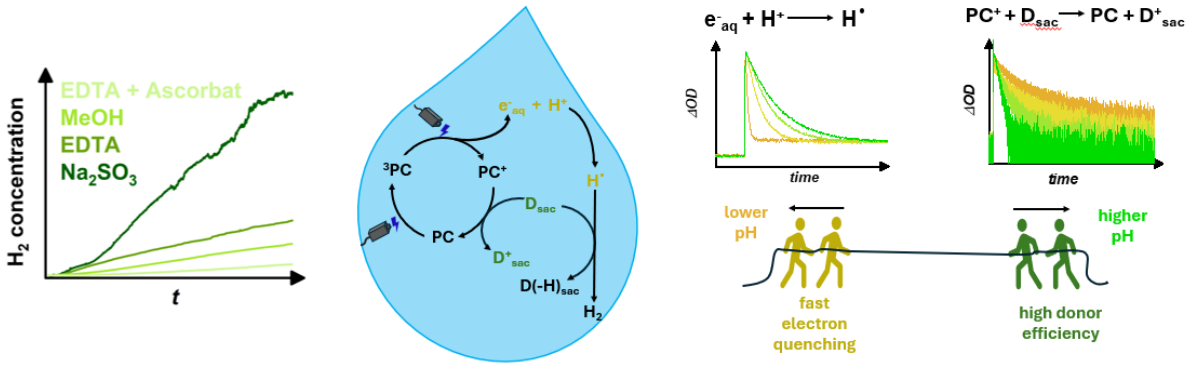
The photocatalytic production of molecular hydrogen offers promising possibilities to solve the complex energy problems of the near future. However, highly desired single-molecule catalysts for efficient light-driven hydrogen generation are scarce.[1,2] Our novel two-photon mechanism in water utilizes hydrated electrons for the generation of hydrogen atoms, which are the key species for the formation of $H_2$. Previously a related catalytic cycle operated under alkaline conditions, precluding the formation of the hydrogen atom due to the lack of protons.[3,4] After successfully realizing the catalytic cycle in acidic water, the performance of the system was optimized. The pH value has to be balanced to provide sufficient proton concentrations for hydrated electron quenching on one hand, and to ensure the activity of the sacrificial donor (that is prone to protonation, thereby losing its activity) on the other hand. Various sacrificial electron donors, including $Na_2SO_3$, EDTA (both alone and in combination with ascorbate), and methanol, were evaluated for their efficiency. Among them, $Na_2SO_3$ emerged as the most promising donor. This resulted in a four-fold enhancement in photocatalytic activity relative to EDTA, which was the second most effective electron donor. A combination of laboratory-scale irradiation experiments and detailed spectroscopic investigations provided deep mechanistic insights into this novel hydrogen-generating mechanism.

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# Novel Deazaalloxazine Derivatives for Photoreductive Catalysis: Synthesis and Photophysical Insights

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A series of 5-aryldeazaalloxazine derivatives have been efficiently synthesized via a one-pot, three-component reaction involving *N,N*-dimethyl barbituric acid, aromatic aldehydes, and anilines. **This straightforward methodology enables rapid access to structurally diverse derivatives functionalized with electron-donating or halogen substituents**, facilitating the development of novel photoredox catalysts without requiring additional purification steps.[1]

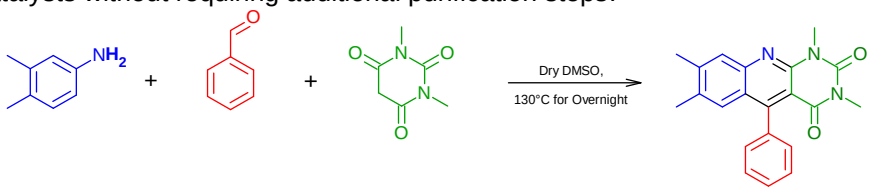


Figure 1.Optimized chemical reaction for novel deazaalloxazine derivatives.[1]

**These deazaalloxazines exhibit exceptional photophysical properties, including the most negative excited-state reduction potentials reported to date, with reducing power comparable to lithium.** [2,3] Moreover, they demonstrate **superior photostability compared to conventional flavins**. The synthesized derivatives have been successfully applied in **photoreductive desulfonylation** (converting sulfonamides and perfluoroalkanesulfonamides to parent amines) and **dehalogenation reactions** (bromo- and fluoroarenes). Additionally, they serve as **efficient singlet oxygen ($^1O_2$) photosensitizers**.

Comprehensive photophysical characterization in *N,N*-dimethylformamide (DMF) revealed fluorescence quantum yields, lifetimes, and radiative/nonradiative rate constants. **The singlet oxygen quantum yields ($\Phi_\Delta$) ranged from 0.066 to 0.30, with 5-'O'-BrPh-substituted derivatives ($\Phi_\Delta$ = 0.26 and 0.22 for 7,8-diMe and 7,8-diMeO variants, respectively) outperforming their 5-'O'-MePh counterparts ($\Phi_\Delta$ = 0.066 and 0.096)**. Transient absorption spectroscopy (µs timescale) further elucidated their excited-state dynamics, correlating structural modifications with enhanced photocatalytic performance.

**This work establishes 5-aryldeazaalloxazines as versatile photoredox catalysts** with applications in organic synthesis and oxidative transformations, **highlighting the critical role of substituent effects in tuning their reactivity**.

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**Acknowledgement:** We thank our collaborative partners (Department of Organic Chemistry, Institute of Chemical Technology, Technicka 5, 16628 Prague 6, Czech Republic) for allowing us to analyse the photophysical and photochemical properties of the synthesized compound and for allowing a nice and coherent presentation for the conference.

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# Photoredox catalysed difluoromethylation–triggered transformations of styrene derivatives

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The difluoromethyl ($CF_2H$) substituent offers great potential for the modulation of biological, physical and chemical properties in new agrochemicals, pharmaceuticals and organic functional materials candidates.[1] Therefore, significant attention has been paid to the preparation of difluoromethyl compounds, using a variety of fluorinating agents such as $SF_4$, HF, DAST and BAST. However, these F sources are toxic and unstable, and forcing reaction conditions are required. More recently, the use of reagents leading to the *in situ* formation of difluoromethyl radical[2] (e.g. $HCF_2I$, $Zn(SO_2CF_2H)_2$) or difluorocarbene[2] (e.g. $HCF_2SO_2Cl$, $HCF_2SO_2Na$) have emerged as powerful strategies. However, these compounds pose practical challenges associated to their preparation, handling and storage and disposal.

Here we report our studies on photocatalytic difluoromethylation reactions using readily available, stable sources of $CHF_2$ radical [3], including difluoromethylation of enolates, oxydifluoromethylation of alkenes (Fig. 1).

We will also present our recent progress in Fe-catalysed oxidative fluoroalkylation with di-/trifluoroacetic acid as sources of fluoroalkyl radicals.

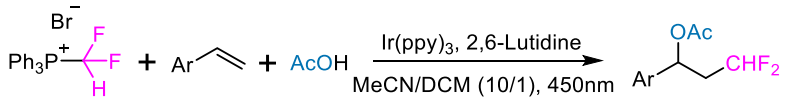


Figure 1. Oxydifouoromethylation of strene

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# Heterostructured Redox Mediator for Photoelectrochemical HMF Oxidation with Simultaneous Hydrogen Production

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Replacing the kinetically demanding oxygen evolution reaction (OER) in conventional photoelectrochemical (PEC) water-splitting systems with an anodic oxidation of biomass-derived compounds offers a promising strategy for enhancing both the process efficiency and economic viability of PEC processes. Among these biomass valorisation reactions, the oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) has gained significant attention. The latter is an important precursor for sustainable bio-based plastics synthesis. Despite its lower thermodynamic barrier compared to the competing OER, direct HMF oxidation is usually hindered owing to the high overpotential on common photoanodes such as $BiVO_4$. As a result, redox mediators are typically required to facilitate the conversion and improve the selectivity toward FDCA. Previous research has demonstrated the effectiveness of adding TEMPO, a well-established redox mediator for organic oxidation, into the electrolyte [1]. TEMPO acted as a homogeneous catalyst, oxidised by the photo-generated holes at the surface of the anode and subsequently regenerated while receiving electrons from the organic species (i.e., HMF and the intermediate products). However, a notable degradation of TEMPO through over-oxidation has been observed during the PEC reaction. Such degradation limited both HMF conversion and the Faradaic efficiency. The use of TEMPO also posed additional challenges including product separation, chemical toxicity and low solubility in aqueous systems.

This study investigated the use of alternative redox mediators with high stability and low process complexity. $Ni(OH)_2$/NiOOH emerged as a promising solid-state redox mediator and has been proven potent for HMF oxidation in electrochemical systems [2,3]. However, the application of this redox couple in the PEC system remained limited as it was generally presumed that constructing $Ni(OH)_2$/NiOOH on photoanodes would favour the competing OER. Herein, we demonstrated a synthesis method for $Ni(OH)_2$ thin film through electrodeposition. The catalyst film was characterised using X-ray diffraction (XRD), in-situ ultraviolet-visible (UV-vis) spectroscopy, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). Electrochemical analysis confirmed the redox behaviour of $Ni(OH)_2$/NiOOH as well as a thorough oxidation path from HMF to FDCA. Subsequently, $Ni(OH)_2$ was uniformly coated onto $BiVO_4$ photoanodes, forming a nanoweb structure as evidenced by SEM. Product quantification following prolonged PEC reaction confirmed the formation of FDCA alongside related intermediates with a Faradaic efficiency of 81%. Further characterisation also showed an excellent stability of the heterostructured photoanodes. The thickness of the $Ni(OH)_2$ coating was manipulated by controlling the deposition time and the pH conditions of the electrolyte for optimal PEC performance.

Kinetic studies revealed that the rate-limiting step was the chemical reaction between the electrochemically produced NiOOH and HMF. Further experiments investigated the temperature dependence of the reaction kinetics, and the activation energy was calculated based on the recorded photocurrent. These results demonstrated that the $Ni(OH)_2$/NiOOH redox couple was a functional mediator for HMF oxidation in PEC systems, providing a stable and cost-effective alternative to traditional options. The proposed solid-state heterojunction strategy also simplified product separation by avoiding the need of soluble additives in the electrolyte, advancing the design of practical PEC systems for organic oxidation.

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# Exploring optical binding inside and outside laser irradiation area toward a rational design of optical matters

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Optical matter refers to a non-equilibrium colloidal self-assembly that emerges exclusively under light irradiation, where nanoparticles (NPs) are optically bound into diverse structures. These assemblies enable significant applications, such as bio-inspired swarming, precisely controlled microrobots, and orderly formed metamaterials[1,2,3]. However, achieving rational design of optical matter demands a comprehensive understanding of the complex interactions and exploration of tunability from both chemical and optical perspectives.

In our work, we observed Au NP swarming behavior, notably finding that Au NPs become bound even outside the directly irradiated laser area. To clarify the system, we divided it into two regions: inside the laser focus and outside the irradiated area (Fig. 1a). Within the laser focus, near-field (NF) and far-field (FF) optical binding are responsible for the optical matter formation (Fig. 1b). We demonstrate that the strength of these bindings can be tuned by electrolyte concentration. Increasing salt concentration promotes NF optical binding, resulting in reduced interparticle distances. For the region outside the irradiated area, we employed a spatial light modulator (SLM) to generate two identical optical traps to probe optical binding effects (Fig. 1c). The interference pattern is visualized by tracking the motion of Au NPs between the traps. At specific separations between the laser beams, synchronized movements of the trapped NPs were observed. To further enhance the tunability of optical matter, we propose manipulating particle shape and laser parameters in future work.

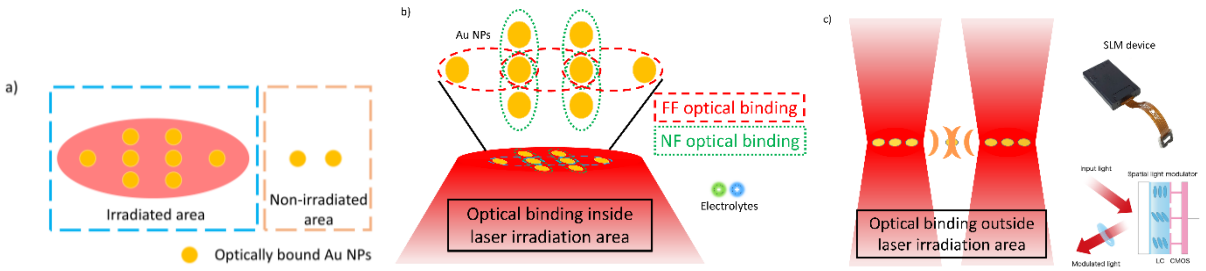


Figure 1. Optical matter formed by interaction of NPs and light. a) Optically bound Au NPs inside and outside laser irradiation area. b) NF and FF optical binding configurations within laser irradiated area tuned by adding electrolytes. c) Optical binding outside laser irradiation area probed by two identical optical traps generated by SLM[4].

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# Optical binding and assembly outside irradiation area: gold nanoparticles guided by gold nanodisk pattern

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The strong scattered light between irradiated plasmonic nanoparticles leads to remarkable light–matter interactions and results in the formation of ordered optical matter of colloidal nanoparticles, where the interparticle separation corresponds to the laser wavelength. This phenomenon is known as optical binding. Under optical trapping condition, where the intense gradient force was involved, the confined nanoparticles exhibited distinctive dynamics. Our group has demonstrated that a single, large, dumbbell-shaped dynamic assembly of 400 nm gold nanoparticles is formed by tightly focusing a linearly polarized 1064 nm laser at the glass/solution interface, a phenomenon termed the "swarming" of gold nanoparticles. [1] Further investigations employing single-particle tracking at the individual nanoparticle level revealed that non-irradiated nanoparticles exhibit a periodic, arc-shaped localization pattern, representing the first experimental evidence of optical binding among non-irradiated and irradiated gold nanoparticles. [2] We further propose that swarming is originated from the abovementioned mutual interactions and scales nonlinearly with increasing particle number, creating an extensive optical binding network. However, due to the pronounced dynamic fluctuations of the nanoparticles and the limitations of single-particle tracking methodologies, such periodic distributions have yet to be observed at the ensemble level.

In this presentation, we employ lithographically fabricated gold nanodisk patterns designed to mimic optical binding structures, and we develop an improved particle detection algorithm to retrieve the high-density localizations of trapped gold nanoparticles. Notably, under the illumination with a circularly polarized laser beam, the initially isotropic assembly becomes anisotropic when the laser is positioned on the gold nanodisk pattern. Furthermore, the localization of non-irradiated gold nanoparticles exhibits several clear, periodic arc-shaped distributions, thereby realizing the proposed optical binding network outside the irradiation area.(Fig. 1) Irradiation time-dependent studies reveal that the positions of these arcs remain nearly unchanged during both the early and saturated stages of swarming, suggesting that the potential minima can be predicted by the preferred localization of non-irradiated particles at the initial stage. We believe that the optical binding network will pave a new way for the fabrication of reconfigurable, dynamic, and large-scale optical matter beyond the geometry of a single tightly focused laser beam.

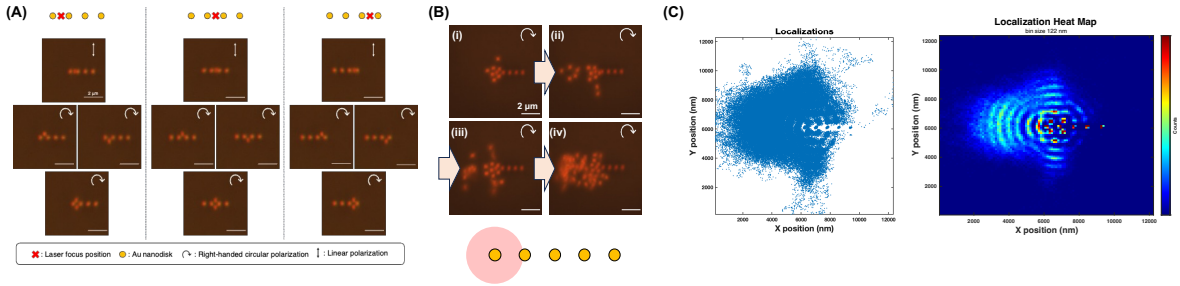


Figure 1. Representative backscattered snapshots at (A) the individual and (B) the ensemble level of swarming. (C) The scatter plot of detected localizations over 2000 frames and its heat map.

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**Acknowledgement:** M.-E. L. thanks the NSTC for the NSTC graduate research fellowship.

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# Nonoplasmonic Hybrid Photoelectrodes for One-step Immunosensing Devices

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Nanoplasmonic hybrid semiconductor/metal bilayer hold significant promise as advanced immunosensors in Point-of-care detection (POCT) applications due to their real-time photoelectric responses. As a consequence of these trends, photoelectric responses related to the improvement of nanoplasmonic hybrid photoelectrode design are increasingly raised. It is noted that nanoscale semiconductors integrated with an Au layer have been widely utilized as immunosensors due to their remarkable photocurrent response. Nevertheless, the challenge for photoelectrode-based immunosensing lies in developing one-step detection protocol specifically focusing on antibody-antigen biorecognition while avoiding the complexities typically associated with conventional approaches. In our previous work, we successfully constructed 2D array of $TiO_2$-nanowire/Au-nanoparticle core-shell heterostructure (TNW/Au-Meta) with large contact areas and great biocompatibility, providing suitable biomolecule loading sites. As visible-light-driven immunosensing device, it can be used for the direct detection of AFP and IgG biomarkers in human serum without complex preparation processes, such as BSA blocking elements and linkers. However, achieving the goal of detecting cTnI is hindered by the limitations of physical immobilization effects. It is found that linear-like cTnI antibodies are adsorbed onto the surface of the TNW through non-covalent immobilization, which increase the dissociation rate of cTnI antibodies from the TNW surface, compromising sensor performance. In this regard, it is necessary to develop a robust surface-functionalized membrane to modify the surface of the immunosensor. In this study, a novel nanoplasmonic hybrid trilayer photoelectrode is developed based on PDA bioadhesive membrane, titanium nanowires, and 2D-arrayed Au-nanoparticle metasurface layer (PDA/TNW/Au-Meta). The PDA membrane facilitate the direct attachment of cTnI antibodies within just 10 minutes without the need for additional crosslinkers. This hybrid photoelectrode facilitates the one-step construction of an immunosensor with a wide detection range of 0.001–1000 ng $mL^{-1}$, a low detection limit of 0.001 ng $mL^{-1}$, and excellent selectivity.

**Funding:** This work was supported by National Science and Technology Council (NSTC), Taiwan (113–2113-M-005-007-, 112-2113-M-005-012-). This work was also financially supported by the 'Innovative Center on Sustainable Negative-Carbon Resources' from The Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) in Taiwan.

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# Fabrication of a Plasmonic Tapered Fiber Probe using Gold Nanoparticle Assemblies for Surface-enhanced Raman Scattering

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## I. Introduction

Tapered fiber tweezers, which utilize the tapered tip of an optical fiber to capture and manipulate microparticles, offer a promising approach for precise optical manipulation. Extending this technique to enable the trapping of not only nanoparticles but also individual molecules could significantly advance the field of nanoscience. For the spectroscopic characterization of trapped molecules and nanomaterials, surface-enhanced Raman scattering (SERS) represents a particularly powerful and sensitive analytical method[1]. Based on this background, we aim to fabricate a SERS probe by assembling plasmonic nanoparticles onto a tapered optical fiber.

## II. Experiments

The tip of a silica optical fiber was tapered by chemical etching in a paraffin-oil/hydrofluoric acid mixture, followed by removal of the polyimide coating. Amino groups were then grafted onto the exposed surface with 3-aminopropyltrimethoxysilane. The functionalized tip was then immersed in a colloidal Au nanoparticle dispersion synthesized via the citrate-reduction method, allowing the nanoparticles to self-assemble on the taper via electrostatic interactions.

## III. Results & Discussion

The fabricated tapered optical fiber tip, along with the surrounding region where gold nanoparticles were assembled, was characterized using a scanning electron microscope (SEM). The fiber tip was successfully tapered to a diameter of less than 1 μm, and gold nanoparticles were densely distributed on the tip surface (Fig. 1). The synthesized Au nanoparticles exhibited an average diameter of approximately 35 nm. The dense assembly of Au nanoparticles is expected to generate localized electromagnetic “hot spots”, thereby significantly enhancing the Raman scattering signals. Based on these results, we believe that the plasmon-tapered optical fiber we have created can be used for SERS analysis.

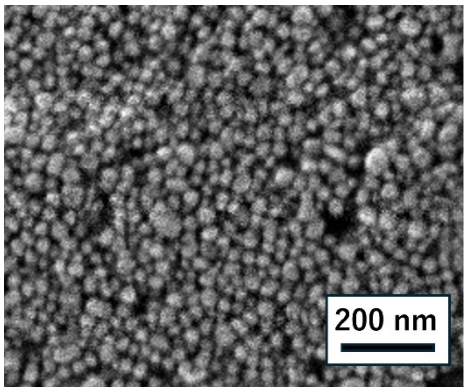


Fig. 1 A SEM Image of gold nanoparticles assembled on the optical fiber.

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# Fabrication of Tapered Optical Fibers Modified with Gold Nanoparticle Assemblies toward Plasmonic Optical Trapping

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## I. Introduction

Optical fiber tweezers trap microparticles by focusing propagating light at the tip of an optical fiber. However, achieving sufficient optical force for manipulating nanomaterials remains challenging. To address this issue, we focused on the localized surface plasmon resonance (LSPR) effect exhibited by noble metal nanostructures, which enhances the local electric field of light. Coupling plasmonic nanoparticles to the fiber tip would enable us to enhance optical force at the fiber tip. We tried to taper optical fibers using a meniscus acid etching process; however, the surface roughness of the tip led to insufficient focusing performance. Such tapered fiber induced undesired photothermal effect (e. g., thermophoresis) during optical trapping. In this study, we aim to develop plasmonic optical fiber tweezers by improving both the tapering process and the gold nanoparticle attachment method.

## II. Experiment

Tapered optical fibers were fabricated using the tube etching method[1]. The optical fiber was immersed in hydrofluoric acid. After removing the polyimide coating of the fiber, the surface was treated with 3-aminopropyltriethoxysilane (APTES), followed by tethering the synthesized gold nanoparticles. A near-infrared fiber laser beam was introduced into the fiber tip for optical trapping of polystyrene nanospheres.

## III. Results and Discussion

Fig. 1 shows a bright-field micrograph of the fabricated fiber tip. An apex angle of the fabricated fiber was determined to be approximately 18°, suggesting that a propagation of light through the optical fiber would be strongly focused at the tip. Additionally, the roughness of surface fabricated by tube etching was improved further. To immobilize gold nanoparticles onto the optical fiber surface, we examined the concentration of APTES and the reaction time during the silanization process. After surface modification, aggregation and precipitation of gold nanoparticles were observed, suggesting that dissolved silane molecules in the nanoparticle dispersion adversely affected the attachment. To address this issue, the APTES concentration was reduced, which successfully suppressed aggregation and multilayer formation. As a result, gold nanoparticles were uniformly attached to the fiber surface. Based on these results, we will fabricate the plasmonic optical fiber and attempt optical trapping.

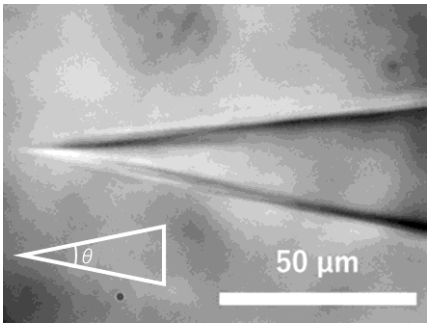


Fig. 1 A bright-field micrograph of a tapered optical fiber

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# Achieving PFAS Degradation through Plasmon-Induced Hot Carrier Generation in Metal Nanoparticles

**Samir Kumar Nayak**, Khushboo Bhardwaj, P. K. Verma, and Sharma S. R. K. C. Yamijala*
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## Abstract

Per- and Polyfluoroalkyl substances (PFAS) are a group of forever synthetic chemicals.[1] They are widely utilized in industries and household appliances because of their remarkable stability and distinctive oil- and water-repellent properties.[2] Despite their broad applications, unfortunately, PFAS are hazardous to all forms of life, including humans. In recent years, the environmental persistence of PFAS has raised significant interest in degrading these substances. However, strong C–F bonds pose challenges in the degradation of PFAS and make the process extremely difficult.

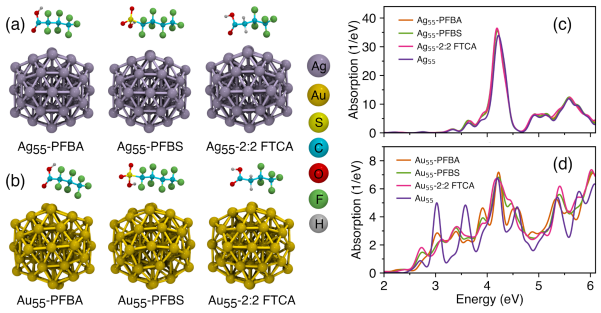


**Figure 1** (a-b) Optimized geometries of NP-PFAS interfaces, and (c-d) the photoabsorption spectra of the bare NPs as well as of NP-PFAS.

Plasmons of noble metal nanoparticles (NPs) offer many exciting applications, including photocatalytic reactions. However, an atomistic understanding of plasmon-driven processes remains elusive. In our work, using the real-time time-dependent density functional theory, we have theoretically studied the real-time formation of plasmons, hot carrier generation, and, subsequently, the direct hot carrier transfer from metal NP to PFAS.[3-4] Our study revealed that although the plasmon decayed significantly by creating hot holes and electrons within the metal nanoparticle, direct hot electron transfer also occurred with a total probability and dominated direct hot hole transfer. The direct hot-electron transferred to PFOA had energies larger than 1 eV, leading to their degradation seen in Ehrenfest dynamics. This is the first work to provide an atomistic picture of plasmon-induced direct hot-carrier transfer from NP to PFAS. We strongly believe that this work generates the impetus to utilize plasmonic NPs to mitigate PFAS.

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# High-resolution imaging of non-equilibrium colloidal self-assembly by photo-fixation

Jagannath Satpathy[1], Jim Jui-Kai Chen[1], Gang Wen[1,2], Hiroshi Masuhara[3], Sudipta Seth[1], Susana Rocha[1], Boris Louis[1], Roger Bresolí-Obach[4], Johan Hofkens[1,5]

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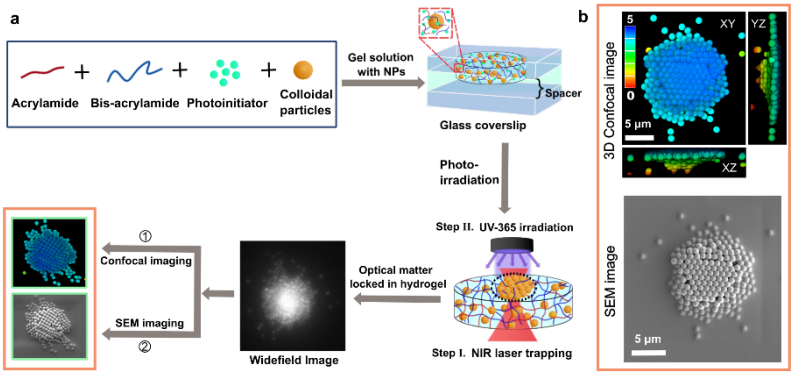
## Abstract

The self-organization of colloidal nanoparticles into complex structures, both in equilibrium and out-of-equilibrium, represents a growing area of interest in colloidal science with significant potential for creating functional materials. While equilibrium assemblies exhibit stable and periodic structures, out-of-equilibrium (or active) assemblies demonstrate dynamic and reconfigurable behavior under external stimuli.[1] Understanding the structure-function relationships in these assemblies remains challenging due to their transient nature and the limitations of current characterization methods. In this work, we present a novel workflow termed: **Fixation and Resolving of Colloidal Active Matter Ensembles (FRAME)**, designed to investigate transient and non-equilibrium colloidal assemblies through a two-step process. First, UV photopolymerization is used to fix the non-equilibrium colloidal assembly within a hydrogel, capturing a snapshot of its dynamic structure. Second, high-resolution imaging techniques, including 3D confocal microscopy and SEM, are used to accurately characterize the fixed assembly.[2]




**FRAME Steps 1–2**: Fixation of non-equilibrium optical matter in a photocrosslinked hydrogel, followed by 3D confocal and SEM imaging. (a) Method Illustration: A gel solution containing 1 µm polystyrene microparticles (PSMPs) is subjected to NIR laser trapping to assemble optical matter, then UV-irradiated to fix the structure for high-resolution imaging. (b) Method Validation: Fluorescent 1 µm PSMPs embedded in the polymer matrix are visualized using 3D confocal and SEM imaging.

We applied FRAME to study **Optical Matter (OM)** structures formed within an optical trap at the glass/water interface.[3] Using this approach, we conducted a detailed analysis of OM structures composed of colloidal nanoparticles ranging from 200 nm to 1 µm. Validation through confocal and SEM imaging confirmed that the FRAME workflow preserves the structural properties of the assemblies without alteration. While FRAME is currently demonstrated with 3D confocal microscopy and SEM, this method can be extended to other high-resolution imaging techniques and spectroscopic techniques, offering expanded opportunities to explore non-equilibrium assemblies. FRAME enables the combination of multiple measurements on the same sample without requiring all modalities in a single setup. This workflow provides a new avenue to study non-equilibrium colloidal assemblies and can be applied toward the rational design of colloidal metamaterials.

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# In-situ Transient Absorption Spectroscopy of the Photoreduction of $CO_2$ on Silver Nanoparticles

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The EU aims to have a net-zero greenhouse gas emission by 2050. Currently, fossil-derived carbon compounds are the backbone of the chemical industry. To reach net-zero emission by 2050, we must find alternative sources of carbon compounds. A promising pathway is to derive carbon compounds through the reduction of $CO_2$. Recently, Jain *et al.* showed that the photocatalytic reduction of $CO_2$ on silver nanoparticles under continuous laser illumination at 514 nm can potentially yield up to $C_4$ products.[1]

Catalysis through hot charge carriers is especially promising because it potentially enables highly selective reaction pathways, making the process viable for the chemical industry.[2] Alternatively, the localized photoinduced heating of the nanoparticle on the (sub-)picosecond timescale can also lead to catalytic conversion, although presumably with lower selectivity.

We aim to understand the photoconversion of $CO_2$ on silver nanoarrays. There are multiple catalytic pathways through which this reaction can occur. In silver nanoparticles, the electrons will collectively resonate and form a localized surface plasmon resonance (LSPR) when excited with visible light. LSPRs last only a few femtosecond before decaying into hot charge carriers, which thermalize further into heat.[3] Thermalization of the hot charge carriers can be avoided by ultrafast transfer into an acceptor molecule, which can initiate the photochemical conversion reaction.

To elucidate the photoinduced electronic and thermal processes and their dynamics in our plasmonic catalyst, we use femtosecond transient absorption spectroscopy under in-situ conditions. We saturate the solution with $CO_2$ and find that the obtained transient absorption signal blue shifts due to $CO_2$ absorbing on the surface of the silver nanoparticle. We also observe a slight change in lifetimes and observe oscillations indicative of surface processes occurring on the nanoparticle, see Fig 1a).

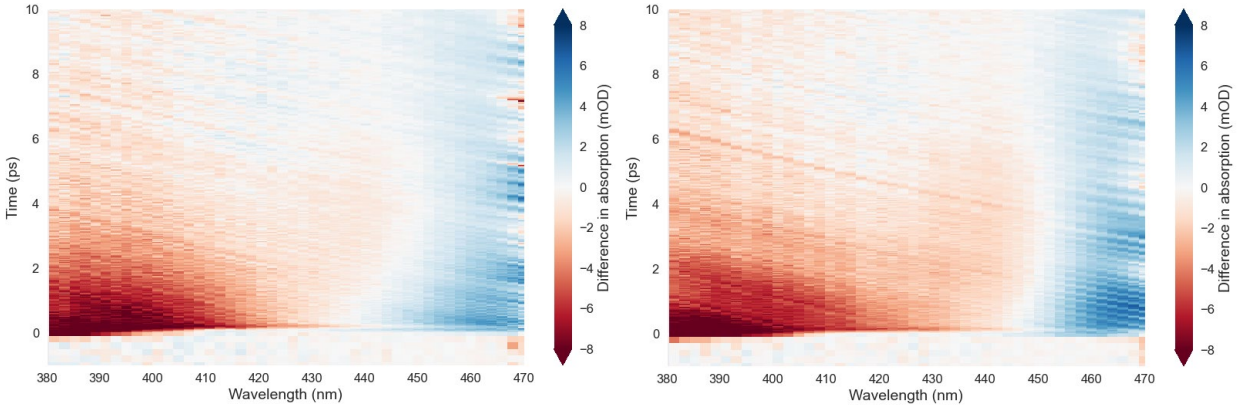


*Figure 1. Transient absorption spectra of Ag nanoparticles in aqueous solution saturated with $CO_2$ (a) and $N_2$ (b). The excitation wavelength used was 480 nm.*

**Funding:** NWO ENW M2 grant

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# Development of Photofixation for Polymer Nanoparticles Trapped by Plasmonic Optical Tweezers

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Excitation of localized surface plasmon resonance (LSPR) of noble metal nanostructures leads to optical trapping of nanoparticles dispersed in solution onto the surface of plasmonic nanostructures. Using such plasmonic optical tweezers, the trapped nanoparticles formed intriguing microstructures such as photonic crystal-like assemblies and the micro-ring patterning [1]. However, once LSPR excitation is stopped, the structures immediately disappear. Additionally, thermophoresis induced by LSPR excitation often hindered the optical trapping behavior. By Overcoming these issues, it would be possible to develop selective trapping and separation techniques at the nanoscale, as well as applications in microscopic spectroscopic analysis of the trapped substances. In this study, we investigated thermophoresis control using surfactants and the fixation of trapped nanoparticles via photopolymerization.

A plasmonic nanostructure was fabricated by assembling gold nanoparticles onto a glass substrate. The sample was prepared by contacting a dispersion of fluorescent polystyrene nanoparticles with the plasmonic substrate. After adding small amounts of surfactants and photofixation reagents to the sample solution, the trapping behaviors were observed using fluorescence microscopy.

Upon LSPR excitation using a near-infrared laser beam, nanoparticles dispersed in solution were trapped and formed assemblies on the substrate. The laser intensity was 20 kW/cm², which is comparable to the intensities typically used in conventional plasmonic optical trapping. Before the addition of the surfactant, the nanoparticles exhibited Brownian motion within the LSPR excitation area. However, the addition of the surfactant reversed the direction of thermophoresis, thereby promoting the formation of nanoparticle assemblies. After forming the assemblies, ultraviolet irradiation successfully fixed the nanoparticle assemblies onto the plasmonic substrate, as shown in Fig. 1.

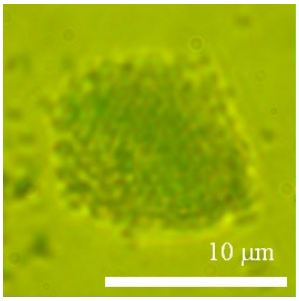


Figure 1. A bright-field micrograph of photofixation of the trapped polymer nanobeads

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# Resonant enhancement of vibrational signal around atomically precise gold nanoclusters seen with stimulated Raman scattering

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Atomically precise gold nanoclusters (AuNCs), due to their properties lying at the boundary between molecules and nanoparticles, have a wide range of potential applications [1]. However, before designing nanoclusters for specific applications, it is essential to understand their structure-properties correlations. We focus on disentangling their complex photophysics, and studying their vibrational properties in solution helps establishing the mentioned correlations.

In here, results of studying the $Au_{25}(PET)_{18}$ nanocluster in solution by means of stimulated Raman spectroscopy (SRS) are presented. Its electronic absorption spectrum is shown in Figure 1a, with markings for the Raman pump wavelengths selected such as to probe both resonant and non-resonant conditions. Remarkably, under resonant excitation at 515 nm we observe a clear enhancement of the solvent vibrational bands (dichloromethane, DCM) in the presence of AuNCs (Fig. 1b), despite the absence of surface plasmon resonance (SPR) in such a small cluster. This observation suggests the involvement of a “chemical” surface-enhanced Raman scattering (SERS). The lack of SPR might offer a unique opportunity to study this chemical enhancement independently of electromagnetic contributions, thereby facilitating a better understanding of this phenomenon and allowing for a more reliable estimation of the enhancement factor. Molecular dynamics simulations of the AuNCs in various solvents, support the findings.

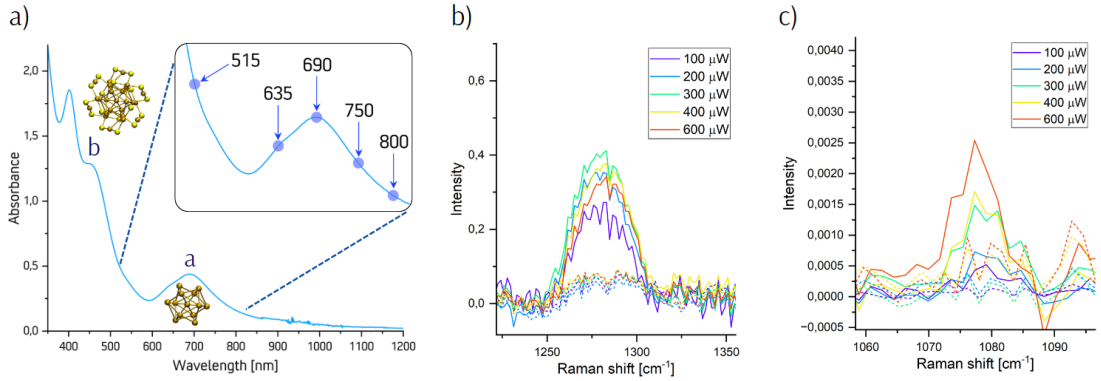


Figure 1. a) Absorption spectrum of Au25(PET)18, b) experimental Raman spectra of DCM in the presence of AuNC (solid lines) and pure DCM (dashed lines), c) a band assigned to the PET ligand.

Moreover, we detected weak Raman bands arising from the nanocluster itself. For excitation at 515~nm, bands corresponding to Au–S–Au bending modes were observed, whereas excitation at 800~nm revealed bands assigned to both Au–S–Au bending and a probable Au core breathing mode. A band at 1080 $cm^{-1}$ (Fig. 1c), associated with the PET ligand, was also observed despite the low sample concentration, further supporting the contribution of a chemical SERS mechanism.

In summary, we started looking for structural information for clarifying the photophysics of AuNCs, and we found an even more interesting and puzzling phenomenon: non-plasmonic Raman enhancement.

**Funding:** National Science Centre (OPUS Grant No. 2021/43/I/ST4/01411)

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# Fiber-based Plasmonic Microreactor for Flow Chemistry

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The European Green Deal aims to reduce the net greenhouse gas emissions to zero by 2050. Consequently, the European Chemical Industry Council stated that we "[…] need to change how we produce […] in less than 30 years […] while remaining globally competitive." [1]. Therefore, we need to develop disruptive and innovative technologies. As a promising example, researchers have investigated flow chemistry driven by light in compact reactors based on polymer hoses, transversally illuminated by UV LEDs [2]. However, the light management of such reactors is comparably poor compared to well-engineered optical systems. This results in high photon "costs" and low photon-to-reaction efficiencies.

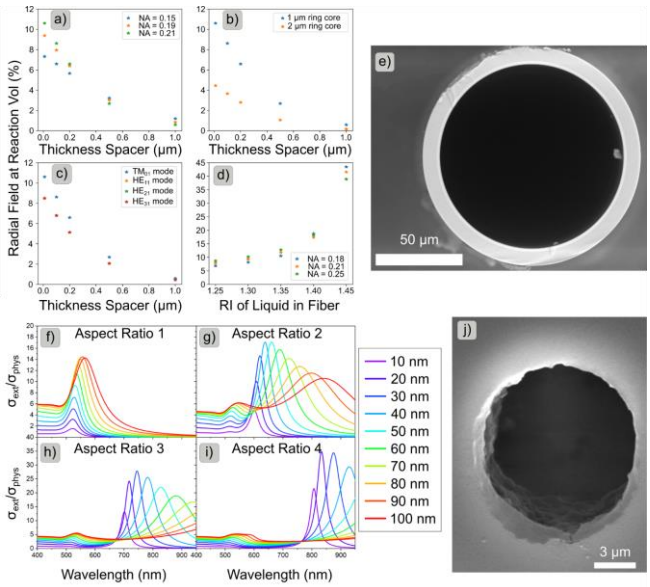


Figure 1: a) – d): Percentage of the radial field at the surface of the reaction volume depending on the thickness of the spacer layer for different numerical apertures (NAs) (a), ring thicknesses (b), modes (c), and depending on the refractive index of the liquid in the reaction volume (d). e): SEM picture of the drawn fiber. f) – i) Plasmon resonances for different side lengths of gold nanorods with an aspect ratio of 1 (f), 2 (g), 3 (h), and 4 (i). j) Close-up electron microscopy picture of the drilled holes to the side of the reactor fiber.

To tackle the high photon "costs" in photo flow reactors, we propose to drive photochemical reactions inside a specialty optical fiber. Our collaborative work is funded by the European Innovation Council (EIC) through the project reaCtor [3] The used specialty fiber is a ring-core fiber with a 100 µm hollow reaction volume. A fiber-based beam converter shapes the single-mode beam of a fiber-coupled laser diode into a donut mode and couples this mode into the ring core of the microreactor fiber. Plasmonic nanorods on the wall of the reaction volume act as efficient scatterers to enhance the light field. They distribute the photon energy to the reactants. Micromachined in-/outlets yield microfluidic connections

Here, we present the current status of our multidisciplinary research efforts. Based on an application-oriented assessment, we numerically design the optical and microfluidic properties of the fiber and fabricate it accordingly. We start the fabrication process with a modified chemical vapor deposition process and draw the as-manufactured preform to a fiber with 125/100 µm outer/inner diameter. We decorate the inner reaction volume of the fiber with plasmonic nanoparticles and fabricate the microfluidic in-/outlets via laser selective etching. In the near future, we will assemble an all-fiber microreactor and benchmark it for photo flow chemistry. We envision employing Bayesian optimization of the flow parameters for a fair comparison to current technology.

**Funding:** The project reaCtor has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No. 101099405.

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# Ultrafast Hot Carrier Decay in Aggregated Plasmonic Systems

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Molecular photoredox catalysts are premier candidates for clean energy reactions such as $CO_2$ reduction and water splitting due to their catalytic selectivity and tunability. However, they typically require high energy excitations through narrowband absorbances. Modern advancements in photocatalysis have focused on a shift toward more efficient catalysts that can harness lower frequency light through both catalyst design and the development of sensitizing agents. Plasmonic materials have emerged as one such light harvesting system due to the localized surface plasmon resonance (LSPR) induced by exciting noble metal nanoparticles with visible light. This phenomenon results in highly absorbing photosensitizers with broad, tunable absorbances across the solar spectrum (UV-NIR) and has demonstrated enhanced catalytic activity for clean energy reactions. The primary challenge of plasmonic photosensitizers lies in their ultrafast relaxation dynamics in which the high-energy electrons generated by the plasmon resonance decay on the order of 100s of femtoseconds. In this work, gold nanoparticles are aggregated by the adsorption of Ru(II) tris(2,2'-bipyridine) ($[Ru(bpy)_3]^{2+}$) to the metal surface to study the photophysical interactions between the plasmon and the molecular catalyst. The aggregation and successful adsorption of $[Ru(bpy)_3]^{2+}$ on the nanoparticle surface are characterized using absorption and Raman spectroscopies. Meanwhile, transient spectroscopies in the optical and x-ray regimes demonstrate unique electron dynamics in the complete system. This study reveals that both nanoparticle aggregation and the adsorbed electron acceptor could contribute to the efficient extraction of plasmon-generated hot carriers and further work that deepens this understanding will provide insight into the application of these light harvesting systems toward photocatalysis and solar cells.

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