ICP2025

32nd International Conference on Photochemistry

13th – 18th July
2025

Book of Abstracts
for Oral Presentations

Status: July 11, 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:

- 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 schedule is as follows:
🔔 Plenary Lecture: 50 minutes (including discussion)
💡 Invited Lecture: 30 minutes (including discussion)
★ Rising Star Lecture: 30 minutes (including discussion)
Contributed Talk: 20 minutes (including discussion)

This Book of Abstracts contains all scheduled oral presentations. For details on poster presentations, please refer to the additional file available on the conference website at www.icp2025.de.

Information for Presenters: We recommend that you present using your own computer, as all lecture rooms are equipped with HDMI connections. If you prefer to use a computer provided by the organizers, please reach out to Christian Ehli at christian.ehli@fau.de. Additionally, if you require an adapter for your presentation, please inform us in advance.

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)

SUNDAY, JULY 13

Opening Ceremony (Venue: RWTH Main Building, Aula)
17:15 – 17:30: Guldi, Dirk M. (FAU Erlangen-Nürnberg); **Wöll, Dominik** (RWTH Aachen University), Opening of the Conference

History of Photochemistry (Venue: RWTH Main Building, Aula)
17:30 – 17:50: Braslavsky, Silvia (Max Planck Institute for Chemical Energy Conversion), "The Photochemical Inheritance of Eduardo Lissi and Juan Grotewold", abstract on page 25 [Frontiers in Photochemical Sciences]

🔔 Opening Lecture (Venue: RWTH Main Building, Aula)
18:00 – 19:00: Nocera, Daniel (Harvard University), "The Bionic Leaf: Surpassing the C- and N- Fixation Processes of Nature", abstract on page 26 [Photochemistry and the Sustainable Environment]

🍸 **19:00:** Welcome Reception (Venue: RWTH Main Building)

MONDAY, JULY 14

🔔 Plenary Lecture (Venue: Eurogress, Europa Saal)

9:00 – 10:00: Wasielewski, Michael (Northwestern University), “Photogeneration and Dynamics of Multi-spin Systems for Quantum Information Applications”, abstract on page 27
[Frontiers in Photochemical Sciences]

Morning Parallel Session A (Venue: Eurogress, Europa Saal)
Session Chair: Richert, Sabine

10:10 – 10:30: Šolomek, Tomáš (University of Amsterdam), “New Modalities in Photochemical Uncaging with Visible Light”, abstract on page 28
[Light-Driven Functional Molecular Systems]

10:30 – 10:50: Kim, Dongho (Yonsei University), “Exploring Intermolecular Coupling and Excited State Dynamics in Perylene Bisimide Systems: From Monomers to Dimers and Beyond”, abstract on page 29
[Light-Driven Functional Molecular Systems]

☕ Coffee break

11:30 – 11:50: Pezzato, Cristian (University of Padova), “Photoacidic Polyelectrolytes”, abstract on page 30
[Light-Driven Functional Molecular Systems]

11:50 – 12:10: Ishow, Eléna (Nantes University), “Cooperative photoswitching materials”, abstract on page 31
[Light-Driven Functional Molecular Systems]

12:10 – 12:30: Nagai, Yuki (Ritsumeikan University), “Anomalous thermal back reaction dynamics in the photochromism of thioindigo in the presence of alkylamide self-assemblies”, abstract on page 32
[Light-Driven Functional Molecular Systems]

Morning Parallel Session B (Venue: Eurogress, K1)
Session Chair: Peneva, Kalina

10:10 – 10:30: Ihmels, Heiko (University of Siegen), “Photochemical conversion, storage and release of light energy with monoaryl-substituted norbornadienes”, abstract on page 33
[The Photophysics and Photochemistry of Solar Energy Conversion]

10:30 – 10:50: Schmidt, Timothy (UNSW Sydney), “Singlet Fission: From fundamentals to devices”, abstract on page 34
[The Photophysics and Photochemistry of Solar Energy Conversion]

☕ Coffee break

11:30 – 11:50: Zieleniewska, Anna (Technical University of Munich), “Elucidating microenvironmental factors governing photothermal conversion”, abstract on page 35
[The Photophysics and Photochemistry of Solar Energy Conversion]

11:50 – 12:10: Sohn, Woon Yong (Chungbuk National University), “Application of Near-Field Heterodyne Transient Grating (NF-HD-TG) Spectroscopy to the Investigation of Photoexcited Charge Carrier Dynamics”, abstract on page 36
[The Photophysics and Photochemistry of Solar Energy Conversion]

12:10 – 12:30: Rau, Sven (Ulm University), “Highly efficient artificial photocatalysts mimicking Photosystem 1”, abstract on page 37
[The Photophysics and Photochemistry of Solar Energy Conversion]

MONDAY, JULY 14

Morning Parallel Session C (Venue: Eurogress, K4/5)
Session Chair: Tschierlei, Stefanie

10:10 – 10:30: Basaric, Nikola (Ruder Boskovic Institute), “Photochemistry of biphenylamine photocages”, abstract on page 38
[Photochemical Reaction Kinetics and Mechanisms]

10:30 – 10:50: Jaworska, Maria (University of Silesia in Katowice), “Photophysical properties of nickel and palladium complexes with porphyrin and corrin. A theoretical perspective”, abstract on page 39
[Photochemical Reaction Kinetics and Mechanisms]

☕ Coffee break

11:30 – 11:50: Klán, Petr (Masaryk University), “(Photo)truncation of Cyanines”, abstract on page 40
[Photochemical Reaction Kinetics and Mechanisms]

11:50 – 12:10: Landgraf, Stephan (TU Graz), “Weak effects on electron transfer reactions – Rethinking of the determination of activation energies in solution”, abstract on page 41
[Photochemical Reaction Kinetics and Mechanisms]

12:10 – 12:30: Troian-Gautier, Ludovic (UCLouvain), “Novel Concepts to Outcompete Thermodynamics and Favor Cage Escape Yields in Bimolecular Electron Transfer Reactions”, abstract on page 42
[Photochemical Reaction Kinetics and Mechanisms]

Morning Parallel Session D (Venue: Eurogress, K8/9)
Session Chair: Ley, Christian

10:10 – 10:30: Gorgon, Sebastian (University of Cambridge), “Thermally Activated Delayed Fluorescence in Open-Shell Organic Molecules”, abstract on page 43
[Enriching Materials Science with Photochemistry]

10:30 – 10:50: Smolentsev, Grigory (Paul Scherrer Institute),”X-ray absorption spectroscopy in the nanoseconds-seconds range to probe rearrangements around catalytic centers induced by light”, abstract on page 44
[Advanced Spectroscopic Methods]

☕ Coffee break

11:30 – 11:50: Strehmel, Bernd (Niederrhein University of Applied Sciences), “Strategies for Oxygen Tolerant Radical Conventional and Controlled Photopolymerization with Less Toxicological Concern and Sustainable Origin”, abstract on page 45
[Enriching Materials Science with Photochemistry]

11:50 – 12:10: Popik, Vladimir (University of Georgia, Chemistry), “Photo-SPAAC ligation-based preparation of sequence defined macromolecules, patterned hydrogels, and macrocycles”, abstract on page 46
[Enriching Materials Science with Photochemistry]

12:10 – 12:30: Dash, Bignya Rani (Indian Institute of Technology, Madras), “Designing Ionic Soft Matter: Liquid Crystalline Ionogels from Protic Ionic Liquids”, abstract on page 47
[Enriching Materials Science with Photochemistry]

MONDAY, JULY 14

Afternoon Parallel Session A (Venue: Eurogress, Europa Saal)
Session Chair: Thomas, George

💡 **14:00 – 14:30: Blum, Suzanne** (University of California, Irvine), “Chemical Reaction Insights through FLIM” (invited lecture), abstract on page 48
[Advanced Spectroscopic Methods]

14:30 – 14:50: Jung, Gregor (Saarland University), “Single-Molecule Photochemistry”, abstract on page 49
[Pushing the Spectroscopic and Microscopic Limits of Single Molecules]

14:50 – 15:10: Nevskyi, Oleksii (Georg-August-Universität Göttingen), “Fluorescence-Lifetime Single-Molecule Localization Microscopy for multiplexing, environmental sensing and 3D imaging”, abstract on page 50
[Pushing the Spectroscopic and Microscopic Limits of Single Molecules]

15:10 – 15:30: Miller, Natalie A. (University of Glasgow), “Single Molecule Spectroscopy of Novel Conjugated Porphyrin Nanorings”, abstract on page 51
[Pushing the Spectroscopic and Microscopic Limits of Single Molecules]

15:30 – 15:50: Louis, Boris (KU Leuven), “On-the-fly local functional imaging of solar cell materials powered by Deep learning”, abstract on page 52
[The Photophysics and Photochemistry of Solar Energy Conversion]

15:50 – 16:10: Lucas, Marie (Laboratoire de Chimie, ENS de Lyon), “Molecular Engineering of AIE Fluorophores for NIR II-NIR I Imaging”, abstract on page 53
[Pushing the Spectroscopic and Microscopic Limits of Single Molecules]

Afternoon Parallel Session B (Venue: Eurogress, K1)
Session Chair: Oppermann, Malte

💡 **14:00 – 14:30: Young, Elizabeth** (Lehigh University), “Understanding Light-Driven Charge Carrier Dynamics for Efficient Solar Conversion in Complete Bifacial Sb_2S_3 Solar Cells using Transient Absorption Spectroscopy” (invited lecture), abstract on page 54
[The Photophysics and Photochemistry of Solar Energy Conversion]

14:30 – 14:50: Cherevan, Alexey (Technische Universität Wien), “Surface-supported All-inorganic Molecular Clusters for Light-driven Water Splitting Reactions”, abstract on page 55
[The Photophysics and Photochemistry of Solar Energy Conversion]

14:50 – 15:10: Karadaş, Ferdi (Bilkent University), “Creating Competing Charge-Transfer Pathways for Photocatalytic Water Oxidation”, abstract on page 56
[The Photophysics and Photochemistry of Solar Energy Conversion]

15:10 – 15:30: Diab, Gabriel Ali (Federal University of São Carlos), “Nickel Co-catalysts on Crystalline Carbon Nitride: Low-Cost Photocatalyst for Efficient Hydrogen Evolution”, abstract on page 57
[The Photophysics and Photochemistry of Solar Energy Conversion]

15:30 – 15:50: Katoh, Ryuzi (Nihon University), “Photoluminescence properties of rutile TiO_2”, abstract on page 58
[The Photophysics and Photochemistry of Solar Energy Conversion]

15:50 – 16:10: Gómez, Roberto (University of Alicante), “Polymer electrolyte membrane photoelectrolyzers for solar hydrogen production: experiments and theory”, abstract on page 59
[The Photophysics and Photochemistry of Solar Energy Conversion]

MONDAY, JULY 14

Afternoon Parallel Session C (Venue: Eurogress, K4/5)
Session Chair: Klán, Petr

💡 **14:00 – 14:30: Alabugin, Igor** (Florida State University), “The Photoredox Paradox: The Roles of Electron Upconversion and Electron Catalysis” (invited lecture), abstract on page 60
[Photoredox Catalysis]

14:30 – 14:50: Bertrams, Maria-Sophie (Universität Mainz), “Mechanistic insights into sensitization via one or two photon processes”, abstract on page 61
[Photochemical Reaction Kinetics and Mechanisms]

14:50 – 15:10: Huijser, Annemarie (University of Twente), “Limiting Molecular Twisting: Upgrading a Donor–Acceptor Dye to Drive Hydrogen Evolution”, abstract on page 62
[Photochemical Reaction Kinetics and Mechanisms]

15:10 – 15:30: Wang, Cui (University of Konstanz), “Photon upconversion via doublet-triplet energy transfer – A bright future for photoactive first-row transition metal complexes”, abstract on page 63
[Photochemical Reaction Kinetics and Mechanisms]

15:30 – 15:50: Ley, Christian (Université de Haute Alsace), “Analyzing Synergy in Photocyclic Three-Component Systems for radical photopolymerization”, abstract on page 64
[Photochemical Reaction Kinetics and Mechanisms]

15:50 – 16:10: Jordan, Caleb (University of Bristol), “Ultrabroadband Two-Dimensional Electronic Spectroscopy of Metalloporphyrin Chromophores in De Novo Protein Maquettes”, abstract on page 65
[Photochemical Reaction Kinetics and Mechanisms]

Afternoon Parallel Session D (Venue: Eurogress, K8/9)
Session Chair: Abrahamsson, Maria

💡 **14:00 – 14:30: Slavíček, Petr** (University of Chemistry and Technology, Prague), “Tuning Cyanine Chromophores: Does Ab Initio Theory Meet Molecular Reality?” (invited lecture), abstract on page 66
[New Theoretical Tools in Photochemistry]

14:30 – 14:50: Malis, Momir (University of Zurich), “Nonadiabatic dynamics simulations in condensed phase systems”, abstract on page 67
[New Theoretical Tools in Photochemistry]

14:50 – 15:10: Kühn, Oliver (University of Rostock), “BSE@GW-Based Spin-Vibronic Quantum Dynamics of Transition Metal Complexes”, abstract on page 68
[New Theoretical Tools in Photochemistry]

15:10 – 15:30: Ottosson, Henrik (Uppsala University), “Why do some heteroaromatics have n,pi* states as their first excited states, while others have pi,pi* states as these?”, abstract on page 69
[New Theoretical Tools in Photochemistry]

15:30 – 15:50: Landi, Alessandro (Università Degli Studi di Salerno), “Bridging Theory and Efficiency: Quantum-Inspired Insights into Organic Solar Cells Performances”, abstract on page 70
[The Photophysics and Photochemistry of Solar Energy Conversion]

15:50 – 16:10: Lindner, Henry (ETH Zurich), “photo-MHAT: Cobalt-Catalyzed Functionalization of Unactivated Olefins under Visible-Light Irradiation”, abstract on page 71
[Photoredox Catalysis]

MONDAY, JULY 14

★ Rising Star Lecture (Venue: Eurogress, Europa Saal)

16:30 – 17:00: Chen, Kai (Robinson Research Institute, Victoria University of Wellington, New Zealand), “Revitalizing Ultrafast Spectroscopy: Innovations in Technique and Application”, abstract on page 72
[Advanced Spectroscopic Methods]

🔔 Plenary Lecture (Venue: Eurogress, Europa Saal)

17:00 – 18:00: Landes, Christy F. (University of Illinois Urbana Champaign), “Plasmonic Pathway to Hybrid Nanomaterials through Energy Transfer”, abstract on page 73
[Frontiers in Photochemical Science]

18:00 – 20:00: Poster Session I (Venue: Eurogress, Foyer) The abstracts can be found in a dedicated Book of Abstracts on the conference website: www.icp2025.de.

TUESDAY, JULY 15

🔔 Plenary Lecture (Venue: Eurogress, Europa Saal)

8:30 – 9:30: Hofkens, Johan (KU Leuven), “Labels and linkers for microscopy: from improved imaging to applications.”, abstract on page 74
[Pushing the Spectroscopic and Microscopic Limits of Single Molecules]

Morning Parallel Session A (Venue: Eurogress, Europa Saal)
Session Chair: Kuimova, Marina

9:40 – 10:00: Douhal, Abderrazzak (Universidad De Castilla La Mancha (UCLM)), “Versatile Photobehavior of Single Crystalline, Non-Stoichiometric Hydrogen-Bonded Organic Frameworks”, abstract on page 75
[Enriching Materials Science with Photochemistry]

10:00 – 10:20: Pelicano, Christian Mark (Max Planck Institute of Colloids And Interfaces), “Boosting the Quantum Efficiency of Ionic Carbon Nitrides for Solar-Driven Fuel Synthesis”, abstract on page 76
[Enriching Materials Science with Photochemistry]

☕ Coffee break

💡 **11:00 – 11:30: Fürstenberg, Alexandre** (University of Geneva), “Encapsulated fluorophores and fluorescence lifetime sensors for super-resolution imaging” (invited lecture), abstract on page 77
[Pushing the Spectroscopic and Microscopic Limits of Single Molecules]

11:30 – 11:50: Filatov, Mikhail (Technological University Dublin), “Enhancement of Intersystem Crossing in Asymmetrically Substituted BODIPY Dyes: Application in Holographic Recording of Diffractive Structures”, abstract on page 78
[Enriching Materials Science with Photochemistry]

11:50 – 12:10: Tsuji, Yugo (Nara Institute of Science and Technology), “Excimer phosphorescence from multiple resonance type dimer”, abstract on page 79
[Enriching Materials Science with Photochemistry]

12:10 – 12:30: Fermi, Andrea (University of Bologna), “Conformation-Controlled Vapochromic Phosphorescence at Room Temperature”, abstract on page 80
[Enriching Materials Science with Photochemistry]

TUESDAY, JULY 15

Morning Parallel Session B (Venue: Eurogress, K1)
Session Chair: Yanai, Nobuhiro

9:40 – 10:00: Grüne, Jeannine (University of Cambridge), "High-Spin State Dynamics and Quintet-Mediated Emission in Intramolecular Singlet Fission", abstract on page 81
[Light-Driven Functional Molecular Systems]

10:00 – 10:20: Pun, Andrew (University of California San Diego), "Design Rules for Triplet-Triplet Annihilation Upconversion Annihilators", abstract on page 82
[Plasmonics & Photonics]

☕ Coffee break

💡 **11:00 – 11:30: Tinnefeld, Philip** (Ludwig-Maximilians-Universität München, Department Chemie), "3D Superresolution Microscopy of Vertical Nucleic Acids on Graphene" (invited lecture), abstract on page 83
[Pushing the Spectroscopic and Microscopic Limits of Single Molecules]

11:30 – 11:50: Link, Stephan (University of Illinois Urbana-Champaign), "Photophysics and Photochemistry of Individual Plasmonic Nanostructures", abstract on page 84
[Plasmonics & Photonics]

11:50 – 12:10: Misawa, Hiroaki (Okayama University), "Role of Quantum Coherence in Hole-Mediated Water Oxidation under Strong Coupling Conditions", abstract on page 85
[Plasmonics & Photonics]

12:10 – 12:30: Baruah, Raktim (Institute of Physical Chemistry, University of Kiel), "Tuning multiexciton properties of colloidal quantum dots via size and surface functionalization", abstract on page 86
[Plasmonics & Photonics]

Morning Parallel Session C (Venue: Eurogress, K4/5)
Session Chair: Landgraf, Stephan

9:40 – 10:00: Ishibashi, Yukihide (Ehime University), "Exciton Migration in Single Copper Phthalocyanine Nanofibers by Femtosecond Pump-Probe Microspectroscopy", abstract on page 87
[Photochemical Reaction Kinetics and Mechanisms]

10:00 – 10:20: Chen, I-Chia (National Tsing Hua University), "Relaxation Dynamics of Hemicyanine Dye Aggregates", abstract on page 88
[Photochemical Reaction Kinetics and Mechanisms]

☕ Coffee break

💡 **11:00 – 11:30: König, Burkhard** (University of Regensburg), "Better Organic Synthesis with Light" (invited lecture), abstract on page 89
[Photoredox Catalysis]

11:30 – 11:50: Ortyl, Joanna (Cracow University of Technology), "Photopolymerization processes in the induction of thermal reactions in the curing of composites", abstract on page 90
[Photochemical Reaction Kinetics and Mechanisms]

11:50 – 12:10: Kohlstedt, Kevin L. (Northwestern University), "A reversible, long-lived photoacid for biological pH-triggers: A time-resolved X-ray study of i-motif DNA folding after a pH-jump", abstract on page 91
[Photochemical Reaction Kinetics and Mechanisms]

12:10 – 12:30: Cruz Neto, Daniel H. (University of Geneva), "Excited Radical Ions in Organic Photocatalysis: A Photophysical Perspective", abstract on page 92
[Photochemical Reaction Kinetics and Mechanisms]

TUESDAY, JULY 15

Morning Parallel Session D (Venue: Eurogress, K8/9)
Session Chair: Blum, Suzanne A.

9:40 – 10:00: Cadranel, Alejandro (FAU Erlangen-Nürnberg), “Ultrafast Optical and Vibrational Studies of Photoinduced Mixed-Valence Ru Polypyridines”, abstract on page 93
[The Photophysics and Photochemistry of Solar Energy Conversion]

10:00 – 10:20: Albinsson, Bo (Chalmers University of Technology), “Triplet-Triplet Annihilation Photon Upconversion: Fundamental Challenges for TTA-UC in Confinement and into the UV”, abstract on page 94
[The Photophysics and Photochemistry of Solar Energy Conversion]

☕ Coffee break

💡 **11:00 – 11:30: D'Souza, Francis** (University of North Texas), “Intervalance (IVCT) and Symmetry Breaking Charge Separation (SBCS) in Far-Red Capturing Chromophore Dimers” (invited lecture), abstract on page 95
[Light-Driven Functional Molecular Systems]

11:30 – 11:50: Latterini, Loredana (DCBB - Università di Perugia), “Photocatalytic activity of Bi_2O_3- based materials for ammonia production”, abstract on page 96
[The Photophysics and Photochemistry of Solar Energy Conversion]

11:50 – 12:10: Yadav, Bharti (University of Padova), “Engineering Reversible Photoacid Systems: Structure-Function Relationships and Stability-Enhancing Strategies for Substituted MCHs”, abstract on page 97
[The Photophysics and Photochemistry of Solar Energy Conversion]

12:10 – 12:30: Zeng, Yi (Technical Institute of Physics and Chemistry, Chinese Academy of Sciences), “Energy and electron transfer in sensitization for photochemical upconversion”, abstract on page 98
[The Photophysics and Photochemistry of Solar Energy Conversion]

Afternoon Parallel Session A (Venue: Eurogress, Europa Saal)
Session Chair: Ito, Syoji

💡 **14:00 – 14:30: Richert, Sabine** (Goethe University Frankfurt), “Photogenerated quartet states for molecular spintronics” (invited lecture), abstract on page 99
[Light-Driven Functional Molecular Systems]

14:30 – 14:50: Ferree, Mariia (LMU München), “Organic semiconductor nanoparticles in CO_2 photoconversion: the need for efficient charge carrier generation and transfer”, abstract on page 100
[The Photophysics and Photochemistry of Solar Energy Conversion]

14:50 – 15:10: Haacke, Stefan (University of Strasbourg - CNRS), “Archaerhodopsin-3: An Ideal Template for Fluorescent Retinal Proteins”, abstract on page 101
[Light-Driven Functional Molecular Systems]

15:10 – 15:30: Parola, A. Jorge (Nova University Lisbon), “Nanomolar Affinity Supramolecular Photoswitching Systems”, abstract on page 102
[Light-Driven Functional Molecular Systems]

15:30 – 15:50: Baggi, Nicolò (Department of Chemical Engineering, Universitat Politècnica de Catalunya, EEBE), “Investigation of ortho-dianthrylbenzenes for Molecular Solar Thermal energy storage and release”, abstract on page 103
[Light-Driven Functional Molecular Systems]

15:50 – 16:10: Durbeej, Bo (Linköping University), “Molecular photogearing without thermal steps”, abstract on page 104
[Light-Driven Functional Molecular Systems]

TUESDAY, JULY 15

Afternoon Parallel Session B (Venue: Eurogress, K1)
Session Chair: D’Souza, Francis

💡 **14:00 – 14:30: S. Baptista, Mauricio** (Universidade de Sao Paulo), “The electrophilic species generated during Type I photosensitized oxidation of lipid membranes play a critical yet underappreciated role in photomedicine and sun care.” (invited lecture), abstract on page 105
[Molecular Photomedicine]

14:30 – 14:50: Yang, Guoqiang (Institute of Chemistry, Chinese Academy of Sciences), “Multifunctional Organic Chromophores for Phototheranostics”, abstract on page 106
[Molecular Photomedicine]

14:50 – 15:10: Lippold, Tim (University of Cologne), “Protection and release of small molecules via chemiluminescent protection groups (CLPGs)”, abstract on page 107
[Molecular Photomedicine]

15:10 – 15:30: Ghimire, Sushant (Nano-institute Munich and Faculty of Physics, Ludwig Maximilian University (LMU) of Munich), “Controlled Shell Growth Enhances Free Exciton Emission in $AgInS_2$ Quantum Dots”, abstract on page 108
[Enriching Materials Science with Photochemistry]

15:30 – 15:50: Gilch, Peter (HHU Düsseldorf), “How Rare is HIGHrISC Behavior in Organic Chromophores?”, abstract on page 109
[Plasmonics & Photonics]

Afternoon Parallel Session C (Venue: Eurogress, K4/5)
Session Chair: Plötz, Evelyn

💡 **14:00 – 14:30: Hutchison, James** (School of Chemistry, University of Melbourne), “Sustainable and Bio-inspired Photonic Structures for Enhanced Photochemistry” (invited lecture), abstract on page 110
[Plasmonics & Photonics]

14:30 – 14:50: Kahnt, Axel (Leibniz-Institut für Oberflächenmodifizierung e.V.), “Photoinduced Electron Transfer in POV Based Systems”, abstract on page 111
[Photochemical Reaction Kinetics and Mechanisms]

14:50 – 15:10: Londi, Giacomo (University of Pisa), “Protein-driven electron-transfer process in a fatty acid photodecarboxylase”, abstract on page 112
[Photochemical Reaction Kinetics and Mechanisms]

15:10 – 15:30: Sachs, Michael (Stanford University), “Ultrafast modulation of solute-solvent hydrogen bonding during electron transfer in iron-ruthenium complexes”, abstract on page 113
[Photochemical Reaction Kinetics and Mechanisms]

15:30 – 15:50: Szabla, Rafał (Wrocław University of Science and Technology), “Shedding UV light on DNA charge transfer”, abstract on page 114
[Photochemical Reaction Kinetics and Mechanisms]

15:50 – 16:10: Telles do Casal, Mariana (KU Leuven), “Assessing anti-Kasha emission in Indigo Carmine: a combined static and dynamic approach”, abstract on page 115
[Photochemical Reaction Kinetics and Mechanisms]

TUESDAY, JULY 15

Afternoon Parallel Session D (Venue: Eurogress, K8/9)
Session Chair: König, Burkhard

💡 **14:00 – 14:30: Thomas, George** (IISER Thiruvananthapuram), “Exciton and Biexciton Dynamics in Semiconductor Nanocrystals” (invited lecture), abstract on page 116
[Enriching Materials Science with Photochemistry]

14:30 – 14:50: Peneva, Kalina (Friedrich Schiller University Jena), “Colorful Catalysis: Noble Metal-Free Photosensitizers in the Age of DYEversity”, abstract on page 117
[Photoredox Catalysis]

14:50 – 15:10: Sikorski, Marek (Adam Mickiewicz University, Poznań), “Flavin anions for photoredox catalysis”, abstract on page 118
[Photoredox Catalysis]

15:10 – 15:30: Horch, Marius (Freie Universität Berlin), “Studying and Controlling Ground-State Catalysts with Light: Cases Studies on Hydrogenases”, abstract on page 119
[Photoredox Catalysis]

15:30 – 15:50: Ohkubo, Kei (The University of Osaka), “Chlorine Dioxide as a Photoredox Catalyst for C-H Oxygenation of Hydrocarbons”, abstract on page 120
[Photoredox Catalysis]

15:50 – 16:10: Manolikakes, Georg (RPTU University Kaiserslautern-Landau), “Modular Synthesis of Sulfones and Sulfonamides via Visible-Light Driven Fixation of Sulfur Dioxide”, abstract on page 121
[Photoredox Catalysis]

★ Rising Star Lecture (Venue: Eurogress, Europa Saal)

16:30 – 17:00: Kim, Woojae (Yonsei University), “Janus-Type Photophysics of Directly-Linked Acene Dimers”, abstract on page 122
[The Photophysics and Photochemistry of Solar Energy Conversion]

🔔 Plenary Lecture (Venue: Eurogress, Europa Saal)

17:00 – 18:00: von Hauff, Elizabeth (TU Dresden / Fraunhofer FEP), “Photochemical Approaches for Device Functionality and Fabrication”, abstract on page 123
[Industrial Photochemistry]

18:00 – 20:00: Poster Session II (Venue: Eurogress, Foyer) The abstracts can be found in a dedicated Book of Abstracts on the conference website: www.icp2025.de.

WEDNESDAY, JULY 16

🔔 Plenary Lecture (Venue: Eurogress, Europa Saal)

8:30 – 9:30: Negri, Fabrizia (University of Bologna, Department of Chemistry "Giacomo Ciamician"), “Shedding Light on Molecular Function: Quantum-Chemical Insights into Luminescence and Photocatalytic Activity”, abstract on page 124
[New Theoretical Tools in Photochemistry]

Morning Parallel Session A (Venue: Eurogress, Europa Saal)
Session Chair: Gilch, Peter

9:40 – 10:00: Mackenzie, Alasdair (Central Laser Facility), “Critical Analysis of Zinc Tetraphenyl Porphyrin as an Entangled Two-Photon Absorption/Fluorescence (eTPA/F) Standard”, abstract on page 125
[Advanced Spectroscopic Methods]

10:00 – 10:20: Vacha, Martin (Institute of Science Tokyo), “Long-range exciton transport and nanoscale photophysics of perovskite and organic meso-hierarchical structures”, abstract on page 126
[Light-Driven Functional Molecular Systems]

☕ Coffee break

💡 **11:00 – 11:30: Steiner, Ulrich** (University of Konstanz), “Spin chemistry of rigid electron-donor-bridge-acceptor triads” (invited lecture), abstract on page 127
[Photochemical Reaction Kinetics and Mechanisms]

11:30 – 11:50: Ploetz, Evelyn (LMU Munich), “Monitoring of Host-Guest Interactions in Metal-organic frameworks (MOFs)”, abstract on page 128
[Advanced Spectroscopic Methods]

11:50 – 12:10: Fernández-Terán, Ricardo (Department of Physical Chemistry, University of Geneva), “Towards Controlling Excited State Reactivity in Organic and Organometallic Systems: A Perspective Through Ultrafast Multidimensional Spectroscopies”, abstract on page 129
[Advanced Spectroscopic Methods]

12:10 – 12:30: Pasanen, Hannu (King Abdullah University of Science and Technology), “Applications of time-resolved reflectance for photophysics”, abstract on page 130
[Advanced Spectroscopic Methods]

WEDNESDAY, JULY 16

Morning Parallel Session B (Venue: Eurogress, K1)
Session Chair: Basaric, Nikola

9:40 – 10:00: Griesbeck, Axel (The University of Cologne), “Deep Light Photochemistry for Medical Applications”, abstract on page 131
[Molecular Photomedicine]

10:00 – 10:20: Huang, Huang Chiao (University of Maryland), “Porphyrin Photochemistry as a Strategy to Overcome ABC Transporter-Mediated Multidrug Resistance”, abstract on page 132
[Molecular Photomedicine]

☕ Coffee break

💡 **11:00 – 11:30: Martínez-Martínez, Virginia** (Universidad del País Vasco, UPV/EHU), “Advanced BODIPY-based Photosensitizers for Enhanced Photodynamic Therapy” (invited lecture), abstract on page 133
[Molecular Photomedicine]

11:30 – 11:50: Novo, Mercedes (Universidade de Santiago de Compostela), “Intrinsic fluorescence as a tool for detecting and quantifying amyloid-β oligomers”, abstract on page 134
[Molecular Photomedicine]

11:50 – 12:10: Berdnikova, Daria (University of Siegen), “Aurones: unexplored visible-light photoswitches for aqueous medium and novel RNA binders”, abstract on page 135
[Molecular Photomedicine]

12:10 – 12:30: Markovitsi, Dimitra (CNRS), “Short wavelength exciton fluorescence of DNA: an indicator for the detection of duplex damage?”, abstract on page 136
[Molecular Photomedicine]

Morning Parallel Session C (Venue: Eurogress, K4/5)
Session Chair: S. Baptista, Mauricio

9:40 – 10:00: Ono, Toshikazu (Kyushu University), “Unique Optical Functions of Al-based Dinuclear Triple-Stranded Helicates: From Multicolor Emission to Triplet-Energy Generation”, abstract on page 137
[Enriching Materials Science with Photochemistry]

10:00 – 10:20: Debroye, Elke (KU Leuven), “Advancing Lead-Free Perovskites for Stable Broad-Range Photodetection”, abstract on page 138
[Enriching Materials Science with Photochemistry]

☕ Coffee break

💡 **11:00 – 11:30: Meyer, Gerald** (University of North Carolina - Chapel Hill), “Encounter Complex Control in Dye-Sensitized Halide Photochemistry” (invited lecture), abstract on page 139
[Frontiers in Photochemical Science]

11:30 – 11:50: Tsuboi, Yasuyuki (Osaka Metropolitan University), “Remote Control of Fluorescence Color by means of Optical Tweezers”, abstract on page 140
[Frontiers in Photochemical Science]

11:50 – 12:10: Börjesson, Karl (University of Gothenburg), “Separating triplet exciton diffusion from triplet–triplet annihilation in solid state triplet-triplet annihilation photon upconversion”, abstract on page 141
[Frontiers in Photochemical Science]

12:10 – 12:30: Inose, Tomoko (Kyoto University), “Novel design of photocleavable molecular tools for targeted intracellular delivery”, abstract on page 142
[Frontiers in Photochemical Science]

WEDNESDAY, JULY 16

Morning Parallel Session D (Venue: Eurogress, K8/9)
Session Chair: Link, Stephan

9:40 – 10:00: Sasaki, Yoichi (Kyushu University), “Optimization of intermolecular interactions for efficient solid-state photon upconversion”, abstract on page 143
[Light-Driven Functional Molecular Systems]

10:00 – 10:20: Capolungo, Chiara (University of Bologna), “Fluorescent detection of micro- and nanoplastics in crowded environmental water samples through a co-staining approach”, abstract on page 144
[Light-Driven Functional Molecular Systems]

☕ Coffee break

💡 **11:00 – 11:30: Vullev, Valentine I.** (University of California, Riverside), “Bioinspired Charge Transfer and Wine-Inspired Photochemistry” (invited lecture), abstract on page 145
[Frontiers in Photochemical Science]

11:30 – 11:50: Pang, Yoonsoo (Gwangju Institute of Science and Technology), “Polariton Dynamics of Gold Nanocubes/Carbocyanine Aggregates Investigated by Femtosecond Transient Absorption Spectroscopy”, abstract on page 146
[Plasmonics & Photonics]

11:50 – 12:10: Yokota, Yukie (Sophia University), “Dye decolorization using liquid phase synthesized Pt nanoparticles as photocatalysts”, abstract on page 147
[Plasmonics & Photonics]

12:10 – 12:30: Oshikiri, Tomoya (Tohoku University), “Chiroptical responses on plasmonic array under modal coupling regime”, abstract on page 148
[Plasmonics & Photonics]

Afternoon Parallel Session A (Venue: Eurogress, Europa Saal)
Session Chair: Fürstenberg, Alexandre

💡 **14:00 – 14:30: Ito, Syoji** (Osaka University), “Photoresponses of molecular systems induced by upconverting photoexcitation: toward super-resolved measurements” (invited lecture), abstract on page 149
[Photoswitches for Super-resolution Fluorescence Microscopy]

14:30 – 14:50: Boixel, Julien (Institut des Sciences Chimiques de Rennes), “Molecular Engineering of Dithienylethene Photochromes: Toward Fully Optical Photo-Activatable Molecular Materials”, abstract on page 150
[Light-Driven Functional Molecular Systems]

14:50 – 15:10: Masuhara, Hiroshi (National Yang Ming Chiao Tung University), “Optical Manipulation for Fabricating Protein-based Soft Matter”, abstract on page 151
[Light-Driven Functional Molecular Systems]

WEDNESDAY, JULY 16

Afternoon Parallel Session B (Venue: Eurogress, K1)
Session Chair: Flors, Cristina

💡 **14:00 – 14:30: Kuimova, Marina** (Imperial College London), “Mapping microscopic viscosity and macromolecular conformation using molecular rotors” (invited lecture), abstract on page 152
[Frontiers in Photochemical Sciences]

14:30 – 14:50: **Nonell, Santi** (Institut Quimic de Sarria), “Small-molecule visible light photocatalytic water oxidation enables oxygen-independent ablation of cancer cells”, abstract on page 153
[Molecular Photomedicine]

14:50 – 15:10: Zaman, Samantha (The University of Melbourne), “Lanthanide-based upconverting nanoparticles and black phosphorus quantum dots for deeper penetrating photodynamic therapy”, abstract on page 154
[Molecular Photomedicine]

Afternoon Parallel Session C (Venue: Eurogress, K4/5)
Session Chair: Ihmels, Heiko

💡 **14:00 – 14:30: Abrahamsson, Maria** (Chalmers University of Technology), “Fuels from the Sun: Understanding and controlling electron and energy transfer reactions in solar energy conversion materials” (invited lecture), abstract on page 155
[The Photophysics and Photochemistry of Solar Energy Conversion]

14:30 – 14:50: Stuhec, Ana (University of Oxford), “Directional Magnetic Sensitivity in Immobilized Cryptochrome 4: Unraveling Nature’s Photochemical Inclination Compass”, abstract on page 156
[Frontiers in Photochemical Sciences]

14:50 – 15:10: Hirata, Shuzo (The University of Electro-Communications), “Selective Lower-Occupied Through-Bond Interactions for Efficient Organic Phosphorescence in Long Wavelength”, abstract on page 157
[Frontiers in Photochemical Sciences]

Afternoon Parallel Session D (Venue: Eurogress, K8/9)
Session Chair: Ueno, Kosei

💡 **14:00 – 14:30: Yanai, Nobuhiro** (The University of Tokyo), “Optical spin hyperpolarization for quantum sensing” (invited lecture), abstract on page 158
[Light-Driven Functional Molecular Systems]

14:30 – 14:50: **Tschierlei, Stefanie** (TU Braunschweig), “Three-Coordinate Cu(I) Complexes of Anionic N-Heterocyclic Carbenes”, abstract on page 159
[Photoredox Catalysis]

14:50 – 15:10: Martínez-Aguirre, Mónica (Imperial College London), “Joint catalyst-surrogacy of a cobalt photocatalyst for carbonylation reactions in flow”, abstract on page 160
[Photoredox Catalysis]

WEDNESDAY, JULY 16

★ Rising Star Lecture (Venue: Eurogress, Europa Saal)

15:30 – 16:00: Oppermann, Malte (University of Basel, Department of Chemistry), “Ultrafast chiral spectroscopy for stereocontrolled photochemistry”, abstract on page 161
[Advanced Spectroscopic Methods]

🔔 Plenary Lecture (Venue: Eurogress, Europa Saal)

16:00 – 17:00: Kojima, Takahiko (University of Tsukuba), “Photocatalytic reactions using metal complexes and non-planar porphyrins”, abstract on page 162
[Photoredox Catalysis]

Presentation by a Sponsor (Venue: Eurogress, Europa Saal)

17:00 – 17:10: Shanghai 3S Technology Co.

🍸 **18:30:** Conference Dinner (Venue: Coronation Hall of the Aachen City Hall) To participate, an additional booking is required when registering.

THURSDAY, JULY 17

🔔 Plenary Lecture (Venue: Eurogress, Europa Saal)

8:30 – 9:30: Lagorio, María Gabriela (University of Buenos Aires Faculty of Exact and Natural Sciences), "Biophotonics. Decoding light signals from living organisms", abstract on page 164
[Frontiers in Photochemical Sciences]

Morning Parallel Session A (Venue: Eurogress, Europa Saal)
Session Chair: Griesbeck, Axel

9:40 – 10:00: Sun, Shih-Sheng (Institute of Chemistry, Academia Sinica), "Excited-State Conformational and Electronic Responses of Fluorescent Charge-Transfer Molecules with Twisted Structural Skeleton", abstract on page 165
[Enriching Materials Science with Photochemistry]

10:00 – 10:20: Favereau, Ludovic (University of Rennes), "Circularly Polarized Room Temperature Phosphorescence in Solution from Purely Organic Chiral Molecular Materials", abstract on page 166
[Enriching Materials Science with Photochemistry]

☕ Coffee break

💡 **11:00 – 11:30: Flors, Cristina** (IMDEA Nanociencia), "Exploring bacteria-surface interactions with a fluorescent membrane tension probe" (invited lecture), abstract on page 167
[Advanced Spectroscopic Methods]

11:30 – 11:50: Bresoli Obach, Roger (Institut Químic de Sarrià), "Illuminating Order: Optical Absorption Forces in Particle Assembly", abstract on page 168
[Enriching Materials Science with Photochemistry]

11:50 – 12:10: Lewandowska-Andralojc, Anna (Adam Mickiewicz University), "Spectroscopic properties of chiral porphyrin self-assembled monolayers on thin ferromagnetic films", abstract on page 169
[Enriching Materials Science with Photochemistry]

12:10 – 12:30: Wu, Bo-Han (National Tsing Hua University), "Triplet Energy Transfer of Monomer and Dimer of Rose Bengal in Methanol and in Polymer Films", abstract on page 170
[Enriching Materials Science with Photochemistry]

THURSDAY, JULY 17

Morning Parallel Session B (Venue: Eurogress, K1)
Session Chair: Kerzig, Christoph

9:40 – 10:00: Ogawa, Makoto (Kyoto University), “Flux Synthesis of Sillén–Aurivillius Phase Oxyiodide Photocatalyst for Visible Light Water Splitting”, abstract on page 171
[The Photophysics and Photochemistry of Solar Energy Conversion]

10:00 – 10:20: Lapini, Andrea (Università di Parma & Lens), “Solid state solvation: a fresh view”, abstract on page 172
[Frontiers in Photochemical Sciences]

☕ Coffee break

💡 **11:00 – 11:30: Ueno, Kosei** (Hokkaido University), “Acceleration of Excited-State Relaxation Dynamics via the Infrared Purcell Effect on Intermolecular Vibrations” (invited lecture), abstract on page 173
[Plasmonics & Photonics]

11:30 – 11:50: Bassani, Dario (Bordeaux University), “Opportunities and challenges in photochemically upcycling polymers”, abstract on page 174
[Photoredox Catalysis]

11:50 – 12:10: Ko, Vincent Chi-Chiu (City University of Hong Kong), “Design of Luminescent Transition Metal Complex Photocatalysts and Recyclable Immobilized Counterparts for Selective Activation”, abstract on page 175
[Photoredox Catalysis]

12:10 – 12:30: Gómez Suárez, Adrián (Bergische Universität Wuppertal), “Photoinitiated Synthesis of 1,1-Dicyanocyclopropanes as a Gateway to β-Aminocarbonyls from Olefins”, abstract on page 176
[Photoredox Catalysis]

Morning Parallel Session C (Venue: Eurogress, K4/5)
Session Chair: Jung, Gregor

9:40 – 10:00: Vallan, Lorenzo (Catalan Institute of Nanoscience and Nanotechnology - ICN2), “Thermochromic paraffin-based microcomposites for smart windows and greenhouses”, abstract on page 177
[Photochemistry and the Sustainable Environment]

10:00 – 10:20: Marinas, Alberto (University of Cordoba), “Synergistic effect of light and acidity on glycerol acetalization over WO_3 catalysts”, abstract on page 178
[Photochemistry and the Sustainable Environment]

☕ Coffee break

💡 **11:00 – 11:30: Kwak, Kyungwon** (1. Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science, Seoul; 2. Department of Chemistry, Korea University, Seoul), “Intra-band Exciton Dynamics of Quantum dot” (invited Lecture), abstract on page 179
[Plasmonics & Photonics]

11:30 – 11:50: Giusto, Paolo (Max Planck Institute of Colloids and Interfaces), “Carbon Nitride Thin Films for Artificial Photosynthesis”, abstract on page 180
[Photochemistry and the Sustainable Environment]

11:50 – 12:10: Jung, Jieun (Nagoya University), “Photocatalytic CO_2 Reduction Mediated by a Mo-Based Complex”, abstract on page 181
[Photochemistry and the Sustainable Environment]

12:10 – 12:30: Hölzel, Helen (JLU Giessen), “Energy Management of Functional Molecular Materials”, abstract on page 182
[Photochemistry and the Sustainable Environment]

THURSDAY, JULY 17

Morning Parallel Session D (Venue: Eurogress, K8/9)
Session Chair: Negri, Fabrizia

9:40 – 10:00: Furuta, Ryoji (Kyushu University), “Helical B–O–B Bridged Complexes: Molecular Design and Chiroptical Functions”, abstract on page 183
[Light-Driven Functional Molecular Systems]

10:00 – 10:20: **Jäger, Michael** (Friedrich Schiller University Jena), “Modular assembly of polymer-based precision assemblies with microsecond charge separation”, abstract on page 184
[Light-Driven Functional Molecular Systems]

☕ Coffee break

💡 **11:00 – 11:30: Kim, Doory** (Hanyang University), “Photochemical Principles and Applications of Super-Resolution Fluorescence Imaging” (invited lecture), abstract on page 185
[Photoswitches for Super-resolution Fluorescence Microscopy]

11:30 – 11:50: Dumele, Oliver (Universität Köln), “All-Organic Spin-State Photoswitches”, abstract on page 186
[Light-Driven Functional Molecular Systems]

11:50 – 12:10: Jankowska, Joanna (University of Warsaw), “Reversing a unidirectional molecular motor: structural design and protocol for an electric-field driven control of the rotation direction”, abstract on page 187
[Light-Driven Functional Molecular Systems]

12:10 – 12:30: Wang, Tianyi (University of Cologne), “Ultrafast Excited-State Dynamics and Inter-Chromophore Interactions in Self-Assembled Coordination Complexes”, abstract on page 188
[The Photophysics and Photochemistry of Solar Energy Conversion]

Afternoon Parallel Session A (Venue: Eurogress, Europa Saal)
Session Chair: Hofkens, Johan

💡 **14:00 – 14:30: Klymchenko, Andrey** (Université de Strasbourg / CNRS), “Light-Harvesting Organic Nanomaterials for Efficient Energy Transfer and Amplified Biosensing” (invited lecture), abstract on page 189
[Enriching Materials Science with Photochemistry]

14:30 – 14:50: **Yang, Jye-Shane** (Department of Chemistry, National Taiwan University), “Stimuli-Responsive Photoluminescence and Photomechanical Effects in Pentiptycene-Based Molecular Crystals”, abstract on page 190
[Enriching Materials Science with Photochemistry]

14:50 – 15:10: Titus, Timi (Indian Institute of Science Education and Research Thiruvananthapuram), “Modulating the Single- and Two-Photon Emission Dynamics in Semiconductor Nanocrystals”, abstract on page 191
[Enriching Materials Science with Photochemistry]

Afternoon Parallel Session B (Venue: Eurogress, K1)
Session Chair: Steiner, Ulrich

💡 **14:00 – 14:30: Marian, Christel** (Heinrich Heine University Düsseldorf), “Simulating the Full Spin Manifold of Triplet Pairs in Singlet Fission” (invited lecture), abstract on page 192
[The Photophysics and Photochemistry of Solar Energy Conversion]

14:30 – 14:50: **Glaser, Felix** (UCLouvain), “Welcome to the Dark Side: Photoactive Iron Complexes with Microsecond Excited-State Lifetimes”, abstract on page 193
[Photoredox Catalysis]

14:50 – 15:10: Nagashima, Yuki (The University of Tokyo), “Organic photoreactions utilizing boron, silicon, and tin elements”, abstract on page 194
[Photoredox Catalysis]

THURSDAY, JULY 17

Afternoon Parallel Session C (Venue: Eurogress, K4/5)
Session Chair: Hutchison, James

💡 **14:00 – 14:30: Eguchi, Miharu** (Waseda University), "Gold Nanoarchitectures for Plasmon-Enhanced Reactions" (invited lecture), abstract on page 195
[Plasmonics & Photonics]

14:30 – 14:50: Kobayashi, Yoichi (Ritsumeikan University), "Multiphoton-Driven Photocatalytic Defluorination of Persistent Perfluoroalkyl Substances and Polymers by Visible Light", abstract on page 196
[Photochemistry and the Sustainable Environment]

14:50 – 15:10: Alfred, Moses (University of Potsdam/Helmholtz Centre Berlin for Materials and Energy), "Structure-Dependent Performance of Cu$_2$O Photocatalysts for Solar-Driven CO$_2$ Conversion", abstract on page 197
[Photochemistry and the Sustainable Environment]

Afternoon Parallel Session D (Venue: Eurogress, K8/9)
Session Chair: Bassani, Dario

14:00 – 14:10: Brenker, Kathrin (opto biolabs GmbH) "Illuminating Insights – how well plate material influences light stimulation efficiency", abstract on page 198
[Advanced Spectroscopic Methods]

14:10 – 14:30: Dubey, Astita (University of Duisburg Essen, Germany), "Highthroughput screening of lead-free halide perovskites using bayesian optimization for photocatalysis", abstract on page 199
[Photochemistry and the Sustainable Environment]

14:30 – 14:50: **Ziegenbalg, Dirk** (Institute of Chemical Engineering, Ulm University), "Reaction Engineering as Key to Transfer Photoreactions to Application", abstract on page 200
[Industrial Photochemistry]

14:50 – 15:10: Ibrahim, Malek (Redeem Solar Technologies), "Reconfigurable Photoflow Reactor for Accelerated Process Development", abstract on page 201
[Industrial Photochemistry]

★ Rising Star Lecture (Venue: Eurogress, Europa Saal)

15:30 – 16:00: Godin, Robert (The University of British Columbia), "Transient Absorption Microscopy of Carbon Nitride Photocatalyst Particles", abstract on page 202
[Advanced Spectroscopic Methods]

🔔 Plenary Lecture (Venue: Eurogress, Europa Saal)

16:00 – 17:00: Stephenson, Corey (The University of British Columbia), "New Tools for Photochemical Reaction Development and Optimization", abstract on page 203
[Photoredox Catalysis]

Closing Ceremony (Venue: Eurogress, Europa Saal)

17:00 – 17:45: Guldi, Dirk M. (FAU Erlangen-Nürnberg); **Wöll, Dominik** (RWTH Aachen University): Poster Awards, Introduction of ICP 2027, Concluding Remarks

FRIDAY, JULY 18

Participation in an optional excursion (Further information can be found on the conference website: www.icp2025.de)

The Photochemical Inheritance of Lissi and Grotewold

Silvia E. Braslavsky[1], **Carlos M. Previtali**[2]

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As part of an ambitious plan for the modernization of the University of Buenos Aires (UBA), and in particular its School of Sciences, in 1959 Eduardo Lissi and Juan Grotewold (L&G) went to the laboratory of A. Trotman-Dickenson in Wales to obtain their PhD degrees. Upon return in 1963, they started a Chemical Kinetics and Photochemistry group in the School of Sciences (UBA). First graduate students were Miguel G. Neumann, Silvia E. Braslavsky, Alberto E. Villa and Carlos M. Previtali (Figure 1).

The military intervention of the Argentinian Universities in 1966 determined the translocation of the group to Santiago, Chile, together with almost all the Inorganic, Analytical and Physical Chemistry Department (DQIAQF) of the School of Sciences. Elsa Abuin and Juan C. (Tito) Scaiano, students at UBA, joined later the L&G group in Chile. Advanced chemistry students at UBA finished their courses at the National University of La Plata (UNLP, 60 km from Buenos Aires, Bs As.) and some entered the group of Hans J. Schumacher in La Plata to do their PhD work. Schumacher was a German Chemist who went to Argentina in 1947 and produced the first photochemistry paper from an Argentinian address in 1950. In 1969, the L&G group dispersed, Lissi and Abuin and Chilean collaborators remained in Chile; Grotewold and Previtali went back to Argentina to the School of Pharmacy (UBA); Braslavsky, Villa and Scaiano left for post-doctoral studies. In 1972-73 Previtali, Braslavsky, Scaiano and Neumann converged in the newly created National University of Rio Cuarto (UNRC) in Argentina. The group dispersed again at the end of 1974 due to political difficulties in Argentina. Scaiano went to Ottawa, Braslavsky returned to her post-doctoral place at Penn State University, later went to Edmonton, and in 1976 to Mülheim. Neumann went to Sao Carlos (Brazil) where he established a productive research group. Previtali remained in Rio Cuarto and Juan J. Cossa joined the group at the UNRC in 1976, after a post-doctoral stay with George Porter. The team in Rio Cuarto became a photochemistry referent group in Argentina. In 1983, with the recovery of democracy, the DQIAQF in Buenos Aires could be re-founded. A Photochemistry group was created at the DQIAQF directed by Enrique San Román and Lelia Dicelio (both Schumacher's PhD students) and coached by Braslavsky (from Germany). Lissi established a Latin-American centre on Photochemistry in Chile with Elsa Abuin, Maria Victoria Encinas, and several Chilean disciples who later started their own research groups. Grotewold went in 1975 to the Chemical Industry in Argentina and contributed to the rebirth of the School of Sciences (UBA) after 1983. Scaiano strongly collaborated with many groups in Chile, Brazil and Argentina

Figure 1. 1993. 30 years L&G group foundation, Encinas, Grotewold, Previtali, Braslavsky, Neumann, Abuin, Villa, Lissi, Scaiano.

Scientific descendants of L&G established research units in Argentina, Chile and Brazil. In spite of difficult political situations, all groups strongly cooperated, exchanged students and postdocs, contributing to create a diversified photochemistry and photobiology community, also interacting with colleagues in the USA and Europe. The ELAFOT meetings (Encuentros Latinoamericanos de Fotoquímica), started by Lissi in Chile in 1982, with so far 15 editions, document such a diversity. The Inter-American Photochemical Society (I-APS) started in 1996 meetings in South America every 5 years, strengthening the ties between the North and the South communities.[1]

Dedication: This presentation is an homage to Eduardo Lissi and Juan Grotewold who, with their knowledge, wisdom and high ethical values, were the guides for our scientific paths.

References:

[1] Braslavsky, S. E., Previtali, C. M. *Photochemistry and Photobiology* **2025**. 10.1111/php.14044

The Bionic Leaf: Surpassing the C- and N- Fixation Processes of Nature

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Hybrid biological | inorganic (HBI) constructs have been created to use sunlight, air and water as the only starting materials to accomplish carbon and nitrogen fixation, enabling the establishment of distributed and renewable Fischer-Tropsch and Haber Bosch cycles. The carbon and nitrogen fixation cycles begin with the Artificial Leaf, which was invented to accomplish the solar fuels process of natural photosynthesis—the splitting of water to hydrogen and oxygen using sunlight—under ambient conditions. The hydrogen from the catalysts of the Artificial Leaf may be interfaced with engineered organisms to power the Bionic Leaf-**C** and Bionic Leaf-**N** to convert carbon dioxide and nitrogen from air into liquid fuels and ammonia, respectively. The solar-to-biomass efficiency of the Bionic Leaf-**C** is 10 times greater than the fastest growing natural biomass. In an alternative approach, using the tools of synthetic biology, CO_2 is fixed with H_2 to polyhydroxybutyrate (PHB), which may be converted intracellularly to provide the energy and the building blocks to make specific liquid fuels (e.g., iso-butanol, iso-pentanol) through metabolically engineered pathways placed in *C. necator*. Here, the solar-to-fuels efficiency of the Bionic Leaf-**C** is >100 more efficient than natural biomass-to-fuels cycles. The hybrid biological-inorganic approach has been elaborated with the creation of the Bionic Leaf-**N**, which exploits an autotropic, nitrogen fixing microorganism, *Xanthobacter autotrophicus* (*X.a.*). As in the Bionic Leaf-**C**, the organism can produce PHB from CO_2 in air and H_2 from water splitting. Drawing on the PHB as a supply of hydrogen and energy, *X.a.* takes nitrogen from air and fixes it in ammonia and "N" biomass. The ammonia produced directly or from the N-biomass diffuses across the *X.a.* membrane and is taken up by plants as a biofertilizer. The Bionic Leaf-N has gone through 200 successful large farm trials. In the latest field trial for leafy vegetables, use of the Bionic Leaf-**N** replaced chemical fertilizer on a 400-acre farm that resulted in the mitigation of 153 metric tons of CO_2 from being released into the atmosphere while enhancing crop yields with no run-off that is responsible for harmful algal blooms. Where are these innovations useful? The use of the simple inputs of only sunlight, air and water to produce fuel (carbon neutral) and food and vitamins (carbon negative) within a sustainable cycle for the biogenic elements of C, N and P is particularly useful to the poor of the world, where large infrastructures for fuel and food production are not tenable.

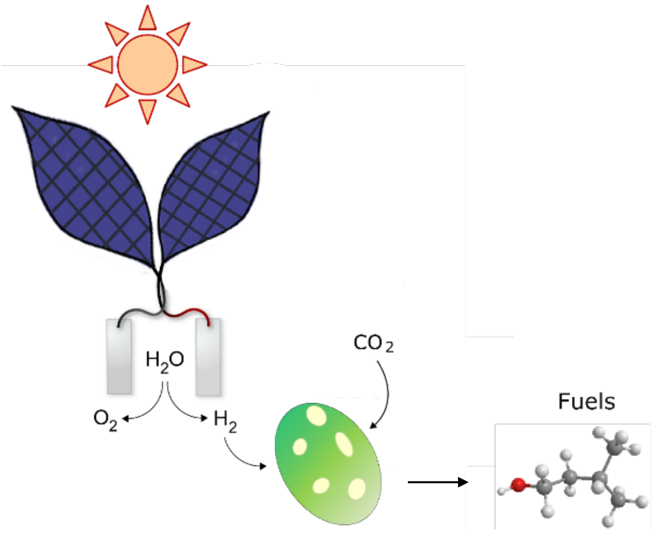

Figure 1. In the Bionic Leaf-**C** performs an artificial photosynthesis. In its design, Photosystems II and I are effectively replaced with hydrogenase, which allows the H_2 produced from inorganic water splitting to power cellular biosynthesis in carbon-fixing organisms to produce biomass or liquid fuels via metabolically engineered pathways at solar-to-biomass and solar-to-fuels efficiencies far exceeding natural photosynthesis.

Photogeneration and Dynamics of Multi-spin Systems for Quantum Information Applications

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Molecular electron spins have emerged as versatile quantum bits (qubits) with wide ranging applications in quantum computing, sensing, and coherent communications at the nanoscale.[1] These applications take advantage of the ability of chemical synthesis to 1) create specific structures with atomic scale spatial control; 2) tailor the magnetic, optical, and electronic properties of the qubits; and 3) construct large-scale ordered arrays of qubits via crystal growth and self-assembly. In order to take further advantage of the tunability of molecular qubits, photon-spin interfaces must be developed to permit addressing and readout of spin information. We will discuss how photo-generated radical pairs as well as stable diradicals can function as spin qubits capable of carrying out quantum operations.

Electron transmission through chiral molecules and materials has been shown to produce highly spin-polarized electrons. This effect is termed Chirality-Induced Spin Selectivity (CISS).[2] Using donor-chiral bridge-acceptor (D-Bχ-A) molecules, we have demonstrated that the CISS effect contributes significantly to the spin dynamics of the photogenerated $D^{\bullet+}$-Bχ-$A^{\bullet-}$ radical pair and does not depend on attaching the molecules to a metal or semiconductor surface.[3,4] We have also shown that ultrafast electron transfer from $A^{\bullet-}$ in a photogenerated spin-entangled radical pair ($D^{\bullet+}$-$A^{\bullet-}$) to a stable radical ($R^{\bullet}$) to yield $D^{\bullet+}$-A-R^{-} can teleport the spin state of $R^{\bullet}$ to $D^{\bullet+}$ across the covalent molecular assembly.[5] Given that CISS essentially imparts triplet character to the radical pair by performing a spin rotation on an electron or hole traversing a chiral molecule, can CISS alter the information teleported? We have now obtained results using a chiral D-Bχ-$R^{\bullet}$ molecule, which show that CISS results in a phase shift in the teleported information that could serve as a means of using CISS to change the nature of the teleported information while preserving its coherence.

Molecular optical-spin interfaces are emerging as promising alternatives to solid state defects such as nitrogen vacancy centers in diamond for quantum sensing applications. We will report on a new theory-guided approach to molecular color centers that utilizes luminescent stable organic diradicals with triplet ground states.[6] Optical spin polarization of the triplet ground state is achieved by spin-selective excited-state intersystem crossing. The triplet ground state is characterized by pulse electron paramagnetic resonance spectroscopy and shows spin coherence times of 20 μs at 5 K. Also, we demonstrate coherent microwave manipulation of the spin-polarized ground state populations and coherences using optically detected Rabi nutations, Hahn echo formation, and echo decay measurements at 85 K. This marks a crucial step towards leveraging the favorable spin relaxation times of organic diradicals for applications as quantum sensors at temperatures that heretofore have been difficult to achieve by molecular color centers.

Acknowledgement: This work was supported by organizations detailed in references [1] and [3-6].

References:

[1] M. R. Wasielewski; M. D. E. Forbes; N. L. Frank; K. Kowalski; G. D. Scholes; J. Yuen-Zhou; M. A. Baldo; D. E. Freedman; R. H. Goldsmith; T. Goodson, III; M. L. Kirk; J. K. McCusker; J. P. Ogilvie; D. A. Shultz; S. Stoll; K. B. Whaley, *Nat. Rev. Chem.* **2020**, *4*, 490-504.

[2] R. Naaman and D. H. Waldeck, *Annu. Rev. Phys. Chem.* **2015**, *66*, 263-281.

[3] H. J. Eckvahl; N. A. Tcyrulnikov; A. Chiesa; J. M. Bradley; R. M. Young; S. Carretta; M. D. Krzyaniak; M. R. Wasielewski, *Science*, **2023**, *382*, 197-201.

[4] H. J. Eckvahl; G. Copley; R.M. Young; M. D. Krzyaniak; M. R. Wasielewski, *J. Am. Chem. Soc.* **2024**, *146*, 24125-24132.

[5] B. K. Rugg; M. D. Krzyaniak; B. T. Phelan; M. A. Ratner; R. M. Young; M. R. Wasielewski, *Nat. Chem.* **2019**, *11*, 981-986.

[6] S. M. Kopp; S. Nakamura; B. T. Phelan; Y. R. Poh; S. B. Tyndall; P. J. Brown; Y. Huang; J. Yuen-Zhou; M. D. Krzyaniak; M. R. Wasielewski, *J. Am. Chem. Soc.* **2024**, *146*, 27935-27945.

New Modalities in Photochemical Uncaging with Visible Light

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Photochemical uncaging has enabled activation and investigation of biochemical processes or release of drugs with precise spatial and temporal control.[1] Uncaging generates well-defined concentration gradients of molecules, such as ATP, glutamate, CO etc., or their mixtures that can be used to investigate underlying mechanisms of fast processes like neuron firing, or they can modulate pharmacokinetics controlling drug efficacy.[2] The research of photochemical uncaging in the past decade has focused on the development of molecular cages in which heterolytic cage–payload bond cleavage is achieved with benign visible or near-IR light.[3-5] However, marginal attention has been paid to transferring this important technology to unexplored chemical environments, such as gas phase, or to execute uncaging using new, alternative concepts in photochemistry.

In my talk, I will tackle both these challenges. I will discuss (i) how photochemical uncaging can be used to gain control of a biopolymer charge state in a molecular beam in high vacuum,[6] and (ii) how molecular strain can transform a photostable metallocene complex (Fig.1) into a functional photocage to activate untapped biochemical agent, Fe^{2+} ions.[7] The former process is highly desirable for applications in quantum metrology, while the latter permits spatio-temporal control over free iron level in a sample, eventually utilizable to induce ferroptosis of cells.

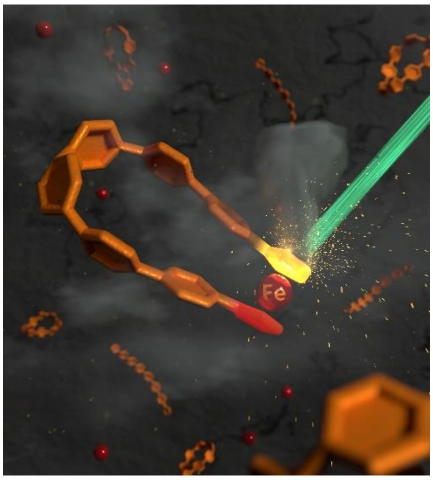

Figure 1. Photoactivation of ferrocene carbon nanohoop as an iron carrier with green light.

Funding: European Research Council (ERC, Grant Agreement No. 949397)

References:

[1] P. Klán, T. Šolomek, C. G. Bochet, A. Blanc, R. S. Givens, M. Rubina, V. Popik, A. Kostikov, J. Wirz, *Chem. Rev.* **2013**, *113*, 119.

[2] G. C. R. Ellis-Davies, *Acc. Chem. Res.* **2020**, *53*, 1593.

[3] T. Šolomek, J. Wirz, P. Klán, *Acc. Chem. Res.* **2015**, *48*, 3064.

[4] R. Weinstain, T. Slanina, D. Kand, P. Klán, *Chem. Rev.* **2020**, *120*, 13135.

[5] P. Štacko, T. Šolomek, *CHIMIA* **2021**, 75, 873

[6] Y. Hua, M. Strauss, S. Fisher, M. F. X. Mauser, P. Manchet, M. Smacchia, P. Geyer, A. Shayeghi, M. Pfeffer, T. H. Eggenweiler, S. Daly, J. Commandeur, M. Mayor, M. Arndt, T. Šolomek, V. Köhler, *JACS Au* **2023**, *3*, 2790.

[7] R. Krecijasz, J. Malinčík, S. Mathew, P. Štacko, T. Šolomek, *J. Am. Chem. Soc.* **2025**, *147*, 10231.

Exploring Intermolecular Coupling and Excited State Dynamics in Perlyene Bisimide Systems: From Monomers to Dimers and Beyond

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Perlyene bisimide (PBI) derivatives have gained attention for their photophysical traits and potential in various optoelectronic devices. This review explores the intermolecular associations and excited state dynamics within PBI-based systems, from monomers to assemblies, crucial for unlocking their potential. It elucidates how linkage manipulation, molecular alignment, and intermolecular associations affect photoexcited states in PBI aggregates. Starting with monomeric PBIs, the review discusses excited state dynamics within cofacially stacked PBI dimers and their intermolecular coupling effects. Long-range dipole-dipole interactions stabilize excimer states, influencing energy transfer. The review investigates mechanisms driving excimer formation and its impact on exciton migration and energy transfer within PBI aggregates. Symmetry-breaking charge transfer (SB-CT) processes in PBI dimers affect charge propagation by inducing transient absorption spectra bands, akin to photosynthetic reaction centers. The emergence of multiexciton states, crucial in singlet fission (SF), is explored, shedding light on molecular arrangement and electronic coupling's role in SF. The interplay among intermolecular interactions in PBI dimers orchestrates photoexcitation dynamics, including excimer generation, SB-CT, and multiexciton generation (MEG). Understanding these processes could lead to innovative materials for enhanced energy harvesting and sustainable energy technologies.

Photoacidic Polyelectrolytes

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Current research in light-to-protonic power conversion systems[1-3] is primarily focused on small organic compounds, with macromolecules receiving comparatively little attention. Here, we synthesized a series of statistical copolymers containing 3-sulfopropyl methacrylate units (SMA) alternated with spiropyran methacrylate units in their open protonated form (MCHMA) (Figure 1a), which can release protons following visible light absorption. We studied the behaviour of these poly(SMA-co-MCHMA) polyelectrolytes in water and found that polymer composition can be used as tool to rationally control their photoacidic characteristics (Figure 1b), whereas polymer constitution significantly enhances the hydrolytic stability of the MCH moieties (Figure 1c). Exposure to mild 500 nm light allows these polyelectrolytes to reversibly dissociate protons, causing metastable fluctuations in the surrounding aqueous medium as large as 3 pH units that can be repeated for at least 6 consecutive hours (Figure 1d). The results presented here hold promise in the fabrication of innovative materials for photocurrent generation.

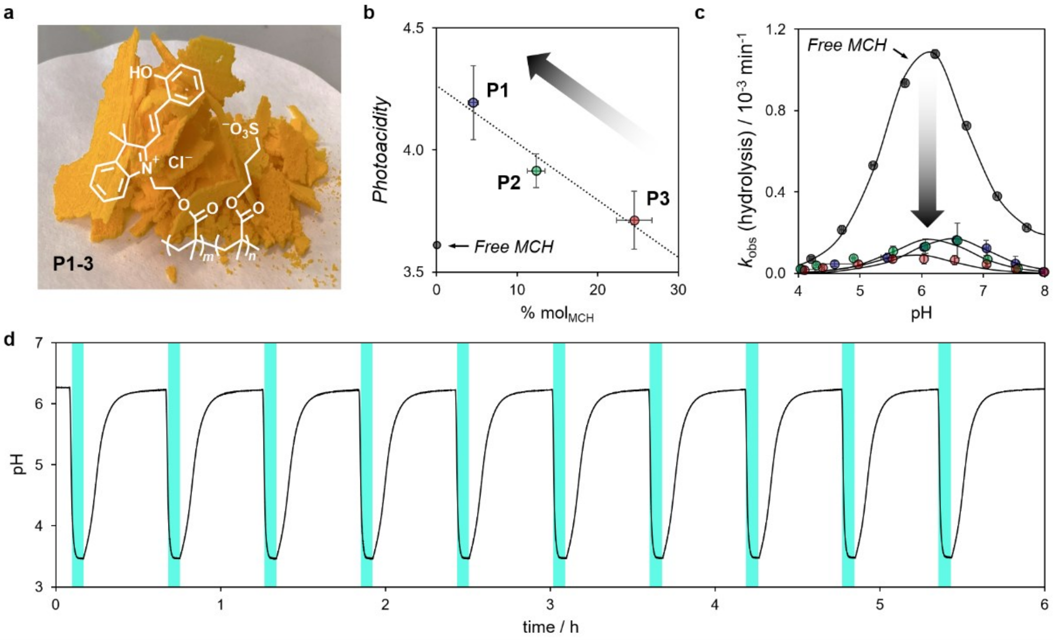

Figure 1. (a) Molecular structure and appearance of poly(SMA-co-MCHMA) polyelectrolytes. Photoacidity (b) and hydrolytic stability vs. pH (c) as a function of polymer composition. (d) pH jump dynamics of the best performing polyelectrolyte, **P1**.

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References:

[1] J. Bae, H. Lim, J. Ahn, Y. H. Kim, M. S. Kim, I.-D. Kim, *Adv. Mater.*, **2022**, *34*, 2201734.

[2] G. S. Phun, R. Bhide, S. Ardo, *Energy Environ. Sci.*, **2023**, *16*, 493.

[3] X. Dai, C. Berton, D. J. Kim, C. Pezzato, *Chem. Sci.* , **2024**, *15*, 19745.

Cooperative photoswitching materials

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Cooperativity represents a fascinating phenomenon that brings considerable benefits in terms of time, space and energy control in many domains[1]. Complexation and release of oxygen by haemoglobin to maintain metabolitic homeostasis are typical amplified effects, thanks to highly synergistic conformational and tension changes, triggered by pH modifications. Such amplification has been exploited in nanomedicine to release drugs in a nonlinear way due to strong electrostatic repulsions caused by protonation/deprotonation sequences[2]. Cooperative phenomena are also involved in spin-crossover molecular systems, where abrupt bistability, triggered by an external stimulus, is highly sought for high-speed memories or switches[3]. Whereas cooperative effects have long been studied in polymeric and liquid crystalline materials[4], very little attention has been paid on small molecule-based functional materials (SMFMs) whose molecular constitution could nicely be harnessed to lead to extensive structural rearrangements under tiny perturbations. This, however, requires high control of the mutual interactions to impulse large actuation that can be transduced at the macroscopic level.

Thanks to the use of glass-forming SMFMs, we show that extensive deformation, photoinduced by light, highly depends on the mutual intermolecular interactions between the individual molecules and can be modulated by varying the ratio of H-bonding entities[5]. Such cooperative effects have been extended to self-assembled photochromic nanoparticles manufactured by flash precipitation[6]. Geometry photoswitching can reversibly be triggered in solution and followed at the single nanoparticle level by combining atomic force microcopy (AFM) and in situ dual illumination. Progressive disintegration of the nanoparticles after several cycles of expansion-contraction caused by alternating vis and UV illuminations could be observed and ascribed to strong adhesion effects (Fig. 1)[7]. The latter results open perspectives into the design of drug-delivery nanocarriers where on-command drug release should better exploit the strong non-covalent intermolecular interactions established at the interface between nanoparticles and biological tissues.

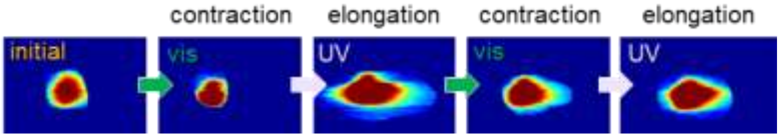

Figure 1. Photoswitching of a single nanoparticle under dual color excitation, followed by AFM.

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References:

[1] a) S. Krause, B. L. Feringa, *Nat. Rev. Chem*. **2020**, *4*, 550-562; b). F. Xu, B. L. Feringa, *Adv. Mater.* **2023**, *35*, 2204413.
[2] J. Wilhelm, Z. H. Wang, B. D. Sumer, J. M. Gao, *Adv. Drug. Deliv. Rev.* **2020**, *158*, 63.
[3] Zhou, H. H. Zhang, H. L. Zheng, Z. T. Xu, H. T. Xu, H. L. Guo, P. N. Li, Y. F. Tong, B. Hu, L. Chen, *Small* **2022**, *18*, 2200679.
[4] S. J. D. Lugger, S; J. A. Houben, Y. Foelen, M. G. Debije, A. P. H. J. Schenning, D. J. Mulder, *Chem. Rev.* **2022**, *122*, 4946.
[5] F. Rodriguez, J. Jelken, N. Delpouve, A. Laurent, B. Garnier, J.-L. Duvail, F. Lagugné-Labarthet, E. Ishow, *Adv. Opt. Mater.* **2021**, *9*, 2100525.
[6] Hoang, S. Olivier, S. Cuenot, A. Montillet, J. Bellettre, E. Ishow, *ChemPhysChem* **2020,** *21*, 2502.
[7] E. Bequet, V. Silvestre, S. Cuenot, E. Ishow, *Small* **2024**, *20*, 2403912.

Anomalous thermal back reaction dynamics in the photochromism of thioindigo in the presence of alkylamide self-assemblies

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Photochromic reactions are widely utilized in various photoresponsive materials, such as solar energy storage systems and photoactuators. In these reactions, photogenerated metastable species typically revert thermally to the original, more stable species, with the reaction rate generally increasing at higher temperatures. Moreover, longer photoirradiation times typically generate a greater amount of metastable species, thereby prolonging the time required for the photoinduced coloration to fade below a visible threshold.

Here, we report anomalous thermal back reaction dynamics observed in the photochromism of thioindigo (ThI, Figure 1a) in the presence of alkylamide self-assemblies. Notably, lower temperatures and longer photoirradiation times promoted faster thermal back reactions, contrary to conventional expectations. These findings are anticipated to contribute to the development of next-generation photofunctional materials.

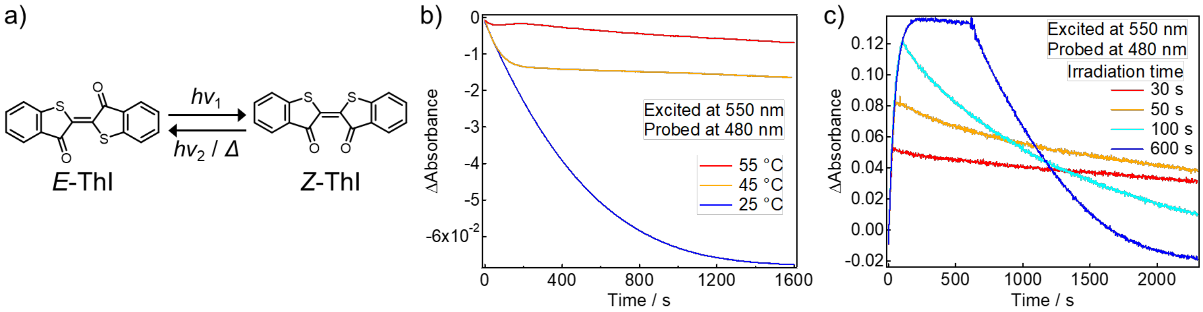

Figure 1. a) Photochromic reaction of thioindigo (ThI), b) Color fading dynamics of ThI with alkylamide self-assembly in toluene at different temperatures after 550-nm light irradiation, c) Coloration and color fading dynamics of ThI with alkylamide self-assembly in toluene at room temperature upon 550-nm light irradiation for different durations.

Upon 550-nm light irradiation, *E*-ThI in toluene was converted to *Z*-ThI (Z ≈ 45% at the photostationary state), followed by a thermal back reaction from *Z*-ThI to *E*-ThI with a half-life of 3.9×10^4 s at room temperature. Interestingly, the addition of an alkylamide, which forms self-assemblies in toluene at room temperature, significantly accelerated the thermal back reaction, although no changes were observed in the absorption spectra of ThI. The acceleration effect became more pronounced with increasing alkylamide concentration; at 30 mM, *Z*-ThI decayed within approximately 100 s.

Strikingly, this acceleration effect diminished at 55 °C, resulting in a slower thermal back reaction compared to that at 25 °C (Figure 1b). This anomalous temperature dependence is likely due to the dissociation of alkylamide self-assemblies at elevated temperatures, thus eliminating the acceleration effect.[1] Furthermore, the acceleration was also influenced by the duration of photoirradiation. Longer photoirradiation times led to faster thermal back reactions (Figure 1c). For instance, photoirradiation for 600 s resulted in nearly complete color fading within 1 h, whereas photoirradiation for only 30 s required a substantially longer time for fading, despite the smaller initial degree of coloration.

Funding: JST PRESTO (JPMJPR22N6), JSPS KAKENHI (JP21K05012, 24K01460, 24K17749), and the Sasakawa Scientific Research Grant from the Japan Science Society.

Reference:

[1] F. Rodríguez-Llansola, B. Escuder, J. F. Miravet, *J. Am. Chem. Soc.* **2009**, *131*, 11478.

Photochemical conversion, storage and release of light energy with monoaryl-substituted norbornadienes

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Molecular solar thermal energy storage (MOST) systems can convert, store and release solar energy in chemical bonds, i.e., as *chemical* energy.[1] For that purpose, photochromic compounds are converted into photoproducts with higher energy, which can be released in the back reaction as heat. One promising MOST system is the intramolecular [2+2] photocycloaddition-cycloreversion cycle between norbornadiene and quadricyclane because of its high energy storage potential. But the parent norbornadiene only absorbs UV light, and the photoisomerization quantum yield is very low, so that there is still need for optimization. Herein, we present monoaryl-substituted norbornadienes as a promising subclass of compounds with improved properties.

The detailed investigation of the photochemical and physico-chemical properties of monoaryl-norbornadienes revealed favorable properties of these compounds for chemical storage of light energy (Fig. 1).[2] For example, the naphthylnorbornadiene **NBD1** (Fig. 1a) has a pronounced red shift of the absorption (Abs.$_{\text{onset}}$: 351 nm), and the corresponding quadricyclane has a long half-life (35 d) and a high energy storage density (361 kJ/kg). As special cases, aryl-linked bis- and trisnorbornadienes, such as derivative **NBD2** (Fig. 1a), have photo isomerization quantum yields of up to 56% and half-lives of the quadricyclane derivatives of up to 14 d. Most notably, the energy storage densities of some quadricyclanes are exceptionally high with a maximum value of 734 kJ/kg (**NBD2**), indicating a huge potential for energy storage. Furthermore, a quantitative photocycloaddition and photocycloreversion can be accomplished with a well-balanced combination of substitution pattern of the arylnorbornadiene and suitable photocatalysts, which absorb in the visible range (Fig. 1B). Whereas the photocyclization is initiated by triplet sensitization, the cycloreversion is triggered by a photoinduced electron transfer (PET) reaction. Under these conditions, the photoreactions can be induced with light from the visible range of the solar spectrum, even upon direct exposure to sunlight.

In this contribution, the photochemical and physico-chemical properties of the arylnorbornadienes as well as the mechanisms of the photoreactions will be presented and discussed in detail.

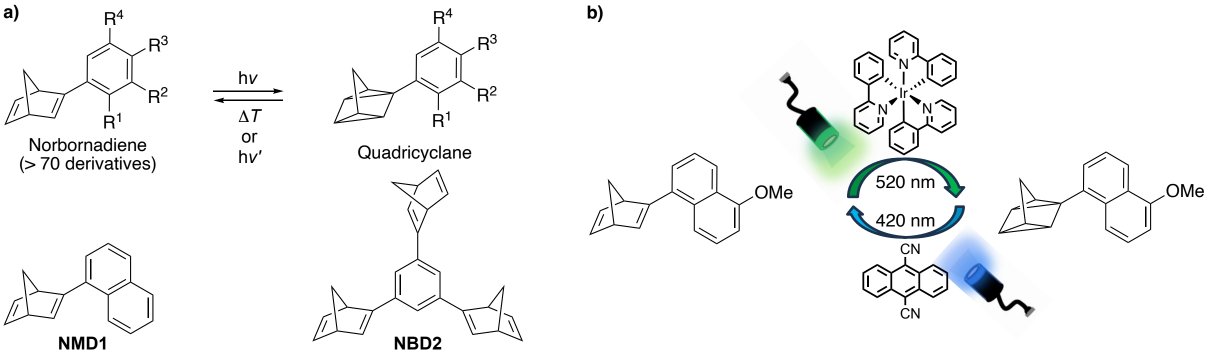

Figure 1. a) Reversible photoisomerization of arylnorbornadienes to quadricyclanes, b) Photo-catalyzed cycloaddition-cycloreversion cycle of a 1-methoxynaphthyl-substituted norbornadiene.

Funding: *House of Young Talents* (University of Siegen), Stiftung Nagelschneider

References:

[1] R. J. Salthouse, K. Moth-Poulsen *J. Mater. Chem. A* **2024**, *12*, 3180.

[2] a) R. Schulte, S. Afflerbach, T. Paululat, H. Ihmels, *Angew. Chem. Int. Ed.* **2023**, *62*, e202309544. b) R. Schulte, S. Afflerbach, H. Ihmels, *Eur. J. Org. Chem.* **2023**, e202201398. c) T. J. B. Zähringer, N. P. Lopez, R. Schulte, M. Schmitz, H. Ihmels, C. Kerzig, *Angew. Chem. Int. Ed.* **2024**, *63*, e202414733.

Singlet Fission: from fundamentals to devices

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There are many applications that demand that the properties of light be controlled by molecular excitons. This includes upconversion applications, where shorter wavelengths are generated from longer wavelengths using triplet fusion, and multiple exciton generation due to singlet fission, where a high energy photon is split into smaller energy packets. In these conjugate processes, an excited state chromophore is necessarily in contact with one or more ground state chromophores, opening up the possibility of excimer formation. What is the role of the excimer in these systems? Is it a trap, or is it an intermediate? By careful analysis of time-dependent photoluminescence and absorption spectroscopy, and consideration of thermodynamical principles, we have concluded that excimers play no useful role at all in the solution phase,[1,2] despite claims to the contrary.[3,4] A more recent report confirmed an emissive triplet fusion intermediate in the solid state.[5] Where does that leave solutions? We carefully analysed the room temperature time-resolved emission of a neat liquid singlet fission chromophore. It exhibits three spectral components: two that correspond to the bright singlet and excimer states, and a third component that becomes more prominent during triplet fusion. This spectrum is enhanced by magnetic fields, confirming its origins in the recombination of weakly-coupled triplet pairs. It is tentatively attributed to strongly coupled triplet pair state. These observations unite the view that there is an emissive intermediate in singlet fission and triplet fusion, distinct from the broad, unstructured excimer emission. This talk will conclude with a short update on silicon-based singlet fission solar cells being developed at UNSW.

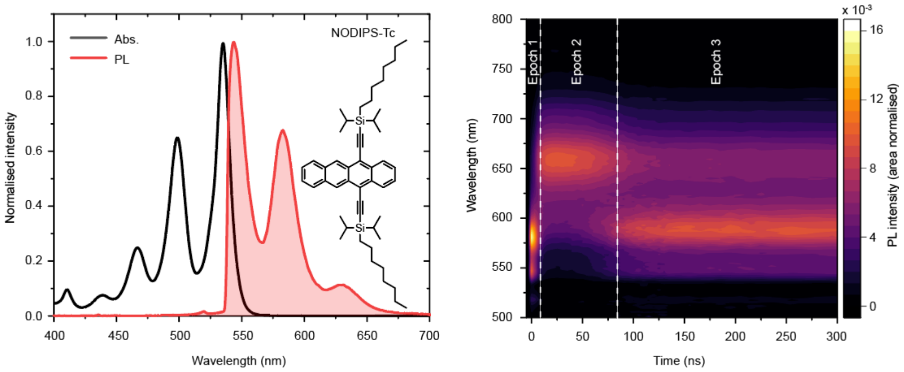

Figure 1. A molecular traffic light! Normalised time-resolved emission of NODIPS-tetracene

Funding: Australian Research Council (Centre of Excellence in Exciton Science CE170100026 (T.W.S.) and FT230100002 (M.J.Y.T.). Australian Renewable Energy Agency, *Low-Cost >30% Efficient Silicon Photovoltaic Solar Cells Achieved Through Singlet Fission*

References:

[1] Cameron B. Dover et al., *Nature Chemistry* **2018,** *10* (3), 305-310
[2] Miroslav Dvořák et al., J. Am. Chem. Soc. **2021,** *143* (34), 13749-13758
[3] Brian J. Walker, et al., *Nature Chemistry* **2013,** *5* (12), 1019-1024
[4] H. L. Stern, et al., *Proc. Nat. Acad. Sci. USA* **2015,** *112* (25), 7656-7661
[5] David G. Bossanyi et al., *Nature Chemistry* **2021**, *13* (2), 163-171
[5] J. Feng, et al., *Nature Chemistry* **2024**, *16,* 1861–1867

Elucidating microenvironmental factors governing photothermal conversion

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Photothermal conversion efficiency depends not only on a material's intrinsic chromophore properties but critically on its surrounding microenvironment (Fig.1). During this presentation, I systematically investigate how interfacial hydration and polymer–protein interactions modulate non-radiative decay and heat release at the nanoscale.[1] By varying polymer chain length and grafting density around a model fluorescent protein, shifts in the heat-generation rate under low-intensity illumination are quantified. It is shown that optimal hydration enhances vibrational energy transfer, while tailored polymer shells impact chromophore aggregates. This factor-by-factor analysis establishes design rules for next-generation light-to-heat materials and lays the groundwork for adaptable microenergy harvesters and self-powered thermal sensors.

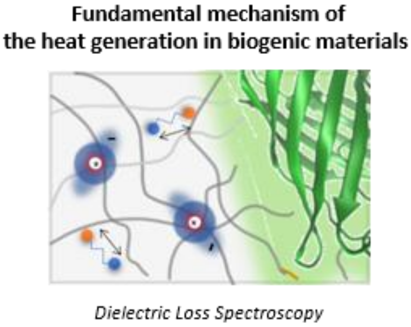

Figure 1. Graphical representation of the microenvironmental impact on photothermal properties of biogenic materials.

Funding: MSCA Fellowship (HeatBLED No. 101066817)

References:

[1] D. Gutiérrez-Armayor, S. Ferrara, M. Nieddu, A. Zieleniewska, R.D. Costa *Adv. Funct. Mater.* **2025**, *35*.

Application of Near-Field Heterodyne Transient Grating (NF-HD-TG) Spectroscopy to the Investigation of Photoexcited Charge Carrier Dynamics

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The heterodyne transient grating (HD-TG) technique is recognized as one of the most powerful time-resolved spectroscopic methods for investigating chemical and physical phenomena at solid-liquid interfaces. This method offers significant advantages, including signal amplification through the mixing of a strong reference field and enhanced detection sensitivity via linearization. Notably, by positioning a transmission grating in front of the target sample, the HD-TG technique can be further simplified and optimized, resulting in what is known as the near-field HD-TG (NF-HD-TG) method. In this approach, the reference and signal fields are automatically generated as the probe light passes through the transmission grating. By adjusting the distance between the grating and the sample, the optical phase difference between the two can be controlled. This adjustment enables the selective detection of only the real part of the refractive index change (Δn(t)), while effectively eliminating contributions from the imaginary part (Δk(t)).

Leveraging these aforementioned advantages, the NF-HD-TG technique has been employed to investigate photoexcited charge carrier dynamics in a variety of photocatalytic materials, including TiO_2, hematite (α-Fe_2O_3), $BiVO_4$, $MAPbI_3$, and others. For instance, our group recently succeeded in determining the activation energy values using the NF-HD-TG method, associated with charge transfer processes between the photoanode surface and the electrolyte, a topic that will be discussed at the conference.

In addition, due to the limited information regarding the energetic positions of trap states present in the target samples, further development of the NF-HD-TG method was necessary. In response to this challenge, our group recently introduced a new spectroscopic technique called the charge carrier-selective HD-TG (CS-HD-TG) method. [1] In this approach, an additional laser (referred to as the "burn laser") was irradiated onto the target sample. (See Figure 1) When the wavelength of the burn laser was tuned to resonate with the energy level of a trap state, it selectively reduced the population of trapped charge carriers. By systematically varying the wavelength of the burn laser, we successfully identified the energetic positions of the trap states.

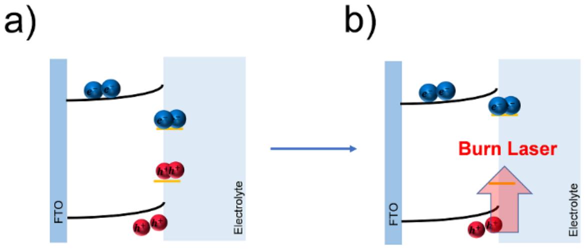

Figure 1. Schematic illustrations of photo-generated charge carriers in a photoanode a) without burn laser and b) with burn laser

We identified the energetic positions of the trap states and discovered that two distinct trap states coexist on the surface of α-Fe2O3, although only one of them serves as an active reaction center for water splitting. In addition, the CS-HD-TG method was employed to investigate the energetic positions of trap states in both α-Fe_2O_3 and ZnO, and these results will also be presented during the session.

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

References:

[1] Y. H. Kim, Y. G. Bae, W. Y. Sohn, *Phys. Chem. Chem. Phys.* **2023**, *25*, 11981.

Highly efficient artificial photocatalysts mimicking Photosystem 1

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Biological photosynthesis has evolved to a highly efficient molecular apparatus where light induced electron transfer processes are precisely tuned with regard to sequence and direction by optimal positioning of functional units. [1] Photosystem 1 is generating a directional electron flow from the P700 to the FNR-catalysis center for $NADH_2^+$ formation over a bridge of several spatially fixed FeS clusters. These highly reactive intermediates are protected by protein environments. A functional mimic of nature's example are multinuclear metal complexes containing a photosensitizing Ru-polypyridyl unit, a catalytically active Rh(III)Cp* unit and a bridging ligand, if containg an alkynyl linkage providing for very efficient electronic coupling already in the ^{1}MLCT state and highly efficient photocatalysis. [2] However, chemical instability of this linkage lead to a search of optimal linking units, which proved futile. [3,4] Inspired by the design of the natural system we those developed a supramolecular protection of the alkynyl link in from of a rotaxane. We present here the synthesis, photophysical and theoretical characterization and the outstanding photocatalytic activities which support the novel concept of supramolecular protection of the Achilles' heel.

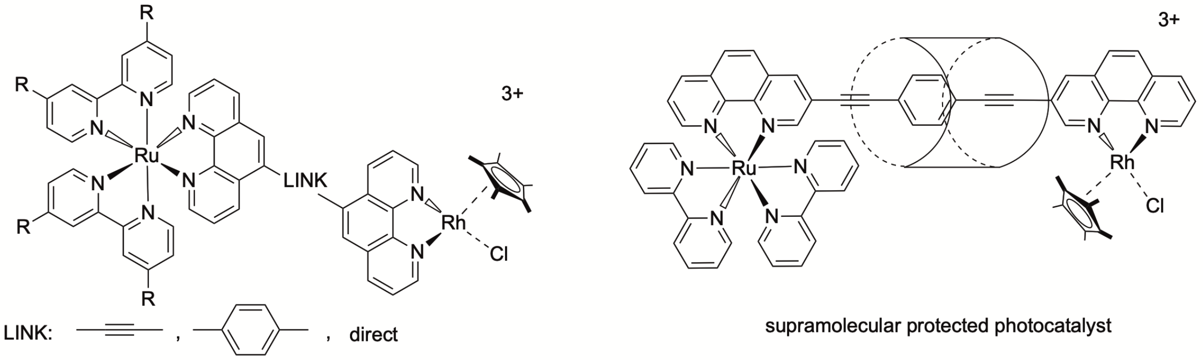

Figure 1. Photocatalysts for visible light driven formation of $NADH_2^+$ and efficient protected novel catalyst

Funding: Deutsche Forschungsgemeinschaft DFG, CRC 234 CataLight, 364549901, A1, B7, C3, C6

References:

[1] R. Blankenship, Molecular Mechanisms of Photosynthesis, 3rd ed. Wiley-Blackwell, **2021**

[2] L. Zedler, P. Wintergerst, A. K. Mengele, C. Müller, C. Li, B. Dietzek-Ivanšić, S. Rau, *Nat. Commun.,* **2022**, 13, 2538

[3] L. Zedler, A. K. Mengele, K. M. Ziems, Y. Zhang, M. Wächtler, S. Gräfe, T. Pascher, S. Rau, S. Kupfer, B. Dietzek, *Angew. Chem. Int. Ed.* **2019**, 58, 13140-13148

[4] M. Semwal, M. Laemmle, E.M. Brohmer, S. Volk, L. Zedler, S. Kupfer, A. Mengele, G. Shillito, S. Rau, B. Dietzek-Ivanšić, Inorg. Chem., **2025** accepted, DOI: org/10.1021/acs.inorgchem.4c04596

Photochemistry of biphenylamine photocages

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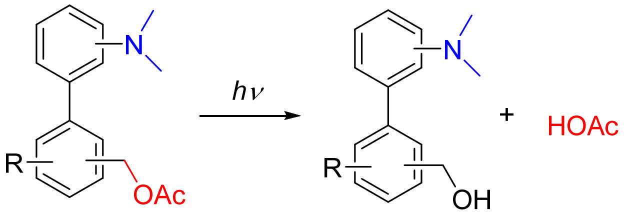
Photocages (photo-removable protective groups) are becoming widely used in biology[1] owing to the development of compounds that can undergo decaging upon excitation by visible light,[2] in processes with spatial and temporal control. However, the ideal photocage for all purposes still does not exist and researchers try to develop better caging groups for various applications.[3] For example, photocages which can be selectively removed by light of different wavelength (also known as chromo-orthogonality) are potentially useful in multistep organic synthesis.[4]

In our research group, we have investigated the photoreactivity of aniline[5] and aminonaphthalene photocages.[6-8] The decaging from aniline derivatives undergoes heterolytically, giving the carbocation as intermediate.[5] On the contrary, the decaging from aminonaphthalenes is homolytic process on the singlet excited state surface giving radical species, which subsequently undergo electron transfer to yield released carboxylic acids ($\Phi_R = 0.01 - 0.22$).[6-8] Further investigation led to the development of differently substituted aminobiphenyl derivatives (Scheme 1) which react more efficiently in releasing carboxylates ($\Phi_R = 0.04 - 0.37$) than aminonaphthalenes. Moreover, we have also demonstrated the applicability of the aminobiphenyl photocages in organic synthesis and biology in the photo-release of different aliphatic and aromatic carboxylic acids. The mechanism of the photodecaging from aminobiphenyls was investigated by fluorescence spectroscopy and laser flash photolysis (LFP).



R = groups that facilitate two-photon absorption

Scheme 1. Photo-release of carboxylic acids from aminobiphenyl photocages.

Funding: Croatian Science Foundation (HRZZ-IP-2024-05-8565)

References:

[1] G. C. R. Ellis-Davies, *Angew Chem. Int. Ed.* **2023**, *62*, e202206083.
[2] R. Weinstain, T. Slanina, D. Kand, P. Klán, *Chem. Rev.* **2020**, *120*, 13135.
[3] P. Klán, T. Šolomek, C. G. Bochet, A. Blanc, R. Givens, M. Rubina, V. Popik, A. Kostikov, J. Wirz, *Chem.Rev.* **2013**, *113*, 119.
[4] P. Shrestha, A. Mukhopadhyay, K. C. Dissanayake, A. H. Winter, *J. Org. Chem.* **2022**, *87*, 14334.
[5] Đ. Škalamera, V. Blažek Bregović, I. Antol, C. Bohne, N. Basarić, *J. Org. Chem.* **2017**, *82*, 12554.
[6] V. Lovrinčević, D. Vuk, I. Škorić, N. Basarić, *J. Org. Chem.* **2022**, *87*, 2489.
[7] V. Lovrinčević, Y. Guo, D. Vuk, I. Škorić, J. Ma, N. Basarić, *J. Org. Chem.* **2023**, *88*,15176.
[8] V. Lovrinčević, D. Zheng, M. Baudin-Marie, M. Marić, L. Uzelac, I. Škorić, J. Ma, D. Vuk, *J. Photochem. Photobiol. A: Chem.* **2024**, *454*, 115715.

Photophysical properties of nickel and palladium complexes with porphyrin and corrin. A theoretical perspective

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Complexes of metals with tetrapyrrole ligands have interesting photophysical properties. Palladium complexes with porphyrin and chlorin derivatives are important for oxygen sensors and photodynamic therapy. Palladium complexes exhibit phosphorescence, whereas complexes of metals such as nickel are neither phosphorescent nor fluorescent.

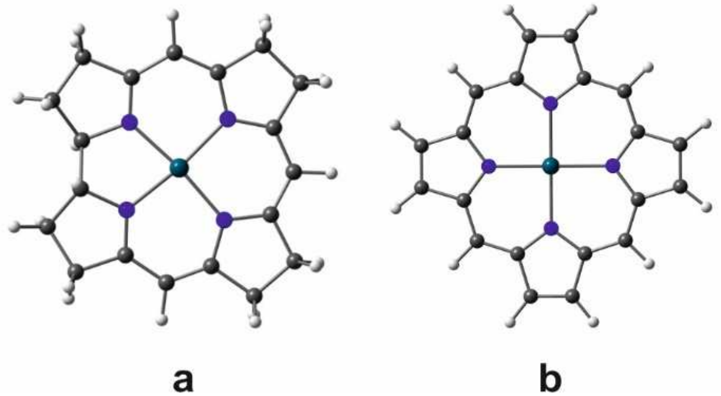

Figure 1. Structure of a) M(II) corrin complex and b) M(II) porphyrin complex (b), where M=Ni, Pd

Quantum chemical calculations with the use of the DFT, TDDFT, CASSCF/NEVPT2 and Spin-Flip DFT methods were performed for palladium(II) porphyrin (Pd(II)Por), palladium(II) corrin (Pd(II)Corr) and corresponding nickel complexes. The structure of the studied complexes is presented in Figure 1. Potential energy curves were determined for various deformations of the porphyrin and corrin rings, such as bending or elongating metal-nitrogen or metal-carbon bonds. Intersections on the energy curves between states of the same multiplicity (Conical Intersections) and different multiplicity (Minimal Energy Crossing Points) were located using the Spin-Flip DFT and CASSCF methods. The deactivation mechanisms of excited states in nickel complexes were determined on this basis. The photophysical properties of nickel complexes were compared with those of palladium complexes.

References:

[1] B. T. Phelan, M. W. Mara and L. X. Chen, *Chem. Commun.*, **2021**, 57, 11904
[2] J. Deng, H. Li, M. Yang and F. Wu, *Photochem. Photobiol. Sci.*,**2020**, 19, 905

(Photo)truncation of Cyanines

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Cyanine dyes are a class of organic, usually cationic molecules containing two nitrogen centers linked through conjugated polymethine chains. They have been found to be widely used as fluorescent probes for labeling nucleic acids and proteins and as photosensitizers in photodynamic therapy, biosensors, and imaging agents. The synthesis[1] and reactivity of cyanine derivatives have been extensively investigated for decades but their further synthetic modifications, especially on the polymethine chains, are still a poorly explored area. In conjunction with applications of cyanine dyes in optical imaging and photochemical drug delivery, Schnermann and co-workers described that excitation of heptamethine cyanine (Cy7) in phosphate-buffered saline leads to the formation of truncated (chain-shortened) pentamethine cyanine (Cy5) in small yields (Figure 1).[2,3] The reported dramatic increase in the phototruncation yield in CAPSO buffer motivated us to perform a deeper study of this reaction and improve the yields. Our mechanistic studies demonstrate that the phototruncation mechanism is a complex photooxidation multi-step process that is related to highly specific buffer constituents.

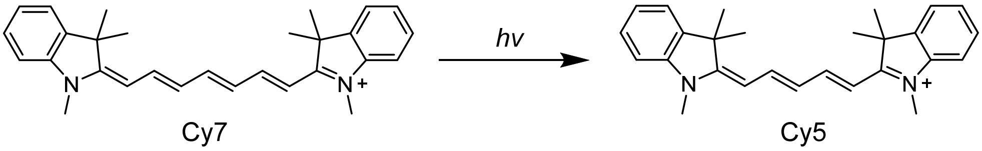

Figure 1. Phototruncation of cyanines.

In addition, we recently demonstrated that truncation of cyanines can also proceed via homogeneous, acid–base-catalyzed nucleophilic exchange reactions in high yields in the dark.[4] We provided critical insight into the reactivity of cyanine polyene chains and elucidated the truncation mechanism and methods to mitigate side processes that can occur during the synthesis of cyanine derivatives.

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References:

[1] L. Štacková, P. Štacko, P. Klán *J. Am. Chem. Soc.* **2019**, *141*, 7155.

[2] S. S. Matikonda, D. A. Helmerich, M. Meub, G. Beliu, P. Kollmannsberger, A. Greer, M. Sauer, M. J.Schnermann *ACS Cent. Sci.* **2021**, *7*, 1144.

[3] H. Fukushima, S. S. Matikonda, S. M. Usama, A. Furusawa, T. Kato, L. Štacková, P. Klán, H. Kobayashi, M. J. Schnermann *J. Am. Chem. Soc*. **2022**, *144*, 11075.

[4] J. Okoročenkova, J. Filgas, N. M. Khan, P. Slavíček, P. Klán *J. Am. Chem. Soc.* **2024**, *146*, 19768.

Weak effects on electron transfer reactions – Rethinking of the determination of activation energies in solution

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The photo-induced electron transfer (PET) plays an important role in many areas of chemistry. Individual changes in the environment, such as an external magnetic field or solvent parameters, can be used to systematically investigate the nature of the PET reaction. As they have proven helpful in clarifying chemical reaction mechanisms, studies on the effects of the local environment on chemical reactions are of great interest.

The physical properties of the solvent influence the rate constant of PET reactions in many ways. The dielectric constant ε and the refractive index n influence the reorientation of the dipoles of the solvent and contribute to the activation energy of the electron transfer reactions [1]. For this reason, solvent-dependent measurements of (P)ET reactions were carried out quite early on. However, the electron transfer kinetics are also influenced by diffusion and thus by the solvent viscosity η. We give an overview of possible individual changes in the reaction environment [2] for thermal ET and PET reactions [3]. Depending on the requirements of the reactants, pure organic solvents and solvent mixtures can be used for these changes.

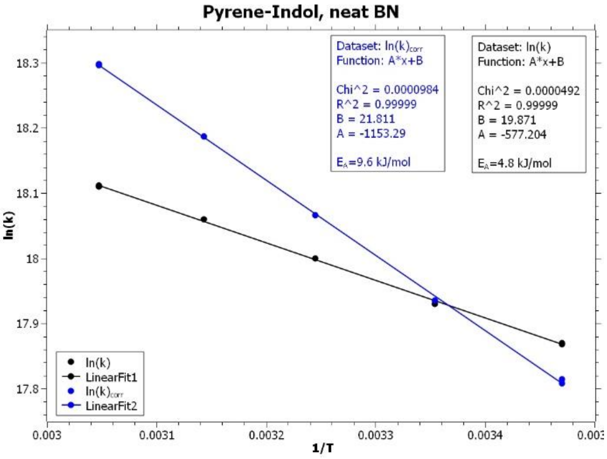

Figure 1. Comparison of the uncorrected and corrected values of an Arrhenius plot for the activation energy in butyronitrile. The difference is a factor of two [4].

In recent studies, we have investigated the temperature dependence of a PET reaction under precisely defined conditions. We could clearly see that increasing the temperature leads to significant changes in the solvent properties and thus to incorrect activation energies. Since this is the rule rather than the exception in (P)ET reactions, we discuss possible ways out of this problem [4].

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References:

[1] M. Berghold, J. Bächle, S. Landgraf, G. Grampp, ChemPhysChem, **2017**, *18*,128.
[2] A. Wankmüller, M. Berghold, S. Landgraf, J. Mol. Liquids, **2021**, *333*, 115880.
[3] S. Landgraf, G. Grampp, K. Rasmussen, T. Suwunwong, P. Choto, New J. Chem., **2024**, *48*, 5392.
[4] unpublished results.

Novel Concepts to Outcompete Thermodynamics and Favor Cage Escape Yields in Bimolecular Electron Transfer Reactions

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In natural and artificial photosynthesis, light absorption and catalysis are separate processes linked together by exergonic electron transfer. Light is commonly used to drive a plethora of organic transformations, but the corresponding reaction mechanisms are not always straightforward.

Here, I will describe two approaches that are currently being developed in our laboratory. This first one is how to control and improve the cage escape process, i.e. the physical separation and solvation of the geminate radical pair formed after excited-state electron transfer. I will present our recent advances in the understanding of the cage escape process using coordination compounds based on rare and earth abundant transition-metal based coordination compounds and correlate it to parameters that include spin, driving force, dielectric constants and temperature to show how these factors can be tuned to modulate the cage escape yields and thus the reaction yields.

In the second part, I will describe our recent approach to in using trifluoroacetate derivatives as $CF_3^{\bullet}$ source for trifluoromethylating reactions. Trifluoroacetate derivatives represent ideal reagents as they are highly abundant and cheap, but their very positive one electron oxidation potential (~2.3 V vs NHE) often hampers their widespread use in photoredox catalysis. Indeed, at these potentials, selectively oxidizing trifluoroacetate over reaction solvent or partner substrates becomes challenging. We present a novel approach that circumvents these limitations through the use of a pentacationic Ir(III) photosensitizer that forms a strong 1:1 ion-pair with trifluoroacetate in acetonitrile and enables rapid and efficient photooxidation of trifluoroacetate in ~90 ps without significant solvent or partner substrate oxidation. The $CF_3^{\bullet}$ radicals so generated are shown to trifluoromethylate a range of partner substrates, including aromatic compounds, heterocycles, natural products and pharmaceutically-relevant products, in moderate yields.

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References:

[1] Aydogan, A.; Bangle, R. E.; Cadranel, A. ; Turlington, M. D. ; Conroy, D. T. ; Cauët, E. ; Singleton, M. L.; Meyer, G. J.; Sampaio, R. N.; Elias, B.; Troian-Gautier, L., *J. Am. Chem. Soc.* **2021**, *143*, 15661-15673.
[2] A. Ripak, A. K. Vega Salgado, D. Pires Valverde, S. Cristofaro, A. de Gary, Y. Olivier, B. Elias, L. Troian-Gautier, *J. Am. Chem. Soc.*, **2024**, *146*, 22818-22828.
[3] F. Glaser, S. De Kreijger, L. Troian-Gautier, *J. Am. Chem. Soc.,* ***2025****, Accepted*
[4] P. Li, C. Bourgois, F. Glaser, S. De Kreijger, A. Cadranel, L. Troian-Gautier, K. Hu, *Submitted*.

TADF in open-shell organic molecules

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High-spin states in organic molecules offer promising tuneability for quantum technologies. Photogenerated quartet excitons are an extensively studied platform, but their applications are limited by the absence of facile read-out. We recently showed that optical read-out in such systems is possible via a luminescent trityl-based radical.[1]

Now we demonstrate a general class of synthetically accessible molecules with quartet-derived luminescence, formed by appending a non-luminescent TEMPO radical to thermally activated delayed fluorescence (TADF) chromophores previously used in OLEDs.[2]

The low singlet-triplet energy gap of the chromophore opens a luminescence channel from radical-triplet coupled states (Fig. 1). We establish a set of design rules by tuning the energetics in a series of compounds based on a naphthalimide (NAI) core. We observe generation of quartet states and measure the strength of radical-triplet exchange. In DMAC-NAI-TEMPO, up to 72% of detected photons emerge after reverse intersystem crossing from the quartet state repopulates the state with singlet character.

This design strategy does not rely on a luminescent radical to provide an emission pathway from the high-spin state. The large library of TADF chromophores promises a greater pallet of achievable emission colours.

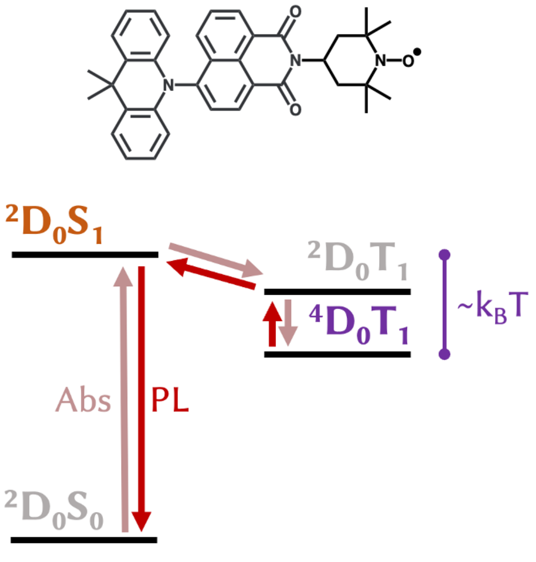

Figure 1. Molecular structure and simplified Jablonski diagram of luminescent DMAC-NAI-TEMPO.

Funding: European Research Council; Royal Society; UKRI; Emmanuel College, Cambridge

References:

[1] S. Gorgon, K. Lv, J. Gruene *et al.*, *Nature* **2023** 620, 538-544.
[2] S. Gorgon, P. Murto, D. Congrave *et al.*, *Adv Mater* **2025** DOI: 10.1002/adma.202501164

X-ray absorption spectroscopy in the nanoseconds-seconds range to probe rearrangements around catalytic centers induced by light.

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An overview of recent developments and applications of light-initiated time-resolved X-ray absorption spectroscopy at the Swiss Light Source (SLS) synchrotron will be given. This includes the development of an instrument for pump-probe measurements covering the time range from 100 ps to a few microseconds using tender X-rays. The instrument is unique for synchrotrons and complementary to those available at some X-ray Free Electron Lasers, in particular SwissFEL. We will show our recent application of this setup to probe carbon-hydrogen bond activation by Rh complex [1]. Two states corresponding to alkane complexation with Rh center and the oxidative addition step were captured using pump-probe XAS at the Rh L_3 edge (Fig. 1. left). This has allowed us to build the molecular picture of C-H bond activation with orbital resolution. Pump-probe XAS in the hard X-ray range, with the main focus on the nanosecond-microseconds range, has been used to study photocatalytic and luminescent materials at SLS for years [2]. Slower light-induced processes in the millisecond range for working photoelectrodes can be probed using modulated light excitation and time-resolved X-ray fluorescence detection. Capabilities for such experiments are more broadly available, they can also be performed at the ESRF synchrotron. Our recent example of such measurements is the investigation of structural changes around Co for oxygen-evolving photoelectrodes with CoP_i catalyst on Fe_2O_3 light-absorber (Fig. 1, right). The role of Co centers, in particular, if they are involved in the accumulation of holes or mainly participate as catalytic centers in the rate-limiting reaction step, is clarified by comparing the transient XAS spectra measured for different electrolytes and applied potentials.

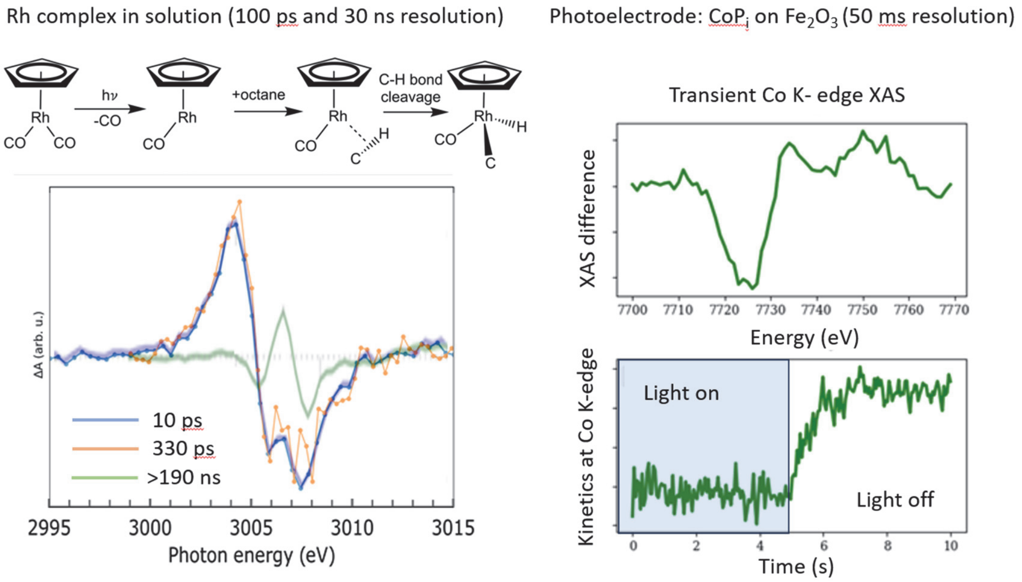

Figure 1. Left: Pump-probe XAS at Rh L3-edge corresponding to C-H bond activation.
Right: Transient XAS at Co K-edge for CoPi-Fe_2O_3 photoelectrode.

References:

[1] Jay et al. *Science* **2023**, 380, 955.

[2] M. Vogt, G. Smolentsev *ChemPhotoChem* **2022,** 6, e202100180

Strategies for Oxygen Tolerant Radical Photopolymerization with Less Toxicological Concern and Sustainable Origin Based on a New Paradigm

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Light-mediated initiation of radical polymerization, connecting to modern application in practice, has been growing in the last decades showing even no drop in the Corona Pandemics. The utilization of this technology has led to the development of systems that exhibit high sensitivity across a broad spectral range, extending from the ultraviolet (UV) to the near-infrared (NIR) region[1].

Oxygen tolerance represents one key parameter. Here, bis(2-amino-5-thienyl)ketones (**BAK**), absorbing in the UV and blue range, operated well in a **PET** mechanism using diaryl iodonium salt (**IS**) and the amine **EMBO** as coinitiator following a protocol to a multi-component photoinitiator[2]. Effective oxygen tolerance mechanistic schemes will be discussed based on photo-DSC and, DSC, and dynamic mechanical analysis (DMA) results. Transient absorption approved efficient reaction between the triplet state of **BAK** and **IS** while no quenching proceeded with **EMBO**. However, both initiated radical polymerization of multi-functional acrylic esters resulting in crosslinked materials. Spectroscopic evaluation of $^1O_2$ formed and electrochemical studies complement the pattern regarding the photophysical properties of **BAK**s. Additional exposure studies and product analysis enabled to setup a mechanism explaining the much bigger oxygen tolerance compared to nowadays systems used in practice. A new paradigm explains the high reactivity even with the triplet state Cytotoxic investigations indicated no remarkable response.

Furthermore, a new heterogeneous one-component photoinitiator based on sustainable carbon nanodots (**CD**), where sustainable furfuraldehyde available from wood waste, served as feedstock, also exhibited a certain oxygen tolerance compared to the traditional phosphine oxide initiator **TPO-L**. **CD**s comprised either oxime ester or diaryl phosphine oxide groups on the surface, which efficiently formed a star-shaped network with improved mechanical performance in applications such as 3D printing. Analysis of photoinitiated radical polymerization by real-time FTIR and photo-DSC indicated a better tolerance under aerobic conditions of both **CD**s compared to **TPO-L** with **UDMA** and **TPGDA** as monomers explainable by the availability of many initiation groups on the surface of the **CD**. Interestingly, the new one component sustainable photoinitiator much better tolerated changes in the initiator loading than classical **TPO-L** systems. Remarkable was also the significant lower cytotoxicity and improved migration resistance compared to **TPO-L**[2] bringing them to broader application uses.

Moreover, confinement of sustainable carbon dots based on cellulose in a rigid matrix based on silica, alginate or zeolite resulted in both conventional and controlled radical photopolymerization. The latter even resulted in control of polymerization with defined architectural design needing at least 9 ppm $CuBr_2$/**L** (L: amine ligand) as cocatalyst, which was successfully approved by chain extension experiments. The confinement resulted in Triplet states as approved by Thermally Activated Delayed Fluorescence (TADF) and Room Temperature Phosphorescence (RTP)[3]. This is as a prerequisite to achieve the necessary performance in radical polymerization. Carbon dots based on cellulose without confinement showed no photoinitiation efficiency.

Acknowledgement: E. Dmitrieva (IFW Dresden) for electrochemical experiments, X. Allonas (U Mulhouse Haute Alsace) for transient absorption experiments, and P. Wang for **CD** confinement experiments.

References:

[1] X. He, L. Zang, Y. Xin, Y. Zou, *Applied Research* **2023**, *2*, e202300030.

[2] X. Luo, X. Liu, H. Guo, R. Li, M. Wang, X. Li, S. Li, S. Liu, J. Li, V. Strehmel, Q. Wang, G. Yilmaz, K. Matyjaszewski, B. Strehmel, Z. Chen, *Nature Protocols*, **2025**, https://doi.org/10.1038/s41596-025-01210-3.

[3] P. Wang, M. Ge, X. Luo, Y. Zhai, N. Meckbach, V. Strehmel, S. Li, Z. Chen, B. Strehmel, *Angew. Chem., Int. Ed.* **2024**, *63*, e202402915.

Photo-SPAAC ligation-based preparation of sequence defined macromolecules, patterned hydrogels, and macrocycles.

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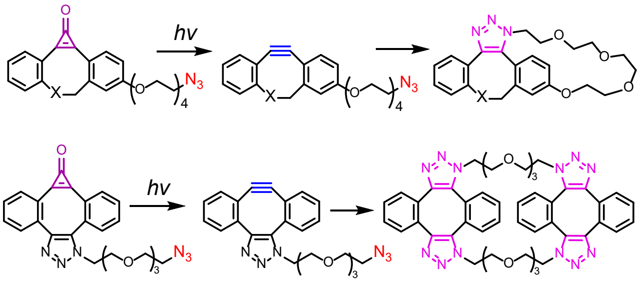
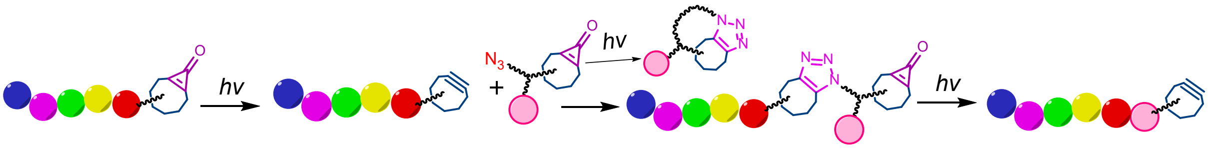
"Photo-SPAAC" click reaction that has been developed in our group is based on the photo-decarbonylation of cyclopropenone moiety incorporated into an 8-membered ring. Cyclopropenone-caged dibenzocyclooctynes (Scheme below) do not react with organic or inorganic azides, nor with common nucleophiles or electrophiles; they also possess excellent thermal and hydrolytic stability. Despite their stability, exposure to UVA or blue light (or NIR pulsed laser) converts them into azide-reactive cyclooctynes in high quantum efficiency and quantitative chemical yield.

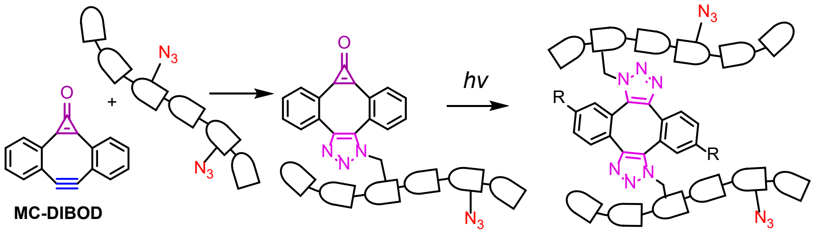
Photo-generated bifunctional cyclooctynes bearing an azide moiety (cyclooctyne-X-azide) undergo very efficient cyclization, even at very high concentration or in the neat form. No dimers or higher oligomers are observed. When the linker between azide group and cyclooctyne is too short to allow for intramolecular reaction, the dimerization is followed by cyclization. This reaction offers and efficient method for the preparation of macrocycles.



Using the bifunctional caged cyclooctynes we have developed a new strategy for the step-by-step assembly of monodispersed sequence defined macromolecules. In this approach, the growing terminus of a macromolecule carries a cyclopropenone-caged cyclooctyne. Upon photochemical activation, the azide-reactive cyclooctyne is revealed. Since the only by-product is the gaseous carbon monoxide, no purification is required at this stage. After the irradiation, a bifunctional monomer that carries azide and caged cyclooctyne moieties at opposite termini is introduced. The latter undergoes rapid SPAAC addition to the macromolecule, producing N+1 cyclopropenone-terminated chain. Then, the process is repeated. The excess of a monomer, which is still required to achieve high sequence fidelity, is deactivated during the subsequent irradiation, as intramolecular cyclization of bifunctional molecule is much faster than intermolecular SPAAC.



Biocompatible biodegradable hydrogels are becoming an important tool in tissue engineering, surgery, wound treatment, etc. SPAAC derivatization of azide-functionalized water-soluble natural polymers (e.g., alginates, GAGs, etc.) with the bifunctional mono-cyclopropanated dibenzocyclooctadiyne (MC-DIBOD) allows for the light-directed cross-linking of the polymer and the formation of a biodegradable hydrogel. The degree of cross-linking, porosity, and mechanical properties of the gel can be readily controlled by the duration and/or intensity of light exposure. In addition, this approach permits the creation of patterns, including 3-D, and gradients of hydrogel properties.



Designing Ionic Soft Matter: Liquid Crystalline Ionogels from Protic Ionic Liquids

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In recent years, significant attention has been given to ionic liquids (ILs) that can form liquid crystals (LCs). Ionic liquid crystals (ILCs), which bridge the ordered structure of crystalline solids and the fluidity of isotropic liquids, have emerged as transformative materials for energy and optoelectronic technologies. Their tunable ionic conductivity, anisotropic behavior, and thermal stability enable applications in sensing, catalysis, solar cells, electrochemistry, and stimuli responsiveness, as well as electro-optical displays.[1] Ionic liquids (ILs) exhibit intrinsic molecular-level heterogeneity, which arises from the coexistence of polar and nonpolar nanoscale domains. This structural complexity arises from the aggregation of ionic headgroups into charged polar regions and the segregation of hydrophobic alkyl chains into apolar domains, as revealed by small- and wide-angle X-ray scattering (SWAXS)[2], and neutron scattering [3]. Notably, fluorescence-based techniques utilizing environment-sensitive molecular probes have become indispensable tools for mapping local heterogeneity within ionic liquids (ILs).[4] Herein, we designed and synthesized a protic ionic liquid (PIL) capable of forming a gel and exhibiting liquid crystalline phases. We explored its molecular structure to assess its suitability as an electrolyte for applications, including dye-sensitized and perovskite solar cells. Phase transitions and morphological characteristics were examined using polarized optical microscopy, which revealed that the PIL demonstrates both lyotropic and thermotropic liquid crystalline behaviors. To further elucidate the microstructure of the neat PIL, we employed multiple fluorescence parameters such as fluorescence intensity, fluorescence anisotropy, and fluorescence lifetime, using both Nile Red (NR) and Nile Blue Sulphate (NBS) as probes. These parameters were effectively used to investigate molecular-level properties such as polarity and microviscosity of the PIL as a function of temperature. By determining the microviscosity of the PIL and comparing it with bulk viscosity measurements (Fig. 1), we confirmed the existence of microheterogeneity within the PIL. These insights not only deepen our fundamental understanding of its molecular environment of PIL but also provide a foundation for the rational design of tailored protic ionic liquid-based materials for diverse energy and optoelectronic applications.

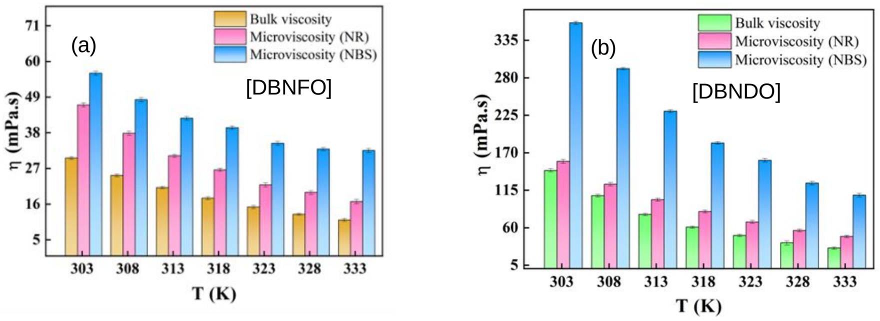

Fig. 1. Temperature-dependent micro- and bulk viscosities of (a) [DBNFO] and (b) [DBNDO] ILs using NR and NBS probes

References:

[1] Goossens, K.; Lava, K.; Bielawski, C. W.; Binnemans, K. Chem. Rev. 2016, 116, 4643−4807.

[2] Russina, O.; Triolo, A.; Gontrani, L.; Caminiti, R. J. Phy. Chem. Lett. 2012, 3, 27–33.

[3] Triolo, A.; Russina, O. J. Phys. Chem. B. 2005, 109, 22061–22066.

[4] Dash, B.R.; Gardas, R.L.; Mishra, A.K. Phys. Chem. Chem. Phys. 2024, 26, 13350–63.

Chemical Reaction Insights through FLIM

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My laboratory is fascinated by understanding how chemical reactions work. Without the right tools to investigate chemical reactions, critical mechanistic details are missed. Thus, my laboratory is also fascinated by tool development. Here the development of fluorescence lifetime imaging microscopy (FLIM) application methods provides the ability to simultaneously image physical and chemical changes inside of polymers in real time during catalytic polymerization. FLIM enables not only an understanding of the dynamic chemical and physical changes inside polymers as they are growing with high spatiotemporal resolution, but also how these two features impact each other and catalytic turnover. Case studies in ring-opening metathesis polymerization (ROMP) include development of spectroscopic (fluorescence-lifetime-imaging) methods for the determination of the molecular weights of growing polymers during ongoing reactions (Fig. 1),[1] identification of the causes of stimuli-responsive assembly–disassembly processes in block-copolymers at the individual-block level,[2] and pinpointing the impact of real-time changing physical parameters inside growing polymers on the catalytic chemical reactivity of monomer insertion and polymer growth.[3] The impact of these microscopic behaviors on macroscopic material properties leads to opportunities for improvement in catalyst efficiency and in tailoring bulk polymer properties.

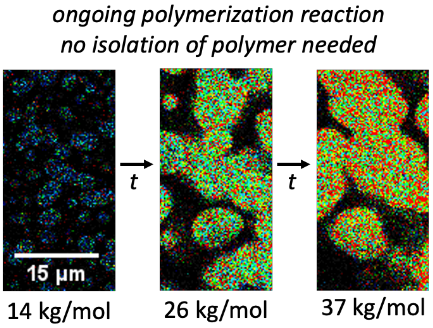

Figure 1. Increasing molecular weight of a polymer imaged using FLIM during an ongoing catalytic polymerization reaction.

Funding: U.S. Department of Energy (DE-SC0016467).

References:

[1] A. I. Garcia, S. A. Blum, *J. Am. Chem. Soc.* **2022**, *144*, 22416–22420.
[2] O. Eivgi, A. C. Ravenscroft, S. A. Blum, *J. Am. Chem. Soc.* **2023**, *145*, 2058–2063.
[3] O. Eivgi, S. A. Blum, *J. Am. Chem. Soc.* **2022**, *144*, 13574–13585.

Single-Molecule Photochemistry

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Besides various schemes of super-resolution microscopy, which are based on reversible switching reactions, single-molecule fluorescence spectroscopy relies on stable fluorophores which should not be prone to photochemical destruction. However, high intensity and/or high number of excitation cycles are mandatory for single-molecule detection by their emission. These experimental conditions predestinates ultrasensitive fluorescence microscopy for studies of photochemical reaction pathways. Our approach is to follow chemical reactions by a change of the fluorescence spectrum.[1,2]

We recently reinvestigated the photooxidation of terrylene,[3] a convenient molecular system accidentally detected more than two decades ago.[4] We found that the excitation wavelength has some impact on the reaction pathway and interpreted this observation as a result of a preformed oxygen-terrylene complex. However, due to the inherent low spectral resolution of two-channel recording setups, we could not analyze whether the two pathways lead to different, fluorescing products. Our attempt to overcome the spectral limitation is to record the emission spectra in a parallelized fashion (Fig.1A).

The same approach is used for investigating the excited-state proton transfer (ESPT).[5] This photochemical reaction is one of the few, if not the only workable for single-molecule studies, which completely proceeds on an adiabatic energy surface, and appears especially appropriate for investigations by fluorescence spectroscopy (Fig. 1B). In contrast to the terrylene photooxidation, the reaction can repeatedly be probed as the reprotonation takes place on the electronic ground state, thus restoring the initial, excitable state.[6,7]

In my presentation, I will compare these two different approaches and show what kind of information can be extracted on the single-molecule level, which cannot be obtained from the ensemble.

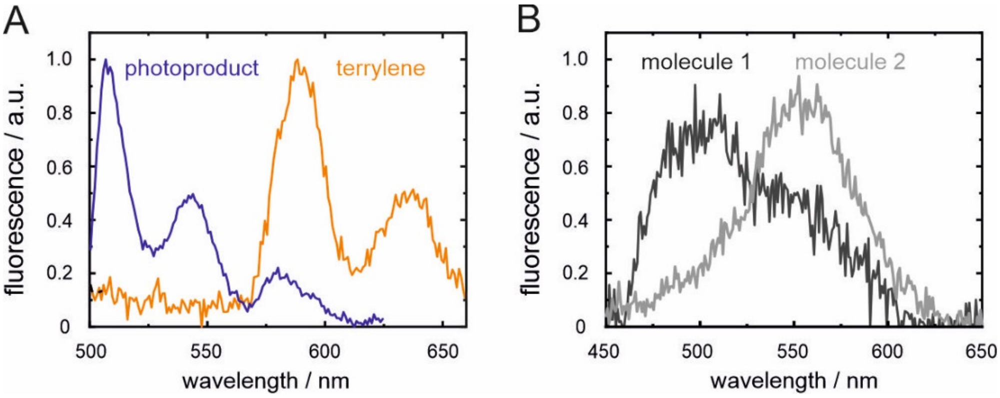

Figure 1. Emission spectra of a) single terrylene molecule and its photoproduct, b) two individual photoacids undergoing different extents of ESPT.

Funding: German Science Foundation (DFG; JU-650/13-1)

Acknowledgement: We thank Luis Pérez-Lustres (Berlin), Roger Kutta, Patrick Nürnberger (both Regensburg), Nicolas Joly (Erlangen), Niklas Sülzner (Bochum) and Thomas Ebbesen (Strasbourg) for helpful discussions, Alexander Grandjean and Matthias Jourdain for contributions at the initial stage of this project.

References:

[1] G. Jung, A. Schmitt, M. Jacob, B. Hinkeldey, *Ann. N.Y. Acad. Sci.* **2008**, *1130*, 131.

[2] J. Menges, A. Grandjean, A. Clasen, G. Jung, *ChemCatChem* **2020**, *12*, 2630.

[3] R. Mhanna, J. Berger, M. Jourdain, S. Muth, R.J. Kutta, G. Jung, *ChemPhysChem* **2025**, *26*, e202400996.

[4] Th. Christ, F. Kulzer, P. Bordat, Th. Basché, *Angew. Chem. Int. Ed.* **2001**, *40*, 4192.

[5] N. Sülzner, G. Jung, P. Nürnberger, *Chem. Sci.* **2025**, *16*, 1560.

[6] M.Vester, T. Staut, J. Enderlein, G. Jung, *J. Phys. Chem. Lett.* **2015**, 6, 1149-1154.

[7] A. Grandjean, L. Pérez-Lustres, G. Jung, *ChemPhotoChem* **2021**, *5*, 1094.

Fluorescence-Lifetime Single-Molecule Localization Microscopy for multiplexing, environmental sensing and 3D imaging

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Fluorescence-lifetime single-molecule localization microscopy (FL-SMLM) adds a powerful dimension to conventional super-resolution techniques by combining precise spatial localization with lifetime-based contrast.[1] We present a versatile FL-SMLM platform that enables multiplexed imaging of spectrally overlapping fluorophores, local environmental sensing and isotropic 3D super-resolution.

By integrating a single-photon detector array into a confocal laser scanning microscope, we combine FL-SMLM with image scanning microscopy (ISM), achieving a twofold improvement in lateral localization precision while maintaining a straightforward implementation.[2] This approach eliminates chromatic aberrations and enables robust multicolor imaging based exclusively on fluorescence lifetime differences.

We further demonstrate the use of FL-SMLM for probing local water content in thermo-responsive microgels by exploiting the differential quenching of red-emitting fluorophores in H_2O versus D_2O environments.[3] This enables nanoscale mapping of hydration dynamics during temperature-induced phase transitions. Additionally, by integrating FL-SMLM with metal-induced energy transfer (MIET) imaging, we achieve isotropic 3D super-resolution reconstructions of subcellular structures.[4]

Taken together, FL-SMLM emerges as a powerful and adaptable platform for multidimensional nanoscale imaging—uniting molecular specificity, environmental sensitivity, and high-precision 3D localization for applications across both biological and materials sciences.

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References:

[1] J. C. Thiele, D. A. Helmerich, N. Oleksiievets, R. Tsukanov, E. Butkevich, M. Sauer, O. Nevskyi, J. Enderlein, *ACS Nano* **2020**, *14*, 14190.

[2] N. Radmacher, O. Nevskyi, J. I. Gallea, J. C. Thiele, I. Gregor, S. O. Rizzoli, J. Enderlein, *Nat. Photonics* **2024**, *18*, 1059.

[3] S. Jana, O. Nevskyi, H. Höche, L. Trottenberg, E. Siemes, J. Enderlein, A. Fürstenberg, D. Wöll, *Angew. Chem. Int. Ed.* **2024**, *63*, e202318421.

[4] J. C. Thiele, M. Jungblut, D. A. Helmerich, R. Tsukanov, A. Chizhik, A.I. Chizhik, M. J. Schnermann, M. Sauer, O. Nevskyi, J. Enderlein, *Sci. Adv.* **2022**, *8*, eabo2506.

Single Molecule Spectroscopy of Novel Conjugated Porphyrin Nanorings

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Conjugated porphyrin nanorings provide a unique opportunity to understand the relationship between the geometry of a molecule and its electronic excited state behaviour. To-date these molecules have been explored using numerous spectroscopic techniques to investigate ultrafast exciton delocalization,[1] anisotropy,[2] and quantum coherence.[3] However, those results have been obtained in ensemble experiments and thus are subject to averaging effects that can hide important details. Here we have used single molecule spectroscopy to measure each nanoring individually and thus disentangle the structure-property relationships.

Three different 18-unit nanorings have been studied, one without a central template, and two with different template rigidities (Figure 1ab). Measuring each molecule individually on a microscope, we observe almost perfect photon antibunching for all three nanorings (Figure 1c), allowing us to determine that they all only support one single exciton on the ring at any one time, indicating a strong degree of electronic coupling over a large distance and the surprising inability of the ring to host two spatially and energetically separate excited states. We also utilize single molecule emission polarisation measurements to understand the different possible orientations of this exciton and observe a noticeable variation between all three nanorings. The ring without a central template can hold a wide number of conformations, and thus shows more diversity of emission orientations, while the two templated rings have more restricted geometries and thus fewer possible orientations. The ring template rigidity also influences the possible emission orientations.

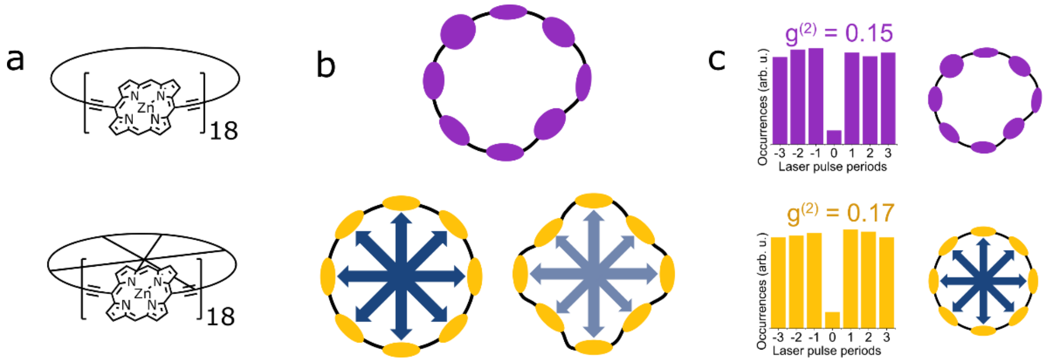

Figure 1. Porphyrin nanorings structures without a template and with templates of varying rigidity (ab). Photon antibunching of the untemplated (c, top) and templated nanoring (c, bottom).

Our work allows exploration of the fundamental behaviour of excited states down at the single molecule level in systems with very defined and controlled geometries. This will aid understanding of the fundamental behaviour of electronic excited states and what controls their delocalisation, interaction, coupling and transition dipole orientations.

Funding: Engineering and Physical Sciences Research Council (EPSRC)

References:

[1] Sprafke, J. K. et al.; Anderson, H.L. *J. Am. Chem. Soc.* **2011**, *133* (43), 17262–17273.
[2] Parkinson, P. et al.; Anderson, H. L.; Herz, L. M. *J. Phys. Chem. Lett.* **2014**, *5* (24), 4356–4361.
[3] Butkus, V. et al.; Anderson, H. L.; Abramavicius, D.; Zigmantas, D. *J. Phys. Chem. Lett.* **2017**, *8* (10), 2344–2349.

On-the-fly local functional imaging of solar cell materials powered by Deep Learning.

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Correlating the structure of materials to their functional properties is a cornerstone challenge in materials science and critical for rational design. This task is particularly difficult in optoelectronic devices, where conventional structural characterization tools (e.g., SEM, X-ray diffraction, AFM) often fail to probe inside multilayer structures or can cause irreversible damage to samples. Conversely, photoluminescence (PL) microscopy is non-invasive and can provide insight into functional properties, such as relative quantum yield, lifetime, and spectral features, but offers limited structural resolution due to the diffraction limit. However, the advancements in super-resolution, particularly the one exploiting blinking, help overcoming this limit. Here, we show correlation clustering imaging (CLIM), a method that exploits intensity fluctuations inherent to Metal halide perovskites, one of the most promising materials for solar cell applications, to resolve functional domain in perovskite films and optoelectronic devices.[1,2] These fluctuations are linked to defects and photochemistry intrinsic to the materials, providing direct insight into their function as a solar cell material. CLIM workflow for functional imaging is shown in Fig. 1. In films, CLIM revealed that in $MAPbI_3$, the functional domain perfectly matches with the structural grain imaged in SEM. Notably, in full solar cell devices, films fabricated under identical conditions exhibit significantly larger functional domains, highlighting the influence of transport layers on domain formation. Furthermore, to enable on-the-fly analysis, we develop D-CLIM, a deep learning model which can separate the functional domain based on spatiotemporal fluctuations in less than a second. This enables us to obtain the functional mapping on-the-fly, during the measurements and directly visualize temporal changes. We envision that CLIM and D-CLIM could serve as powerful tools for in-line quality control and optimization in photovoltaic device manufacturing.

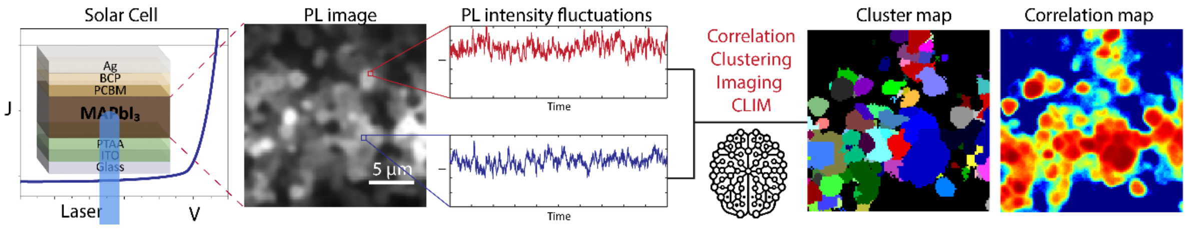

Figure 1. Functional imaging of Solar cell materials using correlation clustering imaging. By analyzing local time correlations in the movie, we can map functional domains in the materials as cluster, and extract and analyze their local dynamic behavior. Deep learning enables us to perform similar analysis, "on-the-fly".

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References:

1. Louis B, Seth S, An Q, Ji R, Vaynzof Y, Hofkens J, et al. In Operando Locally-Resolved Photophysics in Perovskite Solar Cells by Correlation Clustering Imaging. Advanced Materials. 2025 Feb;37(7):2413126.
2. Seth S, Louis B, Asano K, Van Roy T, Roeffaers MBJ, Debroye E, et al. Unveiling the Local Fate of Charge Carriers in Halide Perovskite Thin Films via Correlation Clustering Imaging. Chemical & Biomedical Imaging. 2025 Feb 17;cbmi.4c00113.

Molecular Engineering of AIE Fluorophores for NIR II-NIR I Imaging

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Biological materials exhibit transparency in several near infra-red (NIR) therapeutic windows called NIR-1 (700-900nm), NIR-2 (1000-1500nm) and NIR-3 (Approx. 1700nm). Fluorophores with absorption and emission wavelengths in those windows allow for deeper and clearer imaging than visible light fluorophores [1, 2, 3].

Over the years, our lab has engineered D-π-A dipolar fluorophores for two-photon excitation microscopy, an imaging technique which doubles the excitation, reaching the NIR [4]. While usual fluorophores exhibit aggregation-caused quenching (ACQ), our lab has developed far-red aggregation-induced emission (AIE) dyes, that precipitate into bright fluorescent nanoaggregates in water [5, 6] (Fig. 1.a).

This work focuses on the design of bright AIE far-red fluorophores and their association with NIR ACQ dyes as Förster resonance energy transfer (FRET) donor/acceptor pairs (Fig. 1.b) to produce large Stokes-shift nanoparticles for NIR II-NIR I imaging (Fig. 1.d).

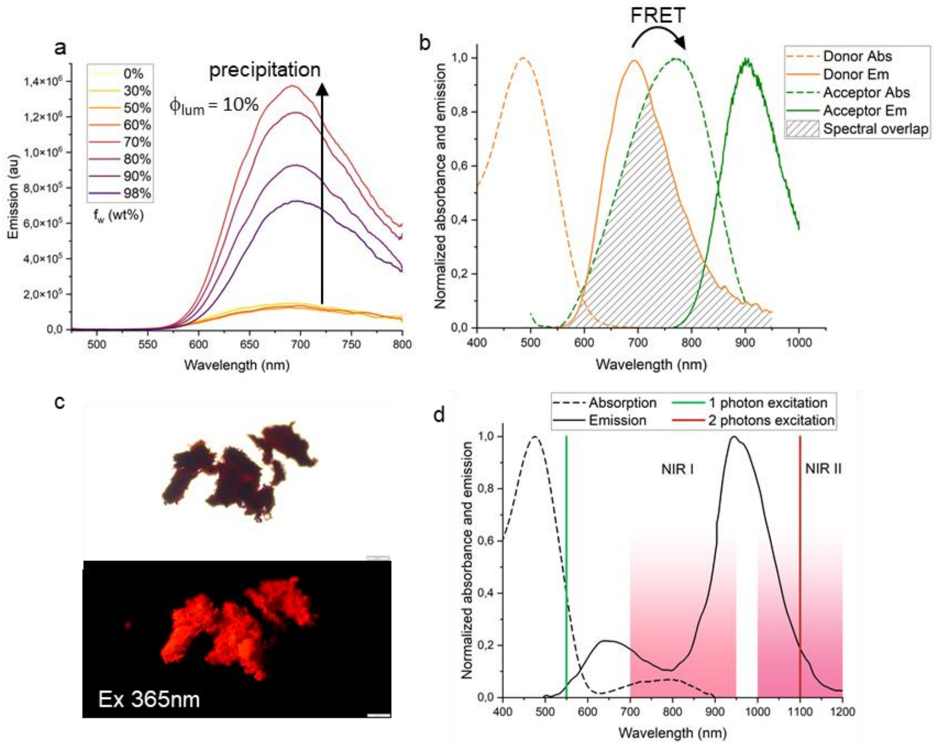

Figure 1. a) Emission spectra in acetone/water mixtures with different water fractions (f_w) b) Absorption and emission spectra of the AIE donor in aggregate and of the ACQ acceptor in chloroform. Spectral overlap for energy transfer is highlighted. c) Microscopy images of the AIE donor powder under white light and 365nm excitation. d) Absorption and emission spectra of AIE FRET donor aggregates doped with ACQ acceptor. Expected wavelength for two-photon excitation microscopy and corresponding one photon excitation wavelength.

Funding: ANR IMAGEin / ANR-22 CE09-0025

References:

[1] Y. Chen, S. Wang, and F. Zhang, *Nat. Rev. Bioeng.* **2023**, *1*, 60.
[2] E. L. Schmidt et al., & G. Hong, *Nat. Rev. Methods Primers* **2024**, *4*, 1.
[3] H. Li, Y. Kim, H. Jung, J. Y. Hyun, I. Shin, *Chem. Soc. Rev*. **2022**, *21*, 8957.
[4] P. Luu, S. E. Fraser, F. Schneider, *Commun. Biol.* **2024**, 7, 1.
[5] M. Rémond, Z. Zheng, E. Jeanneau, C. Andraud, Y. Bretonnière, S. Redon, *J. Org. Chem.* **2019**, *84*, 9965.
[6] S. Redon et al., & Y. Bretonnière, *Dyes Pigm.* **2018**, *156*, 116.

Understanding Light-Driven Charge Carrier Dynamics for Efficient Solar Conversion in Complete Bifacial Sb_2S_3 Solar Cells using Transient Absorption Spectroscopy

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Charge transfer and recombination dynamics are the key to understanding and optimizing photovoltaic devices. However, metallic contacts that are typically used to fabricate devices are incompatible with through-sample ultrafast transient absorption spectroscopy (TAS), a commonly used technique for tracking such photo-induced charge transfer. Therefore, for such TAS measurements, electrodes have often been omitted. This omission results in incomplete solar cells for TAS measurements, the results of which are then compared to standard steady-state PV characterization that takes place on a complete solar cell configuration. This mismatch in the type of samples analyzed (incomplete vs. complete solar cell stacks) has limited previous work based on thin-film Sb_2S_3 absorber layers in establishing the basis of a full mechanism. In this talk I will present how we overcame this challenge by developing new methodology to add a protective layer of ZnO by atomic layer deposition (ALD) on the selected hole transport materials followed by sputtering a transparent, conductive pad of indium tin oxide (ITO) to fabricate complete and transparent (i.e. bifacial) solar cell devices that are compatible with the transmissive measuring conditions of TAS (Figure 1). Photovoltaic characterization reveals similar *J*-*V* curves between bifacial cells and reference cells containing a metallic contact with consistent performance under steady-state illumination. I will discuss how TAS reveals a new mechanism in these bifacial cells ascompared to models previously proposed for similar antimony sulfide-based systems. Several important changes to the mechanism are uncovered. Additional optical modeling of the material stack by calculating the optical electric field distributions in the layers rationalizes the differences in the TAS spectra measured in these studies compared with past incomplete solar cell stacks. These results provide a path to fully characterizing devices by giving a mechanistic understanding of antimony sulfide-based solar devices and facilitating future investigation of the mechanics under variable conditions such as those during solar cell operation.

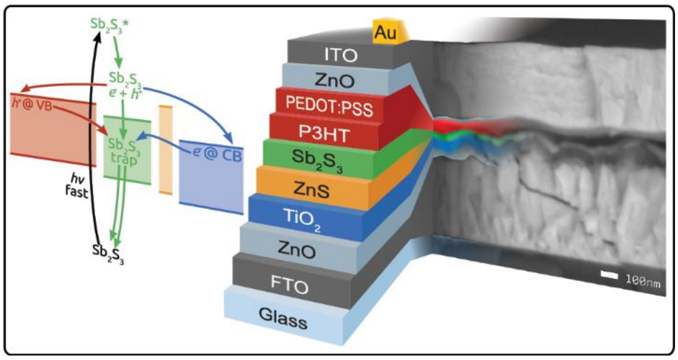

Figure 1. Cross section and energy level diagram of bifacial Sb2S3-based solar cell.

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Surface-supported all-inorganic molecular clusters for light-driven water splitting reactions

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Due to the ongoing global warming and the upcoming energy crises, the exploitation of alternative, renewable energy sources has become a major focus of materials chemistry. The ultimate solution for sustainable energy lies in the concept of solar fuels – commodity chemicals that can be generated from nothing but sunlight and abundant feedstock through heterogeneous photocatalysis. The reactions of water splitting and carbon dioxide photoreduction, however, involve complex multi-electron redox processes that require a rational design of the surface catalytic sites. When working with ill-defined inorganic surfaces, these sites are inevitably hard to study and understand on a truly fundamental level, which limits the development of active and selective photocatalysts.

The field of homogeneous photocatalysis has been evolving independently from its heterogeneous branch, however, it has been much more successful in the purposeful design of organometallic (photo)catalysts assisted by the concepts of coordination chemistry. Molecular photocatalysts, however, face a different set of challenges related to their insufficient redox stability and the need for a molecular photosensitizer required to accomplish the absorption step.

In this talk, I will show that a rational combination of both approaches to photocatalysis can address their challenges and help bridging the gap between the communities. As prime examples of this combination, we employ a diverse set fully inorganic molecular clusters as surface-immobilized co-catalysts for photocatalytic water splitting reactions.[1,2] On one hand, I will discuss covalent attachment of a $[Mo_3S_{13}]^{2-}$ thiometalate anion to photoactive surfaces for light-driven hydrogen evolution.[3] On the other hand, I will present an example of linker-mediated electrostatic binding of $[Co_2W_{11}]^{7-}$ polyoxometalate (POM) onto TiO_2 surface for photocatalytic water oxidation (Fig. 1).[4] In-depth characterization will unravel details of cluster immobilization, structural integrity and molecular nature of the attachment. Photocatalytic experiments and mechanistic studies will shed light on their stability and active sites.

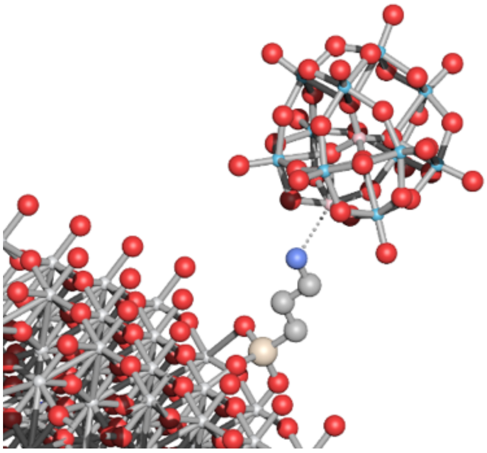

Figure 1. Schematic of the POM attachment.

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References:

[1] A. Cherevan et al., *Advanced Science* **2020**, 7, 1903511.
[2] S. Batool et al., *Advanced Materials* **2024**, 36, 2305730
[3] S. Batool et al., *ACS Catalysis* **2022**, 12, 6641–6650
[4] S. Nandan et al., *ACS Materials Au* **2022**, 4, 505–515

Creating Competing Charge-Transfer Pathways for Photocatalytic Water Oxidation

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Earth-abundant photoactive complexes play a critical role in light-harvesting applications, including dye-sensitized solar cells, artificial photosynthesis, photocatalysis, and photodynamic therapy [1]. The main focus is centered on Fe(II) complexes owing to their isovalency with well-known precious Ru(II), Re(I), and Ir(III) based photosensitizers. However, the implementation of an iron chromophore to a photocatalytic application presents a three-fold problem: i) The metal-to-ligand charge transfer (MLCT) excited state lifetimes of iron complexes fall far short of the performance required for efficient charge separation, ii) they have relatively poor stabilities, and iii) the preparation of a bridging ligand that connects iron to a catalyst, is a synthetic challenge.

Cyanoferrate complexes with bipyridyl ligands were prepared as visible light absorbing photosensitizers. Then, catalytic cobalt sites were connected to the Fe(II) photosensitizer through the bridging cyanide groups to prepare photosensitizer-catalyst dyad assemblies. The charge transfer process in the Fe complexes and Co-Fe dyad assemblies was investigated using femtosecond transient absorption spectroscopy.

In Co-Fe dyad assemblies, Fe sites play a role in both metal-to-metal charge transfer (MMCT) and metal-to-ligand charge transfer (MLCT) processes. Transient absorption spectroscopy experiments reveal a significant MMCT process between Co and Fe sites, which affects the photophysics of Fe(II) photosensitizers by changing the energy levels of ^{5}MC excited states due to the bridging cyanide ligands. The generation of the MMCT state following the MLCT transition renders the Fe-Co dyad catalytically active for water oxidation, as evidenced by our photocatalytic water oxidation results.

Funding: German Science Foundation (Project No. 534960673).

References:

[1] McCusker, J. K.; *Science.* **2019,** 363, 6426, 484-488.
[2] R. Chalil Oglou, R. et al. *ACS Appl. Mater. Interfaces.* **2022**, 14, 18, 21131-21140.
[3] Ahmad, A. A. et al. *Inorg. Chem.* **2022**, 61, 9 3931-3941.

Nickel Co-catalysts on Crystalline Carbon Nitride: Low-Cost Photocatalyst for Efficient Hydrogen Evolution

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The escalating global energy demand and environmental impacts of fossil fuel reliance pose a critical challenge.[1, 2] Photocatalytic H_2 production has emerged as a prominent approach in the ongoing energy transition. However, the significant reliance on precious metals, such as Pt and Pd, for proton reduction, represents a significant obstacle to the widespread adoption of this technology due to their high cost and scarcity.[3] In this work, we present a simple and controlled method to address this challenge by incorporating Ni as co-catalysts into Poly(heptazine imide) - PHI, instead of noble metals, ranging from single atoms to small nanoparticles through a simple cation exchange process. This approach significantly enhances photocatalytic performance of pristine PHI by more than 250-fold. Moreover, we establish a direct correlation between the chemical environment of Ni sites and the photocatalytic activity, with atomically isolated nickel sites exhibiting superior activity. Post-reaction studies reveal increased photoactivity associated with the formation of Ni(0) species during the reaction. The optimal condition achieved efficient H_2 photoevolution (AQY 1.50%) in the absence of noble metals, underscoring its potential as a sustainable solution.

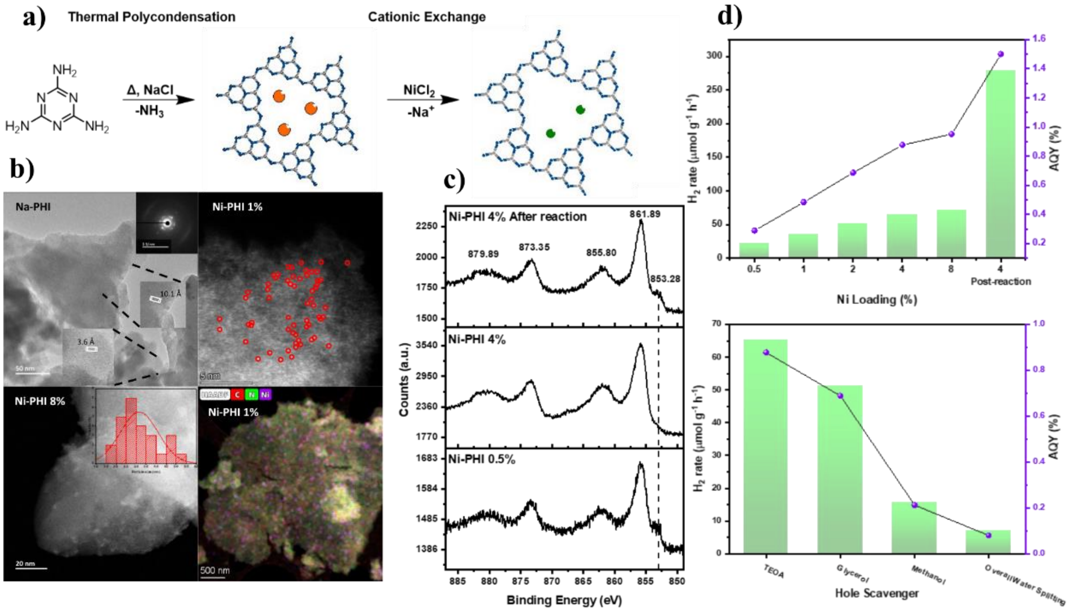

Figure 1. a) Ni-PHI synthesis scheme (Na^+ - Orange, Ni^{2+} - green); b) TEM images: HR-TEM of Na-PHI, AC-HAADF-STEM and EDS mapping of Ni-PHI (1% and 8%+); c) Ni 2p spectra before/after HER for Ni-PHI (0.5% and 4%) and photocatalytic H_2 evolution under different conditions.

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Acknowledgement: The authors are thankful for the CNPEM infrastructure for providing the TEM images.

References:

(1) Younas, M.; Shafique, S.; Hafeez, A.; Javed, F.; Rehman, F. An Overview of Hydrogen Production: Current Status, Potential, and Challenges. *Fuel* **2022**, *316*, 123317. DOI: https://doi.org/10.1016/j.fuel.2022.123317.
(2) Boudellal, M. De Gruyter, 2023. DOI: doi:10.1515/9783110781892.
(3) Zhang, G.; Xu, Y.; Zhu, J.; Li, Y.; He, C.; Ren, X.; Zhang, P.; Mi, H. Enhanced photocatalytic H2 production independent of exciton dissociation in crystalline carbon nitride. *Applied Catalysis B: Environmental* **2023**, *338*, 123049. DOI: https://doi.org/10.1016/j.apcatb.2023.123049.

Photoluminescence properties of rutile TiO_2

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We have studied the charge carrier dynamics of TiO_2 photocatalysts using transient absorption (TAS) [1] and time-resolved microwave conductivity (TRMC) techniques [2]. Recently, in addition to these techniques, we have measured weak luminescence from TiO_2 photocatalysts [3,4]. Theoretical analysis has also been carried out [5] and it was found that in anatase TiO_2, the luminescence originates from excitons and the particulate surface acts as a quenching center of the luminescence. Thus, luminescence measurements would be powerful tool to understand photophysical processes of photocatalysts. Here we show the results of the luminescence study on rutile TiO_2.

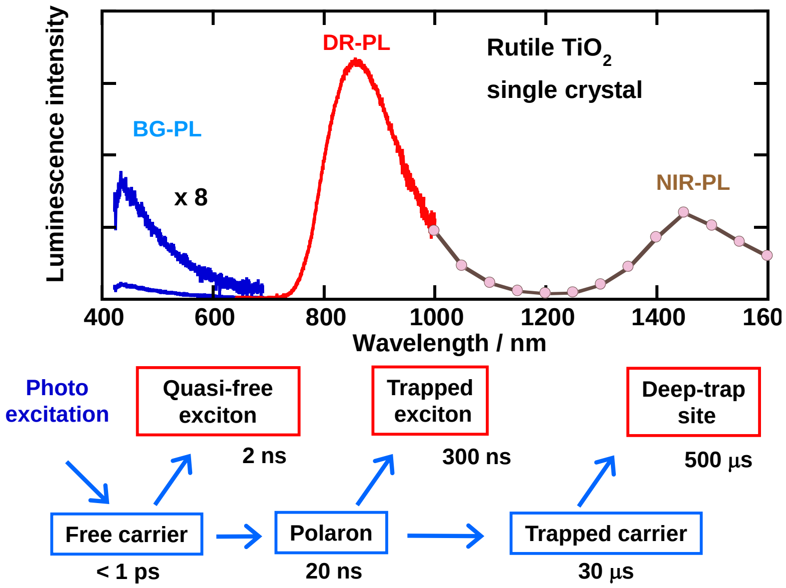

Figure 1. Luminescence spectrum of rutile TiO_2 single crystals. Sequential process of charge carrier dynamics and exciton formation is shown with time constant of each event.

Figure 1 summarizes the origin of the luminescence of rutile TiO_2. Three emission bands are observed in blue-green (BG-PL), deep-red (DR-PL) and near-infrared (NIR-PL) wavelength range. Time-resolved luminescence and TAS measurements were carried out under the same excitation intensity condition. BG-PL was attributed to luminescence from a quasi-free exciton with a lifetime of about 2 ns; DR-PL attributed to luminescence from a trapped-exciton with a lifetime of about 300 ns populated through a polaron; and the NIR-PL attributed to luminescence arose by recombination between a deeply trapped hole and dark electron with a lifetime of about 0.5 ms. Thus, the charge carrier dynamics in rutile TiO_2 can be understood as such a sequential process.

Funding: Nihon University research grant for SDGs related project (no. 24SDG02)

References:

[1] R. Katoh, T. Nakagawa, *J. Phys. Chem. C* **2023**, *127*, 14797.
[2] S. Nakajima, R. Katoh, *J. Mater. Chem. A* **2015**, *3*, 15466.
[3] R. Katoh, K. Takahashi, K. Sugawa, *J. Phys. Chem. C* **2022**, *126*, 20954.
[4] R. Katoh, K. Seki, *J. Chem. Phys.* **2024**, *160*, 174704.
[5] R. Katoh, K. Seki, *J. Chem. Phys.* **2024**, *161*, 124706.

Polymer electrolyte membrane photoelectrolyzers for solar hydrogen production: experiments and theory

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The development of high-efficiency solar hydrogen production devices has been garnering significant interest as a way of transitioning to a zero-carbon energy system. Photoelectrochemical (PEC) tandem cells offer a promising solution to this challenge as they allow for harvesting more sunlight in a productive manner compared to other configurations (single electrode or side-by-side dual systems). However, currently the solar-to-hydrogen efficiencies of such devices are far below the values required to be competitive in the market. Problems related to the short lifespan, high manufacturing cost and poor activity of the semiconductor photoelectrodes are holding back the development of this technology. Despite recent developments [1-3], much effort is still needed on both theoretical and experimental aspects of these devices for achieving a real breakthrough. One way forward may be to develop quasi-solid state PEC cells based on Polymer Electrolyte Membranes (PEM) as they have a flat configuration that facilitates upscaling and integration into panels.

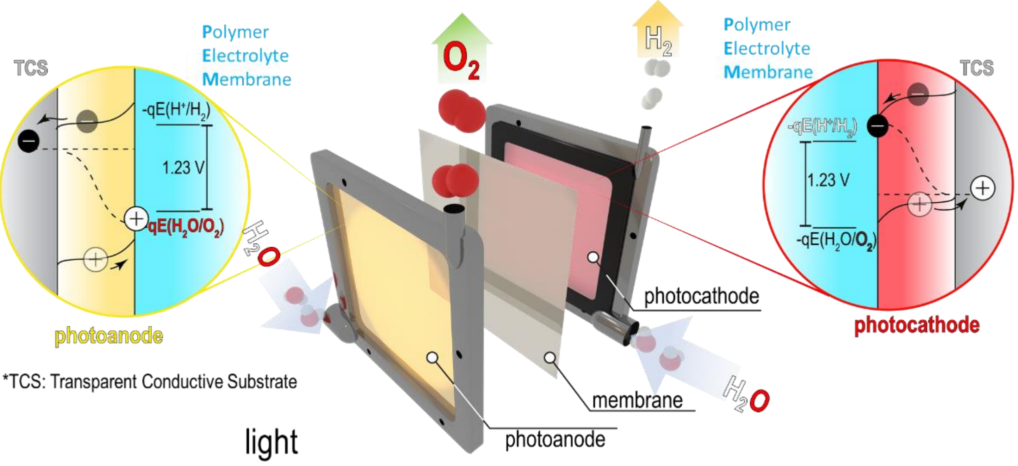

Figure 1. Sketch for a photoelectrochemical tandem cell based on a polymer electrolyte membrane for solar hydrogen production. Band diagrams for both electrodes are also shown.

This contribution will focus on summarizing our recent work in this subject, which encompasses both experiments and theory. Specifically, we have explored a tandem cell configuration integrating tungsten oxide (WO_3) and tungsten selenide (WSe_2), as photoanode and photocathode, respectively, taking advantage of their stability. The cell incorporates a cationic PEM with high ionic conductivity, transparency to solar light, and compatibility with both photoelectrodes. Laboratory-scale prototypes have demonstrated substantial photocurrents and the possibility of producing hydrogen in the absence of an external applied bias.

A macroscopic semi-analytical model for rationalizing the behavior of PEM tandem cells will also be delineated. It is based on the application of the Gärtner model to thin film electrodes illuminated from both the back and the front sides. This model will be used to construct solar-to-hydrogen efficiency maps as a function of the semiconductor bandgaps and other parameters.

Finally, the main challenges for the practical implementation of this technology will be discussed on the basis of the presented results.

Funding: MCIN/AEI/10.13039/501100011033 and EU "NextGenerationEU"/PRTR (TED2021–132697B–I00)

References:

[1] A. Cots at al., & R. Gómez, *ACS Appl. Mater. Interfaces* **2018**, *10*, 25393.

[2] S. Trocino et al., & R. Gómez, A.S. Aricò, *Catalysts* **2020**, *10*, 1319.

[3] D. Monllor-Satoca, M.I. Díez-García, T. Lana-Villarreal, R. Gómez, *Chem. Commun.* **2020**, *56*, 12272.

The Photoredox Paradox:
the Roles of Electron Upconversion and Electron Catalysis

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Although photoredox catalysis is complex from a mechanistic point of view, it is also often surprisingly efficient. In fact, the quantum efficiency of a puzzlingly large portion of photoredox reactions exceeds 100% (i.e., the measured quantum yields (QYs) are >1). Hence, these photoredox reactions can be *more* than perfect with respect to photon utilization. In several documented cases, a single absorbed photon can lead to the formation of >100 molecules of the product, behavior known to originate from chain processes.

In this talk, I explore the underlying reasons for this efficiency, identify the nature of common catalytic chains, and highlight the differences between HAT and SET chains. Our goal is to show why chains are *especially* important in photoredox catalysis and where the thermodynamic driving force, that sustains the SET catalytic cycles, comes from. [1, 2]

I demonstrate how the interplay of polar and radical processes can activate hidden catalytic pathways mediated by electron and hole transfer (i.e., electron and hole catalysis). Furthermore, I illustrate how the phenomenon of redox upconversion serves as the thermodynamic precondition for electron and hole catalysis.

After discussing representative mechanistic puzzles, I analyze the most common bond forming steps where redox upconversion is common (and sometimes unavoidable). In particular, we highlight the importance of 2-center-3-electron bonds as a common motif that allows a rational chemical approach to the design of redox upconversion processes.

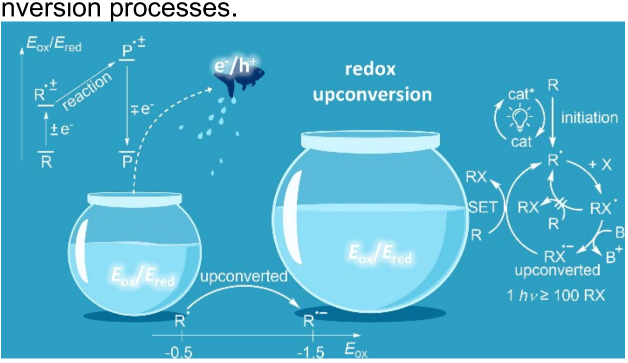

Figure 1. Redox upconversion converts photoredox catalysis into electron catalysis

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Acknowledgement: Parts of this research were conducted using the supercomputer Mogon II offered by Johannes Gutenberg University Mainz (hpc.uni-mainz.de), which is a member of the AHRP (Alliance for High Performance Computing in Rhineland Palatinate, www.ahrp.info) and the Gauss Alliance e.V.

References:

[1] Syroeshkin, M. A.; Kuriakose, F.; Saverina, E. A.; Timofeeva, V. A.; Egorov, M. P.; Alabugin, I. V. *Angew. Chem. Int. Ed.* **2019**, *58*, 5532.

[2] Alabugin, I. V.; Eckhardt, P.; Christopher, K. M.; Opatz, T., *J. Amer. Chem. Soc.*, **2024**, *146*, 27233.

Mechanistic insights into sensitization *via* one or two photon processes

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The photochemical activation of numerous compounds with one photon or two photons is well established in literature and depending on the conditions different pathways are feasible.[1,2] Here we present three projects together with spectroscopic methods for detailed investigations regarding the nature of the underlying mechanism.[3,4,6]

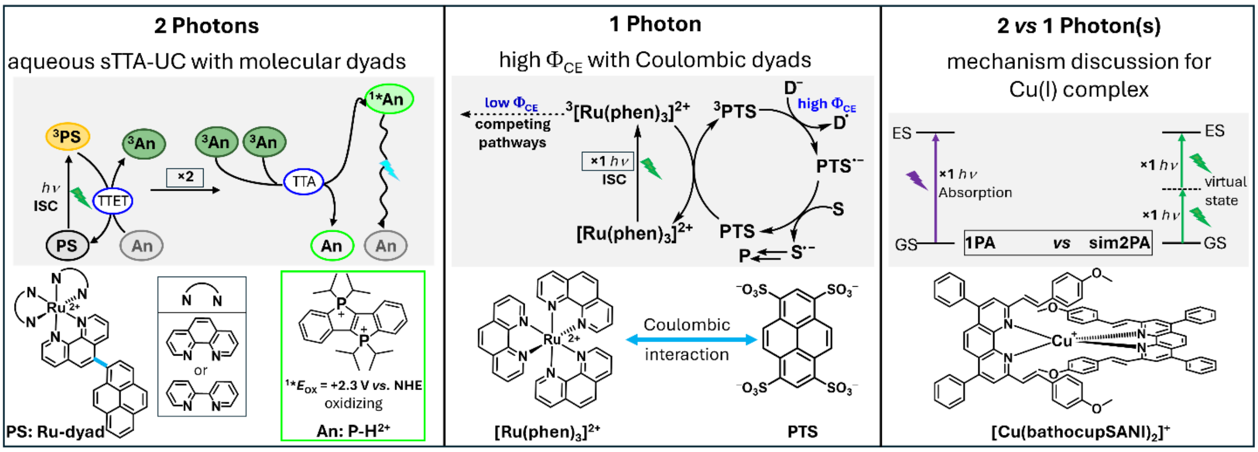

Figure 1: Left (2 $h\nu$): sTTA-UC in water using molecular dyads as photosensitizer (PS) and an annihilator ($P\text{-}H^{2+}$) with a highly oxidizing singlet excited state. Middle (1 $h\nu$): Coulombic dyad for highly efficient electron transfer photocatalysis. Right (1 or 2 $h\nu$): Cu(I) complex for light-intensity based studies.

The first project (Figure 1 left) presents a system for sensitized triplet-triplet annihilation upconversion (sTTA-UC) using water as the solvent. The bichromophoric photosensitizers (PS) are excited with green photons and provide a triplet excited state, which is mainly located on the pyrene unit. We combined the dyads with the annihilator (An: $P\text{-}H^{2+}$) and observed spectroscopic signatures typical for two-photon based upconversion. sTTA-UC provides access to the highly oxidizing singlet excited state of $P\text{-}H^{2+}$, which makes this sensitizer – annihilator combination unique among the limited number of UC systems that operate in aqueous solvents. In contrast to the two-photon mechanism with the molecular dyads as PS, we also employed the parent metal complexes, which only resulted in electron transfer to the annihilator. Hence, for a successful UC system in water, the triplet excited states of the Ru-dyads are essential for their function as PS.[3]

In a second project (Figure 1 middle) we identified a so-called Coulombic dyad by combining the di-cation $[Ru(phen)_3]^{2+}$ with a tetra-anion (PTS) for efficient electron transfer catalysis. $[Ru(phen)_3]^{2+}$ is excited into its triplet exited state using one green photon, followed by fast energy transfer – comparable to the intramolecular energy transfer in molecular dyads – results in a long-lived triplet excited state located exclusively on PTS. Quantitative laser spectroscopy revealed efficient electron transfer (Φ_{CE}~1) from a donor (D) to the ^3PTS producing the corresponding radical anion ($PTS^{\bullet-}$) as reactive intermediate for substrate activation.[4] Finally, we investigated a recently published Cu(I) complex ($[Cu(bathocupSANI)_2]BF_4$)[5] regarding red/NIR light-driven $^1O_2$ generation and subsequent photooxidations. We present easily accessible methods for differentiation between the claimed two-photon mechanism (simultaneous two photon absorption = sim2PA) and the actually occurring direct one-photon absorption (1PA).[6]

Funding: Exploration Grant of the Boehringer Ingelheim Foundation (BIS).

References:

[1] F. Glaser, C. Kerzig, O. S. Wenger, Angew. Chem. Int. Ed. **2020**, *59,* 10266-10284.

[2] R. C. McAtee, E. J. McClain, C. R. J. Stephenson, *Trends Chem.*, **2019**, *1*, 111-125..

[3] M.-S. Bertrams, K. Hermainski, J.-M. Moersdorf, J. Ballmann, C. Kerzig, *Chem. Sci.* **2023**, *14*, 8583-8591.

[4] M. Schmitz, M.-S. Bertrams, A. C. Sell, F. Glaser, C. Kerzig, *J. Am. Chem. Soc.* **2024**, *146*, 25799-25812.

[5] N. Beaucage, Z. Singh, J. Bourdon, S. K. Collins, *Angew. Chem. Int. Ed.*, **2024**, *64,* e202412606.

[6] J. A. Moghtader, M.-S. Bertrams, C. Kerzig, **2025,** *manuscript submitted* (Correspondance to [5]).

Limiting Molecular Twisting: Upgrading a Donor–Acceptor Dye to Drive H_2 Evolution

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The donor–acceptor (D–A) dye 4-(bis-4-(5-(2,2-dicyano-vinyl)-thiophene-2-yl)-phenyl-amino)-benzoic acid (P1) has been frequently used to functionalize NiO photocathodes and induce photoelectrochemical reduction of protons when coupled to a suitable catalyst. Photoinduced twisting of the P1 dye is steered on NiO by co-adsorption of tetradecanoic acid (C_{14}, myristic acid (MA)). Density Functional Theory and time-resolved photoluminescence studies confirm that twisting lowers the energy levels of the photoexcited D–A dye. The apolar environment provided by the MA suppresses photoinduced D–A twisting, retards charge recombination following photoinduced charge separation between P1 and NiO, and provides a larger electrochemical potential increasing the photocurrent. Very interestingly, co-adsorption of MA induces H_2 evolution upon photoexcitation without the presence of an H_2 evolution catalyst. Based on prior art, the formation of H_2 is assigned to the dissolution of Ni^{2+}, followed by reduction and re-deposition of Ni nanoparticles acting as the catalytically active site. It proposes that only excited P1 with suppressed twisting provides the sufficient electrochemical potential to induce deposition of Ni nanoparticles. Our work illustrates the importance of understanding the effects of photoinduced intramolecular twisting and highlights the promise of designing twisting-limited D–A dyes to create efficient solar fuel devices.

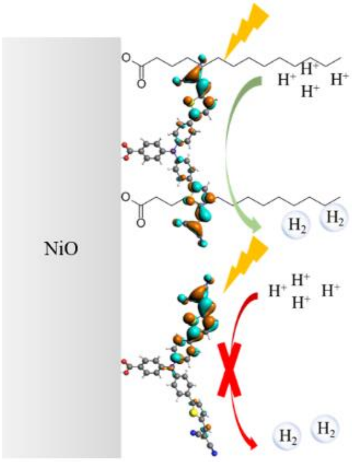

Figure 1. Co-adsorbed MA reduces photoinduced twisting, thereby enabling H_2 evolution.

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References:

[1] K. Zhu, A. Paradelo Rodríguez, M. B. Brands, T. de Haas, F. Buda, J.N.H. Reek, G. Mul, A. Huijser, Adv. Sci. 2024, 11, 2403454.

Photon upconversion via doublet-triplet energy transfer – A bright future for photoactive first-row transition metal complexes

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Recent years, remarkable progresses have been made in developing photoactive first-row transition metal complexes, including chromium, manganese, iron, and cobalt.[1-4] These fundamentally new types of photoactive metal complexes could be highly attractive for energy conversion based applications, such as photon upconversion and photocatalysis, due to the high natural abundance, low cost, and low-energy visible light absorption. However, this remains often challenging, due to their poorly understood and inherently suboptimal photophysical and photochemical properties.

Sensitized triplet-triplet annihilation upconversion (sTTA-UC) converts two low energy photons to one of higher energy, which has become a popular approach in many fields, including bioanalytics, light harvesting, and photocatalysis. This method often relies on triplet photosensitizers with long-lived excited state. Photosensitizers featuring doublet excited states, such as luminescent $3d^3$ chromium(III) and $3d^5$ low-spin iron(III) complexes, remain so far largely underexplored for this purpose.

This contribution will provide some fundamental insights and catalytic strategies of employing luminescent $3d^3$ Cr(III) and $3d^5$ Fe(III) complexes for sensitizing photon upconversion and photocatalysis via underexplored doublet-triplet energy transfer (DTET) to anthracene-based annihilators. Specifically, this includes 1) luminescent mononuclear and dinuclear Cr(III) complexes with spin-flip doublet excited states sensitize photon upconversion via efficient DTET;[5-6] 2) luminescent Fe(III) complex with ligand-to-metal charge transfer (LMCT) doublet excited state sensitizes aerobic photon upconversion via preassociation-enhanced DTET.[7] Driven by the Fe(III)-sensitized photon upconversion, photoredox catalytic radical polymerizations of acrylate monomers are initiated rapidly under aerobic conditions with green light. These studies make a fundamentally important step toward efficient light energy conversion using low-cost first-row transition metals.

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References:

[1] N. Sinha and O. S. Wenger, *J. Am. Chem. Soc.* **2023**, *145*, 4903–4920.
[2] W. R. Kitzmann, J. Moll and K. Heinze, *Photochem. Photobiol. Sci.* **2022**, *21*, 1309–1331.
[3] A. Y. Chan, A. Ghosh, J. T. Yarranton, J. Twilton, J. Jin, D. M. Arias-Rotondo, H. A. Sakai, J. K. McCusker and D. W. C. MacMillan, *Science* **2023**, *382*, 191–197.
[4] D. Kim, V. Q. Dang and T. S. Teets, *Chem. Sci.* **2023**, *15*, 77-94.
[5] C. Wang, F. Reichenauer, W. R. Kitzmann, C. Kerzig, K. Heinze and U. Resch-Genger, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202238.
[6] S. Trippmacher, S. Demeshko, A. Prescimone, F. Meyer, O. S. Wenger and C. Wang, *Chem. Eur. J.* **2024**, *30*, e202400856.

Analyzing Synergy in Photocyclic Three-Component Systems for radical photopolymerization

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In radical photopolymerization, three-component initiating systems, lead to far better radical polymerization performances in comparison with the corresponding two component systems. The third component is able to produce additional initiating radicals, regenerate the photoinitiator forming a photocyclic initiating systems and consume terminating photoproducts happening in two component photoinitiators.[1] However, the respective roles of these reactions are not well defined. Kinetic modeling is then applied to a photocyclic initiating system to provide insights into the synergistic effects observed in a systems based on organic dye, a triazine derivative and a tertiary amine as third component.

The full photochemical reaction of the three-component PIS was studied by ns laser flash photolysis. All photoinduced electron transfer reaction and secondary reactions occur in parallel and the initiating system is consequently named a bicyclic system. The proven competitive photocyclic behavior of the RB^-/TA/MDEA PIS with all measured rate constants is displayed on Figure 1.

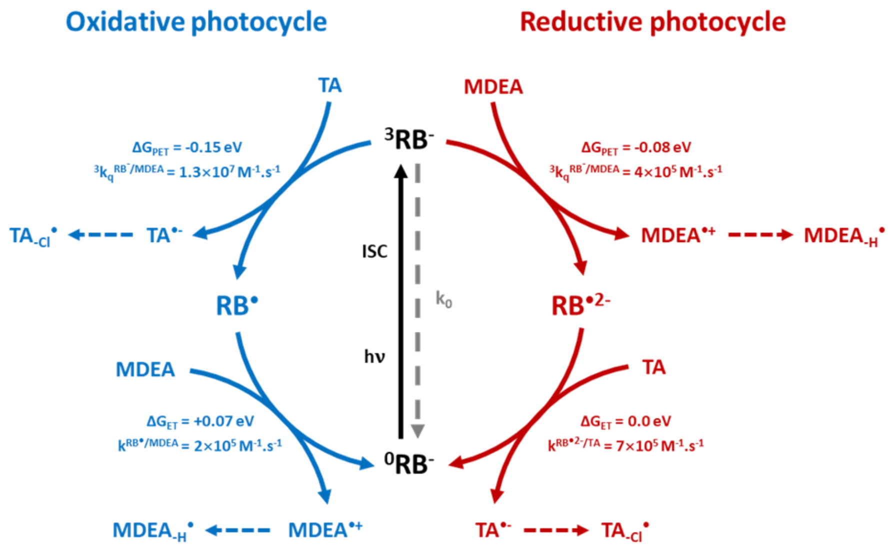

Figure 1. Demonstrated photochemical mechanism of the RB-/TA/MDEA three-component bicyclic photoinitiating system, with measured rate constants.

This reaction scheme was then used to perform kinetic modeling of photopolymerization in neat acrylate monomer to understand the synergistic effect. The simulated data from the complete PCIS model were compared to the experimental photopolymerization kinetics and a good agreement was found between the experimental and simulated data. [2]

This theoretical and experimental approach thus revealed that the consumption of the terminating agent $RB^\bullet$ by MDEA is by far the major way of improvement of the polymerization kinetics for this dual photocyclic system. It would be of particular interest to extend this kind of complementary mechanistic/modeling study to three-component cyclic photoinitiating systems containing other types of photoinitiators (e.g. neutral or cationic dyes) and co-initiators (onium salts, thiols…) to draw more general trends in the synergistic effect occurring within the PCIS.

References:

[1] J. Christmann, S. Shi, A. Ibrahim, C. Ley, C. Croutxé-Barghorn, M. Bessières, X. Allonas, J. Phys. Chem. B, 121 (2017) 1972-1981.
[2] J. Christmann, X. Allonas, C. Ley, A. Ibrahim, C. Croutxé-Barghorn, Macromol. Chem. Phys., (2017) 1600597.

Ultrabroadband Two-Dimensional Electronic Spectroscopy of Metalloporphyrin Chromophores in *De Novo* Protein Maquettes

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Photoactive proteins are essential to driving key chemical processes on Earth, ranging from the initial photoisomerisation reaction which drives vision, to the primary energy- and charge-transfer steps in photosynthesis. Inspired by natural photosynthetic respiratory designs, artificial photoactive proteins have been developed to efficiently fulfil similar roles in a range of tailored functional applications, such as the capacity for long-range electron transport through assemblies of 'molecular wires'. Two-dimensional electronic spectroscopy (2DES) is uniquely disposed to explore the photoinduced dynamics of these systems, as it combines high temporal and spectral resolution to probe chromophore-protein and chromophore-chromophore interactions. We have developed an ultrabroadband boxcars 2DES spectrometer combining ultrafast time resolution (< 8 fs) with full-wavelength reference detection to yield significantly improved signal-to-noise ratios.[1] This greater sensitivity allows for measurements of samples at lower optical densities, and thus concentrations, than typically used in 2DES experiments. We have leveraged this enhanced sensitivity to examine the photochemistry of redox-active *de novo* protein maquettes incorporating different zinc- and iron-containing metalloporphyrin chromophores, which have the potential to form the basis of artificial electron-conducting circuitry.[2] Measurements on the heme-m4D2 protein represent the first probing of the ultrafast photodynamics of the single Fe(II) metalloporphyrin in the absence of a ligand photodissociation channel, providing a model compound to explore Fe(II) excited state dynamics and an important context for the behaviour of multi-heme variants of the 4D2 family of proteins. The comparison with Zn(II) chlorin-e_6 bound to m4D2 highlight the effect of the timescale of pigment-protein interactions through changes in 2DES lineshape (spectral diffusion), and the frequency of impulsively-excited wavepackets within the chromophore reveal additional information on interactions with the surrounding protein, as well as the potential presence of excitonic couplings with neighbouring chromophores, which are pivotal for fast and efficient electron transfer.

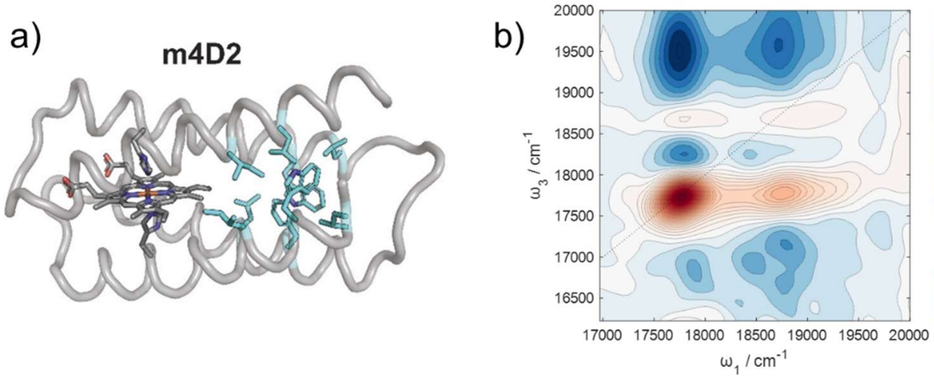

Figure 1. a) Structure of m4D2 protein maquette incorporating a single heme chromophore, b) Example 2DES spectrum of heme in m4D2 at t_2 = 200 fs.

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References:

[1] C. Gajo, C. J. C. Jordan and T. A. A. Oliver, *J. Phys. Chem. A* **2025**, 129, 3537−3551.
[2] G. H. Hutchins *et al*., *Proc. Natl. Acad. Sci. U.S.A.* **2023** 120 (31) e2306046120.

Tuning Cyanine Chromophores: Does Ab Initio Theory Meet Molecular Reality?

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The application of advanced theoretical methods to elucidate the photophysics and photochemistry of organic molecules is a vibrant research field. This talk will emphasize approaches for photophysics calculations, molecular design, and non-adiabatic dynamics, with a particular focus on cyanine dyes. Cyanine dyes are ubiquitous in bioimaging, sensing, optoelectronics, and medicinal applications owing to their tunable photophysical properties[1].The cyanine dyes are familiar even to freshman quantum mechanics students as their electronic structure closely follows the particle-in-a-box model [2].However, as the conjugated chain lengthens, this simple framework breaks down due to symmetry-breaking phenomena such as Peierls distortion or bond length alternation (BLA). We have identified an additional mechanism—out-of-plane rotation (OPR)—that significantly influences optical behavior and show how C1 substitution can generate non-orthodox absorption and emission profiles[3].

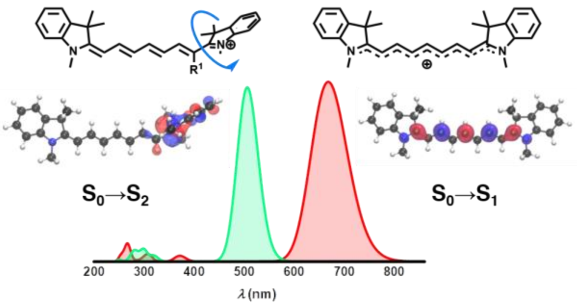

Figure 1. C1´ substitution offers unprecedented way to modify the electronic structure of cyanine dyes.

Beyond photophysics, cyanine dyes exhibit intriguing excited-state reactivity: for example, deuteration can modulate their dynamics and spectral characteristics[4]. We will present accelerated non-adiabatic molecular dynamics simulations that capture long-timescale photochemical processes in these systems. We will also discuss techniques to account for isotope effects.

To contextualize the current capabilities and limitations of *ab initio* photodynamics, we will discuss two exemplar ultrafast photochemical processes: (i) the cis-stilbene isomerization studied via time-resolved photoelectron spectroscopy by multiple groups[5,6], and (ii) the cyclobutanone photochemistry benchmarked by the Photochemistry Prediction Challenge[7]. These case studies highlight both the predictive power and the challenges that remain for theory-driven photochemistry.

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References:

[1] L. Štacková, E. Muchová, M. Russo, P. Slavíček, P. Štacko, P. Klán, J. Org. Chem. 2020, 85, 9776–9790.
[2] J. Autschbach, J. Chem. Educ. 2007, 84, 1840.
[3] O. Bedocchi, J. Polena, J. Okorončeková, P. Slavíček, P. Klán, ChemRxiv 2025, DOI 10.26434/chemrxiv-2025-mf3t3.
[4] H. Janeková, H. C. Friedman, M. Russo, M. Zyberaj, T. Ahmed, A. S. Hua, A. V. Sica, J. R. Caram, P. Štacko, Chem. Commun. 2024, 60, 1000–1003.
[5] T. Jíra, J. Janoš, P. Slavíček, J. Chem. Theory Comput. 2024, 20, 10972–10985.
[6] C. Wang, M. D. J. Waters, P. Zhang, J. Suchan, V. Svoboda, T. T. Luu, C. Perry, Z. Yin, P. Slavíček, H. J. Wörner, Nat. Chem. 2022, 14, 1126–1132.
[7] https://pubs.aip.org/collection/16531/Prediction-Challenge-Cyclobutanone-Photochemistry

Nonadiabatic dynamics simulations in condensed phase systems

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Almost all photochemical reactions encountered in nature, in the lab, or in an industrial photoreactor happen in the condensed phase, usually in solution. Accurate in silico modelling of photochemical processes of photoexcited systems within the condensed phase environment, however, represents a significant theoretical and computational challenge. Not only does the system size increase due to additional environmental molecules that must be accounted for, but the number of electronic states and potential nonradiative deactivation (NRD) pathways also increases. Density functional theory (DFT) based methods, such as the linear-response time-dependent DFT (TDDFT)[1,2] and the delta self-consistent field (ΔSCF)[3] methods, are known for their well-balanced compromise between accuracy and computational efficiency. Given that both methods can incorporate the periodic boundary conditions, they enable sophisticated modelling of NRD processes in the condensed phase with all atoms at the same electronic structure level of theory. Employing them with the nonadiabatic molecular dynamics (NA-MD) simulations, we investigated several photoexcited systems in a condensed phase environment.[4,5,6] NRD mechanisms of *ortho*- and *para*-nitrophenol initiated from the brightest π to π^* singlet excited electronic state have been investigated with trajectory surface hopping NA-MD simulations on a manifold including several (up to twelve in total) singlet and triplet excited electronic states, mutually coupled by the spin-orbit coupling elements computed at the TDDFT level of theory.[4] By careful analysis of such NRD pathways obtained on isolated and in water-solvated nitrophenols, the cage effect exhibited by the surrounding water molecules on electronically excited nitrophenol reduces the number of inter-system crossings and facilitates its NRD deactivation from the first singlet excited electronic states. When the water solvent was modelled at a force field level, as is usually performed when applying the computationally cheaper molecular mechanics/quantum mechanics (QM/MM) approach, the NRD mechanisms resemble more those of the isolated system than when the whole solvent was treated at the same level of theory as the chromophore.[4] Our ΔSCF method enables NA-MD simulations for selected excited electronic states, alleviating the influence of underestimated charge transfer states encountered at the TDDFT level. The NRD mechanism of photoexcited diimine system solvated in water, simulated at all-atom ΔSCF level, elucidated the delicate influence of the hydrogen bonding between its *cis* and *trans* conformers, and its effect on the kinetics of their NRD mechanisms.[5] Similarly, NRD mechanisms of solvated cyclopropanone and its hydrate were investigated at the ΔSCF level. While the solvated photoexcited cyclopropanone exhibits a cage effect, and its photodisociation NRD mechanism into ethylene and carbon monoxide is noticeably reduced compared to its photodisociation in the gas phase, the cyclopropanone hydrate reacts with the water molecules of its first solvation shell during its NRD and gives several different photoproducts.[6] Hydrogen transfer via the Grotthuss mechanism is also exhibited in several trajectories. We have recently improved the ΔSCF method with two new algorithms for maintaining the proper electronic density during its SCF optimisations, which enables a larger number of excited electronic states to converge, and a direct construction of the multi-configurational character excited electronic states and their corresponding properties with the ΔSCF method.[7] This will further improve the methodology for simulating photochemical processes in the condensed-phase systems.

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References:

[1] A.-S. Hehn, B. Sertcan, F. Belleflamme, S. K. Chulkov, M. B. Watkins, J. Hutter, *J. Chem. Theory Comput* **2022**, *18*, 4186

[2] K. Hanasaki, T. F. de Jong, K. Komarov, R. Kumar, M. Mališ, J. Mattiat, L. I. Hernandez Segura, L. Schreder, A. Sinyavskiy, S. Luber, *submitted*

[3] E. Vandaele, M. Mališ, S. Luber, *J. Chem. Phys.* **2022**, *156*, 130901

[4] E. Vandaele, M. Mališ, S. Luber, *J. Chem. Theory Comput.* **2024**, *20*, 3258

[5] M. Mališ, S. Luber, *J. Chem. Theory Comput.* **2020**, *16*, 4071

[6] E. Vandaele, M. Mališ, S. Luber, *Phys. Chem. Chem. Phys.* **2022**, *24*, 5669

[7] A. Sinyavskiy, M. Mališ, S. Luber, *in revision*

BSE@GW-Based Spin-Vibronic Quantum Dynamics of Transition Metal Complexes

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A protocol for generating potential energy surfaces and performing photoinduced nonadiabatic multidimensional wave packet propagation is presented [1]. The workflow starts with the parameterization of a linear vibronic coupling (LVC) Hamiltonian using the Green's function - Bethe-Salpeter Equation (BSE@GW) approach. In a second step, the LVC model is used as input for multi-layer multi-configurational time-dependent Hartree (ML-MCTDH) wave packet propagation. Key to the efficient solution of the time-dependent Schrödinger equation is the choice of the ML tree. To facilitate automated ML tree generation, a spectral clustering algorithm is introduced. It is based on a correlation matrix obtained from nuclear coordinate expectation values of a full-dimensional Time-dependent Hartree (TDH) simulation. The performance of the protocol is tested on the photoinduced spin-vibronic dynamics of a Fe(II) complex (Fig. 1a) [2,3]. It is shown that BSE@GW provides a more robust description of the character of the electronic transitions contributing to the absorption spectrum compared to linear response Time-dependent Density Functional Theory (TD-DFT), Fig. 1b. This finding is in line with previous systematic investigations of first row transition metal excitations [4]. Furthermore, the LVC parameterization is tested against explicit calculations of potential energy curves to find the validity of the linear approximation over a wide range of normal mode elongations. Finally, the flexibility of spectral clustering is used to generate different ML trees, resulting in very different numerical efficiencies for ML-MCTDH propagation. The performance for this, in terms of electronic structure and dimensionality, challenging example is suggesting that the new protocol should be applicable to a wide range of systems.

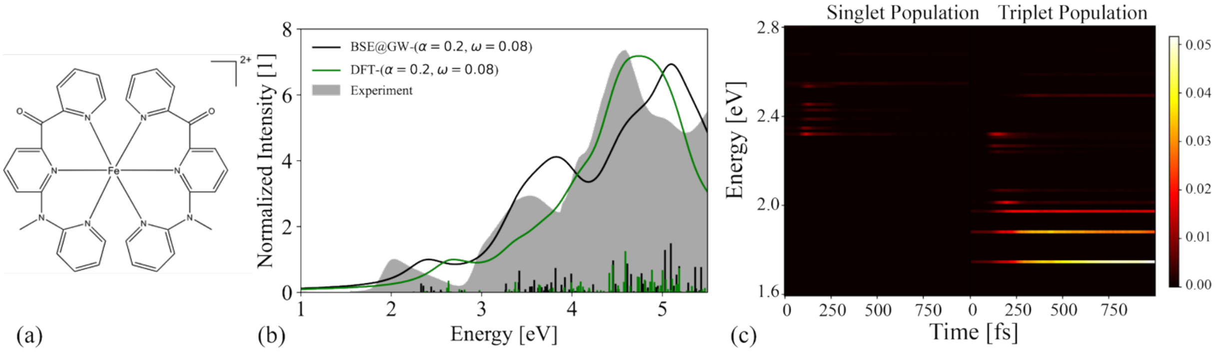

Figure 1. (a) Fe(II) complex studied in this work. (b) Comparison between experimental [2] and calculated absorption spectrum. (c) Energy- and time-resolved population dynamics after ultrafast (40 fs) excitation centered at 2.34 eV. Intersystem crossing is observed on a time scale of a few hundred femtoseconds.

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References:

[1] F. Bogdain, S. Mai, L. González, O. Kühn, ChemRxiv **2025**, https://doi.org/10.26434/chemrxiv-2025-c7zzr-v2.

[2] J. Moll et al. & K. Heinze, *Chem. –Eur. J.* **2022**, *28*, e202201858.

[3] J. P. Zobel et al, & O. S. Bokareva, *Chem. Sci.* **2023**, *14*, 1491–1502.

[4] F. Bogdain, O. Kühn, *J. Chem. Theor. Comp.* **2025**, https://doi.org/10.1021/acs.jctc.5c00140.

Why do some heteroaromatics have n,π* states as their first excited states, while others have π,π* states as these?

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Heteroaromatic molecules are found in areas ranging from biochemistry to photovoltaics.[1] Hitherto there is no simple rationale as to which heteroaromatic compounds have π,π* states as their lowest excited state and which ones have n,π* states as these states. We explore if (anti)aromatic character is a decisive factor, yet, Baird's 4*n* rule on excited state aromaticity is applicable only to the lowest π,π* states.[2] Thus, a different rationale needs to be developed for the n,π* states, and we start at Mandado's 2*n*+1 rule for aromaticity of separate spins.[3,4] Heteroaromatics with (4*n*+2)π-electrons in S_0 and in-plane lone-pairs (n_σ, herein n), will in their n,π* states have 2*n*+2 π_α-electrons and 2*n*+1 π_β-electrons (or *vice versa*), and becomes π_α-antiaromatic and π_β-aromatic. Yet, the antiaromatic π_α- and aromatic π_β-components may not cancel, leading to residual aromatic or antiaromatic character (Fig. 1A). We explore vertically excited triplet n,π* states (^{3}n,π*), which are most readily analyzed, but also singlet n,π* states (^{1}n,π*), and first explain which compounds have n,π* states with aromatic residuals as their lowest excited states. If the π_β-electron population becomes more uniformly distributed upon excitation, the system will have an aromatic residual. Interestingly, five-membered ring (5-MR) heteroaromatics with one or two N, O and/or S atoms (*e.g.*, thiophene and imidazole) never have n,π* states as their first excited states (T_1 and S_1), while this is nearly always the case for six-membered ring (6-MR) heteroaromatics with electropositive heteroatoms, highly symmetric (D_{2h}) diheteroaromatics, and for 5-MR compounds with in-plane lone-pair orbitals at C, *i.e.,* carbenes. Through a comparison between three-, five-, six-, and seven-membered ring carbenes, as well as heavier congeners, we can conclude that six factors impact on the order between the n,π* and π,π* states (Fig. 1B): (*i*) the electronegativity of the heteroatom(s), (*ii*) the valence angle at the heteroatom impacting the lone-pair orbital energy, (*iii*) the number of π-orbitals and π-electrons, (*iv*) the degree of (anti)aromatic character of the n,π* state, (*v*) the electronegativity of atoms adjacent to the heteroatom, and (*vi*) the spatial extent of the n orbital affecting the intra-orbital electron repulsion.[5]

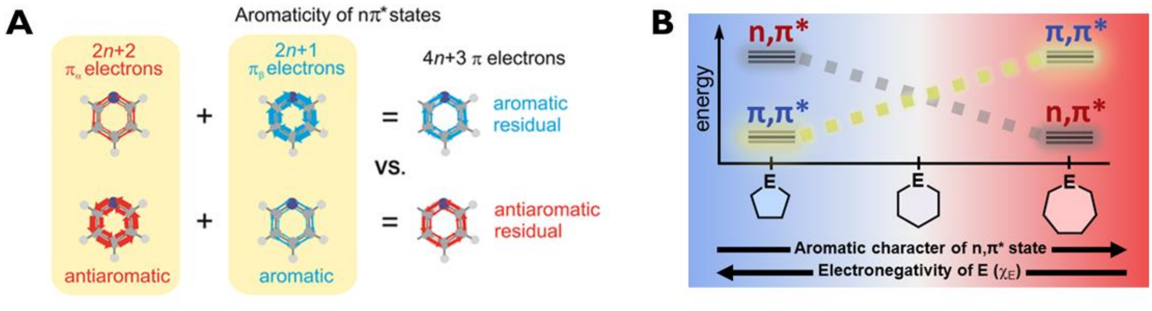

Figure 1: (A) Illustration of why n,π* states have aromatic or antiaromatic residuals. (B) Illustration of factors that influence on the energy order between the lowest n,π* and π,π* states of heteroaromatics.

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References:

[1] Balaban, A. T.; Oniciu, D. C.; Katritzky, A. R. *Chem. Rev.* **2004**, *104*, 2777-2812.
[2] (a) Baird, N. C. *J. Am. Chem. Soc.* **1972**, *94*, 4941-4948. (b) Karas, L.; Wu, J. I. *Nat. Chem.* **2022**, *14*, 723-725. (c) Yan, J.; Slanina, T.; Bergman, J.; Ottosson, H. *Chem. Eur. J.* **2023**, *29*, e202203748.
[3] Mandado, M.; Graña, A. M.; Pérez-Juste, I. *J. Chem. Phys.* **2008**, *129*, 164114.
[4] Proos Vedin, N.; Escayola, S.; Radenković, S.; Solà, M.; Ottosson, H. *J. Phys. Chem. A.* **2024**,*128*, 4493-4506
[5] Proos Vedin, N.; Toldo, J.; Escayola, S.; Radenkovic, S.; Solà, M.; Ottosson, H. *J. Org. Chem*. Submitted.

Bridging Theory and Efficiency: Quantum-Inspired Insights into Organic Solar Cells Performances

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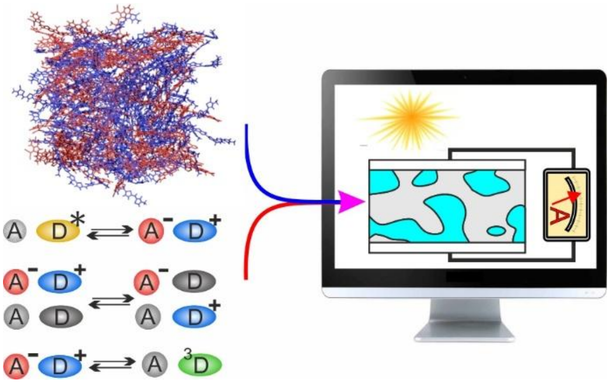
Organic solar cells (OSCs) offer significant advantages over traditional silicon devices, because of their lower costs, easier processability, improved mechanical properties, and chemically-tuneable electronic properties.[1] The identification of novel donors and acceptors boosted up the power conversion efficiency (PCE) up to 19% for bulk heterojunction (BHJ) OSC;[2] however, this value is still lower than their inorganic counterparts, thus hindering their commercialization.

Theoretical studies have the potential to play a key role in the quest for higher PCE, by unravelling structure-property relations which can lead to the identification of new materials with improved properties.[3] Since the overall OSC efficiency depends on the rates of several elementary charge transfer processes which can take place at the donor/acceptor (D/A) interface (e.g. photoinduced hole and electron transfer, excitation energy transfer, and charge recombination), reliable and fast protocols for evaluating such rates from first principles are needed.

Herein, we present a protocol[4] where Fermi's Golden Rule rates for the processes occurring at the interface are computed on a reliable morphology obtained through molecular dynamics simulations using quantum-mechanically derived force fields. This protocol is then applied to predict and compare the performances of different BHJ blends, focusing on particular on the sources of energy losses, a problem of outstanding importance for increasing power conversion efficiency.



Funding: Italian Ministry of University and Research (MUR), PRIN grant 2022XSC9P5.

References:

[1] A. Hedley, *Chem. Rev.*, **2017**, *117*, 796.
[2] R. Zhou, *Nat. Commun.*, **2019**, *10*, 5393; A. Lin, *ACS Energy Lett.*, **2020**, *5*, 2935
[3] E. Pyzer-Knapp, *Annu. Rev. Mater. Res.*, 2015, **45**, 195; R Bombarelli, *Nat. Mater.*, **2016**, *15*, 1120
[4] A. Landi, *J. Mater. Chem. A*, **2021**, *9*, 24849; A. Landi, *ACS Appl. Energy Mater.*, **2024**, *7*, 707

photo-MHAT: Cobalt-Catalyzed Functionalization of Unactivated Olefins under Visible-Light Irradiation

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Metal-hydride hydrogen atom transfer (MHAT) has proven to be an effective strategy for the functionalization of unactivated alkenes under mild conditions. While traditional MHAT conditions prescribe the use of superstoichiometric amounts of reductant, we were able to leverage the beneficial properties of benzothiazinoquinoxalines as organophotocatalysts for the development of methods that combine photochemistry with MHAT reactivity. Herein, we report a general method for the cobalt-catalyzed photo-semipinacol rearrangement of unactivated allylic alcohols to prepare α,α-disubstituted ketones.[1] Key to success was the use of an organic dye under blue-light irradiation to shuttle a cobalt complex between the desired oxidation states. This obviates the need for any stoichiometric reducing or oxidizing agents. The reaction proceeds with alkanes as well as arenes as migrating groups and, importantly, displays reactivity complementary to procedures which employ Brønsted acid.

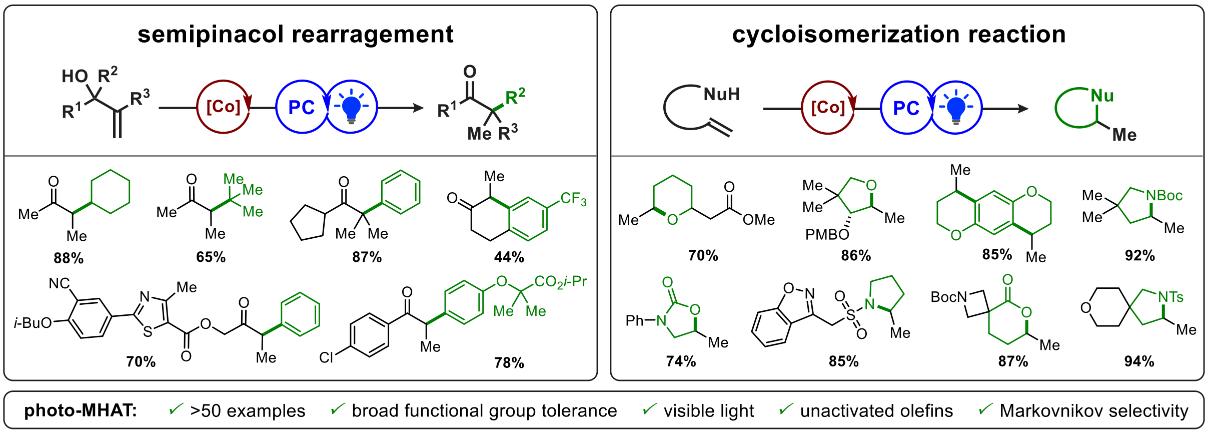

Figure 1. Merging metal-hydride hydrogen atom transfer chemistry and photocatalysis results in fully catalytic reaction conditions for several functionalization reactions of unactivated olefins.

Under identical conditions, we were able to showcase a fully catalytic photo- and cobalt-catalyzed Markovnikov-selective cycloisomerization reaction that utilizes olefins with pendant *N*-, *O*-, as well as *C*-nucleophiles to yield a number of different heterocycles including, but not limited to, pyrrolidines, piperidines, epoxides, tetrahydrofurans, lactones, oxazolidinones, and chromanes.[2,3] The transformation was employed for late-stage drug diversifications and the synthesis of several small natural products which highlights the potential of photo-MHAT for the development of efficient and sustainable synthetic strategies.

Funding: European Research Council (833540)

References:

[1] H. Lindner, E. M. Carreira, *Angew. Chem. Int. Ed.* **2024**, e202407827.

[2] H. Lindner, W. M. Amberg, T. Martini, D. M. Fischer, E. Moore, E. M. Carreira, *Angew. Chem. Int. Ed.* **2024**, e202319515.

[3] H. Lindner, E. M. Carreira, *Org. Lett.* **2025**, 704–708.

Revitalizing Ultrafast Spectroscopy: Innovations in Technique and Application

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Ultrafast spectroscopy has long been a cornerstone for investigating excited-state dynamics across a wide range of scientific disciplines. While conventional techniques have been widely adopted, recent advancements in ultrafast spectroscopic methods and light sources have not only enhanced performance metrics but also opened new application opportunities and enabled the exploration of previously inaccessible aspects of photochemistry. In this talk, I will share my research journey focused on revitalizing traditional ultrafast spectroscopy through the development of novel techniques and the integration of next-generation ultrafast light sources.[1,2]

I will highlight the development of transient grating photoluminescence spectroscopy (TGPLS),[1,3] a technique designed to overcome key limitations of conventional time-resolved photoluminescence methods. By integrating TGPLS with advanced ultrafast light sources beyond conventional Ti:sapphire lasers, we have achieved significant improvements in key performance parameters, including detection bandwidth, signal quality, acquisition speed, and temporal resolution.

As an application example, I will present an ultrafast photoluminescence study of mixed-layer quasi-2D perovskites, an emerging class of materials with great potential for light emission and optical amplification. TGPLS serves as an ideal tool to probe photoexcitation dynamics critical for understanding lasing mechanisms. Using an approach that simultaneously achieves high temporal and spectral resolution, we reveal that while sub-picosecond energy funneling facilitates amplified spontaneous emission, ultrafast singlet-triplet annihilation introduces a bottleneck by quenching singlet excitons within 200 femtoseconds, which effectively suppresses population inversion.[4] This case study demonstrates how advanced ultrafast spectroscopy can provide new insights into key excited-state processes such as energy transfer, lasing dynamics, and singlet-triplet interactions.

By addressing longstanding limitations with innovative solutions, these efforts aim to significantly expand the capabilities of ultrafast spectroscopy and unlock new directions in photochemistry and materials research.

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References:

[1] C.Y. Lin et al., & K. Chen, The Journal of Physical Chemistry Letters, **2025**, *16*: 1081-1087.
[2] R. Ronnie et al., & K. Chen, C.H. Lu, Scientific Reports, **2021**, 11.1: 12847.
[3] K. Chen et al., & J.M. Hodgkiss, The Journal of Physical Chemistry Letters, **2014**, *5*.10: 1732-1737
[4] I. Wagner et al., & K. Chen, Advanced Materials, **2025**, 2419674.

Plasmonic Pathway to Hybrid Nanomaterials through Energy Transfer

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Abstract

Plasmon-induced resonance energy transfer (PIRET) is a promising approach for plasmonic photocatalysis and energy conversion, but challenges include elucidating the mechanism and maximizing its efficiency, both of which are hampered by competing processes. Another challenge is demonstrating that PIRET can photoinitiate reactions that follow efficient pathways compared to bulk processes. We report a plasmon-induced route to plasmonic-polymer hybrid nanomaterials using *in-operando* single-particle spectroelectrochemistry. An energy transfer efficiency of 40% is achievable when the spectral overlap between the gold nanorod scattering and monomer absorption is maximized. We also show that PIRET-initiated polymerization proceeds through a different mechanism than bulk polymerization, supported by spectroscopic evidence and density functional theory calculations, highlighting efficient energy cascade from photon to plasmon to exciton and finally, to new light-initiated chemistry.

Labels and linkers for microscopy: from improved imaging to applications.

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Single molecule spectroscopy has revolutionized numerous scientific disciplines, spanning from catalysis, plasmonics, and polymer physics to biophysics, cell biology, and DNA sequencing. By enabling the detection and characterization of individual molecules, this technique has provided unprecedented insights into molecular interactions and dynamic processes. Moreover, single molecule approaches have played a pivotal role in pushing the resolution of fluorescence microscopy beyond the diffraction limit, leading to significant advancements in imaging.

In this presentation, I will provide an overview of recent single molecule experiments conducted in my laboratory, highlighting how these studies have been closely intertwined with the development of novel microscopy modalities, the synthesis of specialized fluorescent labels, and advances in linker chemistry. A key focus will be our development of FLUOROCODE, a super-resolution optical mapping approach for DNA, which enables precise visualization and structural analysis of genomic sequences at the nanoscale. I will illustrate how fundamental research in this domain has transitioned into real-world applications, including microbiome analysis, and discuss ongoing valorization efforts. This work underscores the synergy between cutting-edge microscopy, innovative chemistry, and applied biotechnology, paving the way for new diagnostic and analytical tools in life sciences.

Funding: ERC, FWO

Acknowledgement: I thank all the coworkers who’s efforts have resulted in the data presented in this lecture

References:

[1] Gang Wen, Volker Leen, Taoufik Rohand, Markus Sauer, Johan Hofkens. Current Progress in Expansion Microscopy: Chemical Strategies and Applications. *Chemical Reviews*. **2023**; 123 (6) 3299-3223

[2] Xiong Chen, Sergey Abakumov, Moa Sandberg Wranne, Vince Goyvaerts, Milena Helmer Lauer, Jana Rubberecht, Taoufik Rohand, Volker Leen, Fredrik Westerlund, Johan Hofkens. Sequence-Specific Minor Groove Binders in Labeling and Single-Molecule Analysis of DNA *J.Am.Chem.Soc* **2025**; 147 (1), 384-396.

[3] Sergey Abakumov, Elizabete Ruppeka-Rupeika, Xiong Chen, Arno Bouwens, Volker Leen, Peter Dedecker, Johan Hofkens. DeepMAP: Deep CNN Classifiers Applied to Optical Mapping for Fast and Precise Species-Level Metagenomic Analysis *ACS Omega* **2025**; 2, 27

Versatile Photobehavior of Single Crystalline, Non-Stoichiometric Hydrogen-Bonded Organic Frameworks

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Hydrogen-bonded organic frameworks (HOFs) composed of multicomponent molecules in a non-stoichiometric composition have drawn great interest due to their tunable properties.[1,2] However, the photobehavior of the single crystals of such mixed HOFs has not been explored. Here, we report on the photobehavior of single crystalline non-stoichiometric HOFs (NS-HOFs). NS-HOFs (**B_TN_T-1**) with various composition ratios were successfully obtained as single crystals from two analogue tetratopic carboxylic acids, possessing naphthalene and benzothiadiazole cores (**NTTA** and **BTTA**, respectively).[3] The heterogeneous distribution of the components was thoroughly confirmed by time-resolved fluorescence single crystals microscopy and local crystallographic analysis using focused synchrotron X-ray radiation. The versatile fluorescence of **B_TN_T-1** behavior depends on the composition ratio and distribution of the component in the single crystals. We observed not only fluorescence bands with various colors such as purple, blue, green and white, depending on the composition ratios, but also different emission bands from a single crystal. We provide details on their emission lifetimes following the composition, emission color and targeted region on single crystals. This work is the first example of single crystal studies applied to organic porous co-crystals (HOFs) and demonstrates unique and versatile optical properties of carboxylic acid-based NS-HOFs. The results provide a concept of creating functional mixed porous materials capable of different and tunable optical properties.

Funding and Acknowledgement: This work was supported by KAKENHI (JP23H04029, JP24K21769, JP24K01468, JP24H00405 and JP24K21717) from JSPS and MEXT Japan, and by grant PID2020-116519RB-I00 funded by MICIU/AEI/10.13039/501100011033 and the European Union (EU), SBPLY/23/180225/000196 funded by JCCM and the EU through "Fondo Europeo de Desarrollo Regional" (FEDER); grant 2022-GRIN-34325 funded by UCLM (FEDER). T. H. thanks financial support by Grant-in-Aid for JSPS Research Fellow (JP24KJ1655). M.H. thanks MICIU for the FPI fellowship PRE2021-099064 financed by MICIU/AEI/10.13059/501100011033 and by FSE +.

References:
[1] Q. Chen, T. Zhang, X. Chen, M. Liang, H. Zhao, P. Yuan, Y.Han, C.-P. Li, J. Hao, P. Xue, *ACS Appl. Mater. Interfaces* 2022, 14, 24509–24517.
[2] T. Hashimoto, R. Oketani, M. Nobuoka, S. Seki, I. Hisaki, *Angew. Chem. Int. Ed.* 2023, 62, e202215836.
[3] T. Hashimoto, M. de la Hoz Tomás, R. Oketani, B. Cohen, M. Naruoka, N. Tohnai, A. Douhal, I. Hisaki, *Angew. Chem. Int. Ed.* 2025, 64, e202419992.

Boosting the Quantum Efficiency of Ionic Carbon Nitrides for Solar-Driven Fuel Synthesis

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Abstract

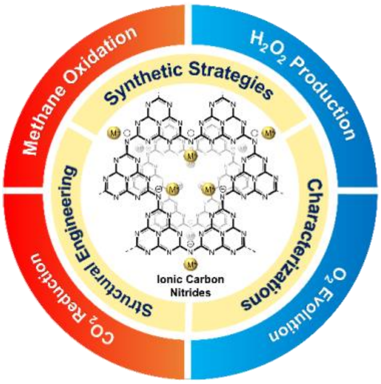

Figure 1. Ionic CNs for solar-driven fuel synthesis.

Solar-driven catalysis using particulate semiconductors represents a promising approach for the sustainable generation of valuable fuels. Metal poly(heptazine imide) (*M*PHI), a new class of crystalline ionic carbon nitrides (CNs), has emerged as a standout photocatalyst due to its efficient visible-light absorption and optimal energy level alignment, which satisfy the requirements for driving H_2O_2 evolution and oxygen evolution. [1, 2] Herein, recent progress in boosting the quantum efficiency of *M*PHI catalysts is presented. We recently discovered that incorporating oxamide during the one-step synthesis of KPHI can induce lattice distortion and activate $n \rightarrow \pi^*$ electronic transition, thereby boosting the photocatalytic H_2O_2 production efficiency. [3] An optimized sample (*2%Ox*-KPHI) demonstrated a significant increase in AQY, achieving 41% at 410 nm—substantially higher than the activities of previously reported ionic CNs for H_2O_2 production. We also developed an innovative approach of KPHI nanocrystal fragmentation induced by incorporating NH_4Cl during its polymerization process. As NH_4Cl decomposes during annealing, it disrupts the block structure of KPHI, leading to the formation of smaller, distorted fragments. This fragmentation further elevated the AQY of KPHI to 49% at 410 nm.[4] Most importantly, we found that NH_4Cl could reduce the polymerization temperature without compromising the performance. The release of NH_3 gas from NH_4Cl decomposition triggers a localized pressure build-up around the CN precursors, which can lower the activation energy required for polymerization. We also identified a way to induce simultaneous integration of boron dopants and nitrogen defects into the KPHI framework through $NaBH_4$ treatment. An optimal catalyst reached an AQY of 4.57% at 420 nm, higher than most of the reported values for CN-based catalysts.[5] Most significantly, the optimal catalyst exhibits outstanding performance even under illumination wavelengths exceeding 450 nm, a feat rarely attained by conventional CNs.

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References:

[1] C. M. Pelicano, M. Antonietti, *Angew. Chem., Int. Ed.* **2024**, *63*, e202406290.

[2] C. M. Pelicano, J. Li, M. Cabrero-Antonino, I. F. Silva, L. Peng, N. V. Tarakina, S. Navalon, H. Garcia, M. Antonietti, *J. Mater. Chem. A* **2023**, *12*, 475.

[3] H. Tong, J. Odutola, J. Song, L. Peng, N.Tkachenko, M. Antonietti, C. M. Pelicano, *Adv. Mater.* **2024**, *36*, 2412753.

[4] J. Bharti, J. Odutola, H. Tong, Z. Tian, V. Shvalagin, M. Antonietti, C. M. Pelicano, *(To be submitted)*

[5] H. Tong, V. Diez-Cabanes, Y. Fang, G. Maurin, M. Antonietti, C. M. Pelicano, *(To be submitted)*

Encapsulated fluorophores and fluorescence lifetime sensors for super-resolution imaging

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The development of super-resolution fluorescence microscopy has led to an active search for dyes with perfected fluorescence properties, and new schemes to improve the brightness and photostability of fluorophores are still in high demand. In biological media, red excitation is usually preferred but red-emitting dyes often display low fluorescence quantum yields in aqueous environments due to specific fluorescence quenching by H_2O in the contact sphere of the fluorophore, as our group has recently shown.[1-2] In addition, very few of the existing fluorophores compatible with super-resolution microscopy display environment-sensitive properties that can be exploited for sensing local interactions at the single-molecule level in multidimensional single-molecule localization microscopy (SMLM) schemes such as spectrally-resolved SMLM or fluorescence lifetime-resolved SMLM (FL-SMLM).

This contribution will on one hand discuss some of the successful encapsulation strategies that our group has developed to improve the brightness of red-emitting dyes using cyclodextrins and cucurbiturils as macrocyclic hosts for SMLM [2-3]. On the other hand, we describe our efforts to exploit or develop environment-sensitive fluorophores compatible with single-molecule detection, with a focus on targetable probes whose lifetime directly reports on their local hydration and which open the door to sensing hydration in biological environments such as protein surfaces and microgels at the nanoscale [2, 4].

Funding: University of Geneva and Swiss National Science Foundation (205321_ 207482)

References:

[1] J. Maillard, K. Klehs, C. Rumble, E. Vauthey, M. Heilemann, A. Fürstenberg, *Chem. Sci.* **2021**, *12*, 1352.

[2] J. Maillard, C. A. Rumble, A. Fürstenberg, *J. Phys. Chem. B* **2021**, *125*, 9727.

[3] L. Briant, J. Maillard, A. Fürstenberg, *Chem. Commun.* **2024**, *60*, 13943.

[4] S. Jana, O. Nevskyi, H. Höche, L. Trottenberg, E. Siemes, J. Enderlein, A. Fürstenberg, and D. Wöll, *Angew. Chem. Int. Ed.* **2024**, *63*, e202318421.

Enhancement of Intersystem Crossing in Asymmetrically Substituted BODIPY Dyes: Application in Holographic Recording of Diffractive Structures

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The development of organic photosensitizers with efficient intersystem crossing (ISC) without relying on heavy atoms is a rapidly expanding field. Among various approaches, spin-orbit charge-transfer intersystem crossing (SOCT-ISC) has emerged as a powerful strategy, particularly for donor-acceptor dyads with orthogonal aromatic fragments, such as meso-aryl BODIPYs (Fig. 1a).[1] In these systems, triplet excited states are generated from a charge-transfer (^{1}CT) state formed by electron transfer between the subunits. A promising alternative for achieving high triplet yields is reducing the singlet-triplet energy gap ($\Delta E_{S\text{-}T}$), which facilitates ISC without the need for heavy atoms via spin-orbit coupling between S_1 and a higher triplet state (T_n), followed by internal conversion to T_1.[2]

In this work, we demonstrate that asymmetrical substitution of the BODIPY chromophore effectively reduces $\Delta E_{S\text{-}T}$, enabling efficient ISC via the $S_1 \rightarrow T_2$ pathway. A comprehensive study of asymmetrical BODIPYs (**aBDP**s, Fig. 1b) revealed that this approach is applicable across a diverse range of substitution patterns. We investigated BODIPYs with an electron-rich alkyl-substituted pyrrolic unit and an electron-deficient pyrrolic unit incorporating carbonyl and/or aryl groups or remaining unsubstituted. The resulting compounds exhibited efficient ISC and singlet oxygen generation with quantum yields (Φ_Δ) of up to 0.76, demonstrating their strong potential as photosensitizers. **aBDP**s were further explored as photoinitiators in a photopolymer for holographic recording of diffractive structures. The lead compound, **aBDP8**, exhibited remarkable photopolymerization efficiency, achieving a diffraction efficiency of up to 71% in holographic transmission gratings.[3]

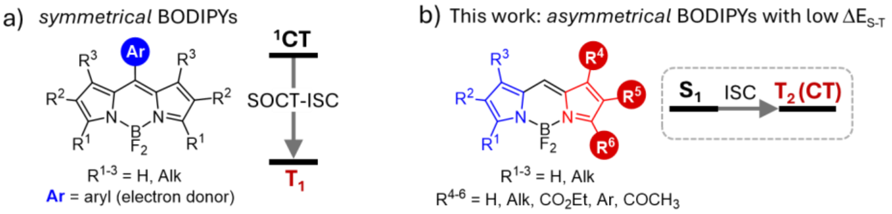

Figure 1. General structures of a) symmetrical BODIPY donor-acceptor dyads undergoing the SOCT-ISC process and b) asymmetrical BODIPY dyes forming triplet excited states via the $S_1 \rightarrow T_2$ pathway.

Our findings suggest that tuning molecular asymmetry represents an effective approach for controlling ISC in BODIPY-based photosensitizers. Moreover, this strategy can be synergistically combined with other methods to create hybrid systems with multiple ISC pathways contributing to triplet excited states formation.

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References:

[1] M.A. Filatov, *Org. Biomol. Chem.* **2020**, *18*, 10-27.

[2] C. M. Marian, *Annu. Rev. Phys. Chem.*, **2021**, *72*, 617.

[3] M.A. Filatov, T. Mikulchyk, M. Hodée, M. Dvoracek, V.N.K. Mamillapalli, A. Sheehan, C. Newman, S.M. Borisov, D. Escudero, I. Naydenova, *J. Mater. Chem. C*, **2025**, doi: 10.1039/D4TC04850D

Excimer phosphorescence from multiple resonance type dimer

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Persistent room-temperature phosphorescent (RTP) materials hold great potential for various applications, including bioimaging and optoelectronic devices. In particular, RTP originating from excimer phosphorescence have recently attracted growing interest [1,2]. However, the underlying mechanism of excimer phosphorescence remains unclear. In this study, we used covalently bonded dimers as a strategy to clarify the spatial arrangement and interactions between chromophores, potentially enabling a more precise understanding of the photophysical properties of excimer phosphorescence. For this purpose, we synthesized covalently linked dimers using molecular linkers, aiming to elucidate the excitation processes responsible for excimer phosphorescence. As a monomer, we focused on a multiple resonance type molecule, a planar molecule known for its efficient intersystem crossing due to a small ΔE_{ST} arising from multiple resonance effect [3]. To modulate the interaction between the monomer units, we synthesized compound **1** and **2** with different linkers: naphthyl and biphenyl groups. Photophysical measurements revealed that compound **1**, which has a co-facial geometry through its naphthalene linker, exhibited excimer phosphorescence formed via intersystem crossing from an initially generated singlet excimer state.

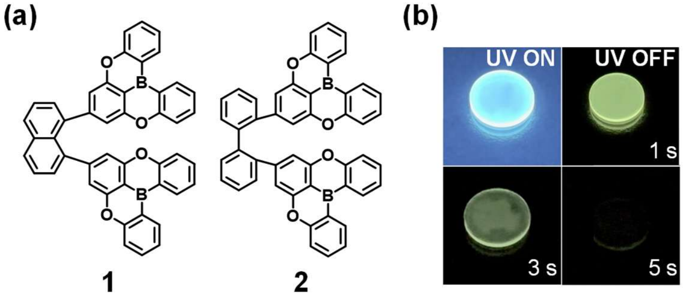

Figure 1. (a) Chemical structures of **1** and **2**, and (b) photographs of the luminescence **1** in PMMA film under UV irradiation and after removal of the UV lamp at room temperature.

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References:

[1] Z, Liu et al., *Light Sci. Appl.* **2022**, *11*, 142.
[2] Z, Deng et al., *Adv. Mater.* **2024**, *36*, 2311384.
[3] H. Hirai et al., *Angew. Chem., Int. Ed.* **2015**, *54*, 13581–13585.

Conformation-Controlled Vapochromic Phosphorescence at Room Temperature

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Molecular and inorganic materials with tailored luminescent properties in the solid phase have been extensively studied over recent decades. More recently, increasing attention has been devoted to materials capable of exhibiting enhanced room-temperature phosphorescence (RTP) in the solid state, a phenomenon most commonly observed in metal complexes. In contrast, achieving RTP in organic materials still remains a significant challenge and the rational control of key luminescence parameters – including emission energy, lifetime, and quantum yield – is still difficult to realise in all-organic systems.[1,2] This limitation often hampers the development of efficient, stimuli-responsive organic triplet emitters.

Persulfurated benzenes are an intriguing class of RTP molecules, whose structural flexibility in principle allows for the reversible response of luminescence upon application of external stimuli. Although the influence of several factors on the RTP – such as aggregation, polymorphism, and intramolecular conformation – has been explored, the tuning of luminescence through chemical stimuli remains elusive for this class of compounds.[3] Recently,[4] we have focused our attention on a class of decorated persulfurated benzenes that exhibit reversible phosphorescence color switching in the solid state (see Fig. 1). This behavior is induced by conformational changes triggered by the uptake/release of solvent molecules. Quantum-chemical calculations support the experimental findings and suggest that the observed luminescence modulation originates from the emission of triplet states of different electronic character. Such materials hold promise for applications in sensing, anti-counterfeiting, and optoelectronics, where tunable and switchable luminescence is highly desirable.

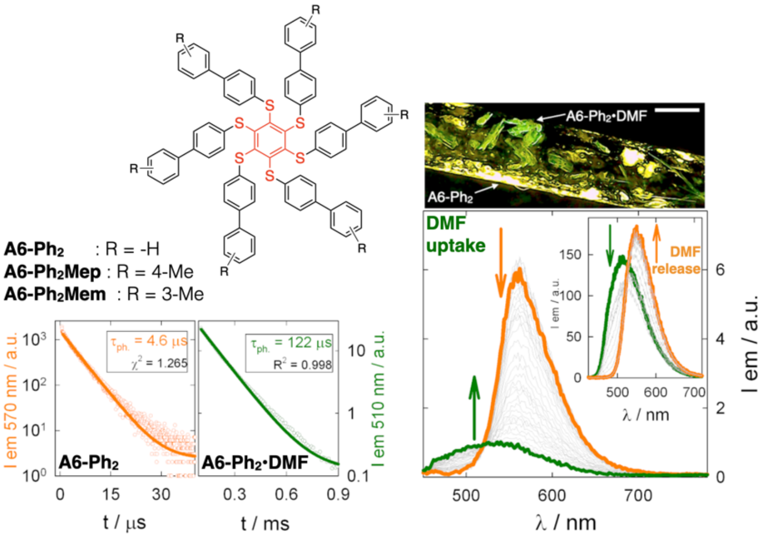

Figure 1. Persulfurated benzenes as vapochromic RTP solid-state emitters.

Funding: National project PRIN "Photogen" (2022AWXS83).

References:

[1] M. Baroncini, G. Bergamini, P. Ceroni, *Chem. Commun.* **2017**, *53*, 2081.
[2] W. Zhao, Z. He, B. Z. Tang, *Nat. Rev. Mater.* **2020**, *5*, 869.
[3] A. Fermi, S. d’Agostino, Y. Dai, F. Brunetti, F. Negri, M. Gingras, P. Ceroni, *Chem. Eur. J.* **2024**, *30*, e202401768.
[4] A. Fermi, S. Gahlot, E. Jorand, S. d’Agostino, Y. Dai, F. Negri, C. Moustrou, M. Gingras, P. Ceroni, *ChemRxiv* **2025**; doi:10.26434/chemrxiv-2025-t8ggf.

High-Spin State Dynamics and Quintet-Mediated Emission in Intramolecular Singlet Fission

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High-spin states are crucial in various organic applications, spanning from optoelectronics to quantum information and singlet fission (SF). This talk focuses on the formation and emission properties of quintet and triplet states in SF systems. The principle is based on a photoexcited singlet exciton rapidly decaying into spin-correlated triplet pairs, forming singlet, triplet and quintet states, before dissociating into free triplets (Fig. 1). While extensive studies have addressed triplet formation and its role in photoluminescence, optical emission involving quintet states remains largely unexplored. Additionally, strategies to tune SF systems for controlled triplet multiplication via molecular design are still of high interest.

We focus on novel concepts of intramolecular singlet fission based on units of the SF-active chromophore diphenylhexatriene (DPH). A particular focus will be on DPH-based oligomers – especially dimers and trimers – which allow tunable geometry for accessing different spin regimes[1]. We employ a set of unique spin-sensitive techniques to investigate high-spin state formation and emission, including optical spectroscopy, such as transient absorption (TA) and magnetic field-dependent photoluminescence (magPL), as well as electron paramagnetic resonance (EPR) and optically detected magnetic resonance (ODMR), to probe the formation and evolution of high-spin states.

We show that quintet states form robustly across all architectures and, remarkably, mediate delayed photoluminescence that persists even at room temperature. However, the efficiency of triplet separation is highly dependent on the number of chromophores and the molecular arrangement. We identify the trimer Me-$(DPH)_3$ as a model system for pure singlet fission, with triplet pair formation occurring exclusively via SF – unlike linear $(DPH)_2$ and $(DPH)_3$ which show intersystem crossing as a contributing or even dominant pathway. These results establish a framework for controlling high-spin state evolution and emission in organic materials, with relevance for exciton multiplication and optically addressable spin states.

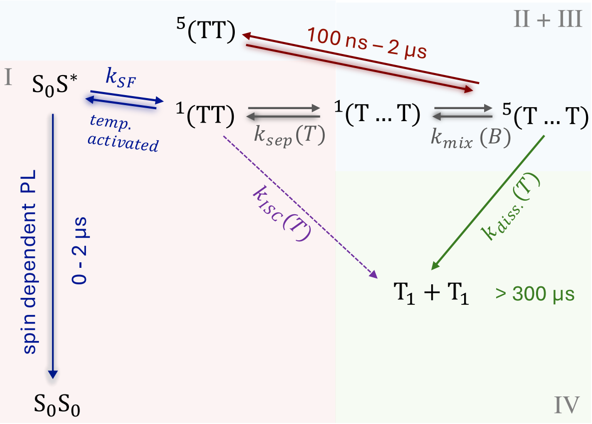

Figure 1. Spin-sensitive techniques probe the formation and evolution of high-spin states and pathways involved in intramolecular singlet fission.

Funding: Engineering Physical Sciences Research Council (EP/W017091/1).

Acknowledgement: We thank the Centre for Advanced Electron Spin Resonance (CAESR) at the University of Oxford, the Lord Porter Ultrafast Laser Spectroscopy Laboratory at the University of Sheffield, and the Freie Universität Berlin for access to instrumentation and facilities used in this work.

References:

[1] Grüne, J., Montanaro, S., Bradbury, T.W., et. al. 2024. High-Spin State Dynamics and Quintet-Mediated Emission in Intramolecular Singlet Fission. arXiv preprint arXiv:2410.07891.

Design Rules for Triplet-Triplet Annihilation Upconversion Annihilators

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Photon upconversion (UC) is a photophysical process where low energy photons are combined into one of higher energy. Among mechanisms of UC, triplet-triplet annihilation (TTA) UC has received widespread attention as it can occur efficiently even at sub-solar incident flux. This enables a wide scope of applications, ranging from enhancing photovoltaic efficiency, to anti-counterfeiting, to improved 3D printing, among many others.[1]

TTA upconversion requires two species, a sensitizer which absorbs low energy photons, and an annihilator which emits high energy photons. Despite the breadth of applications of TTA upconversion, few families of TTA-UC annihilators have been explored, with most work focusing on unstable acene-based annihilators.

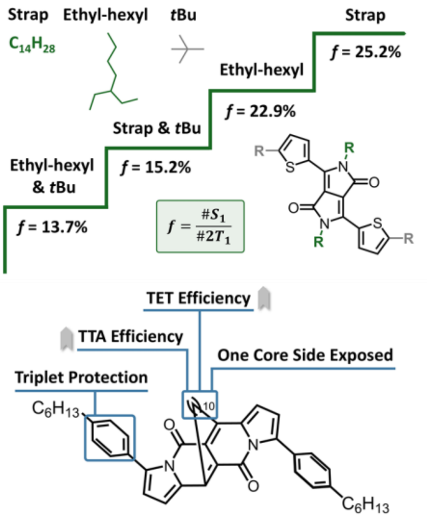

Figure 1. Examples of annihilator design rules for enhanced TTA-UC efficiency.[1]

Herein, I will discuss our work developing design rules for optimized TTA-UC (Fig. 1). By focusing on novel families of annihilators based on well-studied organic semiconductors, we can develop libraries of molecules that are easily derivatized. This allows the development of structure-function relationships, to synthesize optimized annihilators with enhanced efficiencies compared to the commonly used acene-based annihilators.[2,3] Furthermore, we can develop design-rules for optimized TTA-UC in the solid state,[4] which will be crucial for the widespread application of TTA-UC.

Funding: University of California San Diego start-up funds

References:

[1] L. Naimovičius, A. B. Pun, *Trends Chem.* **2025**, Accepted.

[2] L. Naimovičius, S. K. Zhang, A. B. Pun, *J. Mater. Chem. C* **2024**, *12*, 18374-18380

[3] A. J. Lyons, L. Naimovičius, S. K. Zhang, A. B. Pun, *Angew. Chem. Int. Ed.* **2024**, *63*, e202411003.

[4] L. Naimovičius, L. Wolek, S. K. Zhang, A. B. Pun, *In Preparation*

3D Superresolution Microscopy of Vertical Nucleic Acids on Graphene

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Superresolution microscopy at physiological conditions suffers from slow imaging compared to the kinetics of Brownian motion that requires stable alignment of the structures imaged. We discovered that DNA adopts a vertical orientation on graphene that aligns it for superresolution interrogation of nucleic acid structural features such as lesions, bents and bulges.[1] It also opens the door for superresolution microscopy of DNA-protein interactions in an unprecedented manner. We show dynamics of DNA repair proteins with single nucleotide resolution of diffusion along the DNA. As nanometric 3D resolution can be achieved by a combination of graphene energy transfer[2] and pMINFLUX,[3] we envision the approach to complement single-molecule FRET as tool for dynamics structural biology of nucleic acids and their protein interactions.

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References:

[1] A. M. Szalai, G. Ferrari, L. Richter, J. Hartmann, M. Z. Kesici, B. Ji, K. Coshic, M. R. J. Dagleish, A. Jaeger, A. Aksimentiev, I. Tessmer, I. Kaminska, A. M. Vera, P. Tinnefeld, *Nat Methods* **2025**, *22*, 135-144.

[2] J. Zähringer, F. Cole, J. Bohlen, F. Steiner, I. Kamińska, P. Tinnefeld, *Light: Science & Applications* **2023**, *12*, 70.

[3] F. Cole, J. Zähringer, J. Bohlen, T. Schröder, F. Steiner, M. Pfeiffer, P. Schüler, F. D. Stefani, P. Tinnefeld, *Nature Photonics* **2024**, *18*, 478-484.

Photophysics and Photochemistry of Individual Plasmonic Nanostructures

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A surface plasmon in a metal nanoparticle is the coherent oscillation of the conduction band electrons leading to both absorption and scattering as well as strong local electromagnetic fields. These fundamental properties have been exploited in many different ways, including surface enhanced spectroscopy and sensing, photocatalysis, photothermal cancer therapy, and color display generation. Chemical synthesis and assembly of nanostructures are able to tailor plasmonic properties that are, however, typically broadened by ensemble averaging. Single particle spectroscopy together with correlated imaging is capable of removing heterogeneity in size, shape, and assembly geometry and furthermore allows one to separate absorption and scattering contributions. In this talk I will discuss our recent work on distinguishing the different contributions that cause plasmon decay as probed by the homogeneous single-particle linewidth in conjunction with ultrafast transient absorption and emission spectroscopy.[1-8] In particular, I will focus on plasmon damping due to energy and charge transfer from the metal to its environment with the goal to mechanistically understand how energy conversion from an incident photon to a plasmon and then a localized excitation can be maximized while circumventing fast metal-intrinsic internal conversion that simply leads to heat generation.

References:

[1] T. Yuan, X. Guo, S. A. Lee, S. Brasel, A. Chakraborty, D. J. Masiello, S. Link, *ACS Nano* ***2025**, 19*, 10277.

[2] B. Ostovar, S. A. Lee, A. Mehmood, K. Farrell, E. K. Searles, B. Bourgeois, W. -Y. Chiang, A. Misiura, N. Gross, A. Al-Zubeidi, J. A. Dionne, C. F. Landes, M. Zanni, B. G. Levine, S. Link, *Sci. Adv.* ***2024**, 10*, eadp3353.

[3] A. Jones, E. K. Searles, M. Mayer, M. Hoffmann, N. Gross, H. Oh, A. Fery, S. Link, C. F. Landes, *J. Phys. Chem. Lett.* ***2023**, 14*, 8235.

[4] H. Oh, E. K Searles, S. Chatterjee, Z. Jia, S. A. Lee, S. Link, C. F. Landes, *ACS Nano* **2023**, *17*, 18280.

[5] S. A. Lee, C. T. Kuhs, E. K. Searles, H. O. Everitt, C. F. Landes, S. Link, *Nano Lett.* ***2023**, 23*, 3501.

[6] S. A. Lee & S. Link, *Acc. Chem. Res.* **2021**, *54*, 1950.

[7] S. S. E. Collins, E. K. Searles, L. J. Tauzin, M. Lou, L. Bursi, Y. Liu, J. Song, C. Flatebo, R. Baiyasi, Y.-Y. Cai, B. Foerster, T. Lian, P. Nordlander, S. Link, C. F. Landes, *ACS Nano* **2021**, *15* 9522.

[8] B. Foerster, M. Hartelt, S. Collins, M. Aeschlimann, S. Link, C. Sönnichsen, *Nano Lett.* **2020**, *20*, 3338/

Role of Quantum Coherence in Hole-Mediated Water Oxidation under Strong Coupling Conditions

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We have recently demonstrated that employing a photoanode exhibiting modal strong coupling between a Fabry–Pérot nanocavity and localized surface plasmon resonance (LSPR) leads to a notable increase in the efficiency of photoelectrochemical water oxidation.[1] In this system, a TiO_2 thin film deposited on a reflective gold layer serves as a nanocavity, forming the so-called TA structure. Upon loading gold nanoparticles (AuNPs) that support LSPR onto the TiO_2 surface, the resulting ATA structure allows for the formation of two distinct hybrid optical modes via the interaction between the cavity and LSPR modes. Compared to the conventional AT structure that lacks such coupling, the ATA photoanode shows enhanced light-harvesting ability and significantly improved catalytic performance for water oxidation. This improvement is attributed to quantum coherence established among the LSPR modes of multiple AuNPs through the nanocavity.[2]

To gain deeper insight into how quantum coherence contributes to the activity enhancement, we carried out a kinetic study. Temperature-dependent transient absorption measurements of electrons injected into TiO_2 revealed a very low activation energy for electron–hole recombination (Ea(r)), indicating that the injected electrons are predominantly trapped in shallow states. Furthermore, from the temperature dependence of incident photon-to-current conversion efficiency (IPCE), we derived the activation energy for water oxidation intermediate formation (Ea(1)). When the lower-energy branch (LB) of the hybrid mode in ATA was excited, Ea(1) was significantly higher than that in the AT structure. In contrast, excitation of the upper branch (UB) gave rise to comparable Ea(1) values to AT. These findings suggest that holes generated under LB excitation possess more negative electrochemical potentials, and that spectral overlap between UB and LB enables interbranch transitions, thereby influencing hole energetics.

Moreover, the frequency factor for intermediate formation in the ATA structure was approximately 40 times larger than that in the AT structure, providing strong evidence that quantum coherence induced by modal strong coupling increases the reaction cross-section and accelerates hole-mediated water oxidation.[3]

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References:

[1] X. Shi, K. Ueno, T. Oshikiri, Q. Sun, K. Sasaki, H. Misawa, *Nat. Nanotechnol.*, **2018**, *13*, 953.
[2] Y. Liu, X. Shi, T. Yokoyama, S. Inoue, Y. Sunaba, T. Oshikiri, Q. Sun, M. Tamura, H. Ishihara, K. Sasaki, H. Misawa, *ACS Nano*. **2023**, *17*, 8315.
[3] E. Cao, X. Shi, H. Inoue, T. Oshikiri, Y-E. Liu, H. Misawa, *J. Phy. Chem. C*, 2**025**, *129*, 1590.

Tuning multiexciton properties of colloidal quantum dots via size and surface functionalization

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Quantum dots (QDs) exhibit unique optoelectronic properties arising from size-dependent quantum confinement of electronic wavefunctions. A key feature of QDs is their capacity to host multiple interacting exciton pairs, termed as 'multiexcitons'. Multiexcitons can be generated either via simultaneous absorption of multiple photons or via multiexciton generation (MEG), wherein a high-energy photon (at-least twice the bandgap) creates multiple excitons. Multiexcitons are of significant interest for applications such as nanocrystal lasers, photovoltaics, and photocatalysis. In photocatalysis, efficient carrier transfer to catalytic centers necessitates long-lived multiexciton states. However, multiexcitons typically undergo rapid non-radiative Auger recombination (hundreds of picoseconds) due to strong electron–hole wavefunction overlap. Strategies such as tuning QD size, shape, and surface chemistry have shown promise in extending multiexciton lifetimes. A detailed understanding of how QD structural parameters influence these lifetimes is essential for advancing multiexciton-based QD applications.

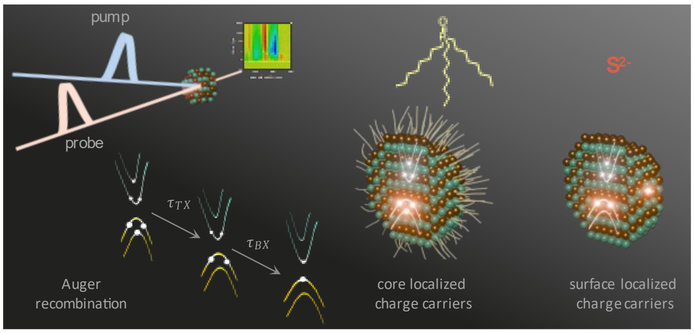

Figure 1. Illustration of TA spectroscopy, Auger recombination model, and surface trapping of carriers influenced by surface ligands.

In this study, we demonstrate the use of excitation intensity dependent broadband transient absorption spectroscopy to identify multiexciton species via their distinct spectral signatures. This approach provides detailed insights into multiexciton relaxation dynamics and enables determination of multiexciton binding energies. Excitation intensity-dependent datasets are globally analyzed using a Markov Chain Monte Carlo (MCMC) based target analysis, allowing simultaneous modeling of spectrally resolved data across varying excitation intensities. Using this approach, multiexcitons up to the tetraexciton (i.e., four bound excitons) are detected. As a target material, we investigate colloidal CdSe QDs with different sizes and surface functionalizations: trioctylphosphine oxide (TOPO) and sulfide (S^{2-}). The two surface functionalizations allow a comparison of weak (with TOPO) and strong (with S^{2-}) surface carrier localization effect on multiexciton properties. The analysis reveals that multiexciton lifetimes are primarily governed by carrier wavefunction overlap. Increased QD size and surface-induced carrier localization (as in S^{2-}-capped QDs) reduce wavefunction overlap, resulting in extended multiexciton lifetimes and diminished multiexciton binding energies.

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References:

[1] R. Baruah, K. Kumar, J. Dellith, M. Wächtler, ChemRxiv, **2025**; doi:10.26434/chemrxiv-2025-zd0zm (just accepted by PCCP)

Exciton Migration in Single Copper Phthalocyanine Nanofibers by Femtosecond Pump-Probe Microspectroscopy

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Phthalocyanines (Pc) have excellent environmental and thermal stability and stable semiconducting properties under ambient conditions. Since a fundamental understanding of the excited-state dynamics in the solid phase provides essential application information, numerous ultrafast spectroscopic studies on the exciton relaxation processes in colloidal particles and thin films of various Pc materials have been reported. These results were obtained as an ensemble average because the colloidal particles and vapor-deposited thin films included various sizes and shapes of Pc nanostructures. However, since the excited-state relaxation process will strongly depend on size or shape distributions, ultrafast spectroscopy at a single nanoparticle level is indispensable. This study investigated the exciton diffusion dynamics in individual copper phthalocyanine single-crystalline nanofibers (CuPc-NFs) by a home-built femtosecond pump and probe single-nanoparticle spectroscopic system.[1]

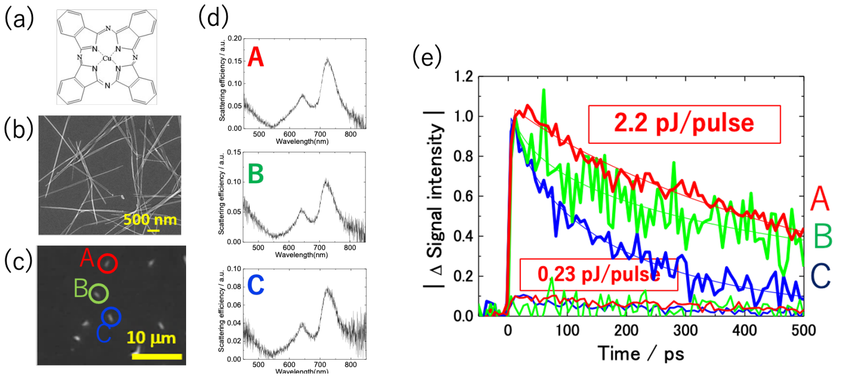

Figure 1. a) Molecular structure of CuPc. b) FE-SEM image of CuPc-NFs. c) Dark-field image of CuPc-NFs deposited on a glass coverslip. Three circles indicate measured single CuPc-NFs. d) Light-scattering spectrum of each CuPc-NF. e) Laser fluence dependence of the time profiles of the transient signal in a single CuPc-NF at two different laser fluences of 0.23 and 2.2 pJ pulse^{-1}. The pump and probe wavelengths were 397 nm and 530 nm, respectively. Solid lines were calculated curves based on the exciton-exciton bimolecular annihilation process.

The ns laser fragmentation method obtained the colloidal solution of CuPc-NFs having a width of 25±6 nm and a length of 100 to 2000 nm, as shown in Figure 1b.[2] After individual CuPc-NFs were deposited on a glass coverslip by spin-coating a drop of the 100-fold diluted colloid in ethyl acetate, we selected a single CuPc-NF (Figure 1c) and examined the light-scattering spectrum and the laser fluence dependence of the excited-state relaxation time profiles. Although the light-scattering intensity differed, the same spectral shapes assigned to the crystalline phase of β form were shown at all CuPc-NFs (Figure 1d). The time profiles of the excited-state absorption at low laser fluence were flat and independent of the nanofibers in Figure 1e. On the other hand, at high laser fluence, the fast decay due to the exciton-exciton annihilation process was observed in all CuPc-NFs. Based on the rate constant of the exciton-exciton annihilation, the exciton diffusion coefficient (D) in a 1-dimensional stack of CuPc molecules in a single nanofiber was estimated. As a result, the estimated D value was 0.0086 cm^2 s^{-1} for A, 0.049 cm^2 s^{-1} for B, and 0.096 cm^2 s^{-1} for C. Considering that the light-scattering intensity in Figure 1d will strongly correlate with the particle size, the discrepancy of the D value will originate from the nanofiber length. At the presentation, we will discuss the detailed exciton diffusion process from the viewpoint of the length, including the results of CuPc-NFs having another crystalline phase.

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References:

[1] Y. Ishibashi, T. Asahi, *J. Phys. Chem. Lett.*, **2016**, 7, 2951-2956.
[2] R. Kihara, S. Imada, T. Kawai, T. Asahi, *App. Surf. Sci.*, **2019**, 478, 532-538.

Relaxation Dynamics of Hemicyanine Dye Aggregates

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The relaxation mechanisms of the excited states of the monomer and the H-aggregate of a Hemicyanine dye diphenyl aminostyryl pyridinium (DPPy) are investigated. Its structure is shown in Fig. 1. We used time-resolved fluorescence techniques: time-correlated photon counting and frequency up-conversion to detect the emission. Density functional theory calculations were carried out on the character of the electronic states and three internal rotations. The emission quantum yield of S_1 of the monomer is very low in all solvents, indicating a high proportion of non-radiative relaxation. Basically, the relaxation of monomer S_1 can be roughly separated into five time components, and those are assigned ot fast relaxation $\tau_{v,S1}$ (<0.5 ps), solvent relaxation $\tau_{sol,S1}$ (1–2 ps), conical intersection decay $\tau_{CI,S1}$ (3–10 ps), a non-radiative relaxation $\tau_{nr,S1}$ (tens of ps), and fluorescence lifetime $\tau_{fluo,S1}$ (hundreds of ps). Two non-radiative relaxation pathways $\tau_{CI,S1}$ and $\tau_{nr,S1}$ result in extreme low emission yield. In high polar solvents, the energy barrier through $\tau_{nr,S1}$ is lowered, and quite a fraction of molecules relax via this pathway $\tau_{nr,S1}$. However, the $\tau_{CI,S1}$ pathway still predominates. While in medium to low polar solvents, the crossing barrier through $\tau_{nr,S1}$ is relatively increased, energy relaxation is dominated by the conical intersection pathway $\tau_{CI,S1}$. The H-aggregates clearly appeared in medium to low polarity solvents and exhibited an absorption band near 360 nm. They possess much superior fluorescence yield to the monomer. The emission curves of H-aggregates are composed of four time components and assigned as fast relaxation $\tau_{v,H}$ (~0.05 ps), solvent relaxation $\tau_{sol,H}$ (1–2 ps), dissociation to monomer $\tau_{dis,H}$ (30–300 ps), and fluorescence lifetime (2.5–3.5 ns). Dissociation to monomer reduces the emission efficiency of the excited state. The aggregation tends to be unstable in polar solvent. Fluorescence anisotropy measurements show that the H-aggregates consisted of roughly two monomers. Overall, H-aggregates exhibit neither conical intersection nor non-radiative relaxation pathway as in the monomer, and thus their fluorescence quantum yield and lifetime are higher. Consequently, it may produce more reactive oxygen species (ROS) compared to the monomer.

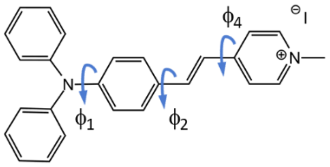

Figure 1. Structure of hemicyanine dye.

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Better Organic Synthesis with Light

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The last two decades have seen the development of many synthetic methods that utilize sensitized or direct photochemistry to facilitate organic reactions under milder conditions, typically near room temperature. These methods also open new reaction pathways that are impossible with thermal chemistry.[1] We will focus on organic reactions that can only be performed photochemically, which yield higher energy products than the starting materials and enable reactions with better predictability and overall efficiency.[2]

The first class of reactions we discuss consists of redox-neutral reactions requiring light energy input.[3,4] The ideal atom economy of these reactions and their excellent energy efficiency make these transformations ideal candidates for preparing chemicals on a larger scale. Cross-coupling reactions are among the most important organic synthesis reactions in both industry and academia. We will examine how photochemistry can enhance the performance of this class of reactions. The new concept of adaptive dynamic homogeneous catalysis (AD-HoC) utilizes light to control the redox state of catalytically active species, enabling the rapid and predictable cross-coupling of all classes of nucleophiles with halogenated arenes and heteroarenes.[5] Alternatively, reaction conditions for on-water photochemistry[6] facilitate the formation of electron-donor-acceptor complexes and their activation for cross-coupling.

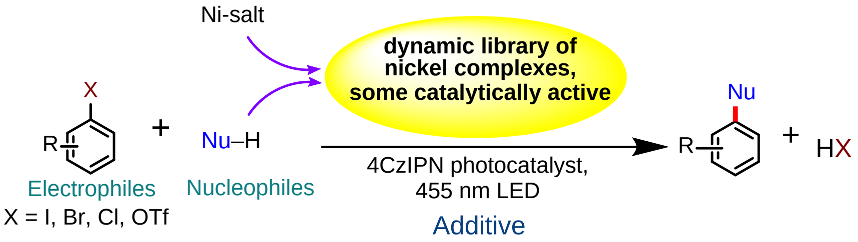

Figure 1. Fast and predictable cross-coupling with adaptive dynamic homogeneous catalysis (AD-HoC).

The examples illustrate the opportunities that arise from combining catalysis with photochemistry. Current challenges include our limited mechanistic understanding of many processes, which necessitates more detailed photophysical investigations. The future for improved catalysis is bright!

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References:

[1] Marzo, L.; Pagire, S.G.; Reiser, O.; König, B. *Angew. Chem. Int. Ed.* **2018**, *57*, 10034 – 10072.

[2] Wang, H.; Tian,Y.- M.; König, B. *Nature Rev. Chem.* **2022**, *6*, 745 – 755.

[3] Schmalzbauer, M.; Svejstrup, T.D.; Fricke, F.; Brandt, P.; Johansson, M.J.; Bergonzini, G.; König, B. *Chem* **2020**, *6*, 2658 – 2672.

[4] Ritu, D. Kolb, N. Jain, B. König, *Adv. Synth. Catal.* **2023**, *365*, 605 – 611.

[5] Ghosh, I.; Shlapakov, N.; Karl, T.A.; Düker, J.; Nikitin, M.; Burykina, J.V.; Ananikov, V.P.; König, B. *Nature* **2023**, *619*, 87-93.

[6] Tian, Y.- M.; Silva, W.; Gschwind, R.M.; König, B. *Science* **2024**, *383*, 750-756.

Photopolymerization processes in the induction of thermal reactions in the curing of composites

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Photopolymerization processes in the induction of thermal reactions represent an innovative approach to curing composites.[1] In this method, UV/vis radiation activates photoinitiators, leading to the formation of active centers that initiate a chain reaction of polymerization. The exothermic heat generated in the early phase of the reaction supports further curing, increasing the depth of penetration and homogeneity of the structure. The selection of photoinitiators with the right absorption spectrum, thermal stability and efficient active centers generation is crucial for precise control of the reaction rate and final material properties.[2] The technology finds applications in the production of protective coatings, structural components, microfabrication and 3D printing.

This work presents new systems for initiating photopolymerization processes that have been used to produce polymeric materials including composites using acrylic and epoxy monomers by VPP.

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References:

[1] G. Malucelli, A. Mariani, *ACS Omega* **2024**, *9*, 25448–25456.

[2] A. Jagtap, A. More, *Polym. Bull* **2022**, 79, 8057–8091

A reversible, long-lived photoacid for biological pH-triggers: A time-resolved X-ray study of i-motif DNA folding after a pH-jump

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To directly probe DNA conformational dynamics in real time, it is essential to employ a method that can rapidly and controllably alter the environmental conditions driving these transitions. A key factor influencing the formation of i–motifs and G–quadruplexes is pH, since protonation of cytosine residues stabilizes the i–motif, while the G–quadruplex responds to availability of cations and local charge distributions. However, conventional pH modulation techniques, such as chemical titration or buffer exchange, often lack the temporal precision needed to capture rapid structural rearrangements. To overcome this limitation, a merocyanine photoacid [1], which undergoes photoactivation in the visible spectrum, is used to induce a rapid and reversible pH drop (Fig. 1). This approach provides an ideal tool for triggering and studying the dissociation of dsDNA into these noncanonical structures with high temporal control. Here, the pH–dependent dissociation of dsDNA, folding of the i–motif [2], and structural response of the G–quadruplex is investigated by probing the conformational dynamics on the microsecond to millisecond time scales using time-resolved x-ray solution scattering (TRXSS) (Fig. 1). The structural dynamics [3] in response to the rapid pH change initiated by the merocyanine photoacid provide structural insight into the formation of noncanonical DNA structures and represent the first pH-jump TRXSS experiment using a reversible merocyanine photoacid.

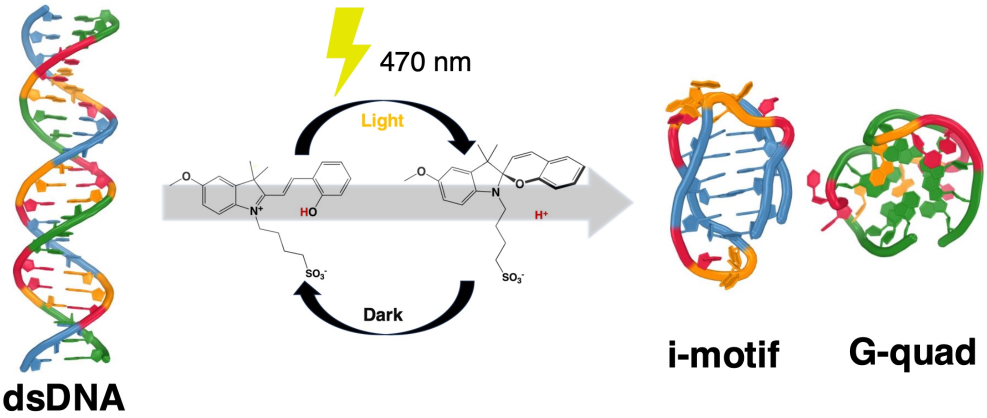

Figure 1 Merocyanine photoacid used to switch to drive dsDNA to folded ssDNA structures. The photoacid releases the proton upon exposure to visible light and is fully reversible when exposed to the dark. The proton release occurs within nanoseconds and stability of the conjugate base lasts > seconds. dsDNA will dissociate into i–motif and G–quadruplex structures upon lowering of the pH < 5.2 with a photoacid. We demonstrated the reversibility of the photoacid and structural transition within a 5 min dark time.

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Acknowledgement: We thank Arnold Chan for initial pH-jump measurements of i-motif. The merocyanine photoacid was synthesized at Northwestern University courtesy of Prof. Karl Scheidt's research group. The TRXSS experiments were performed at the ID09 beamline of the ESRF. We appreciate the support from Matteo Levantino at ESRF for his help and support in collecting the X–ray solution scattering data.

References:

[1] L. Wimberger, et al. & J.E. Large, *JACS* **2021**,143, 20758–20768.
[2] A.M. Chan et al., & L.X. Chen, *JACS*, **2024**, *146*, 33743-33752.
[3] A.K. Nijhawan et al., & K.L. Kohlstedt, *J. Phys. Chem. B*, **2021**, *125*, 12401-12412.

Excited Radical Ions in Organic Photocatalysis: A Photophysical Perspective

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The use of excited organic radical ions as photocatalysts for thermodynamically challenging synthetic reactions has been a topic of intense research in the past few years. Since the first report on the use of the excited radical anion of a perylene diimide derivative ($^{2}\mathrm{PDI}^{\bullet-*}$) as a photocatalyst for the reduction of aryl halides in what came to be known as consecutive photoinduced electron transfer (conPET) mechanism,[1] many questions have been raised as the mechanism is constantly under scrutiny. This process is based on the excitation of PDI in the presence of a sacrificial electron donor, reductively quenching $^{1}\mathrm{PDI}^{*}$ to generate its radical anion form. From there, a second photon excites $^{2}\mathrm{PDI}^{\bullet-}$ and produces the species that is claimed to be the photocatalyst in the synthetic reaction. One of the main points of scrutiny in this mechanism is the very short lifetime of the D_1 excited state of $^{2}\mathrm{PDI}^{\bullet-*}$ (145 ps),[2] making it highly unlikely for this species to engage in any diffusion-driven electron transfer process with a substrate. Previous studies have attributed the observed photocatalytic activity to photoproducts of the decomposition of $^{2}\mathrm{PDI}^{\bullet-*}$,[2] or even considered a pre-association between the excited radical anion and the substrate,[3] but a full description of the mechanism involving this elusive species is still missing. Our photophysical approach to this problem consists in photochemically generating the radical ion species and later probing its excited state properties via ultrafast optical absorption spectroscopy by using a double pump excitation strategy. Starting from a neutral ground state PDI derivative (Figure 1, left panel), we take an unusual pathway for the generation of the elusive $^{2}\mathrm{PDI}^{\bullet-}$ in high concentration. We first induce the population of the excited triplet state of the dye ($^{3}\mathrm{PDI}^{*}$) by using halogenated electron donors (D1),[4] resulting in a high yield of $^{3}\mathrm{PDI}^{*}$ that peaks at 20 ns with characteristic absorption bands at 470, 505, and 555 nm (Figure 1, right panel).

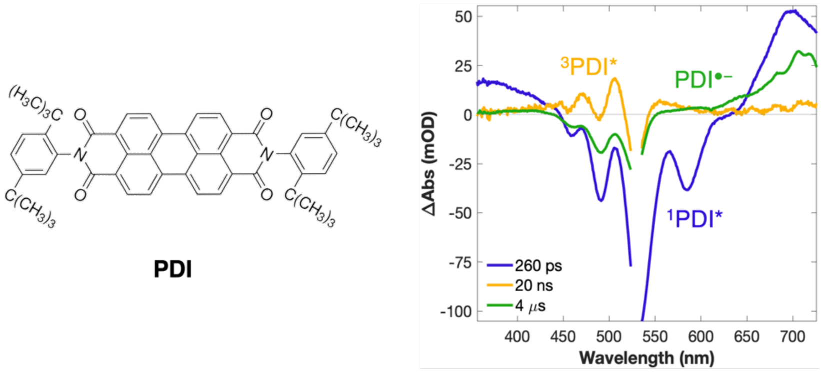

Figure 1. Chemical structure of the PDI derivative used in this work (left) and transient absorption spectra at selected delay times. λ_{pump} = 532 nm

Once populated, $^{3}\mathrm{PDI}^{*}$ can be efficiently quenched by a second electron donor (D2) to yield the free $^{2}\mathrm{PDI}^{\bullet-}$ species whose maximal concentration is observed 4 μs after excitation as evidenced by its intense absorption features above 600 nm (Figure 2, right panel). From there, a second actinic pump can be used to selectively populate the excited state of the photogenerated radical anion, probing its ultrafast dynamics in the presence and absence of aryl halide substrates, therefore shining some light on the photocatalytic mechanism for the full photochemical scheme.

References:

[1] I. Ghosh, T. Ghosh, J.I. Bardagi, B. Konig., *Science* **2014**, *346*, 725-728.
[2] M. Marchini, A. Gualandi, L. Mengozzi, P. Franchi, M. Lucarini, P.G. Cozzi, V. Balzani, P. Ceroni. *Phys Chem Chem Phys* **2018**, *20*, 8071-8076.
[3] B. Pfund, D. Gejsnaes-Schaad, B. Lazarevski, O.S. Wenger. *Nat Commun* **2024**, *15*, 4738.
[4] O. Nicolet, E. Vauthey. *J. Phys. Chem. A* **2003**, *107*, 5894.

Ultrafast Optical and Vibrational Studies of Photoinduced Mixed-Valence Ru polypyridines

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In natural photosynthesis, visible-light absorption triggers the formation of a charge-separated state that contains an oxidized special pair $[P_A{\cdot}P_B]^{\bullet+}$ with a mixed-valence configuration, and a reduced chlorophyll counterpart $Chl_A^{\bullet-}$. This is, formally, a photoinduced mixed-valence (PI-MV) system, where charge-transfer counterparts, absent in the traditionally studied ground-state analogs, play a key role. The "excited-state Creutz-Taube ion" $\{Ru^{II}(\mu pz^{\bullet-})Ru^{III}\}$[1] and other PI-MV systems based on MLCT or LMCT excited states have recently emerged as the simplest models for excited-state elector transfer. The energy and shape of photoinduced inter-valence charge transfer (PI-IVCT) bands monitored with ultrafast optical transient absorption spectroscopy (fsTAS) provide critical information about electronic coupling, reorganization energies and energy barriers for the intramolecular electron transfer in these systems. However, electron delocalization is a matter of the relative rates of thermal electron transfer versus solvent motions and/or intramolecular vibrations, and therefore ultrafast vibrational spectroscopy (fsIR) is the ultimate tool to determine the excited-state electron transfer timescales. In this presentation, I will show how PI-MV interactions determine excited-state reactivity towards short-range energy transfer and electron transfer,[2] similar like in the photosynthetic reaction center. Next, I will address the fine tuning of PI-MV interactions using different substitutions in bimetallic complexes,[3] reaching a fully delocalized Class III behavior despite structural asymmetry (Fig. 1).[4] Finally, I will communicate the first dynamic observation of a Class II-III behavior.

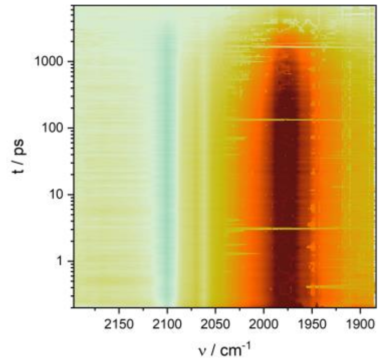

Figure 1. fsIR spectroscopy of $[Ru(tpy)(bpy)(CN)Ru(py)_4(DMAP)]^{3+}$ under 480 nm excitation, in acetonitrile at room temperature. The broad, intense and down-shifted C≡N stretching signal indicates a Class III behavior.

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References:

[1] G. E. Pieslinger, I. Ramírez-Wierzbicki, A. Cadranel, *Angew. Chem. Int. Ed.* **2022**, *61*, e202211747.
[2] P. S. Oviedo, L. M. Baraldo, A. Cadranel, *Proc. Natl. Acad. Sci.* **2021**, *118*, e2018521118.
[3] I. Ramírez-Wierzbicki, L. Sanchez Merlinsky, G. E. Pieslinger, S. Domínguez, L. D. Slep, L. M. Baraldo, A. Cadranel, *Chem. Eur. J.* **2024**, e202402700.
[4] T. Ullrich, I. Ramírez-Wierzbicki, L. D. Slep, A. Cadranel, *Angew. Chem. Int. Ed.* **2025**, e202422633.

Triplet-Triplet Annihilation Photon Upconversion: Fundamental Challenges for TTA-UC in Confinement and into the UV

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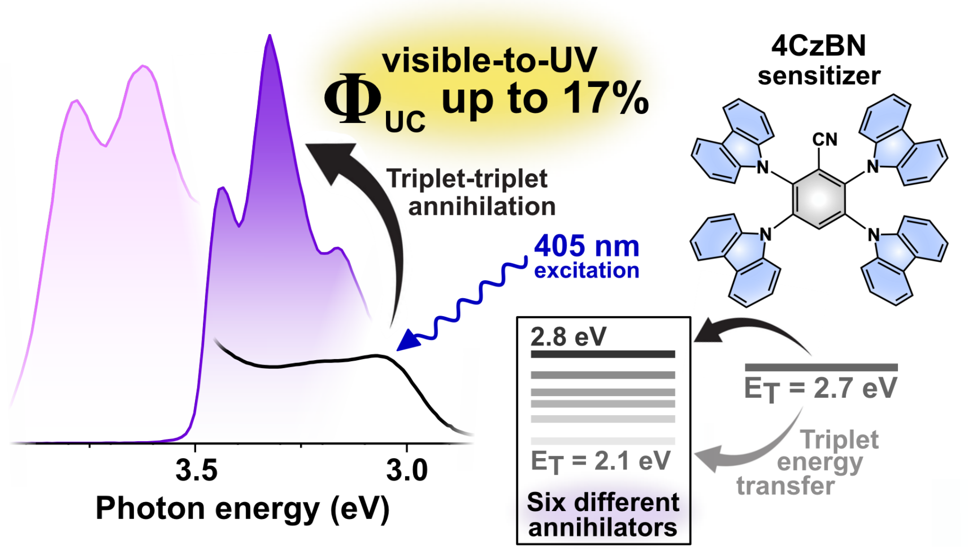
Triplet-triplet annihilation photon upconversion (TTA-UC) is a process in which triplet excitons combine to form emissive singlets. While high TTA-UC quantum yields have been reported for freely diffusing systems in the visible region, there are only a few examples of visible-to-UV transformations in which the quantum yield reaches 10% and upconversion in solid-state materials or under confinement is still poorly understood. In this presentation I will discuss recent progress in the field along with a few examples from our lab addressing the challenges with upconversion in the solid state, under confinement, and into the UV.



TOC Figure from Olesund, A.; Johnsson, J.; Edhborg, F.; Ghasemi, S.; Moth-Poulsen, K.; Albinsson, B., Approaching the Spin-Statistical Limit in Visible-to-Ultraviolet Photon Upconversion. *J Am Chem Soc* **2022**, *144*, 3706-3716.

Intervalance (IVCT) and Symmetry Breaking Charge Separation (SBCS) in Far-Red Capturing Chromophore Dimers

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Intervalence charge transfer (IVCT),[1-3] is a process observed in chromophore dimers comprised of two identical redox centers differing in their oxidation states by one unit. The odd electron shuffles between the two chromophore entities, resulting in an IVCT transition band in the near-IR region. Studying such processes helps us understand the fundamentals of electron transfer events in complex molecular and biomolecular systems. Conversely, symmetry breaking charge separation (SBCS) is a phenomenon where appropriate symmetrically disposed chromophore dimers create a charge-separated state (CSS) upon light illumination with the hole and electron residing on different chromophores, i.e., Ch_0-Ch_0 + $h\nu \rightarrow Ch^{+}$-Ch^{-}.[4-6] In contrast to the typical donor-acceptor (D-A) systems where 500 mV or more energy is lost to form D^{+}/A^{-} from the singlet excited state, the small energy loss (<100 mV) in SBCS leads towards maximum utilization of capture solar light.[4-6] Consequently, studying this phenomenon in synthetic inorganic and organic molecular systems holds great promise for constructing next-generation artificial solar energy conversion devices that perform at higher efficiencies.

Spectroelectrochemistry,[7], where applying a constant potential corresponding to either the oxidation or the reduction process of a compound of interest covering visible-IR regions in a thin-layer optical cell, is an essential technique in studying IVCT and SBCS. Often, such data is utilized to characterize the IVCT and SBCT products in transient absorption of spectral studies and to seek kinetic information of different events. The present talk focuses on our recent findings on these two processes in molecular dimers of near-infrared capturing chromophores, such as π-extended BF_2-chelated dipyrromethene[6] and phthalocyanines.[8] The design principles to witness IVCT and SBCS and the key outcomes will be summarized.

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References:

(1) Sun, D.; Rosokha, V. S.; Kochi, J. K. J. Am. Chem. Soc. ***2004****,126, 1388-1401.*

(2) *Ramirez-Wierzbicki, I.; Cotic, A.; Cadranel, A. ChemPhysChem.* ***2022***, 23, e202200384

(3) Khan, F.; Jang, Y.; Patil, Y.; Misra, R.; D'Souza, F. *Angew. Chem. Int. Ed*. **2021**, 60, 20518 – 20527.

(4) Whited, M. T.; Patel, N. M.; Roberts, S. T.; Allen, K.; Djurovinch, P. I.; Bradforth, S. E.; Thompson, M. E. *Chem. Commun*. **2012**, 48, 284–286.

(5) Hong, Y.; Schlosser, F.; Kim, W.; Wurthner, F.; Kim, D. *J. Am. Chem. Soc*. **2022**, *144*, 15539−15548.

(6) Yahagh, A.; Kaswan, R. R.; Kazemi, S.; Karr, P. A.; D'Souza, F. *Chem. Sci*. **2024**, *15*, 906–913.

(7) Lozeman, J. J. A.; Fuhrer, P.; Olthuis, W.; Odijk, M. *Analyst*, **2020**, *145,* 2482-2509.

(8) Kaswan, R.F.; Molina, D., Ferrer-López, L.; Ortiz, J.; Karr, P.A.; Sastre-Santos. Á.; D'Souza, F. *Angew. Chem., Int. Ed. Engl.* **2025**, *e202502516i.*

Photocatalytic activity of Bi_2O_3- based materials for ammonia production

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Ammonia (NH_3) is an essential compound with widespread applications, primarily as a key ingredient in agricultural fertilizers and pharmaceutical products.[1,2] At the present, the Haber–Bosch (H-B) process, developed in 1909, remains the predominant industrial method for NH_3 synthesis; the severe requirements of H-B and the considerable CO_2 emissions, foster the search for sustainable production methods. Among the various approaches explored, photocatalysis[3–4] has emerged as a promising methology, leveraging solar energy to drive the conversion of nitrogen (N_2) into ammonia under ambient conditions. In these last years, Bismuth-based materials have attracted particular interest due to their suitable electronic structures, efficient charge carrier separation, and responsiveness to visible light: Figure 1a-b.[9]

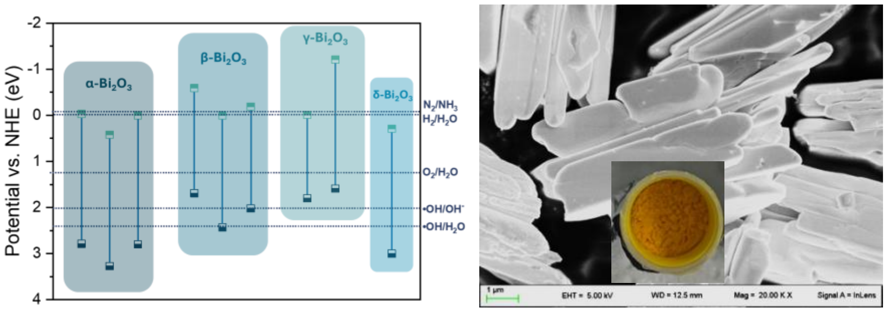

Figure 1. Energy diagram for Bi_2O_3 nanostructured materials; SEM images of Bi_2O_3 and pitcher of the powders

In this study, we focus on α- and β-Bi_2O_3 as a photocatalysts for ammonia production, aiming to optimize the reaction conditions and enhance NH_3 yield. The photocatalysts have been fully characterized and the ammonia evolution rates determined in different experimental conditions. Data will be presented to relate the material properties and the ammonia production rates, in other to rationalize the role of photocatalyst electronic and optical behavior for nitrogen photofixation.

References:

[1] S. Zhang, Y. Zhao, R. Shi, G.I.N. Waterhouse, T. Zhang, EnergyChem, **2019**, 1(2), 100013
[2] K. Ithisuphalap, H. Zhang, L. Guo, Q. Yang, H. Yang, G. Wu, Small Methods **2019**, 3, 1800352.
[2] L. Hollevoet, M. De Ras, M. Roeffaers, J. Hofkens, J. A. Martens, ACS Energy Letters **2020** 5 (4), 1124-1127
[3] Valentini F, Grigoras AM, Vaccaro L, Latterini L., Carbon Energy. **2024**;6(12):e545.
[4] Grigoras AM, Valentini F, Latterini L, Vaccaro L., Green Energy & Environment. **2025**;10(4), 733-755

Engineering Reversible Photoacid Systems: Structure-Function Relationships and Stability-Enhancing Strategies for Substituted MCHs

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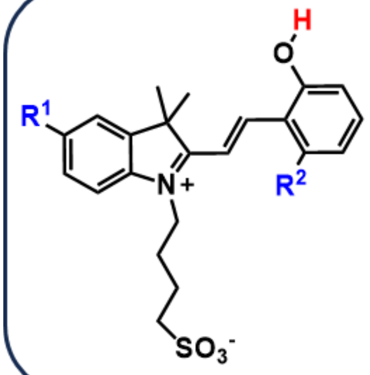
The development of reversible photoacids with enhanced chemical stability in aqueous environments is essential for their application in light-controlled pH-switching systems.[1,2] This work focuses on the synthesis and screening of library (Fig. 1) of diversely substituted merocyanine photoacids (MCHs) to identify structural motifs that optimize three critical parameters: photoacidity (Π), quantum yield (Φ), and stability towards hydrolysis ($k_{obs,hyd}$). Recent studies indicate that while Π typically spans ~3-4 pK units,[3] both Φ and $k_{obs,hyd}$ are highly sensitive to subtle molecular modifications.



Entry	R_1	R_2
1	H	H
2	OMe	H
3	H	OMe
4	OMe	OMe

Figure 1. Library of substituted merocyanines **1**-**4** investigated in this study.

To address these challenges, we propose three strategic structural modifications: (1) functionalizing the indolenine moiety with electron-donating groups (*i.e.*, -OMe group) to simultaneously enhance p*K*a values and hydrolytic stability;[4] (2) introducing electron-donating groups (*i.e.*, -OMe group) on the phenol ring to increase water compatibility without perturbing photochemical behavior; (3) keeping butyl-1-sulfonate groups to improve solubility and modulate zwitterionic character. [5-6] These approaches have been systematically evaluated using a suite of experimental and theoretical techniques such as NMR, UV-Vis titrations, and photochemical pH-jump analyses. The findings have deepened our understanding of structure-property relationships in MCHs and advance the design of robust, water-compatible photoacid systems.

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References:

[1] C. Berton, D. M. Busiello, S. Zamuner, E. Solari, R. Scopelliti, F. Fadaei-Tirani, K. Severin, C. Pezzato, *Chem. Sci*., **2020**, *11*, 8457.

[2] X. Dai, C. Berton, D. J. Kim, C. Pezzato, *Chem. Sci.,* **2024**, *15*, 19745.

[3] L. Wimberger, S. K. K. Prasad, M. D. Peeks, J. Andréasson, T. W. Schmidt, J. E. Beves, *J. Am. Chem. Soc.* **2021**, *49*, 20758.

[4] C. Berton, C. Pezzato, *Eur. J. Org. Chem*. **2023**, *26*, e202300070.

[5] C. Berton, D. M. Busiello, S. Zamuner, R. Scopelliti, F. Fadaei-Tirani, K. Severin, C. Pezzato, *Angew. Chem. Int. Ed.* **2021**, *60*, 21737.

[6] L. Wimberger, J. Andréasson, J. E. Beves*, Chem. Commun*., **2022**, *58*, 5610.

Energy and electron transfer in sensitization for photochemical upconversion

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Photochemical upconversion, also known as triplet-triplet annihilation upconversion (TTA upconversion), has great potential in solar energy conversion, anti-counterfeiting, displays and other applications. TTA upconversion generally involves a two-component system consisting of a triplet sensitizer (donor) and an annihilator (acceptor). Fig. 1 shows the simplified energy diagram of a TTA upconversion system. The sensitizer is in charge of capturing lower-energy photons, converting to its triplet state, and delivering the triplet energy to the annihilator through triplet energy transfer. Two triplet excited annihilators undergo TTA, generating a ground-state annihilator and a singlet excited one of higher-energy that emits the upconverted delayed fluorescence. Various sensitizers, including organic and inorganic compounds have been developed to improve the excitation wavelength range, anti-Stokes shift and efficiency of TTA systems.[1] In our work, several unconventional triplet energy transfers between sensitizers and annihilators were investigated. Efficient thermally activated triplet energy transfer has been established for TTA upconversion, overcoming a significant energy barrier between sensitizer triplets and annihilator triplets. Furthermore, the subtle interplay between nanocrystals sensitizers and annihilators were studied by means of time-resolved spectroscopies.[2-3] These studies provide a rational design for triplet energy extraction from different types of sensitizers for efficient photochemical upconversion.

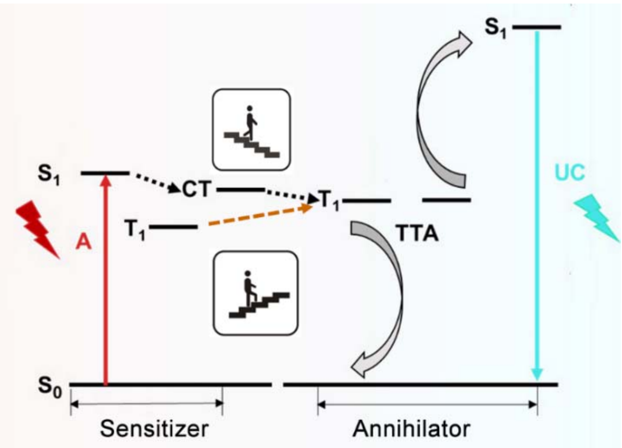

Figure 1. Schematic energy diagram of sensitization in triplet-triplet annihilation upconversion

Funding: National Natural Science Foundation of China (22273117, 22273110 and 22090012)

References:

[1] N. Yanai, N. Kimizuka *Acc. Chem. Res.* **2017**, *50*, 2487.
[2] G. W. Luo, Y. P. Liu, Y. Zeng, T. J. Yu, J. P. Chen, R. Hu, G. Q. Yang, Y. Li *J. Mater. Chem. C*. **2022**, *10*, 8596.
[3] P. F. Niu, G. W. Luo, T. J. Yu, J. P. Chen, R. Hu, G. Q. Yang, Y. Zeng, Y. Li *J. Mater. Chem. C*. **2023**, *11*, 13213.

Photogenerated quartet states for molecular spintronics

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In the presence of a stable radical, such as a nitroxide, the triplet state of an organic chromophore may be generated efficiently upon photoexcitation by a spin-allowed process referred to as enhanced intersystem crossing (EISC). If the exchange interaction J_{TR} between the chromophore triplet state and the radical doublet state is large, compared to other electronic or magnetic interactions active within the system, quartet states may be formed by triplet–doublet spin mixing (cf. Fig. 1).

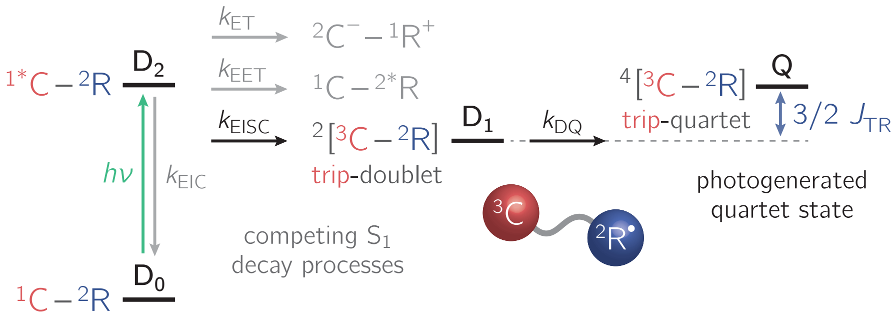

Figure 1. Simplified photoscheme of a chromophore–radical dyad eventually leading to the formation of photogenerated quartet states. The numeric superscripts indicate the spin multiplicity. Abbreviations: C – chromophore; R – radical; Q – quartet state; D – doublet state; EIC – enhanced internal conversion; ET – electron transfer; EET – excitation energy transfer; EISC – enhanced intersystem crossing.

Our recent work, on a number of different chromophore–radical combinations, revealed that such photogenerated quartet states may exhibit the right optical and magnetic properties to be suitable for a range of applications in the emerging field of molecular spintronics, such as optoelectronic and quantum sensing devices.[1-9] They can be initialised by light in a pure initial spin state, are long-lived, and exhibit spin coherence times that are much longer than typical pulse microwave-driven gate operation times, even at moderate temperatures (80 K).

Combining complementary spectroscopic approaches with insight from *ab-initio* calculations, our studies are focussed at exploring how to control the optical and spin properties of the quartet states by rational design. In this contribution, we aim to shed light on the factors influencing the rate and yield of triplet state formation, the magnitude of J_{TR}, as well as the quartet state spin coherence times.

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References:

[1] T. Quintes, M. Mayländer, S. Richert, *Nat. Rev. Chem.* **2023**, *7*, 75.
[2] M. Mayländer, S. Chen, E. R. Lorenzo, M. R. Wasielewski, S. Richert, *J. Am. Chem. Soc.* **2021**, *143*, 7050.
[3] M. Mayländer, O. Nolden, M. Franz, S. Chen, L. Bancroft, Y. Qiu, M.R. Wasielewski, P. Gilch, S. Richert, *Chem. Sci.* **2022**, *13*, 6732.
[4] M. Mayländer, T. Quintes, M. Franz, X. Allonas, A. Vargas Jentzsch, S. Richert, *Chem. Sci.* **2023**, *14*, 5361.
[5] M. Mayländer, P. Thielert, T. Quintes, A. Vargas Jentzsch, S. Richert, *J. Am. Chem. Soc.* **2023**, *145*, 14064.
[6] M. Mayländer, K. Kopp, O. Nolden, M. Franz, P. Thielert, A. Vargas Jentzsch, P. Gilch, O. Schiemann, S. Richert, *Chem. Sci.* **2023**, *14*, 10727.
[7] P. Thielert, M. El Bitar Nehme, M. Mayländer, M. Franz, S. Zimmermann, F. Fisch, P. Gilch, A. Vargas Jentzsch, M. Rickhaus, S. Richert, *Chem. Sci.* **2024**, *15*, 7515.
[8] M. Mayländer, I. V. Khariushin, A. Vargas Jentzsch, S. Richert, *J. Phys. Chem. Lett.* **2024**, *15*, 5935.
[9] I. V. Khariushin, P. Thielert, E. Zöllner, M. Mayländer, T. Quintes, S. Richert, A. Vargas Jentzsch *Nat. Chem.* **2025**, https://doi.org/10.1038/s41557-024-01716-5.

Organic semiconductor nanoparticles in CO_2 photoconversion: the need for efficient charge carrier generation and transfer

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Photocatalytic CO_2 reduction, powered by abundant renewable solar energy, could facilitate the transition to a carbon-neutral future. It could mitigate the intermittency of solar energy by generating storable solar fuels, which in turn could seamlessly integrate with existing energy conversion and distribution systems.

Developing efficient photocatalysts for solar-to-fuel energy conversion requires a deep understanding of photophysical processes occurring in them upon photoexcitation, such as free charge carrier generation and further charge/energy transfer[1]. In this study, we investigated charge carrier dynamics of organic semiconductor nanoparticles (NPs) composed of donor-acceptor blends – specifically, PM6:$PC_{71}BM$, PM6:Y6, and PCE10:ITIC – functionalized with noble metal cocatalysts (Ag or Au), which were employed in visible-light-driven CO_2 conversion[2].

Using time-resolved photoluminescence (TRPL), we showed that the metal cocatalysts and a sacrificial electron donor facilitate exciton dissociation in the organic NPs. Additionally, employing transient absorption (TA) and photoinduced absorption (PIA) spectroscopies, we rationalized the observed selectivity of the developed NPs towards particular CO_2 conversion products and proposed plausible free charge carriers generation and extraction mechanisms. The yield of CO_2 reduction reaction products appears to depend on the amount of photogenerated charge carriers which accumulate at the surface of the metal cocatalysts and are able to drive the reaction. Therefore, improving the efficiency of charge transfer from the organic NPs to the metal cocatalysts is likely essential for advancing the photocatalytic activity of the developed NPs in CO_2 conversion.

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References:

[1] J. Kosco, S. Gonzalez-Carrero, C. T. Howells, T. Fei, Y. Dong, R. Sougrat, G. T. Harrison, Y. Firdaus, R. Sheelamanthula, B. Purushothaman, F. Moruzzi, W. Xu, L. Zhao, A. Basu, S. De Wolf, T. D. Anthopoulos, J. R. Durrant, I. McCulloch, *Nature Energy*. **2022**, *7*, 340–351.

[2] M. Ferree, J. Kosco, N. Alshehri, L. Zhao, C. S. P. De Castro, C. Petoukhoff, I. McCulloch, M. Heeney, F. Laquai, *Sustainable Energy Fuels*. **2024**, *8*, 2423-2430.

Archaerhodopsin-3: An Ideal Template for Fluorescent Retinal Proteins

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Archaerhodopsin-3 (AR-3) is a light-driven transmembrane proton pump found in *Halorubrum sodomense*, that has emerged as an interesting platform for optogenetics [1], since the wild-type (wt) form and a large variety of mutants [2] display good fluorescence levels, depending on the cellular transmembrane voltage. Multiple mutants were reported over the years, with fluorescence quantum yields (FQY) reaching up to 1.2%, in the best cases, which is still low as compared to the most fluorescent natural neorhodopsin (NeoR) [3]. Experimental and theoretical studies aiming at a rational understanding of the mutation-induced ≈100-fold increase of FQY, as compared to wt AR-3, were disclosed recently for the Quasar and Archon families [4,5]. In the present contribution, we focus on the double mutant DETC and the quintuple mutant Arch-5 [2, 6]. A combination of different spectroscopic techniques (fluorescence, transient absorption and Raman scattering), either steady-state or with time resolution down to the 50 fs, allows us to establish that the long-lived fluorescence in the mutant comes from a one-photon excitation process, unlike wt AR-3. Both all-*trans/*15-*anti* and 13-*cis/*15-*syn* isomers of the protonated Schiff base retinal (PSBR) cation contribute to the fluorescence in the mutants with slightly different excited state lifetimes (ESL). The temperature-dependence of the ESL's allows us to determine the exc. state barrier height, which prevents photo-isomerisation. Indeed, as compared to wt AR-3, the isomerization QY is found to be > 15 times smaller for DETC, and close to zero for Arch-5 [6].

In a recent quantum chemistry treatment, some us showed that the extended ESLs of AR-3 mutants and of NeoR are due to unusual properties in the electronic character of the first excited state (diradical instead of charge transfer), which give rise to the formation of an energy barrier for increasing $C_{13}=C_{14}$ dihedral angle [5]. In this contribution, we will show that the same electronic properties and unusual dynamic proton re-localisation are found for wt AR-3 as well, but without the existence of an excited state barrier [6]. Indeed, our experiments show that the photo-isomerisation occurs on a 300-fs time scale with vibrational coherences surviving in the photo-products. As the simulations show, the latter are due to excited state wavepackets along the C13-methyl and C14-H wag motions, the phase of which controls the outcome of the reaction, productive 13-*cis* isomerization vs. non-productive all-*trans* backreaction [6].

In summary, we will present new fundamental results, including the identification of D95 and D222 and main counter ion. The exceptional electronic structure of the PSBR in AR-3, makes this protein an ideal template for further development of improved rhodopsin-based genetically encoded voltage indicators (GEVIs).

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References:
[1] J. M. Kralj et al, Nat. Methods, **2011**, 9, 90–95.
[2] R. Scott McIsaac et al PNAS, **2014**, 111, 36, 13034-13039.
[3] M. Broser et al., Nat. Commun., **2020**, 11, 5682.
[4] A. Silapetere et al., Nat. Commun., **2022**, 13, 5501.
[5] L. Barneschi et al, Nat. Commun., **2022**, 13, 6432.
[6] K. Herasymenko et al., Chem. Sci, **2025**, 16, 761-774.

Nanomolar Affinity Supramolecular Photoswitching Systems

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Host-guest pairs offer attractive noncovalent binding motifs for constructing diversified supramolecular systems (e.g., rotaxanes), molecular machines, and self-assembled materials. In recent years, our research group has been interested in the design and development of water-soluble photoresponsive host-guest binding pairs, envisioning potential applications in biology and materials science.[1–6] We have developed and characterized photoswitchable dithienylethene (DTE) – cucurbit[*n*]uril (CBn) supramolecular systems with sub-picomolar affinities that can be exploited for drug delivery (Fig. 1).[1,3] This remarkable affinity can be modulated with light stimulation owing to the exceptional selectivity ($K_{\mathrm{closed}}/K_{\mathrm{open}}$ up to 10000-fold) displayed by CB8 towards the closed DTE isomers. In this communication, results from our recent work on the binding kinetics and thermodynamics and of the photoswitching ability of CB8:DTE host-guest systems will be presented, to provide important hints towards the design of novel host-guest pairs with photomodulated binding stability and dynamics.

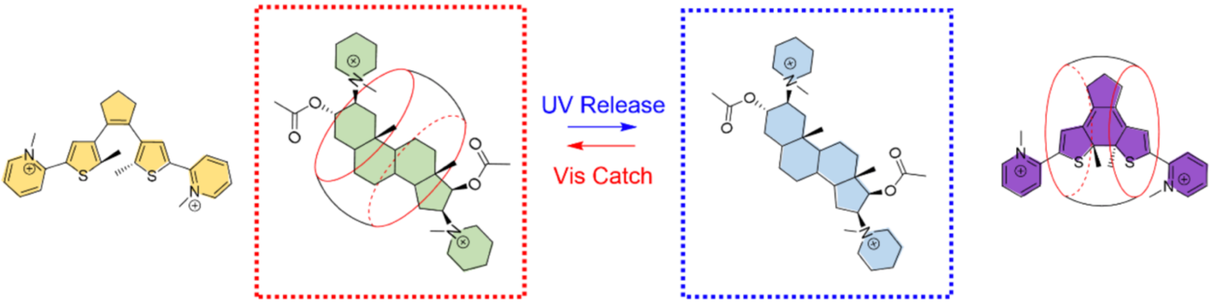

Figure 1. Light-controlled binding and release of a steroidal drug from a cucurbituril receptor using a DTE as a competitor with photocontrolled affinity.

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References:

[1] P. Ferreira, B. Ventura, A. Barbieri, J. P. Da Silva, C. A. T. Laia, A. J. Parola, N. Basílio, *Chem. Eur. J.*, **2019**, *25*, 3477

[2] M. Colaço, P. Máximo, A. J. Parola, N. Basílio, *Chem. Eur. J.*, **2021**, *27*, 9550

[3] P. Máximo, M. Colaço, S. R. Pauleta, P. J. Costa, U. Pischel, A. J. Parola, N. Basílio, *Org. Chem. Front.*, **2022**, *9*, 4238.

[4] J. Chen-Wu, P. Máximo, P. Remón, A. J. Parola, N. Basílio, U. Pischel, *Chem. Commun.*, **2023**, *59*, 3431.

[5] M. Colaço, J. Ewert, J.-S. von Glasenapp, U. Pischel, R. Herges, N. Basílio, *J. Am. Chem. Soc.*, **2025**, *147*, 734.

[6] A. Seco, S. Yu, A. Tron, N. McClenaghan, F. Pina, N. Basílio, A. J. Parola, *Chem. Eur. J.*, **2021**, *27*, 16512.

Investigation of *ortho*-dianthrylbenzenes for Molecular Solar Thermal energy storage and release

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Aiming to develop renewable energy storage concepts to address the escalating global energy consumption, several photochromic molecules (e.g. azobenzenes, norbornadienes, etc.) are explored for Molecular Solar Thermal (MOST) energy storage applications.[1-3] Among them, anthracenes, whose potential application as Solar Thermal Fuels (STFs) was already proposed in 1909,[4] are experiencing nowadays an increasing interest towards this objective, both in solid state[5] and in solution. In particular, *ortho*-dianthrylbenzenes (first reported as photochromic molecules by Kubo and co-workers)[6] have emerged as interesting photoswitches thanks to their good optical properties and long-term energy storage.[7] In this work, the properties of these systems for a potential MOST application are presented and the possible means to achieve on-demand energy release are discussed.[8]

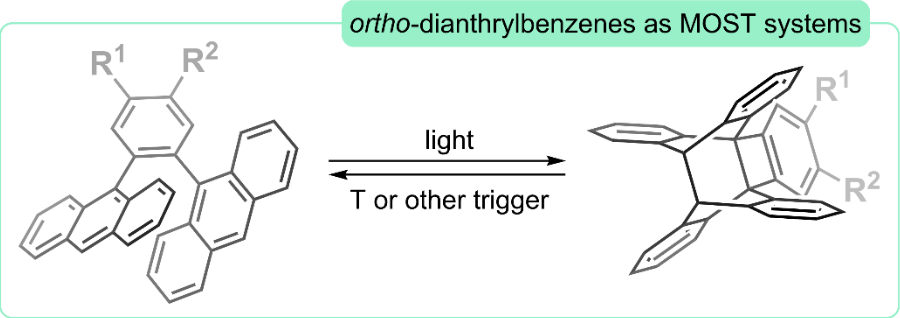

Figure 1. Structures of *ortho*-dianrthylbenzenes and their photoisomers.

Funding: European Research Council (ERC) under grant agreement CoG, PHOTHERM–101002131.

References:

[1] L. Dong, Y. Feng, L. Wang, W. Feng, *Chem. Soc. Rev.* **2018**, *47*, 7339.
[2] Z. Wang, H. Hölzel, K. Moth-Poulsen, *Chem. Soc. Rev.* **2022**, *51*, 7313.
[3] J. Usuba, G. G. D.Han, *Trends Chem.* **2023**, *5*, 577.
[4] G. Jones II, S.-H. Chiang, P. T. Xuan, *J. Photochem.* **1979**, *10*, 1.
[5] S. Chakraborty, H. P. Q. Nguyen, J. Usuba, J. Y. Choi, Z. Sun, C. Raju, G. Sigelmann, Q. Qiu, S. Cho, S. M. Tenney, K. E. Shulenberger, K. Schmidt-Rohr, J. Park, G. G. D. Han, *Chem* **2024**, *10*, 3309.
[6] T. Nishiuchi, S. Uno, Y. Hirao, T. Kubo, *J. Org. Chem.* **2016**, *81*, 2106.
[7] N. Baggi, L. M. Muhammad, Z. Liasi, J. L. Elholm, P. Baronas, E. Molins, K. V. Mikkelsen, K. Moth-Poulsen, *J. Mater. Chem. A*, **2024**, *12*, 26457.
[8] Z. Hussain, N. Baggi, L. M. Muhammad, A. Müller, A. Dreuw, K. Moth-Poulsen, O. Brummel, J. Libuda, *manuscript in preparation*.

Molecular photogearing without thermal steps

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The construction of molecular photogears that can achieve through-space transmission of the unidirectional double-bond rotary motion of light-driven molecular motors onto a remote single-bond axis is a formidable challenge in the field of artificial molecular machines.[1] In this talk, I will present two designs of such photogears that employ completely different working mechanisms,[2,3] and describe computational assessments of their efficiency based on both static quantum chemical calculations and non-adiabatic molecular dynamics simulations. While computational studies have made many important contributions to the design and characterization of molecular motors, their role in advancing molecular photogearing has been less prominent. In this sense, the results described herein are quite unique.

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References:

[1] A. Gerwien, F. Gnannt, P. Mayer, H. Dube, *Nat. Chem.* **2022**, *14*, 670.
[2] E. M. Arpa, S. Stafström, B. Durbeej, *Chem. Eur. J.* **2024**, *30*, e202303191.
[3] E. M. Arpa, B. Durbeej, To be submitted.

The electrophilic species generated during Type I photosensitized oxidation of lipid membranes play a critical yet underappreciated role in photomedicine and sun care.

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Oxidative damage to cellular membranes is strongly correlated with the efficacy of photoinduced cell death, a process central to photodynamic therapy (PDT) and ultraviolet (UV)-induced skin damage.[1-3] Direct-contact reactions between photosensitizers and membrane lipids drive the formation of lipid peroxides and reactive aldehydes, which compromise membrane integrity, induce pore formation, and propagate oxidative damage beyond initial reaction sites.[3-4] Beyond their membrane-disrupting effects, these lipid-derived electrophiles act as redox signaling molecules and disrupt autophagy, contributing to long-term cellular dysfunction.[5] In sun-exposed skin, the accumulation of such electrophiles promotes lipofuscin formation and other oxidation end-products, exacerbating photosensitivity to visible light.[6] Understanding these mechanisms is crucial for developing advanced sun protection strategies and optimizing PDT protocols. This discussion will explore novel approaches for mitigating electrophile-mediated photodamage and designing next-generation photosensitizers with enhanced therapeutic efficacy.

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] EL Bastos, FH Quina, MS Baptista. Endogenous Photosensitizers in Human Skin. Chem Rev 2023, 123 (16), 9720.

[2] WK Martins et al. Parallel damage in mitochondria and lysosomes is an efficient way to photoinduce cell death. Autophagy 2019, 15 (2), 259-279.

[3] TT Tasso et al. Photobleaching efficiency parallels the enhancement of membrane damage for porphyrazine photosensitizers. J Am Chem Soc 2019, 141, 15547.

[4] I Bacellar, et al. Photosensitized membrane permeabilization requires contact-dependent reactions between photosensitizer and lipids. J Am Chem Soc 2018, 140, 9606.

[5] S Schalka, et al. The skin redoxome. JEADV 2022, 36 (2), 181-195.

[6] PN Tonolli et al. The phototoxicity action spectra of visible light in HaCaT keratinocytes. J Photochem Photobiol B: Biology 2023, 243, 112703.

Multifunctional Organic Chromophores for Phototheranostics

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Phototheranostics is a light-based single platform that simultaneously integrates therapeutic and diagnostic capabilities, aiming to enable real-time and convenient assessment and optimization of the efficacy and safety of therapeutic regimens in precision medicine. As the core component of phototheranostics, phototheranostic agents must have two or more functionalities, i.e. targeting, sensing or imaging, superimposed therapeutic function, etc. Organic chromophores are highly attractive candidates for phototheranostic systems due to the broad spectral response, tunable energy levels and structural diversity. A common strategy in designing phototheranostic systems (shown in Figure 1) involves the integration of imaging modalities, such as photoluminescence, chemiluminescence or photoacoustic imaging motifs, with therapeutic modalities of photodynamic therapy (PDT) or photothermal therapy (PTT). In our lab, several types of organic multifunctional chromophores have been developed, such as derivatives based on triarylboron, dibenzylideneaceton and triphenylamine AIEgens, [1,2,3] some of which have been successfully applied in phototheranostic applications. In this presentation, the design strategies, photophysical properties and theragnostic performance for these organic phototheranostic agents will be discussed.

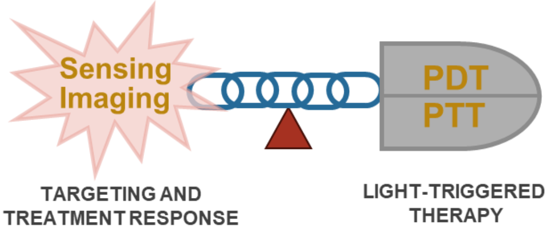

Figure 1. Schematic illustration of the phototheranostic platform.

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References:

[1] X.Y. Li, X. D. Guo, L. X. Cao, Z. Q. Xun, S. Q. Wang, S. Y. Li*, Y. Li*, and G. Q. Yang*, *Angew. Chem. Int. Ed.,* **2014**, *53*, 7809-7813.

[2] C. L. Yang; R. Hu*; F. X. Lu; X. D. Guo; S. Q. Wang, Y. Zeng*, Y. Li, and G. Q. Yang*, *Chem. Commun.* **2019**, *55*, 3801-3804.

[3] W. T. Wang, Y. Jian, Y. H. Luo, X. D. Guo, S. Q. Wang, R. Hu*, Q. X. Zhou*, Y. Zeng, G. Q.Yang*, *Mater. Lett.,* **2023**, *330*, 133285.

Protection and release of small molecules via chemiluminescent protection groups (CLPGs)

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Abstract:

In synthetic chemistry, protection and release of functional groups (**FG**) are highly important tools[1]. The protecting group (**PG**) is removed in the deprotection step and the original reactivity is recovered. A light-induced removal, either by direct absorption or by photocatalytic methods, involves the electronic excitation of the PG-FG couple and subsequent cargo release. These groups are named photoremovable (or photoreleasable) protecting groups (**PRPG**)[1].

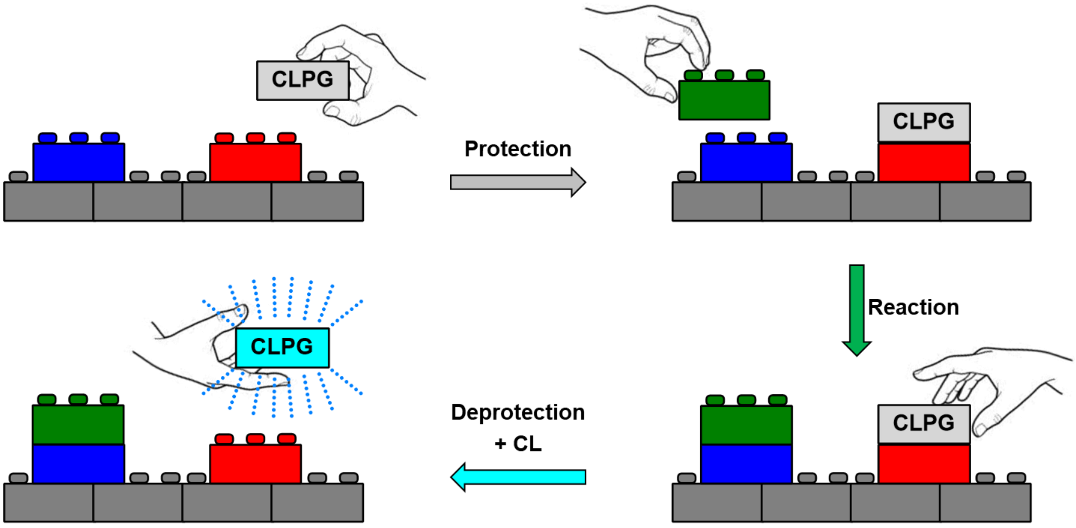

Figure 1: Simplified scheme for the concept and application of a CLPG.

However, the photon may also be emitted as a consequence of the release process, i.e., through chemiluminescence (CL), which we refer to as a chemiluminescent protecting group (**CLPG**, Fig. 1). Chemiluminescent compounds are generally small molecules activated by oxidation processes, primarily through the action of triplet oxygen, leading to the formation of unstable strained peroxides[2]. Every chemiluminescent compound, such as peroxalates, adamantane dioxetanes, and coumaranones, can be tuned into a PG[2]. The latter represent the most versatile class of compounds for chemiluminescence[3,4]. Their basic scaffold allows various synthetic modifications to alter the emission wavelength or facilitate linkage to other building blocks. Consequently, spatio-temporal detection of the release becomes possible.

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References:

[1] Kocienski, P. *Protecting Groups: Foundations of Organic Chemistry*, Thieme: Stuttgart, Germany, 3. Ed., 2005.

[2] M. Vacher, I. F. Galván, B.-W. Ding, S. Schramm, R. Berraud-Pache, P. Naumov, N. Ferré, Y.-J. Liu, I. Navizet, D. Roca-Sanjuán, W. J. Baader, R. Lindh, *Chem. Rev.* **2018**, *118*, 6927-6974.

[3] T. Lippold, A. G. Griesbeck, R. Herzhoff, M. S. Wickleder, L. Straub, N. T. Flosbach, *Photochem* **2023**, *3*, 373-389.

[4] T. Lippold, J. Kosolapova, N. T. Flosbach, R. Herzhoff, A. G. Griesbeck, M. Wickleder, *Chem. Commun.* **2025**, DOI: 10.1039/D4CC06150K.

Controlled Shell Growth Enhances Free Exciton Emission in $AgInS_2$ Quantum Dots

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Environmentally-benign I-III-VI quantum dots are gaining increasing attention as promising candidates for next-generation light-emitting and energy-harvesting devices due to their non-toxic composition, tunable band gap, environmental stability, and water solubility. However, intrinsic defects such as cation and anion vacancies, interstitials, and antisites suppress their excitonic features and significantly affect their optical properties.[1] Therefore, their precise surface engineering is crucial to minimize defect states and enable well-defined excitonic characteristics. Here, we synthesize and investigate $AgInS_2$ quantum dots that exhibit dual emission: a weak, narrow band-edge emission attributed to free excitons and a dominant, broad, red-shifted luminescence arising from surface-related defect states.[2] To enhance their optical quality, we explore two surface coating strategies using wide-bandgap materials to form type-I core/shell structures. While GaS_x coating typically forms an amorphous, non-epitaxial interface, it still leads to substantial enhancement of free-exciton emission by effectively passivating surface and trap states. Remarkably, a compositionally tailored $AgGaS_x$ shell not only further amplifies free-exciton emission but also promotes epitaxial shell growth, thereby improving interface quality. Photoluminescence spectroscopy reveal efficient carrier relaxation from the shell into the core, facilitating free-exciton recombination. These findings highlight the pivotal role of shell composition in governing interface quality and excitonic behavior, offering a viable strategy for developing highly luminescent I-III-VI quantum dots.

Funding: This work is supported by the Bavarian State Ministry of Science and Arts and by the LMU Munich through the grant "Solar Technologies go Hybrid" (SolTech).

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References:

[1] L. Yang, et al., *Nano Lett.* **2023**, *23*, 2443.

[2] J. G. Mann, E. Kostyurina, M. Döblinger, B. Nickel, J. Feldmann, S. Ghimire, *Adv. Opt. Mater.* **2025**, under review.

How Rare is HIGHrISC Behavior in Organic Chromophores?

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In the HIGHrISC[1,2] or hot exciton process[3], reverse intersystem crossing (rISC) from a higher triplet state $T_{n\geq 2}$ to the S_1 state occurs (see Fig. 1). The process has attracted some interest in the OLED community since it may convert triplet excitons generated by electron-hole recombination into light. HIGHrISC behavior is in conflict with Kasha´s rule stating that excited (organic) molecules rapidly relax to their lowest excited state of a given spin multiplicity (mostly singlet or triplet). Despite this, there is occasional experimental evidence for HIGHrISC behavior in the pre-OLED literature.[4,5]

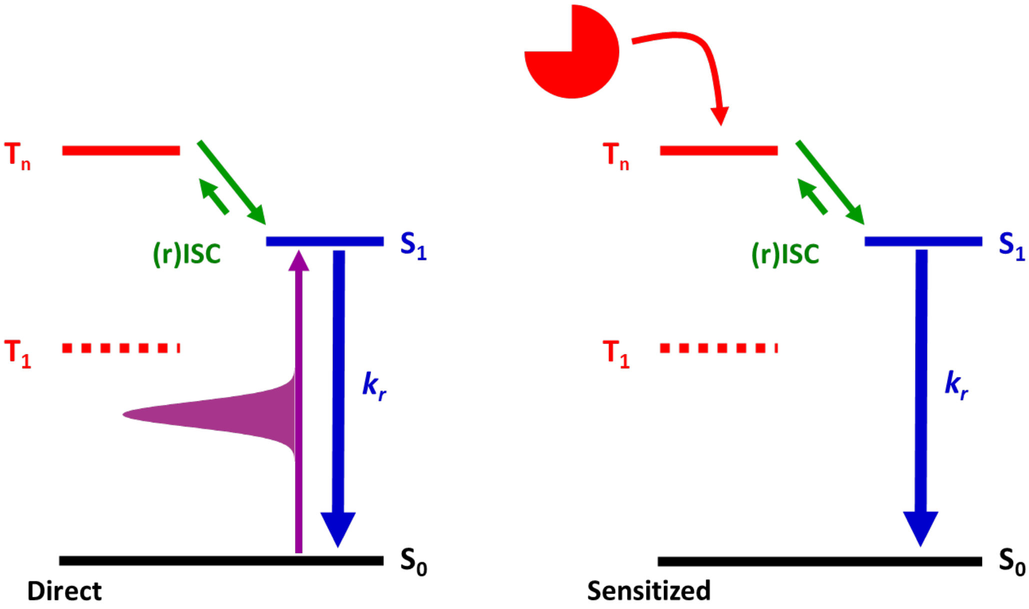

Figure 1. Investigation of HIGHrISC behavior *via* direct (left) and sensitized (right) excitation. In the direct excitation experiment, the chromophore is promoted to the S_1 state by a laser pulse. Provided that the T_n state is in energetic reach, the equilibration of the two states can be monitored by time resolved spectroscopy. A suitable molecular sensitizer transfers population to the T_n state which is ensued by rISC and fluorescence emission.

Our group has extensively studied aromatic carbonyls like xanthones, thioxanthones, and acridones with respect to HIGHrISC behavior. Experimental evidence for this behavior relying on direct[6] and sensitized[7] excitation (Fig. 1) will be presented together with corroborating quantum chemical computations[8,9]. Approaches to optimize chromophores with respect to HIGHrISC will be summarized[2]. Some general considerations concerning the occurrence of HIGHrISC will conclude the presentation.

Funding: Deutsche Forschungsgemeinschaft GRK 2482 “ModISC”, Fonds der Chemische Industrie (Kekulé scholarship for Matthias Jantz).

References:

[1] K.A. Thom et al., J. Phys. Chem. Lett. **2021**, 12, 5703.
[2] M. Jantz et al., Phys. Chem. Chem. Phys. **2025**, DOI: 10.1039/D4CP04781H
[3] Y. Xu, P. Xu, D. Hu, Y. Ma, Chem. Soc. Rev. **2021**, 50, 1030.
[4] R.A. Keller, Chem. Phys. Lett. **1969**, 3, 27.
[5] L.H. Catalani, T. Wilson, J. Am. Chem. Soc. **1987**, 109, 7458.
[6] D. Wöll et al., J. Am. Chem. Soc. **2007**, 129, 12148.
[7] C. Torres Ziegenbein et al., Chemphyschem **2017**,18, 2314.
[8] V. Rai-Constapel et al., J. Phys. Chem. A **2014**,118, 11708.
[9] M. Bracker, C.M. Marian, M. Kleinschmidt, J. Chem. Phys. **2021**,155, 014102.

Sustainable and Bio-inspired Photonic Structures for Enhanced Photochemistry

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Our lives are increasingly improved by light-driven technologies, whether they be for display and lighting, or cheaper and more carbon-neutral energy production. The next generation of optoelectronic devices may contain light-absorbing materials (e.g. pigments) for flexibility and cost-effectiveness, but also photonic structures -micro/nanostructures that trap and manipulate light- to increase efficiency. A continuing challenge however is to find better ways to combine pigments and photonic structures. Arrangements that drive strong light-matter interactions, generating polaritonic resonances, may be particularly useful in driving not only new device efficiency but also new routes to useful chemistry [1].

While metallic/plasmonic photonic structures show excellent performance in this space, sustainable and biodegradable alternatives will become increasingly important. Nature has engineered its own examples of the close interaction between photonic structures and pigments, examples of which are found on the surfaces of butterfly and beetle wings (Fig. 1) [2,3]. These structures are thus naturally evolved corollaries to the synthetic pigment/photonic structures that are of so much interest for enhanced photochemistry, such as plasmonic and polaritonic chemistry. This talk covers our recent work on reverse engineering the morphology- and pigment-induced light interactions found on butterfly and beetle wings as bioinspiration for next-generation photonic structures for enhanced photochemistry using lightweight, flexible and sustainable materials [3,4].

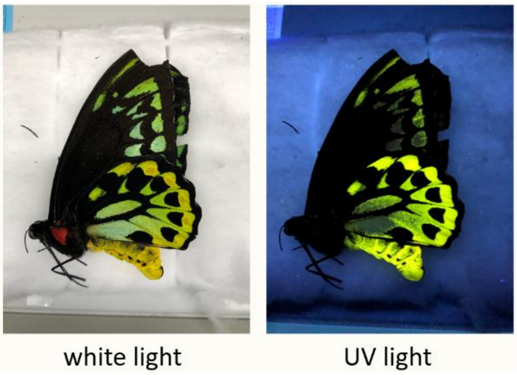

Figure 1. Australia's Cairns Birdwing butterfly displays not only structural colour, but also pigment coloration (and fluorescence), with strong interactions between the two, suggesting sustainable alternatives to metallic photonic structures for enhancing photochemistry and organic devices.

Funding: Australian Research Council (ARC) Future Fellowship (FT180100295), Centre of Excellence in Exciton Science (CE170100026), and LIEF (LE210100151) schemes, and the University of Melbourne Hallmark Research Initiative on Bioinspiration.

References:

[1] K. Hirai, J.A. Hutchison, H. Uji-i, *Chemical Reviews* **2023**, 123, 8099.
[2] B.D. Wilts, A. Matsushita, K. Arikawa, D.G. Stavenga, *J. R. Soc. Interface* **2015**, 12, 20150717.
[3] L. Ospina-Rozo, N. Priscilla, J.A. Hutchison, A. van de Meene, N.W. Roberts, D. Stuart-Fox, A. Roberts, *Materials Today Advances* **2023**, 18, 100363.
[4] G. E. Akinoglu, D. Quan, E. Rokhsat, J.A. Hutchison, *Advanced Functional Materials* **2024**, 34, 2403657.

Photoinduced Electron Transfer in POV Based Systems

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Understanding photo-induced electron transfer processes in inorganic-organic systems based on polyoxometalates is of great interest for a wide range of potential applications in the field of memristor devices, light sensing, optoelectronics, and solar light conversion. In recent years, the electronic features of polyoxometalates like polyoxyvanadate (POV) fused with electron donors have been at the forefront of investigations. In this contribution, results regarding the investigations of electron transfer processes in polyoxyvanadate systems are presented.[1,2] For these investigation time-resolved photophysical and complementary radiation chemical techniques like, for example, nanosecond laser photolysis and electron pulse radiolysis were employed (Fig. 1). As an example, our results demonstrate electron transfer processes occurring from the photoexcited lutetiumphthalocyanine as electron donor to the polyoxyvanadate forming a rather long-lived charge separated state with a lifetime of 170 ns in THF.[1]

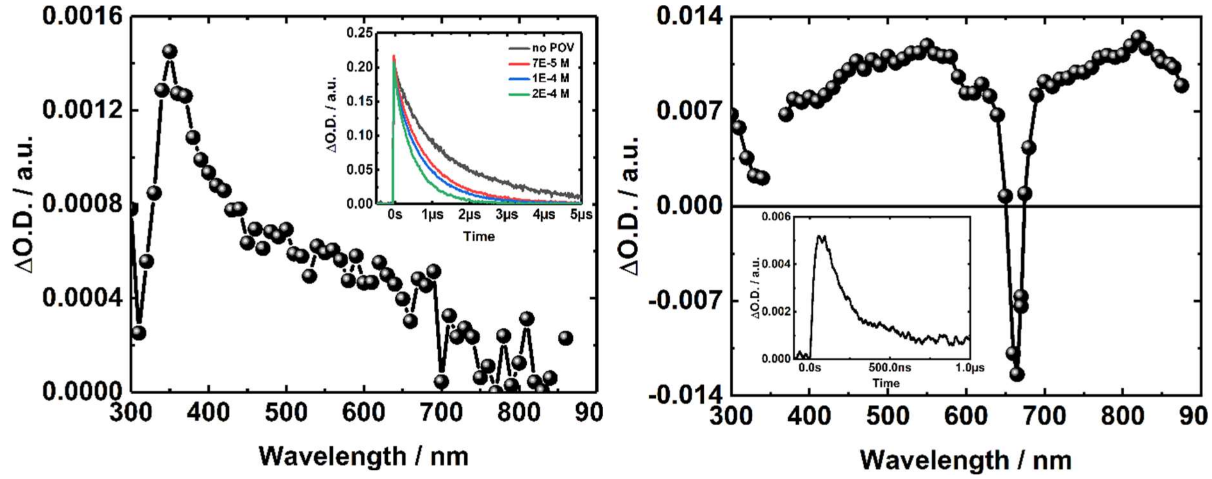

Figure. 1 left: Pulse radiolysis transient absorption spectrum of 1x10–4 M $(nBu_4N)_4[HV_{12}O_{32}Cl]$ in N_2 saturated water containing 5 vol% t-butanol 10 µs after the electron pulse (10 MeV, 10 ns, 30 Gy/pulse). Inset: Corresponding time absorption profiles at 720 nm showing the decay of e_{aq}^{-} at different $(nBu_4N)_4[HV_{12}O_{32}Cl]$ concentrations. Right: Nanosecond laser photolysis transient absorption spectrum of LuPc-$(nBu_4N)_3[HV_{12}O_{32}Cl]$ in N_2 saturated THF 150 ns after excitation at 355 nm (5 ns FWHM, 5 mJ/pulse). Inset: Corresponding time absorption profiles at 830 nm depicting the decay of the characteristic transient absorption of the $LuPc^{\bullet+}$.

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References:

[1] I. Werner, J. Griebel, A. Masip-Sanchez, X. Lopez, K. Załęski, P. Kozłowski, A. Kahnt, M. Boerner, Z. Warneke, J. Warneke, K. Y. Monakhov, *Inorg. Chem.* **2023**, *62*, 3761.

[2] E. Vogelsberg, J. Griebel, I. Engelmann, J. Bauer, F. Taube, B. Corzilius, S. Zahn, A. Kahnt, K. Y. Monakhov, *Adv. Sci*, **2024**, *11*, 2401595.

Protein-driven electron-transfer process in a fatty acid photodecarboxylase

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Naturally occurring photoenzymes are rare in nature, but among them, fatty acid photodecarboxylases derived from *Chlorella variabilis* (*Cv*FAPs) [1,2] have emerged as promising photobiocatalysts capable of performing redox-neutral, light-induced decarboxylation of free fatty acids (FAs) into C1-shortened *n*-alka(e)nes. Using a hybrid QM/MM approach combined with a polarizable embedding scheme, we identify the structural changes of the active site and determine the energetic landscape of the forward electron transfer (fET) from the FA substrate to the excited flavin adenine dinucleotide. We obtain a charge-transfer diradical structure where a water molecule rearranges spontaneously to form an H-bond interaction with the excited flavin, while the FA's carboxylate group twists and migrates away from it. Together, these structural modifications provide the driving force necessary for the fET to proceed in a downhill direction (Fig. 1). Moreover, by examining the R451K mutant where the FA substrate is farther from the flavin core, we show that the marked reduction of the electronic coupling is counterbalanced by an increased driving force, resulting in a fET lifetime similar to the WT, thereby suggesting a resilience of the process to this mutation. Finally, through QM/MM molecular dynamic simulations we reveal that, following fET, the decarboxylation of the FA radical occurs within tens of ps, overcoming an energy barrier of ~0.1 eV. Overall, by providing an atomistic characterization of the photoactivation of *Cv*FAP, this work can be used for future protein engineering.[3]

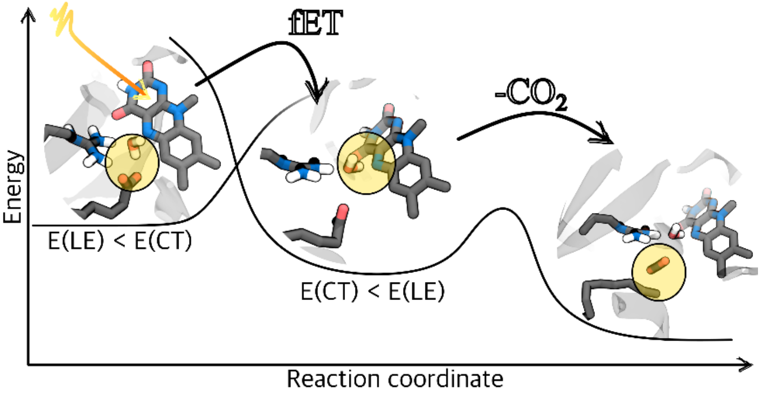

Figure 1. The forward electron transfer (fET) and decarboxylation mechanism in FAPs.

Funding: European Research Council under the Grant ERC-AdG-786714 (LIFETimeS)

References:

[1] D. Sorigué et al., *Science*, **2017**, *357*, 903–907
[2] D. Sorigué et al, *Science*, **2021**, *372*, eabd5687.
[3] G. Londi et al. *JACS Au* **2025** *5* (1), 158-168

Ultrafast modulation of solute-solvent hydrogen bonding during electron transfer in iron-ruthenium complexes

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Transition metal complexes (TMCs) are widely used as catalysts for photochemical energy conversion processes in liquid environments. However, the development of design guidelines for such molecular assemblies is impeded by an incomplete understanding of the coupling between their electronic and nuclear dynamics, including the interplay of TMCs with their liquid environment upon photoexcitation. Probing the involved processes requires high spatial sensitivity towards the transfer of electron density, and the ability to capture atomic motion on ultrafast timescales – a combination which is not readily available for optical transient spectroscopic techniques.

X-ray free electron lasers (XFELs) have transformed ultrafast science in recent years. They provide tuneable and extremely bright X-ray pulses with a typical pulse duration of <30 fs, which can be used to capture photoinduced electronic and atomic motion in molecules and materials.[1] Applied to TMCs, XFEL probes are sensitive to the local electronic structure with element-specificity as well as to intra- and inter-molecular structural reorganization at an atomic level.[2]

In this talk, I will present work on the impact of solute-solvent interactions on photoinduced electron transfer in a linear trimetallic cyanide-bridged iron-ruthenium complex (FeRuFe), carried out at the LCLS XFEL facility at SLAC National Accelerator Laboratory. The experiment is performed in a pump-probe geometry on a liquid jet, where a visible/near-infrared pump induces a metal-to-metal charge transfer (MMCT) between Ru and Fe which is followed by an ultrafast back-electron-transfer. We capture the ensuing dynamics with simultaneous ultrafast X-ray emission spectroscopy (XES) and X-ray solution scattering (XSS) in solvents of differing hydrogen-bonding strength, including water, methanol and acetonitrile. XES is sensitive to the oxidation and spin state of the Fe centres and XSS provides information on atomic motion in solute and solvent, as demonstrated recently.[3]

We reproduce our experimental scattering signals computationally through molecular dynamics simulations, yielding atomistic insight into the coupled motions of FeRuFe and its solvent shell following photoexcitation. The resulting molecular level understanding of solvent reorganization coupled to electron transfer demonstrates that the strength and type of solute-solvent interactions are a central factor in determining the outcome of photoinduced charge transfer processes in TMCs.

Funding: This work is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division under Contract No. DE-AC02-76SF00515.

References:

[1] Schoenlein, R.; Elsaesser, T.; Holldack, K.; Huang, Z.; Kapteyn, H.; Murnane, M.; Woerner, M. Recent Advances in Ultrafast X-Ray Sources. *Philos. Trans. R. Soc. Math. Phys. Eng. Sci.* **2019**, *377* (2145), 20180384.

[2] Gaffney, K. J. Capturing Photochemical and Photophysical Transformations in Iron Complexes with Ultrafast X-Ray Spectroscopy and Scattering. *Chem. Sci.* **2021**, *12* (23), 8010–8025.

[3] Biasin, E.; Fox, Z. W.; Andersen, A.; Ledbetter, K.; Kjær, K. S.; Alonso-Mori, R.; Carlstad, J. M.; Chollet, M.; Gaynor, J. D.; Glownia, J. M.; Hong, K.; Kroll, T.; Lee, J. H.; Liekhus-Schmaltz, C.; Reinhard, M.; Sokaras, D.; Zhang, Y.; Doumy, G.; March, A. M.; Southworth, S. H.; Mukamel, S.; Gaffney, K. J.; Schoenlein, R. W.; Govind, N.; Cordones, A. A.; Khalil, M. Direct Observation of Coherent Femtosecond Solvent Reorganization Coupled to Intramolecular Electron Transfer. *Nat. Chem.* **2021**, *13* (4), 343–349.

Shedding UV light on DNA charge transfer

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Photoinduced electron transfer is one of the most common consequences of the absorption of UV light by nucleic acids. It leads to the population of long-lived excited charge transfer (CT) states, which often involve several stacked nucleobases in a DNA strand. Recently, we demonstrated that such CT states are responsible for photoprotective mechanisms[1], such as the nonenzymatic self-repair of cyclobutane pyrimidine dimers in specific DNA sequences[2,3,4]. However, the efficiency of DNA CT is generally difficult to predict simply based on sequence information and redox potentials of nucleobases. In this talk, I will present how structural factors such as stacking overlap (see Fig. 1) and population of CT-active conformers can affect the efficiency of photoinduced DNA charge transfer and the associated self-repair of cyclobutane pyrimidine dimers[2]. I will also show that CT and self-repair yields can be greatly improved by alternative DNA bases such as 2,6-diaminopurine[3]. In the final part of the talk, I will explain why commonly used rate theories, such as the Marcus equation, fail to capture even the qualitative trends in DNA CT rates. I will discuss how microcanonical rate theory can be used to accurately estimate the rates of photoinduced electron transfer and those of other competing photoinduced processes.

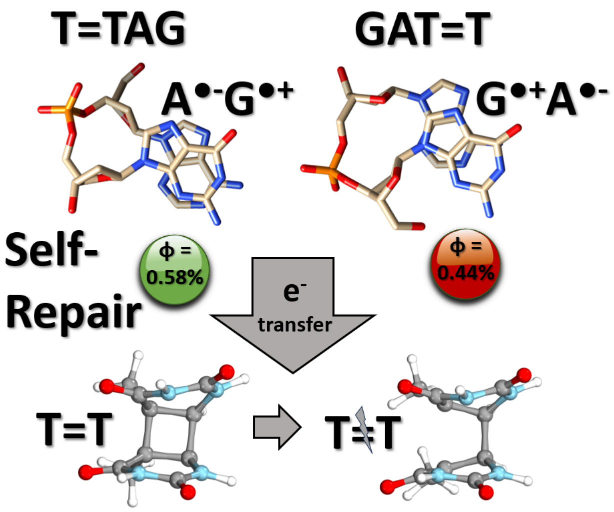

Figure 1. Stacking overlap strongly affects the rates and yields of photoinduced DNA charge transfer and the associated DNA self-repair process.

Funding: National Science Centre Poland (2020/37/B/ST4/04092 to R. S.)

References:

[1] K.E. Szkaradek, P. Stadlbauer, J. Sponer, R.W. Góra & R. Szabla, *Chem. Commun.* **2020**, 56, 201-204.

[2] C.L., Kufner, S., Crucilla, D. Ding, P. Stadlbauer., J. Šponer, J.W. Szostak, D.D. Sasselov & R. Szabla, *Chem. Sci.* **2024** 15, 2158-2166.

[3] R. Szabla,M. Zdrowowicz, P. Spisz., N.J. Green, P. Stadlbauer, H. Kruse, J. Šponer & J. Rak, *Nat. Commun.* **2021**, 12, 3018.

[4] R. Szabla, H. Kruse, P. Stadlbauer, J. Šponer & A.L. Sobolewski, *Chem. Sci.* **2018** 9, 3131–3140

Assessing anti-Kasha emission in Indigo Carmine: a combined static and dynamic approach

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Indigo is a historically important dye, known for its remarkable photostability. While previous studies on the origin of this photostability are restricted to the photophysics of Indigo at the first excited state (S_1), where a fast internal conversion from S_1 is mediated by the presence of a crossing with the ground state (S_0) [1-4], recent experimental findings suggest the presence of emission originating from higher excited state when the system is excited at 390 nm, i. e. anti-Kasha luminescence, which enhances the established understanding of Indigo's excited-state behavior.

Given the complexity of Indigo's photophysics due to the interplay of three possible isomers (keto, enol and dienol forms), it is difficult to disentangle its photophysics to understand the origin of the anti-Kasha behaviour. Moreover, the photophysics of Indigo at higher excited states presents a challenge for the available theoretical tools. First, because it combines inherently anharmonic processes, such as proton transfer, and processes with longer timescales, such as emission. While the first aspect requires excited-state dynamics for an accurate description of the bond breaking, the second is better treated with a static approach based on Fermi's golden rule [5]. In both cases, the treatment of higher excited state becomes also a challenge for the electronic structure level used.

In this study, we used a series of static methods to compute the excited-state decay rate constants of Indigo and explore its possible deactivation mechanisms. We show that the observed emission originates from the keto form of Indigo's S5 state or the enol form of Indigo's S_4 state. We also employ excited-state dynamics at the MNDO/ODM2 level, incorporating solvent effects through the QM/MM scheme, to approximate the proton transfer process.

This study not only clarifies the mechanistic origins of anti-Kasha behaviour in Indigo but also illustrates the power of integrating multiple theoretical strategies to understand the behaviour of molecules at the excited state.

Funding: FWO.

References:

[1] Yamazaki, S.; Sobolewski, A. L.; Domcke, W. Phys. Chem. Chem. Phys. 2011, 13 (4), 1618–1628.

[2] Roy, P. P.; Shee, J.; Arsenault, E. A.; Yoneda, Y.; Feuling, K.; Head-Gordon, M.; Fleming, G. R. J. Phys. Chem. Lett. 2020, 11 (10), 4156–4162.

[3] Pina, J.; Sarmento, D.; Accoto, M.; Gentili, P. L.; Vaccaro, L.; Galvão, A.; Seixas de Melo, J. S. J. Phys. Chem. B 2017, 121 (10), 2308–2318.

[4] Cui, G.; Thiel, W. Phys. Chem. Chem. Phys. **2012**, 14 (35), 12378.

[5] Do Casal, M. T.; Veys, K.; Bousquet, M. H. E.; Escudero, D.; Jacquemin, D. J. Phys. Chem. A **2023**, 127 (48), 10033–10053.

Exciton and Biexciton Dynamics in Semiconductor Nanocrystals

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Developing semiconductor systems for light energy harvesting and optoelectronic applications requires an in-depth understanding of exciton and biexciton dynamics, as well as charge delocalization of photogenerated carriers. Compared to binary (II–VI and III–V) semiconductor nanocrystals (NCs), lead halide perovskite nanocrystals (PNCs) offer several notable advantages due to their defect tolerance. The first part of the presentation will explore the dynamics of bound charge carriers in both binary semiconductor NCs and lead halide PNCs using time-resolved emission spectroscopy. Our findings reveal that trap depth plays a vital role in exciton dynamics in semiconductor quantum dots, whereas the biexciton quantum efficiency in cesium lead bromide PNCs is influenced by the number of facets. In the second part of the talk, I will present strategies to enhance electron delocalization in semiconductor heterostructures and vertex-oriented cube assemblies of perovskites. In the last part, I will explain the effect of the plasmonic field on the photoluminescence properties of semiconductor NCs in the presence of Au nanoparticles and Au nanofilms by precisely tuning the distance between the two components. I will also discuss how plasmonic fields influence PL lifetimes associated with first and second exciton recombination in a cascade two-photon emission process.

[1] E. K. Vishnu *et al.*, J. Phys. Chem. C 125, 25706-25716 (2021).

[2] E. M. Thomas *et al.*, ACS Energy Lett. 7, 2856-2863 (2022).

[3] A. Garai *et al.*, J. Am. Chem. Soc. 145, 13989-13999 (2023).

[4] E. K. Vishnu *et al.*, J. Phys. Chem. C 128, 4373-4382 (2024).

[5] M. P. Varghese *et al.*, J. Phys. Chem. C 128, 10945-10954 (2024).

[6] S. Bera *et al.*, J. Am. Chem. Soc. 146, 20300-20311 (2024).

[7] T. Titus *et al.*, Nano Lett. 24, 10434-10442 (2024).

[8] L. Paul *et al., Chem. Sci. 15, 20263-20273 (2024).*

Colorful Catalysis: Noble Metal-Free Photosensitizers in the Age of DYEversity

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The inexpensive cost, natural abundance, and chemical tunability of organic photoactive materials make them attractive candidates for molecular artificial photosynthetic systems. In our recent work, we have developed and synthesized photostable organic photosensitizers, such as perylene monoimides, BODIPY dyes as well as ketocoumarins for application in light driven reactions (Fig. 1) .[1-3] We established a versatile synthetic approach to prepare photostable rylene monoimides capable of sensitizing $[Mo_3S_{13}]^{2-}$ clusters in aqueous solution for visible-light-driven hydrogen evolution. The influence of substituents on the nature and lifetime of the excited state upon visible light excitation is explored in detail. Furthermore, we demonstrate how the photocatalytic activity of photosensitizers and catalysts in general can be significantly enhanced by incorporation into macromolecular templating agents such as soft matter matrices.[4,5]

Figure 1. Conceptual illustration of a ketocoumarin dye photosensitizer enabling visible-light-driven hydrogen evolution in aqueous solution.

Funding: DFG, SFB TRR 234 Catalight, Project A03

References:

[1] Hagmeyer, N.; Costabel, D.; Hofmeister, E.; Nabiyan, A.; Max, J.; Schacher, F. H.; Peneva, K.; Dietzek‐Ivanšić, B.. ChemPhotoChem **2024**, 8 (n/a), e202400150

[2] D. Costabel, R. T. D. De, F. Jacobi, J. Eichhorn, K. Hotzel, A. Nabiyan, C. Neumann, A. Turchanin, S. Kupfer, F. H. Schacher, S. Rau, B. Dietzek-Ivansic, K. Peneva, ACS Catalysis **2023**, 13, 7159-7169.

[3] D. Costabel, A. Nabiyan, A. Chettri, F. Jacobi, M. Heiland, J. Guthmuller, S. Kupfer, M. Wächtler, B. Dietzek-Ivansic, C. Streb, F. H. Schacher, K. Peneva, ACS Applied Materials & Interfaces **2023**, 15, 20833-20842.

[4] G. Knorr, K. Hotzel, A. Chettri, A. Skabeev, M. Wächtler, B. Dietzek-Ivansic, K. Peneva, J Mater Chem A **2023**, 11, 23260-23269

[5] D. Kowalczyk, G. Knorr, K. Peneva, D. Ziegenbalg, React Chem Eng **2023**, 8, 2941-3212.

Flavin anions for photoredox catalysis

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Flavins are well-established catalysts in oxidative photoredox chemistry, but their application in reductive photocatalysis remains limited due to the instability of reduced flavin intermediates[1,2,3]. This work introduces a novel strategy leveraging the anionic form of 10-unsubstituted isoalloxazine, generated in situ from 3-methyllumichrome (1a-H) under basic conditions, as a potent photoredox catalyst for reductive transformations[4].

Deprotonation of 1a-H with tetrabutylammonium acetate (TBAOAc) in acetonitrile yields a resonance-stabilised anion (2a$^-$) with distinct isoalloxazinic spectral properties, including a visible absorption maximum at 447 nm and long-lived fluorescence ($\tau_F \approx 8.0$ ns). Density functional theory (DFT) calculations confirm the dominance of isoalloxazinic character in 2a$^-$, contrasting with the less stabilised anions derived from conventional alloxazines. Cyclic voltammetry reveals a dramatically lowered oxidation potential for 2a$^-$ (E_p = +1.09 V vs SCE) compared to neutral 1a-H (+2.09 V), enabling potent photoreduction under visible light (470–505 nm).

The catalytic utility of 2a$^-$ was demonstrated in the reductive dehalogenation of activated bromoarenes, achieving an 84% yield of benzonitrile from 4-bromobenzonitrile, and in a C–P coupling reaction with trimethyl phosphite. Remarkably, the system operates efficiently under aerobic conditions, a rare feat for reductive photoredox processes. Transient absorption spectroscopy and Stern–Volmer analysis corroborate electron transfer from photoexcited 2a^{-*} to substrates (k_q up to 5×10^9 M^{-1}s^{-1}), with the singlet excited state playing a dominant role.

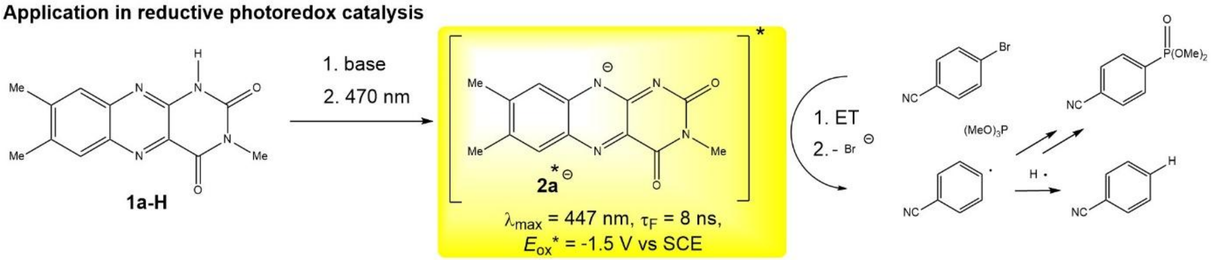

Figure 1. Application of the flavin-10-ide anion **2a^{-*}** in photoredox catalysis developed in this work.

This study establishes flavin-10-ide anions as a new class of photoredox catalysts that combine ease of generation, visible-light activation, and exceptional stability. The work expands the synthetic toolbox for flavin-mediated reductions while providing mechanistic insights into the interplay between tautomerism, deprotonation, and photocatalytic activity. The strategy opens avenues for developing flavin-based systems for challenging reductive transformations under ambient conditions.

Funding: Czech Science Foundation (24-11386K); National Science Centre of Poland (UMO-2023/05/Y/ST4/00062)

References:

[1] M. Schmalzbauer, M. Marcon, B. König, *Angew. Chem. Int. Ed*. **2021**, *60*, 6270.
[2] R. Cibulka, M. Fraaije, Flavin-based catalysis: Principles and applications, Wiley-VCH, **2021**.
[3] M. Sikorski, I. Khmelinskii, E. Sikorska, Spectral Properties of Flavins, in: R. Cibulka, M. Fraaije (Eds.), Flavin-Based Catalysis, Wiley-VCH, **2021**, pp. 67-96.
[4] D. Prukała, E. Zubova, E. Svobodová, L. Šimková, N. Varma, J. Chudoba, J. Ludvík, G. Burdzinski, I. Gulaczyk, M. Sikorski, R. Cibulka, *Chem. Sci*. **2025**, accepted.

Studying and Controlling Ground-State Catalysts with Light: Cases Studies on Hydrogenases

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Hydrogenases catalyze the reversible cleavage of dihydrogen (H_2) into protons and electrons. [NiFe] and [FeFe] hydrogenases accomplish this reaction by utilizing sophisticated base-metal active sites containing sulfur-rich Ni and Fe centers that carry biologically uncommon CO and CN^- ligands. Thus, these metalloenzymes represent valuable model systems for sustainable energy conversion and bio-inspired catalyst design.

Although operating as ground-state catalysts in Nature, [NiFe] and [FeFe] hydrogenases exhibit pronounced light sensitivity and photochemical reactivity. For instance, almost all active and inactive states of the [NiFe] catalytic center can be photochemically transformed to tautomeric forms by reversible ligand dissociation from Ni and/or Fe. The most prominent example is a Fe(II),Ni(III) catalytic intermediate carrying a bridging hydride between Ni and Fe (Ni_a-C), which can be photolyzed to yield a formal Fe(II),Ni(I) species with a protonated cysteine ligand (Ni_a-L). Combining spectroscopic techniques and computational tools, we have demonstrated that a similar process can also be accomplished for a congeneric Fe(II),Ni(II) state (Ni_a-SR).[1,2] While Ni_a-C photolysis represents a local tautomerization of the [NiFe] center only, photolysis of Ni_a-SR is a net redox process of the catalytic site that involves light-driven electron transfer towards FeS clusters within the enzyme. Omitting the ground-state intermediate Ni_a-C, this direct interconversion of Ni_a-SR and Ni_a-L represents a photochemical shortcut of the catalytic cycle that integrates multiple redox sites of the enzyme. Processes of this type were detected in multiple [NiFe] hydrogenases and, more recently, also in [FeFe] hydrogenases. In addition, light-driven electron transfer in hydrogenases could even be initiated by excitation of canonical [4Fe4S] clusters, highlighting the universal potential to control biological redox cascades with light.

All previously known photo reactions of hydrogenases, including the newly discovered non-local process discussed above, start from the photolysis of an extraneous ligand that represents a substrate derivative or an inhibitor. Recently, we found that the opposite can also be accomplished.[3] Here, two catalytic Fe(II),Fe(II) hydride states of [FeFe] hydrogenases ($H_{hyd:red}$ and $H_{hyd:ox}$) were photo-generated from Fe(I),Fe(I) intermediates ($H_{sred}H^+$ and $H_{red}H^+$) *via* an oxidative addition mechanism. This newly observed photo process (1) contrasts hydride photolysis in [NiFe] hydrogenase, (2) indirectly identifies the controversially discussed structures of the $H_{sred}H^+$ and $H_{red}H^+$ parent states, (3) offers the potential to photochemically accelerate H_2 oxidation, and (4) highlights the plethora of unexpected photo processes in hydrogenases.

In total, these studies highlight the diversity of photo reactions in hydrogenases, including local and non-local as well as dissociative and associative processes. Moreover, our findings demonstrate the possibility of using light for studying and manipulating these enzymes, with the potential to control their catalytic bias or reactivity. In a more general sense, this statement extends to other ground-state catalysts and (biological) redox cascades whose intrinsic light-sensitivity may be utilized for creating an additional layer of photochemical control.

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Acknowledgement: We thank all collaborators who contributed to the cited studies.

References:

[1] E. Siebert, M. Horch, Y. Rippers, J. Fritsch, S. Frielingsdorf, O. Lenz, F. Velazquez Escobar, F. Siebert, L. Paasche, U. Kuhlmann, F. Lendzian, M.-A Mroginski, I. Zebger, P. Hildebrandt, *Angew. Chem. Int. Ed.* **2013**, *52*, 5162.

[2] C. Karafoulidi-Retsou, C. Lorent, S. Katz, Y. Rippers, H. Matsuura, Y. Higuchi, I. Zebger, M. Horch, *Angew. Chem. Int. Ed.* **2024**, *63*, e202409065.

[3] C. Lorent, S. Katz, J. Duan, C. J. Kulka, G. Caserta, C.Teutloff, S. Yadav, U.-P. Apfel, M. Winkler, T. Happe, M. Horch, I. Zebger, *J. Am. Chem. Soc.* **2020**, 142, 5493.

Chlorine Dioxide as a Photoredox Catalyst for C-H Oxygenation of Hydrocarbons

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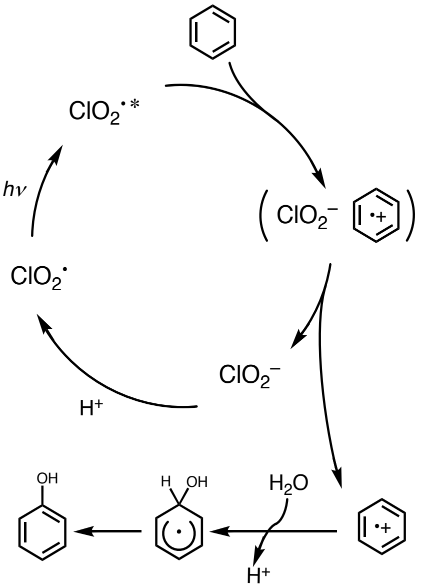
Extensive efforts have been devoted towards the development of methods for the direct conversion from methane (CH_4), ethane (CH_3CH_3), or other abundant natural gasses into useful products, such as the corresponding alcohols, aldehydes, ketones, and carboxylic acids, as liquid fuels and precursors of chemical and pharmaceutical products. Selective aerobic oxygenation of CH_4 into liquid products without the concomitant formation of CO_2 and CO has served as an elusive target reaction. The one-step transformation of CH_4 into methanol (CH_3OH) is carried out in nature using methane monooxygenases. However, under chemical conditions, the selective oxygenation of CH_4 to CH_3OH with molecular oxygen (O_2) has been unknown because the oxidation of oxygenated products, CH_3OH and formic acid (HCOOH) is much easier than that of CH_4, leading to over-oxidation products such as CO and CO_2. Here we report that oxygenation of methane photochemically occurred in the presence of $ClO_2^{\bullet}$. The yields of methanol and formic acid as products were 17% and 82%, respectively, with a methane conversion of 99% in a two-phase system comprising perfluorohexane and water under ambient conditions. The reaction occurred by the efficient radical chain process.[1–3]

UV-light irradiation of chlorine dioxide radical results in the excited state of one-electron reduction potential to be E_{red}^{*} = +3.22 V vs. SCE. The highly oxidative power of chlorine dioxide at the excited state allowed electron-transfer oxidation of benzene and cyclohexane as hydrocarbon substrates to yield the corresponding oxygenated products. The reaction is initiated by the formation of photoexcited state of $ClO_2^{\bullet}$. Electron transfer from benzene (Eox = 2.48 V vs SCE) to the excited state of $ClO_2^{\bullet}$ occurs to form radical ion pair composed of benzene radical cation and ClO_2^-. Phenol as a final product is formed from the reaction between benzene radical cation and H2O as shown in Scheme 1.



Scheme 1 Mechanism of photochemical oxygenation of benzene with $ClO_2^{\bullet}$

We also found a C-C coupling reaction leading to toluene in the photochemical reaction of benzene with methane.

Funding: This work was supported by JSPS KAKENHI Grants (JP24K21770 to K.O.) from MEXT, Japan

References:

[1] K. Ohkubo, K. Hirose, T. Shibata, T. Takamori, S. Fukuzumi, *J. Phys. Org. Chem.* **2017**, *30*, e3619.
[2] K. Ohkubo, K. Hirose, *Angew. Chem. Int. Ed.* **2018**, *57*, 2126.
[3] Y. Itabashi, H, Asahara, K, Ohkubo, *Chem. Commun.* **2023**, *59*, 7506.

Modular Synthesis of Sulfones and Sulfonamides via Visible-Light Driven Fixation of Sulfur Dioxide

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Molecules containing a sulfonyl (-SO_2-) functionality, such as sulfones or sulfonamides, play an important role in organic chemistry and have found widespread application, in particular in medicinal chemistry. In the last years, the visible-light mediated fixation of sulfur dioxide (SO_2) has emerged as a versatile tool for the sustainable synthesis of sulfones and sulfonamides.[1]

Herein, novel approaches for a three-component synthesis of sulfones[2] and sulfonamides[3] using sulfur dioxide as key building block are reported. All methods are based on a visible-light mediated generation of SO_2-centered radicals from suitable carbon- or nitrogen-radical precursors and SO_2. The reactivity of the in situ generated sulfonyl or sulfamoyl radicals can be harnessed for the construction of structurally diverse sulfones and sulfonamides in combination with different terminal trapping agents.

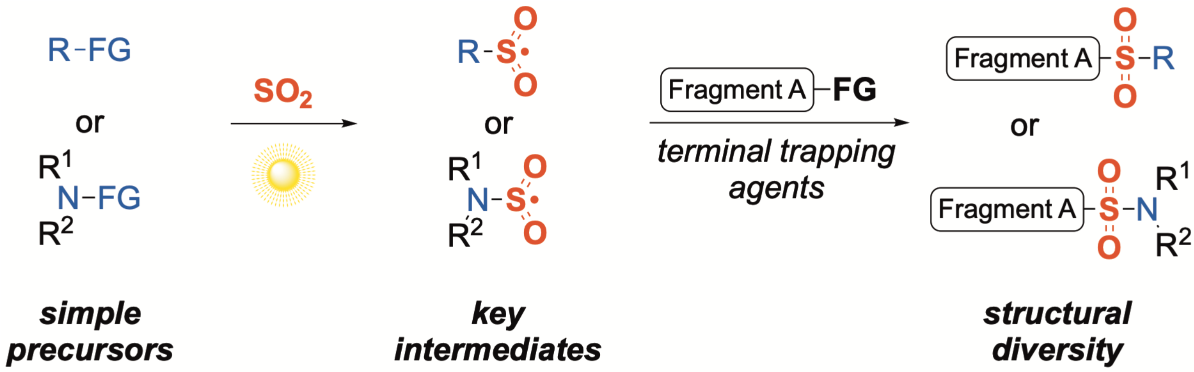

Figure 1. Graphical Abstract.

Overall, these processes enable a highly modular construction of the sulfonyl functionality using sulfur dioxide as key building block and visible-light light as sole driving force.

Funding: Landesforschungsinitiative Rheinland-Pfalz (Research Focus Area *NanoKat*) and German Research Fundation (DFG)

References:

[1] a) S. P. Blum, K. Hofman, G. Manolikakes, S. R. Waldvogel, *Chem. Commun.*, **2021**, *57*, 823; b) K. Hofman, N.-W. Liu, G. Manolikakes, *Chem. Eur. J.*, **2018**, *24*, 11852.

[2] a) Z. Chen, N.-W. Liu, M. Bolte H. Ren, G. Manolikakes, *Green Chem.*, **2018**, *20*, 3059; b) N.-W. Liu, Z. Chen, A. Herbert, H. Ren, G. Manolikakes, *Eur. J. Org. Chem.*, **2018**, 5725; c) S. Sittel, A. C. Sell, K. Hofmann, C. Wiedemann, J. P. Nau, C. Kerzig, G. Manolikakes, K. Heinze, *ChemCatChem*, **2023**, e202201562.

[3] a) N.-W. Liu, S. Liang, G. Manolikakes, *Adv. Synth. Catal.*, **2017**, *359*, 4117; b) T. R. Arroio, J. P. Nau, K. Hofman, C. Förster, S. L. Faber, S. Becker, K. Heinze, G. C. Clososki, G. Manolikakes, *Adv. Synth. Catal.*, **2024**, *367*, e202401065; c) K. Hofman, M. Friedrich, G. Manolikakes, *ChemCatChem*, **2024**, e202401899.

Janus-Type Photophysics of Directly-Linked Acene Dimers

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Most optoelectronic processes in organic semiconducting materials are predominantly intermolecular in nature. This means that the kinetics and efficiencies of light-induced phenomena—such as energy and electron transfer, excimer formation, singlet fission, and triplet-triplet annihilation—are strongly influenced by intermolecular geometries.[1,2] Understanding these structure-property relationships is thus essential for the rational control of intermolecular interactions driving these processes in the solid state. However, overcoming the intrinsic structural disorder in the solid state remains a major challenge. Tailored molecular dimers have therefore been extensively studied as model systems to investigate fundamental solid-state photophysics. With their more precisely defined structures compared to chromophores in thin films, molecular dimers allow for controlled through-bond and through-space couplings. This often facilitates the development of design principles informed by a robust library of structure-property relationships governing the excited-state photophysics of organic semiconductors. Yet, this approach assumes that molecular dimers have a single, well-defined static structure. In this talk, I will delve into the limitations of this assumption and highlight the importance of structural diversity in organic photophysics, with a particular focus on the differing photophysical behaviors of directly-linked acene dimers that arise solely from syn- or anti-type connectivity differences.[3,4]

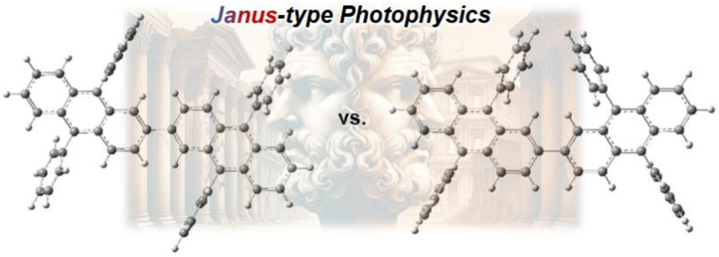

Figure 1. The concept of Janus-type photophysics in acene dimers

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References:

[1] D. Bialas, E. Kirchner, M. I. S. Röhr, F. Würthner, *J. Am. Chem. Soc.* **2021**, *143*, 4500.
[2] N. J. Hestand, F. C. Spano, *Chem. Rev.* **2018**, *118*, 7069.
[3] B. Kang, D. Yim, J. Kim, H. Choi, K. M. Lim, J. Oh, N. A. Panjwani, H. Kim, W. Kim. *Submitted*.
[4] B. Kang, J. Yi, W. Kim. *Manuscript in preparation*.

Photochemical Approaches for Device Functionality and Fabrication

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Functional interfaces are central to solid-state and electrochemical energy conversion and sensing technologies. In this talk, I will explore how impedance spectroscopy can be applied to study in-situ interfacial dynamics and electronic structures in photochemical devices. Specifically, I will demonstrate how impedance models can serve as rapid diagnostic tools to identify performance losses under operational conditions [1,2]. The presentation will begin with an overview of impedance spectroscopy, covering its mathematical foundations, data representation conventions, and methods for selecting measurement points, assessing data reliability, and interpreting results. I will also present case studies of impedance analysis applied to emerging photovoltaic technologies [3,4].

Beyond energy conversion, photochemistry offers powerful opportunities for advancing device fabrication, enabling innovative strategies to create functional interfaces and complex structures. In the second part of the talk, I will discuss how photochemically-driven film fabrication can facilitate rapid, tailored production of functional materials. This approach is exemplified by a novel volumetric additive manufacturing method for printing microstructured piezoelectric sensors [5].

This presentation aims to provide insights into the convergence of photochemistry, device engineering, and fabrication processes, highlighting new pathways toward sustainable energy and sensing technologies.

References:

[1] E. von Hauff, J. Phys. Chem C, 123 (2019) 11329.
[2] E. von Hauff and D. Klotz, J. Mater. Chem. C, 10 (2022) 742-761.
[3] Tulus, J. Wang, Y. Galagan, E. von Hauff, J. Mater. Chem. C, 11 (2023) 2911-2920
[4] Tulus, L. A. Muscarella, Y. Galagan, S. C. Boehme, E. von Hauff, Electrochim. Acta 433 (2022) 141215
[5] A. Frick, W. A. van Vliet, A. Zukauskaite, O. Zywitzki, T. Modes, A. Kostenko, E. von Hauff, Adv. Mat. Tech., (2024) 2301469

Shedding Light on Molecular Function: Quantum-Chemical Insights into Luminescence and Photocatalytic Activity

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Luminescent molecules constitute a versatile class of functional materials with wide-ranging applications in fields such as light-emitting devices, bioimaging, and, more recently, quantum technologies. Within this domain, diradicals have recently emerged as promising alternatives to conventional radicals.[1] Although many diradicals are intrinsically non-emissive, largely due to efficient internal conversion processes that facilitate exceptional photothermal conversion[2], Thiele hydrocarbon derivatives (see Fig.1a) exhibit high photoluminescence quantum yields [3]. In this context, I will present a summary of our recent computational investigations that highlight the unique optoelectronic properties of these novel molecular systems. Among luminescent materials, in recent years, there has been growing interest in solid-state materials capable of exhibiting efficient room-temperature phosphorescence, a phenomenon that remains particularly challenging to achieve in purely organic systems. Our recent investigations have focused on a series of arylthio-substituted persulfurated benzenes (see Fig. 1b), for which we have elucidated the underlying mechanisms governing their phosphorescent behavior[4]. Beyond conventional applications in optoelectronics, metal-free phosphorescent compounds are attracting attention as promising photocatalysts. In this context, I will present our studies on BODIPY derivatives specifically designed to facilitate the generation of long-lived triplet excited states[5], as well as our recent characterization of singlet excited states exhibiting potent photoreductant activity[6].

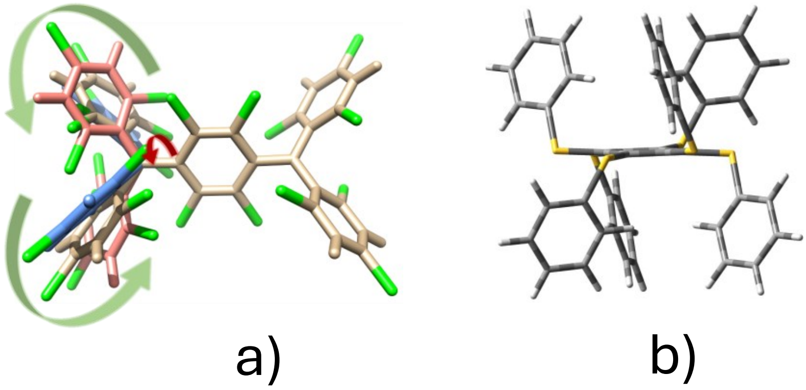

Figure 1. Luminescent organic molecules: a) the diradicaloid Thiele derivative, TTH, b) one conformer of a persulfurated benzene

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References:

[1] Y. Zhu, et al., *Angew. Chem. Int. Ed.* ***2025**, 64, e202423470*.
[2] Y. Ji, et al., *Angew. Chem. Int. Ed.* **2023**, *62*, e202311387.
[3] A. Punzi et al., *J. Am. Chem. Soc.* **2023**,*145*, 20229.
[4] A. Fermi et al., *Chem. Eur. J.* **2024**, *30*, e202401768.
[5] E. Bassan et al., *ChemCatChem* **2023**, e202201380.
[6] F. Calogero et al., *Angew. Chem. Int. Ed.* **2024**, *63*, e202411074.

Critical Analysis of Zinc Tetraphenyl Porphyrin as an Entangled Two-Photon Absorption/Fluorescence (eTPA/F) Standard

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Entangled Two-Photon Absorption/Fluorescence (eTPA/F) Spectroscopy is a technique which is suggested to offer increased signal to noise over a classical process in the single-photon-pair power regime. It has also been purported to offer new chemical selectivity that is different to classical two-photon excitation. However recent works have cast doubt on some of the earlier findings, especially in commercially available dyes used for system characterisation and as standards [1].

We have constructed a simple and flexible ET optical system to determine possible eTPF and eTPA. At 812 nm, we observe 2500 coincidences per mW of pump power (1-80 mW, 406 nm) at 10 % entangled visibility, in line with expected SPDC generation without detector saturation. Using both the chemical standard zinc tetraphenylporphyrin and a highly conjugated probe with ultra-high classical TPA, we present data and evidence that ETPA is not observable with these systems.

We use the methodology of counts per mW pump power for coincidence rate and absorption comparison to allow accurate absorption calculations over time. In our ETPA setup we measure a coincidence loss ratio over a wide power range in agreement with previous literature ZnTPP measurements (rabs ratio of 0.23); however we also observe single photon absorption losses from ZnTPP under the same photon pair rates (rabs ratio of 0.16,).

We also use the related very high classical-TPA cross-section dye molecule PYYP which shows no one-photon absorption and no eTPA absorption at the 812 nm wavelength. This reflects the observation of other recent studies on rhodamine 6G of re-evaluating eTPA methodology.

Funding: Guy Foundation Grant 002

References:

[1] Parzuchowski, K. M., Mikhaylov, A., Mazurek, M. D., Wilson, R. N., Lum, D. J., Gerrits, T., Camp, C. H., Stevens, M. J., & Jimenez, R. (**2021**). Setting Bounds on Entangled Two-Photon Absorption Cross Sections in Common Fluorophores. *Physical Review Applied*, 15(4), https://doi.org/10.1103/PhysRevApplied.15.044012

Long-range exciton transport and nanoscale photophysics of perovskite and organic meso-hierarchical structures

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Meso-hierarchical systems, such as low-dimensional supramolecular structures or superlattices exhibit specific properties, including long-range transport of charges or excitons, potentially leading to novel optoelectronic properties and functionality. We use single molecule spectroscopy in combination with atomic force microscopy to examine new properties and functions at various scales from individual supramolecular structures to complex meso-hierarchical systems.

For sub-wavelength size $CsPbBr_3$ perovskite quantum dot (QD) superlattices (Fig. 1a) we observe collective blinking and photon bunching phenomena at room temperature. Individual superlattices composed of thousands of QDs exhibit two-level blinking (Fig. 1b) similar to that of a single QD, demonstrate photon bunching with a degree of up to 2.75 (Fig. 1c), and have photoluminescence (PL) lifetimes significantly longer individual QDs (Fig. 1d). These observations are consistent with long-range migration of singlet excitons which are trapped at a local defect in the superlattice and form biexcitons, the cascade-like emission of which gives rise to the observed photon bunching. These findings establish perovskite QD superlattices as a promising platform for room-temperature collective optical phenomena and quantum light generation.

Further, we used position-dependent PL lifetime technique to study long-range exciton transport in supramolecular nanofibers. While nanofibers self-assembled from bis(phenylethynyl) anthracene linked with two dendritic hydrophilic structures show exciton diffusion coefficient on the order of 0.1 cm^2/s, the exciton diffusion in anthracene dimer nanotubes is much slower, on the order of 0.01 cm^2/s. This difference reflects differences in structural order and stability between the two mesostructures, and points to the need of well-defined and fixed chromophore arrangement for the realization of long-distance exciton transport in molecular systems.

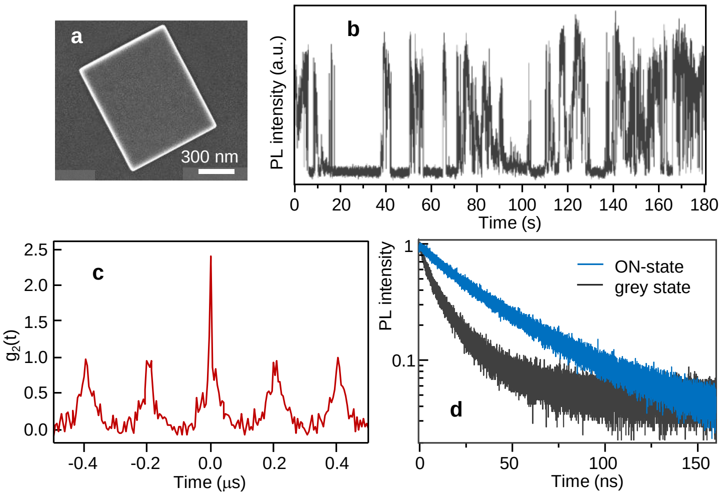

Figure 1. a) SEM image of a typical $CsPbBr_3$ perovskite quantum dot superlattice; b) Two-level blinking of a single superlattice; c) Second-order correlation function of PL from a single superlattice showing photon bunching; d) PL lifetime from ON and grey states of the blinking trace.

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'.

Spin chemistry of rigid electron-donor-bridge-acceptor triads

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Photochemically active, covalently linked electron donor–bridge–acceptor triads (DBAs) have long attracted the interest of photochemists working on solar energy storage, due to their resemblance to photosynthetic reaction centers. More recently, attention has shifted toward their potential applications in quantum information science. This is because the spin-correlated radical pairs generated through photo-induced charge separation (CS) can form spin-correlated—and potentially entangled—qubit pairs, Here DBAs offer the advantage of rational chemical design.

In this talk, we will present the fundamentals of spin chemistry of DBAs in a nutshell, and briefly review the results of 15 years of collaboration between our research groups in Würzburg, Novosibirsk and Konstanz.

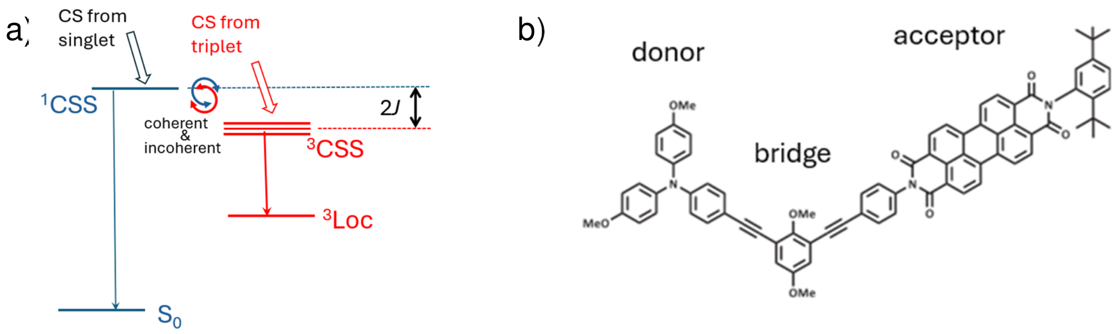

Figure 1. a) Spin chemical reaction scheme.b) Structure of typical DBA used in our work

According to the reaction scheme in Fig. 1a, CS—with a corresponding spin-specific population of charge-separated states (CSS)—can occur from an initially photoexcited singlet or triplet state. Similarly, there are spin-specific pathways leading out of the CSS multiplet, which exhibits singlet-triplet (S/T) splitting due to twice the exchange interaction *J*, along with possible Zeeman splitting of the triplet state. Variations in these parameters give rise to a wide range of magnetic field effects (MFEs) on CSS decay, that is controlled by coherent and incoherent spin transitions in the CSS multiplet. A prototype structure of the triads investigated, as shown in Fig. 1b, typically consists of a substituted triarylamine (TAA) as the electron donor. The nitrogen nuclear spin dominates the hyperfine coupling (hfc) observed in the magnetic field effects (MFEs), but weaker hfcs from ^{1}H and ^{13}C nuclei have also been sensitively detected via magnetic field-dependent photo-CIDNP. Transition metal complexes, as well as conjugated or non-conjugated purely organic bridges with functionally tailored substituents, serve as bridges, while naphthalene or perylene diimide act as acceptors. Structural variations were specifically aimed at exploring the factors that determine the exchange interaction *J*, as revealed by a characteristic 2*J* resonance in the MFE, its correlation with electron transfer rates, and decoherence effects arising from fluctuations in *J*. A major objective was to investigate the mechanisms of spin conversion within the CSS multiplet. Anisotropic hyperfine coupling (hfc) and g-tensor anisotropy were identified as the mechanisms of spin relaxation and were quantitatively analyzed through quantum dynamical simulations. An optical method was developed to detect spin quantum beats in the population ratio of ^{1}CSS and ^{3}CSS, arising from coherent spin transitions induced by isotropic hfc. Although the two CSS spin states cannot be distinguished by optical absorption alone, a second, so-called push laser pulse enables interrogation of the spin state by exciting the system to a higher electronic level, where "immediate" recombination to singlet or triplet products occurs. Since recombination to the singlet state results in a fluorescent excited singlet, this technique offers the potential to observe spin effects at the single-molecule level.

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Monitoring of Host-Guest Interactions in Metal-organic frameworks (MOFs)

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Metal-organic frameworks (MOFs) are a versatile class of crystalline materials formed by inorganic building units that are linked to organic molecules via strong bonds. Their large structural variety leads to widespread applications [1], including gas separation, and storage leveraging their remarkable porosity and tunable pore size. While the influence of the crystal structure of MOF crystals is well understood, the role of particle morphology and defects in shaping their properties remains challenging to elucidate. Conventional characterization methods provide bulk-information, omitting the single-particle level. High-resolution imaging and diffraction techniques like SEM, provide single-particle resolution but are limited in throughput and are often invasive, hindering *in situ* studies.

To address this gap, we developed a multimodal optical spectroscopy and imaging correlation analysis called MOSAIC [2-3]. MOSAIC enables correlative, label-free analysis of functional materials *in situ*, and combines nonlinear microscopy, Raman spectroscopy with fluorescence lifetime imaging (FLIM) in one imaging system. I will present our developed imaging system MOSAIC and discuss how FLIM supported by Raman allows for studying MOFs, including their material composition, crystal structure, morphology, host-guest interactions and thermodynamic properties for applications in environmental sensing and chemical storage [4].

Funding: Deutsche Forschungsgemeinschaft (DFG; PL 696/4-1)

References:

[1] Tittel J, Knechtel F, Ploetz E, *Adv. Funct. Mater.* **2024**, 2307518

[2] Fuchs A, Mannhardt P, Hirschle P, Wang H, Zaytseva I, Ji Z, Yaghi OM, Wuttke S, Ploetz E, *Adv. Mater.* **2022**; *34*, 2104530.

[3] Fuchs A, Knechtel F, Wang H, Ji Z, Wuttke S, Yaghi OM*, Ploetz E*, *J Am Chem Soc*. **2023**; *145*, 14324.

[4] Andreo J, Dutta S, Barroso-Garcia N, Ejsmont A, Baumgartner B, Janakowska A, Tittel J, Marcée R, Frankowski M, Weckhuysen BM, Ploetz E*, Goscianska J*, Wuttke S*, DOI: 10.21203/rs.3.rs-3353195/v1

Towards Controlling Excited State Reactivity in Organic and Organometallic Systems: A Perspective Through Ultrafast Multidimensional Spectroscopies

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Controlling excited-state reactivity by bond-specific IR excitation is an active and fundamental field of research.[1] Herein, I will show examples of our ongoing research towards the control of excited-state photoreactivity, including electron and charge transfer, excited state symmetry breaking (ES-SB), and proton transfer, in a series of organic and organometallic chromophores.

We probed the excited-state dynamics of D–A–D chromophores which exhibit ES-SB upon photoexcitation,[2,3] with the aim of examining the effect of selective IR excitation of the C≡C stretching modes of the π bridge in the electronically excited state. In the second stage, we modified these chromophores, introducing intrinsic rotational asymmetry, observing some intriguing differences. In a third step, we aim to understand the role of the overall redox state of the molecule in the ES-SB dynamics—akin to inorganic mixed-valence complexes.

In parallel, we examined the photodynamics of symmetric Pt(II) bis-acetylide complexes with either a *cis*- or *trans*- arrangement of the two acetylide ligands, investigating also the role of the conjugation length and electronic properties of the substituent on the ligand framework.[4]

One last system we examined involves proton transfer (PT) in a symmetric molecule with two independent PT sites. In this case, a single-sided ultrafast excited-state intramolecular PT reaction takes place, followed by isomerisation. Multipulse experiments enable us to observe the ground-state back PT reaction, and to investigate the effects of a secondary trigger into the potential for driving a second PT reaction.

Using time-resolved electronic and vibrational spectroscopies, as well as transient 2D-IR (tr2DIR) and mixed 2D spectroscopies (e.g. 2D-VE), we probe the ultrafast relaxation dynamics, intramolecular vibrational and vibronic couplings, and solvation effects. By focussing on the C≡C stretching modes (1950–2250 cm^{-1}), which directly participate on the electron/charge transfer pathways, we can gain a unique perspective. We combine these spectroscopic methods with calculations, (spectro)electrochemistry and the design and synthesis of new molecules.

Altogether, we observe a marked solvent dependence of the ES-SB dynamics of the organic D–A–D system, however with a lack of “permanent” control over the outcome of the photoexcitation process. Ongoing investigations into other organic and organometallic systems will provide further answers on the generality of this approach, whilst providing design criteria for functional molecules and materials.

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References:
[1] Delor, M., Weinstein, J. A., et al. *Science* **346**,1492-1495 (2014).
[2] Dereka, B., Vauthey, E., et al. *Nat. Commun.* **11**, 1–11 (2020).
[3] Dereka, B., Rosspeintner, A., Li, Z., Liska, R. & Vauthey, E. *J. Am. Chem. Soc.* **138**, 4643–4649 (2016).
[4] J. C. López-López, Y. H. Nguyen, C. Jiang and T. S. Teets, *Inorg. Chem.* **62**, 17843–17850 (2023).

Applications of time-resolved reflectance for photophysics

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Time-resolved absorption spectroscopy (TAS) is a commonly utilized method for analyzing photoinduced reactions. It follows the reactions and evolution of the excited state from the changes it introduces to the absorption spectrum of the sample. However, changes in absorption properties are always accompanied by changes in the refractive index and reflectivity, which complicates the time-resolved measurements of any film samples such as the highly popular perovskites and other thin-film materials [1]. But with complications also come opportunities as changes in refractive index enable time-resolved measurements in reflection mode. I aim to highlight the applications offered by time-resolved reflectance (TRS) measurements for tracking the excited state charge carriers as they traverse through the device layers in an oral and poster presentation for advanced spectroscopic methods.

While time-resolved reflectance is necessary for correcting reflection changes in TAS [2], it has added sensitivity to the spatial distribution of charge carriers and interfacial phenomena. Looking at the distribution of charge carriers and their diffusion over time provides a way to measure the charge carrier mobility perpendicular to the film surface. Most methods for measuring charge carrier mobility can only provide it in horizontal direction, which is problematic for polycrystalline films where horizontal mobility across grain boundaries does not correspond to the real-world performance in applications like thin-film solar cells [3]. Figure 1a provides an example of a carrier diffusion measurement in perovskite where altering the pump wavelength reveals carrier trapping at the surface [4].

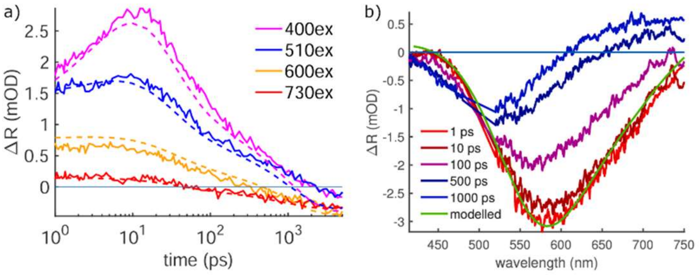

Figure 1: a) TRS signal sensitive to charge carrier diffusion with different pump wavelengths in perovskite [4].
b) TRS charge transfer signal in TiO_2-Si system [6].

Measuring charge transfer from one material to another is one of the most common use cases of TAS, as it is a critical factor for any practical device. Reflectance is naturally sensitive to the interfaces, providing an alternative way to discover charge transfer features. We recently utilized it for tracking charge transfer from perovskite to C_{60} and determining the charge retention time with different interfacial passivates [5]. The sensitivity of time-resolved reflectance can be further maximized by manipulating the thin-film interference, which we have used in the past to track charge transfer from Si to TiO_2 (Figure 5b) [6]. With optimized thin-film interference we were even able to determine the charge carrier distribution in the 50 nm thick TiO_2 layer after it received the charges from Si.

Figure 1b measurements on TiO2-Si also exemplify how reflection mode enables time-resolved measurements on non-transparent samples. This expands TAS methodology to any samples deposited or grown, for instance, on silicon wafers for photonic applications [7].

The downside of TRS is that it is subject to thin-film interference, which has to be modelled in order to determine the underlying photoinduced absorption and refractive index and carrier distribution. This adds further complexity compared to the traditional transmission mode measurements. Luckily, modelling thin-film interference is a fairly basic topic in photonics, and we have openly available software for applying those models to time-resolved signals.

Deep Light Photochemistry for Medical Applications

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Photodynamic therapy is a useful treatment for skin diseases and skin cancer. When translating the principle of action (dyes, light, oxidative damage) to deeper tissue treatments, a limiting factor is the penetration depth of the electromagnetic radiation. This problem can be overcome by combining a photodynamic substrate with a photosensitiser/catalyst using 'deep light', which is specifically released at the site of action or has deep penetration. Two concepts are described in which the three components are combined and studied for their synergistic photodynamic effect:

PDT effects, i.e. singlet oxygen generation using Cerenkov luminescence as a deep light source. The second concept focuses on the photoinduced degradation of the pharmacologically active artemisinin. For the first concept, following the development and application of a spectroscopic detection method for singlet oxygen, it was shown that Cerenkov radiation from the decay of the isotope gallium-68 is sufficient to induce a PDT effect. The second concept of deep light activation of artemisinin uses dyads and triads of triplet photosensitizers and natural antimalarial and antitumour agents from the artemisinin natural peroxide family[1].

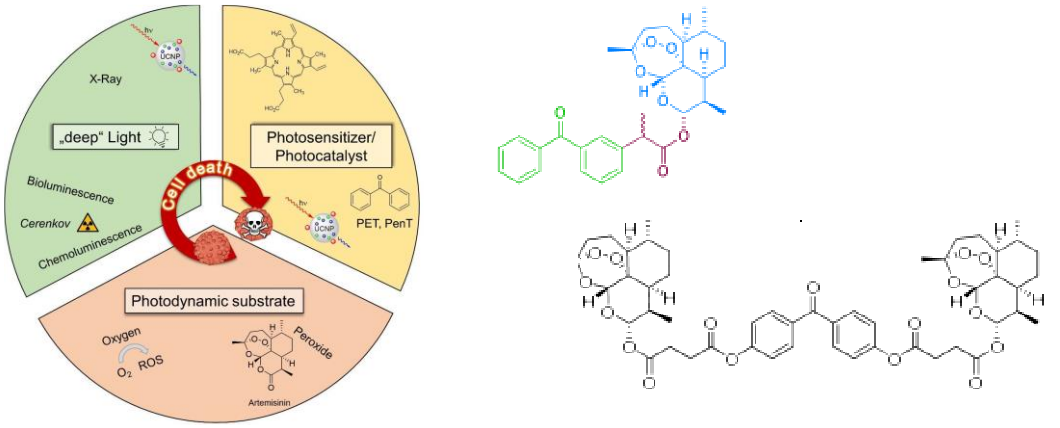

Figure 1. Concepts for light-triggered applications: deep light activation, photosensitization, and photodynamics using the artemisinin natural peroxide family. Dyad from ketoprofen (green) + dihydroartemisinin (blue) and the benzophenone / artesunate triad.

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References:

[1] A. G. Griesbeck, M. Bräutigam, M. Kleczka, A. Raabe, *Molecules* **2017**, *22*, 110.

[2] C. Bold, A. G. Griesbeck, H. Dochtermann, J. F. W. Van Stiphoudt, manuscript in preparation.

Porphyrin Photochemistry as a Strategy to Overcome ABC Transporter-Mediated Multidrug Resistance

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Drug resistance is a complex, multifactorial phenomenon that has been extensively studied in microbiology, where it evolves rapidly. It also presents a major challenge in cancer therapy, with notable similarities to microbial resistance. The term "multidrug resistance" (MDR) is commonly used in both fields and refers to several mechanisms through which cells develop resistance. A primary mechanism involves the action of ATP-binding cassette (ABC) transporters, which expel therapeutics from cells or bind to them, preventing effective action at target sites. Other resistance mechanisms include the overexpression of anti-apoptotic proteins and enhanced DNA repair pathways.

This presentation will explore how photochemistry can be harnessed to overcome ABC transporter-mediated MDR[1]. Using in silico, in vitro, and in vivo models, we have demonstrated that porphyrin photochemistry can selectively damage ABC transporters overexpressed in chemo-resistant cancer cells through three key mechanisms[2],[3]: (i) Reduction of ATPase activity – impairing the energy-dependent function of ABC transporters, (ii) Induction of ABC transporter protein crosslinking – potentially altering transporter stability, and (iii) Inhibition of ABC transporter expression and function – reducing the capacity for drug efflux. Our findings suggest that porphyrin-based photochemistry offers a promising strategy to counteract MDR in cancer therapy.

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References:

[1] Obaid G, Celli JP, Broekgaarden M, Bulin AL, Uusimaa P, Pogue B, Hasan T, **Huang HC**. *Nat Rev Bioeng.* **2024**, 2(9):752-769.

[2] Rahman I, Liang B, Sajid A, Ambudkar S, **Huang HC**. *Photochem Photobiol.* **2025**, 101(1):188-205.

[3] Liang BJ, Lusvarghi S, Ambudkar SV, **Huang HC**. *ACS Pharmacology & Translational Science*. **2021**, 4(5):1578-1587

Advanced BODIPY-based Photosensitizers for Enhanced Photodynamic Therapy

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Photosensitizers (PSs) are applied in a wide range of fields, including photodynamic therapy (PDT), photocatalytic processes, and optoelectronics. PDT stands out as a promising minimally invasive approach for treating cancers and microbial infections. This method relies on the activation of PSs by light to produce reactive oxygen species (ROS), which selectively damage pathological cells. Nevertheless, traditional PSs, such as porphyrins and phthalocyanines, are often hindered by drawbacks like limited photostability, poor aqueous solubility, and suboptimal ROS production. These shortcomings have prompted the development of next-generation PSs with superior photophysical and chemical characteristics.

In this context, boron-dipyrromethene (BODIPY) dyes have emerged as versatile and efficient PS scaffolds, thanks to their robust photostability, strong absorption in the visible spectrum, tunable optical properties, and chemical flexibility for functionalization. Through strategic modifications of the BODIPY core, we have developed advanced derivatives capable of generating singlet oxygen with extended triplet-state lifetimes, or achieving enhanced selectivity in biological systems. This work focuses on various design strategies for BODIPY-based PSs (Figure 1). The specific systems studied include: (i) halogenated BODIPY derivatives with mitochondrial targeting ability [1]; (ii) compact donor–acceptor BODIPY dyads optimized for intramolecular charge transfer [2,3]; and (iii) BODIPY–fullerene conjugates exhibiting efficient energy transfer processes[3].

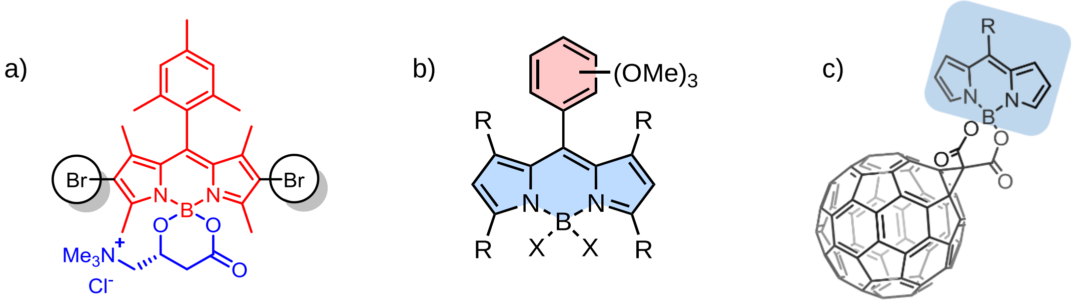

Figure 1: Examples of functionalization of BODIPY chromophore. a) conjugation with biomolecule (L-carnitina); b) introduction of electron-donating groups at meso position; or c) direct anchoring to fullerene C60

The newly synthesized BODIPY derivatives were extensively characterized through experimental spectroscopic techniques, including transient absorption spectroscopy (fs-TA and ns-TA), as well as computational simulations based on time-dependent density functional theory (TD-DFT). The integration of theoretical and experimental data allowed us to elucidate the underlying photophysical properties of these compounds to determine mechanistic details, particularly the key factors governing triplet state population. The potential applicability as theragnostic agents (imaging and treatment) of some derivatives was demonstrated through in vitro studies, assessing their cellular uptake, subcellular localization, and phototoxic effects by analyzing the internalization, localization and phototoxic action.

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References:

[1] L. Maierhofer, R. Prieto-Montero, T. Cubiella, A. Díaz-Andrés, N. Morales-Benítez, D. Casanova, V. Martínez-Martínez, M.-D. Chiara, E. Mann, J. L. Chiara. *J Mater Chem B* **2025**, *13*, 4430.

[2] R. Prieto-Montero, A. Díaz-Andrés, A. Prieto-Castañeda, A. Tabero, A. Longarte, A. R. Agarrabeitia, A. Villanueva, M.J. Ortiz, R. Montero, D. Casanova, V. Martínez-Martínez. *J Mater Chem B* **2023**, *11*, 169.

[3] Manuscript in preparation

Intrinsic fluorescence as a tool for detecting and quantifying amyloid-β oligomers

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The early detection of amyloid-β (Aβ) oligomers in biological fluids is a crucial objective for advancing Alzheimer's disease (AD) diagnosis and developing effective therapeutic interventions, including vaccines.[1,2] Soluble Aβ oligomers, rather than mature fibrils, are increasingly recognized as key neurotoxic agents, emphasizing the importance of detecting these early aggregation states.[3]

Our work provides a detailed characterization of the early aggregation processes of Aβ(1–42) and Aβ(1–40) peptides.[4,5] Using fluorescence correlation spectroscopy (FCS), we determined their critical aggregation concentrations (*cac*) and revealed distinct oligomerization pathways: Aβ(1–42) forms stable micelle-like oligomers (~50 monomers) at a nanomolar concentrations (~90 nM),[4] whereas Aβ(1–40) exhibits two aggregation steps ($cac_1 \approx 0.5$ μM and $cac_2 \approx 19$ μM) involving metastable and stable oligomeric species.[5] Additionally, we demonstrated that serum albumin proteins, particularly human serum albumin (HSA), interact strongly with Aβ monomers and promote the disaggregation of Aβ oligomers, suggesting a protective role *in vivo*.[6]

In this work, we explore the potential of the intrinsic Aβ fluorescence as a label-free method for detecting Aβ oligomers.[7] Our results show that aggregation induces a visible emission band (~500 nm) distinct from tyrosine autofluorescence, which correlates with oligomer concentration. This aggregation-induced emission (AIE) provides a direct optical signature of early aggregation events. We are currently deepening the mechanistic understanding of this phenomenon and refining the fluorescence characterization of Aβ oligomers.

Combining intrinsic fluorescence detection with extrinsic probes based on proton and electron transfer, such as 2-cyano-6-hydroxybenzothiazole[8] and 6-amino-2-cyanobenzothiazole[9], and implementing machine learning methodologies for spectral analysis,[10] we aim to develop robust, non-invasive approaches for the quantification of Aβ oligomers in biomimetic fluids.

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References:

[1] K. L. Viola, M. A. Bicca, A. M. Bebenek, D. L. Kranz, V. Nandwana, E. A. Waters, C. R. Haney, M. Lee, A. Gupta, Z. Brahmbhatt, W. Huang, T.-T. Chang, A. Peck, C. Valdez, V. P. Dravid, W. L. Klein, *Front. Neurosci.* **2022**, *15*..
[2] J.-H. Lee, C. Ostalecki, T. Oberstein, S. Schierer, E. Zinser, M. Eberhardt, K. Blume, B. Plosnita, L. Stich, H. Bruns, R. Coras, J. Vera-Gonzales, M. Maler, A. S. Baur, *eBioMedicine* **2022**, *77*.
[3] E. N. Cline, M. A. Bicca, K. L. Viola, W. L. Klein, G. Perry, J. Avila, P. I. Moreira, A. A. Sorensen, M. Tabaton, *Journal of Alzheimer's Disease* **2018**, *64*, S567–S610.
[4] M. Novo, S. Freire, W. Al-Soufi, *Sci Rep* **2018**, *8*, 1783.
[5] S. Illodo, W. Al-Soufi, M. Novo, *Archives of Biochemistry and Biophysics* **2024**, *761*, 110179.
[6] D. Cora, W. Al-Soufi, M. Novo, *International Journal of Biological Macromolecules* **2025**, 140367.
[7] M. Novo, S. Illodo, J. Seijas, F. Rodríguez-Prieto, W. Al-Soufi, **2025**, DOI 10.26434/chemrxiv-2025-3mdgs.
[8] S. Illodo, Study of Biomolecular Self-Assembly and Host-Guest Association Using Spectroscopic and Microscopic Techniques, PhD Thesis, Universidade de Santiago de Compostela, **2024**.
[9] D. Cora, A. Arias-Rodríguez, B. Fernández, A. Hervés-Pardavila, N. Carro-Varela, M.C. Ríos-Rodríguez, M. Mosquera, M. Novo, F. Rodríguez-Prieto, *submitted* **2025**.
[10] S. Hernández, S. M. Valladares-Rodríıguez, M. Novo, W. Al-Soufi, Early Detection of Alzheimer's Disease via Amyloid Aggregates: A Systematic Review of Plasma Spectral Biomarkers Using Machine Learning Approaches, *submitted* **2025**.OSF Preprints. doi:10.31219/osf.io/vs4cx_v1

Aurones: unexplored visible-light photoswitches for aqueous medium and novel RNA binders

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Aurones are natural or synthetic flavonoids that have been isolated from plant sources more than 70 years ago.[1] The broad spectrum of biological activities of aurones led to extensive studies of these molecules as potential drug candidates possessing antiviral, antibacterial, antifungal, antitumor, antioxidant effects and so on.[1] At the same time, aurones, together with hemiindigo and hemithioindigo, which are known as remarkable photoswitches, belong to the hemiindigoid family. However, the photoswitching of aurones has been scarcely studied, so far.[2] The aim of our work was, therefore, to explore the surprisingly neglected photoswitching properties of aurones and to investigate potential applications of these compounds for RNA targeting.

- In the first sub-project, aurone derivatives have been introduced for the first time as a novel class of visible-light photoswitches ***for aqueous medium*** possessing good quantum yields, high conversions in photostationary states and remarkably long (up to 7 years) lifetimes of the photoisomers (Fig.1A).[2]

- In the second sub-project, we have identified a novel aurone derivative which binds to the mutant RNA CAG repeat expansions and inhibits toxic RNA–protein interactions *in vitro* in the Huntington's disease model (Fig. 1B). To the best of our knowledge, this is the first example of an RNA binder based on the aurone scaffold, which, therefore, provides a proof-of-principle for the application of aurone photoswitches as a platform for the design of RNA-targeting ligands.[3]

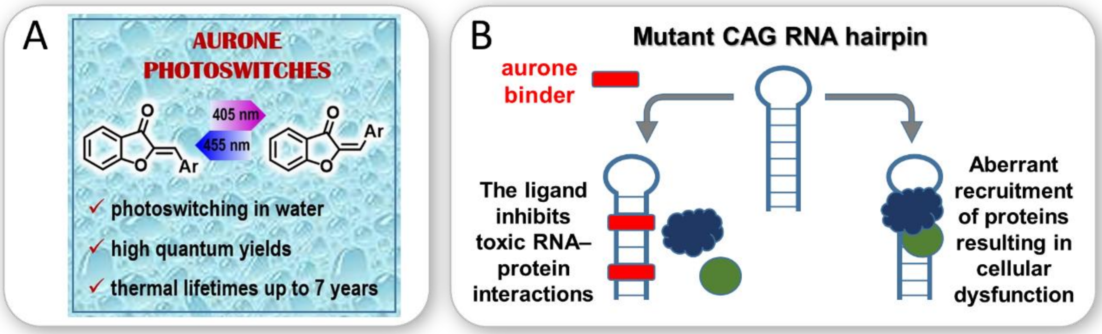

Figure 1. (A) Photoswitching of aurones. (B) Schematic representation of the inhibitory effect of the aurone binder on the toxic huntingtin RNA–protein interactions.

References:

[1] G. Sui, T. Li, B. Zhang, R. Wang, H. Hao, W. Zhou, *Bioorg. Med. Chem*. **2021**, *29*, 115895.

[2] D. V. Berdnikova, *Chem. Eur. J*. **2024**, *30*, e202304237.

[3] G. Ballarin, M. Biasiotto, A. Reisbitzer, M. Bolte, S. Krauß, D. V. Berdnikova, *RSC Med. Chem.* **2024**, *15*, 3092.

Short wavelength exciton fluorescence of DNA: an indicator for the detection of duplex damage?

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The detection of DNA damage by probing its intrinsic fluorescence started to be explored 50 years ago. So far, these investigations have been based on the emission of a specific class of lesions, the pyrimidine (6−4) pyrimidone photoadducts, which are stronger emitters than undamaged DNA. But in light of recent advances on the UV-induced primary processes, such a perspective does not seem well-founded. In contrast, the short-wavelength (<310 nm) fluorescence component of undamaged double helices is instead quite promising [1].

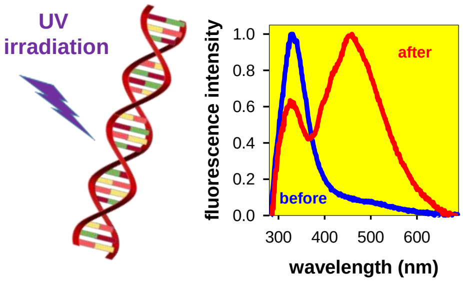

Figure 1. Fluorescence spectra of calf thymus DNA recorded before (blue) and after (red) irradiation at 267 nm. Excitation wavelength: 255 nm

The excited states of DNA and their relaxation depend strongly on the electronic coupling and, therefore, on conformational disorder. Despite this complexity, giving rise to a multitude of emitting states, three limiting types can be distinguished: (i) $\pi\pi^*$ states, (ii) excimer/exciplexes with strong charge transfer character and (iii) Frenkel excitons, encompassing a weak charge transfer character, the emission of each type being prominent, respectively, at 330 – 360 nm, above 400 nm and below 310 nm [2].

The short wavelength emission is ubiquitous in duplexes, including genomic DNA [3]. It represents the longest-living fluorescence component, decaying on the ns time scale and is characterized by small positive anisotropy values (0.02-0.05). Theoretical calculations assigned this unexpected emission to excitons arising from a mixing of pyrimidine Frenkel excitons with purine-to-pyrimidine charge transfer states, extended over at least four nucleobases across both strands [4]. Due to their collective nature, their fluorescence is extremely sensitive to the local environment: it decreases when conformational motions increase and it vanishes completely in single strands. This behavior could be exploited for detecting DNA damage, because the formation of dimeric photoproducts or other nucleobase adducts provoke local distortions within double helices. Thus, not only the fluorescence of the reacted nucleobases disappears, but also the nucleobases located on the opposite strand acquire a single strand character, favoring exciplex emission, and thus shifting the spectrum toward longer wavelengths, and shortening its lifetime.

The qualitative conclusions drawn from fundamental studies, need to be implemented by systematic measurements in view of monitoring specific lesions. To this end, both the spectral and temporal features of the mixed exciton fluorescence could be considered. Would this approach prove realistic, it could be possibly used for optoelectronic devices sensing the damage caused, not only by UV irradiation, but also by other sanitizing agents and anticancer therapies.

References:

[1] D. Markovitsi, *ACS Omega* **2024**, *9*, 26826.
[2] T. Gustavsson, D. Markovitsi, *Acc. Chem. Res.* **2021**, 54, 1226-1235.
[3] T. Gustavsson, D. Markovitsi, *J. Phys. Chem. Lett.* **2023**, *14*, 2141.
[4] L. Martinez-Fernandez, F. Santoro, R. Improta*, Acc. Chem. Res.* **2022**, *55*, 2077.

Unique Optical Functions of Al-based Dinuclear Triple-Stranded Helicates: From Multicolor Emission to Triplet-Energy Generation

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In recent years, there has been growing interest in sustainable, high-performance luminescent materials, and complexes of light main-group elements have been attracted attention because of their low cost and low toxicity. Despite aluminum (Al) being the most abundant and inexpensive metal source among earth-crust elements, research on Al-based luminescent complexes remains very limited, and understanding their structure–property relationships is still a key challenge. In this context, our group has recently focused on the design and synthesis of Al-based complexes to explore new functional dyes, including circularly polarized luminescence derived from their inherent chirality.[1,2] Here, we report a series of Al(III)-based dinuclear triple-stranded helicates constructed from two Al(III) ion and three ligands, in which systematic ligand modification enables tuning of emission color from blue to near-infra-red (NIR) under UV-light irradiation (Figure 1). X-ray crystal crystallography and DFT calculation revealed that the metal–ligand twist angle is the kye to modulates the emission wavelength. [3] In the solid-state, mechanical grinding disrupts the crystalline states into amorphous states, triggering a dramatic mechanochromic shift in absorption and emission that can be fully reversed by solvent treatment. [4] Furthermore, appropriate combination of different ligands sufficiently generates inter-ligand charge transfer (ILCT) states, [5] together with internal heavy-atom effect, promote the formation of excited triplet-state formation and singlet-oxygen generation. In this presentation, we will also discuss the fundamental photophysical properties of these helicates using transient absorption spectroscopy. These findings highlight Al(III)-based dinuclear triple-stranded helicates as structurally tunable, functionally diverse luminescent dyes, paving the way to for their application in advanced photofunctional materials, devise fabrications, and photocatalytic systems.

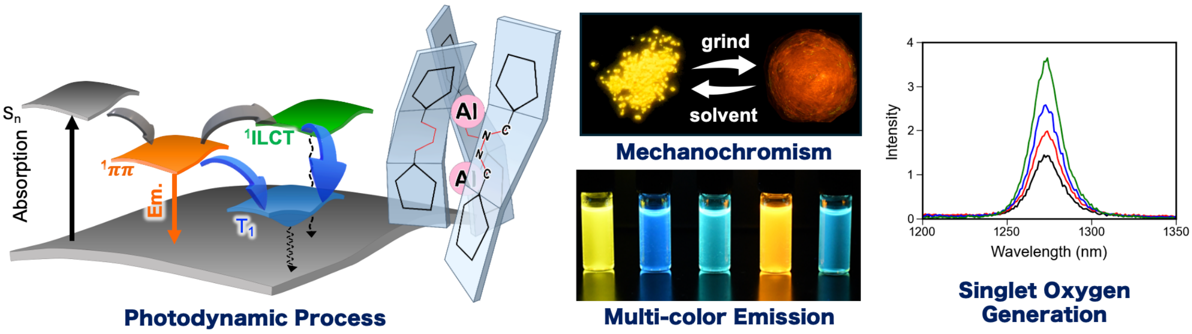

Figure 1. Overviews of studies on aluminum(III)-based dinuclear triple-stranded helicates for their design, tunable photophysical properties, and applications.

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References:

[1] T. Ono and Y. Ooyama, *Dalton Trans.* **2025**, *54*, 6361.
[2] T. Ono *et al*., *Angew. Chem. Int. Ed.*, **2021**, *60*, 2614
[3] K. Ueno and T. Ono *et al*., *Inorg. Chem.*, **2024**, *63*, 6296.
[4] T. Umeki and T. Ono et al., in preparation.
[5] Y. Konishi and T. Ono *et al*., *Inorg. Chem.*, **2024**, *63,* 11716.

Advancing Lead-Free Perovskites for Stable Broad-Range Photodetection

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Metal halide perovskites have emerged as a transformative class of semiconductors for optoelectronic devices, owing to their remarkable properties, including efficient light absorption, tunable bandgaps, and excellent charge carrier transport. These low-cost materials have already revolutionized solar energy conversion, achieving power conversion efficiencies surpassing 25% within a decade, outpacing traditional silicon-based photovoltaics.

While the performance of perovskites is well-documented, their long-term stability remains a critical challenge, particularly for lead-based perovskites that are prone to ion migration and degradation. This talk will focus on the development and application of lead-free perovskites as sustainable alternatives for next-generation optoelectronics, emphasizing their potential in low- to high-energy photodetectors.

By micro-engineering the chemistry of $Cs_2AgBiBr_6$, a lead-free double halide perovskite, we have developed durable platforms that exhibit high photoresponse and low dark current, reflecting enhanced device stability. Through controlled Cs- and Bi-site doping with monovalent metal ions (e.g., Rb), organic cations (e.g., imidazolium), and trivalent lanthanides (e.g., Eu), we demonstrate significant improvements in charge transport and X-ray sensitivity - up to an order of magnitude.[1,2] Moreover, our work provides a deeper understanding of the relationship between the materials' intrinsic properties and their photophysical performance. Advanced spectroscopic techniques are employed to elucidate the interplay between crystalline structure and charge carrier dynamics, providing insights into the mechanisms driving their optoelectronic behavior.
Additionally, the photodetection range of $Cs_2AgBiBr_6$ is extended from X-rays to near-infrared radiation, showcasing its versatile properties for future optoelectronic applications.[3]

This work highlights the promise of lead-free perovskites in addressing stability and environmental concerns, establishing a foundation for their broader adoption in advanced photonic technologies.

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References:

[1] Keshavarz, M.; Debroye, E.; Ottesen, M.; Martin, C.; Zhang, H.; Fron, E.; Küchler, R.; Steele, J.; Bremholm, M.; Van de Vondel, J.; Wang, H.; Bonn, M.; Roeffaers, M.; Wiedmann, S.; Hofkens, J. Tuning the Structural and Optoelectronic Properties of $Cs_2AgBiBr_6$ Double Perovskite Single Crystals Through Alkali Metal Substitution. *Advanced Materials*, **2020**, *32, 40*, 2001878.

[2] Valli, D.; Zhang, H.; Betuiak, M.; Romolini, G.; Meulemans, A.; Escudero, D.; Seth, S.; Zhao, Q.; Zhu, Z.; Bonn, M.; Belas, E.; Grill, R.; Wang, H.I.; Hofkens, J.; Debroye, E. Enhancing the X-ray sensitivity of $Cs_2AgBiBr_6$ double perovskite single crystals through cation engineering. *ACS Applied Optical Materials*, **2024**, *2, 10*, 2075-2084.

[3] Valli, D.; Vanden Brande, R.; Herreman, V.; Li, Q.; Romolini, G.; Chen, J J.-K.; Shameem, K.M.M; Sun, L.; Zhao, Q.; Pradhan, B.; Hofkens, J.; Debroye, E. Noble Metals Doping in Lead-Free Double Perovskite Single Crystals: Achieving Near-Infrared to X-ray Broadband Photodetection. *Small Science, **2025**, 10.1002/smsc.202500135*

Encounter Complex Control in Dye-Sensitized Halide Photochemistry

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Many important photochemical transformations are initiated by bimolecular reactions between a molecular excited state and an electron donor or acceptor. A key step in the composite mechanism for such reactions involves formation of an *encounter complex* in which the excited state and the quencher are held in proximity within a solvent cage.[1] This presentation considers what we as photochemists really understand about these putative encounter complexes and raises the question of how they can be controlled? This question is addressed by providing a historic perspective on encounter complexes and solvent cages in photochemistry followed by our own recent attempts to control the encounter complex structure through synthetic design of Ru(II) and Ir(III) photocatalysts for halide oxidation and photo-release. Some representative examples include photocatalysts with cationic functional groups that drive bond forming reactions;[2] hydrogen bonding groups that stabilize reactants in the solvent cage,[3,4] and strong oxidizing power for determination of halogen atom one-electron reduction potentials.[5] In one particular example, chloride photorelease/migration was observed when the metal-to-ligand charge transfer excited state dipole was directed towards the halide ion, but not when the dipole was directed away from the halide, Fig.1.[4] The free energy for stabilization within the encounter complex has been determined by competitive kinetic measurements.[2] These and other examples provide new directions for photochemical investigations of encounter complexes where enhanced cage escape yields may enable practical applications.

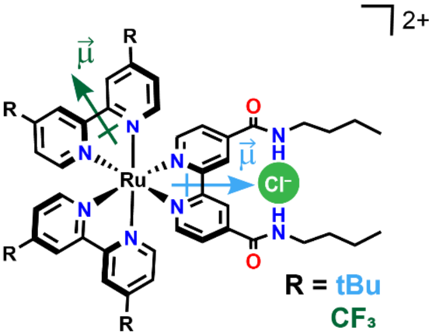

Figure 1. Metal-to-ligand charge transfer (MLCT) excitation results in chloride migration/release when the excited state was localized on the halide associated ligand (R = tertiary butyl) and not when the excited state was localized on an ancillary ligand (R = CF_3).

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References:

[1] M.J. Goodwin, J. Dickenson, A Ripak, A.M. Deetz, J. McCarthy, G.J. Meyer, L. Troian-Gautier *Chem. Rev.* **2024**, *124*, 7379.

[2] A.M. Deetz, G.J. Meyer *J. Am. Chem. Soc. Au* **2022**, *2,* 985.

[3] M.J. Goodwin, A.M. Deetz, P.J. Griffin, G.J. Meyer *Inorg. Chem.* **2024**, *63*, 15772.

[4] D. Turlington, L. Troian-Gautier, R.N. Sampaio, E. Beauvilliers, G.J. Meyer *Inorg. Chem.* **2019**, *58*, 3316.

[5] A.M. Deetz, L. Troian-Gautier, S.A.M. Wehlin, E.J. Piechota, G.J. Meyer *J. Phys. Chem. A* **2021**, *125*, 9355.

Remote Control of Fluorescence Color by means of Optical Tweezers

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Beautiful fluorescence is very attractive in chemistry. For further applications of fluorescence, it is much important to control and modulate fluorescence color. So far, various techniques and methodologies have been proposed and demonstrated to control and modulate fluorescence color. All these approaches require touching the fluorescent material; modification of molecular structure, exchanging solvents (solvatochromism), applying mechanical stress, and so on.

In contrast, by using optical tweezers, we propose novel techniques that enable us to control and modulate fluorescence color in a remote and non-contact manner. We demonstrate that optical tweezers can control initial photochemical processes such as solvation, excimer formation, and FRET.

Here we show 3 examples of the remote control of fluorescence Color (FC) by means of optical tweezers.

(1) FC based on solvatochromism of a dye-decorated chain polymer on a nanostructured Si crystal [1]

(2) FC based on excimer formation of perylene (linked to a chain polymer) on a nanostructured Si crystal [2]

(3) FC based on FRET in a polymer droplet [3], which is described here briefly.

Förster resonance energy transfer (FRET) is ubiquitous in optical processes in the natural world. We propose a methodology which uses an optical force to control its efficiency without contact in an aqueous solution of a thermo-responsive polymer, polyvinyl methyl ether (PVME). Focused irradiation of a near infrared laser beam into the solution resulted in the formation and trapping of a single polymer droplet. We show that the polymer concentration in the droplet is controllable by changing the optical force from the laser light. The polarity inside the droplet decreases with increasing the optical force. When small amounts of dye molecules, $\boldsymbol{D}$ (energy donor) and $\boldsymbol{A}$ (energy accepter), are dissolved in the polymer solution, $\boldsymbol{D}$ and $\boldsymbol{A}$ are absorbed (extracted) into the droplet. The concentrations of $\boldsymbol{D}$ and $\boldsymbol{A}$ are controllable by the optical force. Based on this mechanism, we succeed in inducing FRET between $\boldsymbol{D}$ and $\boldsymbol{A}$, and can control the FRET efficiency. Finally, we demonstrate the modulation of fluorescence color of the droplet from blue, green, yellow, to an orange color simply by changing the optical force. This is shown in Figure 1. The concept and technique are unique and will open a new channel to develop droplet chemistry and photochemistry.

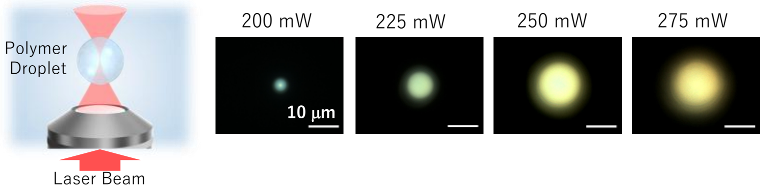

Figure 1. Fluorescence color control of a polymer droplet by an optical force.

References

[1] T. Nagai et al. & Y. Tsuboi, *ACS Appl. Nano Mater*. **2023**, 6, 180–189

[2] R. Takao et al., & Y. Tsuboi, *Angew. Chem. Int. Ed*. **2022**, *61*, e202117227.

[3] T. Nagai et al. & Y. Tsuboi, *Advanced Optical Materials*., **2024**, 12, 2400302.

Separating triplet exciton diffusion from triplet–triplet annihilation in solid state triplet-triplet annihilation photon upconversion

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Exciton diffusion is of importance in for instance organic light emitting diodes and solar cells, as well as in solid state triplet-triplet annihilation photon upconversion (TTA-UC). For TTA-UC to be technologically relevant within solar harvesting, solid-state TTA-UC systems need to be developed.[1] The biggest problem going from solution to solid state, is replacing molecular diffusion by exciton diffusion. Exciton hopping requires orbital overlap and therefore an annihilator concentration approaching the neat state, which in turn result in significant concentration induced quenching of the annihilator singlet state. Thus, a pressing fundamental matter in purely solid state TTA-UC films is achieving efficient excited state energy transfer between species whilst maintaining the annihilators favorable photophysical properties. I will propose that hetero-TTA could be a solution of achieving efficient exciton diffusion without causing concentration quenching of the annihilator.[2] I will start with proposing an energy flowchart that allows the triplet energy transfer function to be separated from upconversion and emission (Fig. 1). This by the utilization of a hetero-TTA based mechanism using a low concentration of annihilator within a mediator matrix in the solid state. Furthermore, I will give spectroscopic evidence of hetero TTA in the solid state, and corroborate the conditions were hetero-TTA is the predominant mechanism with simulations using the Monte-Carlo method. The developed Monte-Carlo simulations will also be used to assess the effect of exciton diffusion and Förster radius on the yield of energy transfer in doped dye films. It is found that the yield of energy transfer to a great deal is a function of exciton diffusion, which is beneficial in organic light emitting diodes but detrimental in solid state TTA-UC.

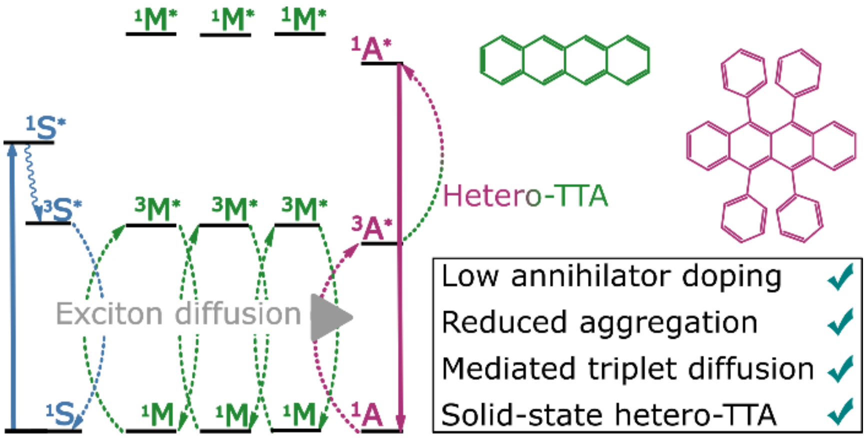

Figure 1. Schematic diagram of the energy transfer pathways and the photon upconversion mechanism. Photon absorption and ISC occurs on the sensitizer (S), and triplet energy transfer to the mediator (M) proceeds with high efficiency. Exciton diffusion between mediators is rapid and occurs over long distances, resulting in hetero-TTA at the annihilator (A) sites

References:

[1] A. J. Carrod, V. Gray, K. Börjesson, *Energ. Environ. Sci.* **2022**.

[2] A. J. Carrod, A. M. Berghuis, V. N. Gopalakrishnan, A. Monkman, A. Danos, K. Börjesson, *Chemical Science* **2025**, *16*, 1293-1301.

Novel design of photocleavable molecular tools for targeted intracellular delivery

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Photoresponsive materials have become indispensable tools in the life sciences, enabling optical control over a wide range of cellular phenomena—from fluorescence-based visualization of biological processes to light-triggered bio-functional molecular release for activity modulation. Among these, photocleavable molecules have played an important role in spatiotemporal control, traditionally used for light-stimulated pro-drug activators. More recently, the potential application of these systems as optogenetic tools for controlling cellular functions at the subcellular or molecular level has also been demonstrated.[1]

Despite their broad potential, conventional photocleavable molecules face major challenges in chemical biology and cell biology applications, due to the trade-off between high photocleavage efficiency and chemical stability under aqueous or enzymatic environments.

To address this limitation, we introduce a new concept in photocleavable molecular design: the introduction of a trimethylsilyl (TMS) group at a position remote from the photolabile bond within coumarin scaffolds (Fig. 1).[2] The remotely introduced TMS group sterically protects the hydrolysis-sensitive carbonyl bond and simultaneously stabilizes the photoexcited cationic species through the β-silyl effect, thereby enhancing photocleavage efficiency. Our remote silyl-based design strategy can be readily extended to other types of photocleavable molecules, offering water- and enzyme-stable, highly efficient photo-triggers with tunable absorption wavelength. Moreover, we successfully conjugated this novel coumarin derivative with proteins and confirmed efficient, light-induced protein release from a solid support material, while maintaining hydrolysis stability.

We further show the power of these molecules by integrating them with a plasmonic-nanowire-based single live-cell endoscopy technique.[3] The hybrid platform enables direct, light-triggered efficient delivery of proteins into the nuclei of living cells, exemplifying the convergence of molecular-level photochemical design and nanophotonic technology, and opening a path toward next-generation tools for high-precision optical manipulation of cellular function.

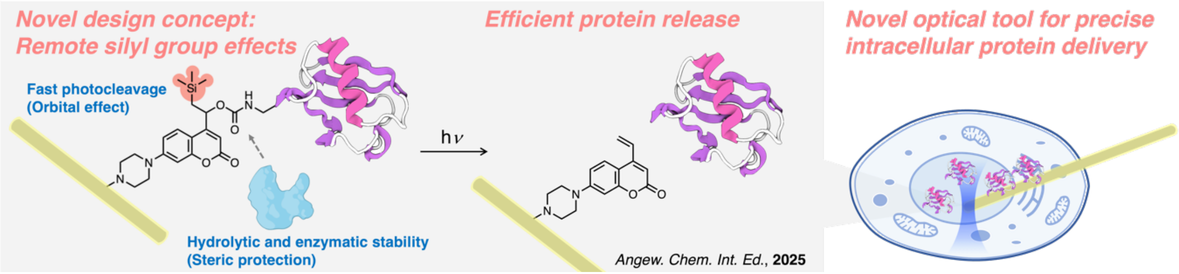

Figure 1. Novel optical tool for spatiotemporally controlled precise intracellular delivery via integration of a novel photocleavable molecular tool with plasmonic nanowire-based single live-cell endoscopy.

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References:

[1] H. Ewers *et al.*, *Nat. Methods*, **2024**, *21*, 666.
[2] M. Yoshimura, T. Inose *et al.*, *Angew. Chem. Int. Ed.* **2025**, e202502376.
[3] G. Lu, H. Uji-i *et al.*, *Adv. Mater.*, **2014**, *26*, 5124.

Optimization of intermolecular interactions for efficient solid-state photon upconversion

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Triplet–triplet annihilation-based photon upconversion (TTA-UC) is a molecular-based methodology for converting low-energy photons into high-energy photons under solar irradiance. Recent advances in developing superior triplet energy acceptors for visible-to-ultraviolet TTA-UC have accelerated its applications in photocatalysis and photoreactions[1]. Although studies in solution have highlighted the importance of bulky substituents in preventing excimer formation and suppressing non-radiative decay through triplet–ground state interactions[2], the optimal molecular design for solvent-free solid-state TTA-UC remains unclear. Here, we control intermolecular electronic interactions based on a unique molecular design in which alkyl chains are introduced at the sp^3 carbons of the highly emissive 5,10-dihydroindeno[2,1-a]indene (DHI) skeleton. These alkyl chains at sp^3 carbons spatially protect the upper and lower π-planes of the DHI chromophore. This new acceptor design allows for controlled intermolecular interactions in the crystalline state, enabling fast diffusion of triplet energy while suppressing singlet and triplet quenching (Figure 1b); the DHI derivatives showed high fluorescence quantum yields and high sensitizer dispersibility, which result in a high absolute UC efficiency of 3.8 % and remarkably low threshold excitation intensity threshold (I_{th}) of 1.2 mW cm^{-2}.

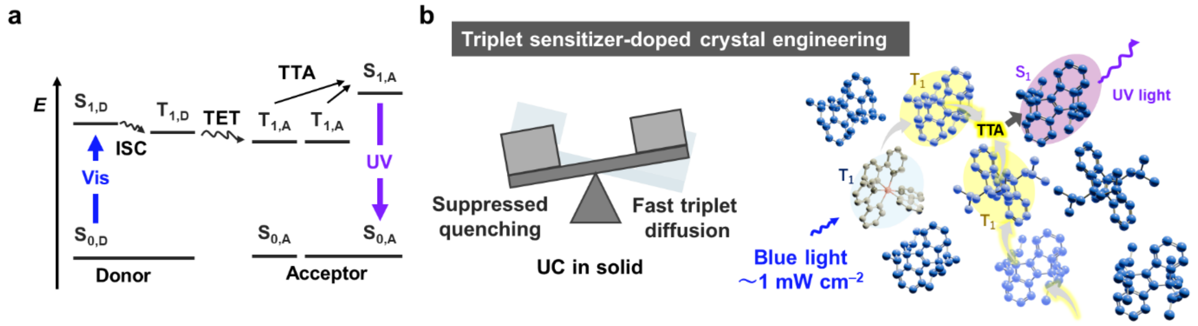

Figure 1. a) An energy diagram of the TTA-UC process from visible to ultraviolet light, b) Crystal engineering for highly efficient solid TTA-UC systems that simultaneously achieve suppression of the excited singlet and triplet quenching, fast triplet diffusion, and donor solubilization.

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References:

[1] M. Uji, T. J. B. Zähringer, C. Kerzig, N. Yanai, *Angew. Chem. Int. Ed.*, **2023**, *62*, e202301506.

[2] A. Olesund, S. Ghasemi, K. Moth-Poulsen, B. Albinsson. *J. Am. Chem. Soc.* **2023**, *145*, 22168–22175.

[3] N. Harada, H. Shoyama, N. Boonmong, K. Mizukami, Y. Watanabe, P. Zhao, M. Ehara, Y. Sasaki, N. Kimizuka, 2025, ChemRxiv preprint DOI: 10.26434/chemrxiv-2025-mmh9d-v2.

Fluorescent detection of micro- and nanoplastics in crowded environmental water samples through a co-staining approach

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In the last decades plastic pollution is dramatically increasing due to human activities; the potential most dangerous plastic fragments are those with sizes lower than 5 mm, the so-called micro- and nanoplastics (MNPs), given their ubiquity and bioavailability.

The detection of MNPs is extremely complex, but a possible solution can be represented by luminescence-based methods, since they allow the development of fast, easy, cheap and sensitive techniques. In particular, fluorescence microscopy can allow the MNPs detection through the staining of the plastic particles with suitable fluorescent probes.[1]

With this aim, we synthetized a fluorogenic probe based on a biopolymer – hyaluronic acid – functionalized with a fluorophore – rhodamine B – (HA-RB).[2] Indeed, in an aqueous environment, hyaluronic acid functionalized with a fluorophore like rhodamine B forms hydrated nanometric aggregates in a colloidal suspension, in which the fluorophores undergo self-quenching processes for proximity issues, causing a decrease in emission quantum yield and fluorescence lifetime. In presence of micro- or nanoplastics, HA-RB can wrap them, inducing an increase in the distance among the dyes, with a consequent luminescence recovery (Fig. 1a). This strategy enabled the detection of MNPs with sizes approaching the resolution limit of confocal fluorescence microscopy (approximately 250 nm).

However, with fluorescence-based staining methods the identification of MNPs may be challenging in complex matrices, such as environmental samples, where numerous organic and inorganic contaminants may also be labelled and thus mistaken for plastic particles.

To overcome this limitation, we implemented a co-staining strategy by employing an array of fluorescent probes with distinct spectral emission profiles and different affinities for plastics and contaminants. Specifically, we combined HA-RB, which emits in the red region and can stain both MNPs and contaminants, with DAPI and methylene blue (MB), which preferentially stain organic and inorganic interferences rather than MNPs, and emit in the blue/green and near-infrared regions, respectively.

By using confocal fluorescence microscopy – a rapid and sensitive technique – this combination of probes enables the discrimination of plastic particles in environmental water samples without the need for sample pre-treatment (Fig. 1b), thereby improving detection accuracy and selectivity and reducing the occurrence of false positives.

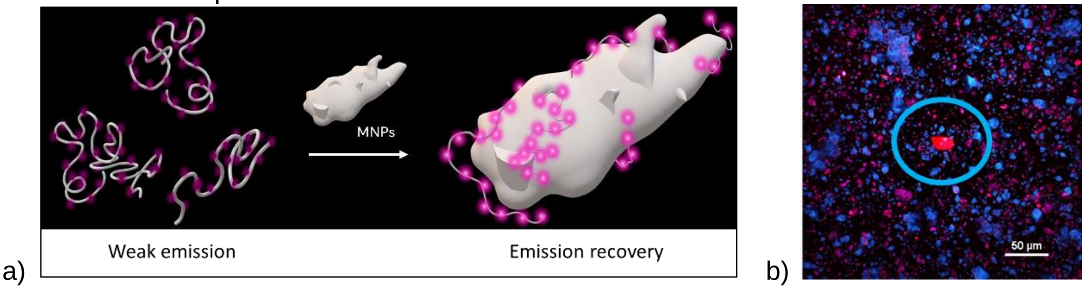

Figure 1. a) Mechanism scheme of the interaction between hyaluronic acid functionalized with rhodamine B and MNPs. b) Confocal image with four channels (blue, green, red and NIR, colored in violet) of an environmental sample stained with the three fluorescent probes, in which an element is colored only by HA-RB (red emissive) so it can be identified as a plastic particle.

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References:

[1] C. Capolungo, D. Genovese, M. Montalti, E. Rampazzo, N. Zaccheroni, L. Prodi, *Chem. Eur. J.*, **2021**, *27*, 17529–17541.

[2] M. Cingolani, D. Genovese, E. Rampazzo, N. Zaccheroni, L. Prodi, *Environ. Sci.: Nano*, **2022**, *9*, 582–588.

Bioinspired Charge Transfer and Wine-Inspired Photochemistry

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Charge transfer (CT) sustains life on earth and ensures our modern ways of leaving possible[1]. CT is at the centre of photosynthesis and cellular respiration. Biomimetics and biological inspiration, therefore, offer vital paradigms for CT control and energy management[2]. Concurrently, dipoles are ubiquitous and their multifaceted effects on CT still remain largely unexplored. Adopting anthranilamide structural motifs, we design and develop bioinspired molecular electrets to explore emerging dipole effects on CT[2]. (Possessing ordered electric dipoles, electrets are the electrostatic analogues of magnets.) Even a single electret residue can rectify CT and exert enormous effects on CT kinetics[3,4]. With persistence length exceeding 2 nm, anthranilamide electret oligomers shorter than five residues are practically rigid[5]. This rigidity allows obtaining valuable high-energy X-ray scattering (HEXS) signals that confirm the electret structures in solution phase. Nevertheless, the macrodipoles of these conjugates show picosecond fluctuations with amplitudes amounting to a factor of two or three from the average values[6]. How universal are such unusually large dipoles fluctuations, and can they be the reason for fast CT processes that do not necessarily appear thermodynamically favorable? To inject holes in electron-rich electrets and initiate CT cascades, we resort to diketopyrrolopyrroles (DPPs) that are good photooxidants[4,7]. For generating and transferring high-energy holes, however, we resort to less electron-rich anthranilamide residues for the electrets and develop pyranoflavyliums (PFs) based on structures of pigments formed during the maturation of red wines. The PFs are potent photooxidants and exhibit good photostability. (How easy is to clean stains from red wine?) PFs have strong absorption in the visible spectral region and their reduction potentials can be as high as -0.2 V vs. SCE, placing them among the best metal-free organic photooxidants. The pyranoflavyliums and the anthranilamide electrets present a valuable bioinspired toolbox for exploring the emergence of new CT phenomena essential for technology advances.

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References:

[1]. J. Derr et al., *Phys. Chem. Chem. Phys.* **2020**, *22*, 21583.
[2]. V. I. Vullev, *J. Phys. Chem. Lett.* **2011**, *2*, 503.
[3]. D. Bao et al., *J. Am. Chem. Soc.* **2014**, *136*, 12966.
[4]. M. Krzeszewski et al., *Angew. Chem. Int. Ed.* **2018**, *57*, 12365.
[5]. O. O'Mari, M. Y. Yang, W. Goddard, V. I. Vullev, *J. Phys. Chem. B* **2025**, *129*, 1750.
[6]. M. Y. Yang, O. O'Mari, W. Goddard, V. I. Vullev, *J. Am. Chem. Soc.* **2024**, *146*, 5162.
[7]. A. Purc et al., *J. Am. Chem. Soc.* **2016**, *138*, 12826.

Polariton Dynamics of Gold Nanocubes/Carbocyanine Aggregates Investigated by Femtosecond Transient Absorption Spectroscopy

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Molecular polaritons are quasiparticles that arise when the confined electromagnetic fields, for example, in a photonic cavity, are strongly coupled to a resonant molecular transition. When confined inside or near the plasmonic cavity of metal nanostructures, a small number of dye molecules show efficient polaritonic properties via localized surface plasmon resonances (LSPR). In this work, we report ultrafast polariton dynamics of gold nanocubes (AuNCs) / carbocyanine (TDBC) aggregates by femtosecond transient absorption spectroscopy.[1] Fig. 1 compares the femtosecond transient absorption results with nonresonant (403 nm), upper polariton (UP; 550 nm), and lower polariton (LP; 620 nm) excitations. The electron-phonon and phonon-phonon scattering dynamics of AuNCs were removed with the separate measurements without TDBC aggregates. The excited-state absorption bands of the coherent plasmon-exciton coupling states show ultrafast (60-70 fs) deexcitation dynamics relevant to the Rabi splitting (0.15-0.17 eV) between the UP and LP bands. Interestingly, the ground-state bleachings of the UP and LP states show excitation-dependent recovery dynamics. The recovery of UP bleaching bands appears much slower (1.8 ps) with the LP excitations, compared to all other ground-state bleaching dynamics (0.3-0.5 ps). Polarition deexciation dynamics depending on the selective excitation of the UP and LP states, and on the LSPR bands of AuNCs (60 vs. 100 nm in length) will be discussed compared to similar plasmonic polariton systems. Our reports provide fundamental experimental evidence of ultrafast polariton dynamics, which exhibit strong correlations with the LSPR of plasmonic metal nanostructures.

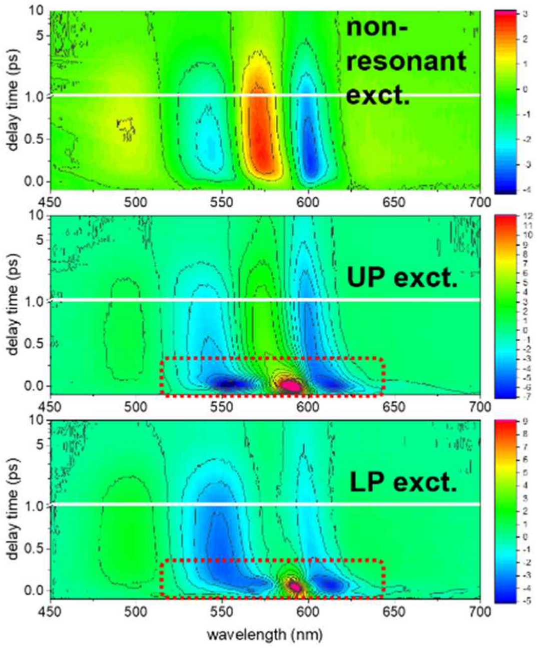

Figure 1. Transient absorption results of gold nanocubes (AuNCs)/carbocyanine aggregates with the nonresonant (403 nm), upper polariton (550 nm) and lower polariton (620 nm) excitations.

Funding: National Research Foundation of Korea (RS-2020-NR049542, RS-2021-NR059060, RS-2023-00210768, and RS-2023-00220174)

References:

[1] Y.-M. Lee, H. Choi, S.-E. Kim, J. Kim, H. W. Kim, J.-E. Park, *Nano Lett.* **2024**, *24*, 16115-16123.

Dye decolorization using liquid phase synthesized Pt nanoparticles as photocatalysts

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Pt is widely used as a catalyst for hydrogenation, dehydrogenation, oxidation reactions, and exhaust gas purification. Since smaller particle size increases the unit surface area and the number of catalytically active sites per unit mass, Pt nanoparticles are also being actively studied. On the other hand, Pt nanoparticles, like gold and silver, interact with light to induce local surface plasmon resonance (LSPR), with Pt nanoparticles of approximately 29 nm in diameter exhibit an LSPR peak in the UV region.[1]. Compared with gold and silver, Pt nanoparticles have been less studied, and the photocatalytic activity of Pt nanoparticles based on plasmon resonance is unclear. In this study, we synthesized Pt nanoparticles with LSPR in the visible to near-infrared region and used them as catalysts to compare their catalytic activity in the decolorization reaction of dye molecules such as methyl violet under light irradiation.

Figure 1(a) shows a scanning electron microscope image of Pt nanoparticles synthesized by the seed-mediated method. The average particle size of the Pt nanoparticles was 38 nm and the particle shape was dendritic. Although not shown here, the synthesized Pt nanoparticles had a peak wavelength in the UV region and showed broad absorption spectra up to the near-infrared region due to plasmon resonance. The absorption spectra of aqueous methyl violet solution with Pt nanoparticles as catalysts are shown in Figure 1(b) for different reaction times under near-infrared irradiation. The reaction time was set to 0 min immediately after irradiation with near infrared light from an Xe lamp (wavelengths of 780 nm - 940 nm). At 0 min, an absorption peak of methyl violet at a wavelength of 586 nm was observed, but the peak intensity decreased with increasing irradiation time, and the reaction was terminated after 60 min. The same experiment was performed in the dark, and the intensity of absorption peak did not change even after 60 minutes. The results of similar experiments at different irradiation wavelengths suggested that the decolorization reaction is enhanced by LSPR of synthesized dendritic Pt nanoparticles induced by near-infrared light.

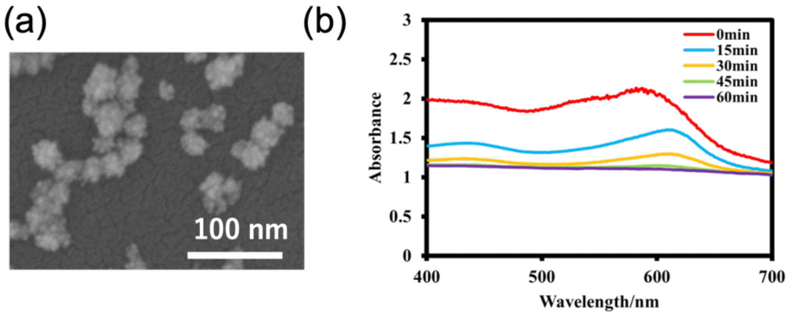

Figure 1. (a) Scanning electron microscope image of synthesized dendric Pt nanoparticles. (b) Time dependence of the absorption spectra of methyl violet aqueous solution under near infrared irradiation using Pt nanoparticles as catalysts.

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References:

[1] N. C. Bigall, *et al.*, *Nano Lett.*, **2008**, 8(12), 4588-4592.

Chiroptical responses on plasmonic array under modal coupling regime

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Numerous studies have examined on the interactions between circularly polarized light (CPL) and materials. Localized surface plasmon resonances (LSPRs), which are collective oscillations of the conductive electrons of the metallic nanostructure, confine propagating light near the nanostructures and enhance the localized electric field, known as the near field. Chiral plasmonic structures and incident light with optical chirality induce helical near fields[1-3].

The configuration and arrangement of plasmonic particles also play important roles in determining their chiroptical responses[4]. In this study, we fabricated Au nano-windmills (Au-NWs) on a Fabry-Pérot (FP) nanocavity of TiO_2 on Au-film. The Au-NWs were composed of a cluster of isotropic Au nanodisks with a two-dimensional chiral arrangement[5]. We discuss chiroptical responses on Au-NWs coupled with the FP nanocavity.

Au-NW was a cluster of Au nanodisks (Au-NDs) with a two-dimensional chiral arrangement bearing three-fold rotational symmetry. We fabricated two types of Au-NWs with different Au-ND diameters on a TiO_2 layer with a thickness of 60 nm on a Au/SiO_2 substrate (Au-NWs-1 and Au-NW-2, Figure 1a). We measured the differential absorption spectra of the left- and right-handed CPL irradiations. The differential absorption spectrum of TiO_2/Au without Au-NWs did not show a significant signal, indicating that the FP nanocavity alone did not exhibit a chiroptical response (Figure 1b). In contrast, the differential absorption spectra of the Au-NWs on the TiO_2/Au-film show clear negative signals. Furthermore, the wavelengths of the negative signals correspond to the diameters of the Au-NDs. These results suggest that modal coupling between the LSPR and FP nanocavity modes induces chiroptical responses in Au-NWs with a chiral arrangement. Near-field analyses by numerical simulation revealed that the Au-NWs coupled with the FP nanocavities formed a collective mode in the near field, and the collective mode represented the chiroptical response in the far field.

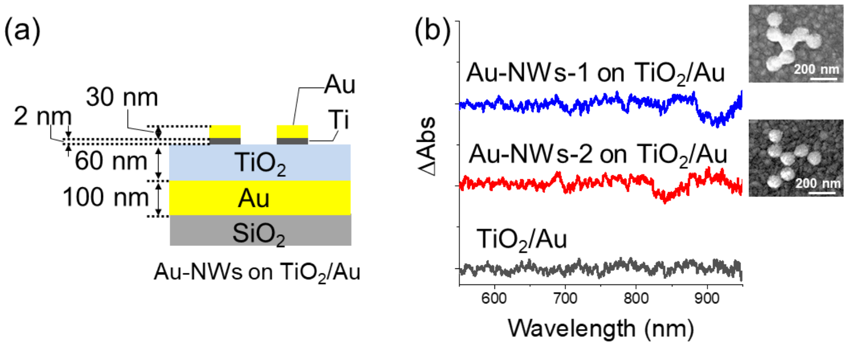

Figure 1. a) Cross-sectional view of Au-NWs on TiO_2/Au. b) Differential absorption spectra of Au-NWs on TiO_2/Au. The insets show scanning electron microscopy images of the Au-NWs on TiO_2/Au.

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References:

[1] S. Hashiyada, T. Narushima, H. Okamoto, *J. Phys. Chem. C* **2014**, *118*, 22229-22233.

[2] T. Oshikiri, Q. Sun, H. Yamada, S. Zu, K. Sasaki, H. Misawa, *ACS Nano* **2021**, *15*, 16802-16810.

[3] S. Zu, Q. Sun, E. Cao, T. Oshikiri, H. Misawa, *Nano Lett.* **2021**, *21*, 4780-4786.

[4] S. Zu, Y. Bao, Z. Fang, *Nanoscale* **2016**, *8*, 3900-3905.

[5] T. Oshikiri, Y. Matsuo, H. Niinomi, M. Nakagawa, *Photochem. Photobiol. Sci.* **2024**, *24*, 13-21.

Photoresponses of molecular systems induced by upconverting photoexcitation: toward super-resolved measurements

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Photoexcitation is a primary process in photochemical reactions; to produce an excited state, a molecule is typically irradiated with light of a wavelength resonant with its one-photon-allowed absorption band. However, a molecule can also be excited using photons with energies lower than the absorption band through processes such as multiphoton absorption or thermally assisted photoabsorption. Hereinafter, we refer to such excitation as upconverting excitation. This excitation method enables selective photoexcitation of target molecules using low-energy photons, facilitating localization of the excited state beyond the diffraction limit and making it highly suitable for super-resolution measurements.

In recent years, we have investigated the photoreaction mechanisms of molecular systems induced by upconverting excitation and have applied these findings to super-resolution measurement. In this presentation, we introduce examples including monochromatic excitation fluorescence switching (MEFS) of diarylethene derivatives (DAEs) using thermally assisted upconverting excitation, and super-resolution measurement based on it. We also demonstrate real-space measurement of excitation energy transfer using upconverting nanoparticles as local excitation sources. Figure 1 shows an example of MEFS of a DAE induced by thermally assisted upconverting excitation. This DAE, in its open form (**1o**, non-fluorescent), undergoes isomerization to the closed form (**1c**, fluorescent) upon UV irradiation. Upon visible light irradiation, **1c** emits fluorescence while simultaneously undergoing reversible isomerization back to the open form. Typically, fluorescence switching of the DAE requires both UV and visible light sources. However, thermally assisted upconverting excitation enables both cyclization and cycloreversion using monochromatic visible light, leading to spontaneous fluorescence blinking (Figure 1b). This allows for super-resolved localization microscopy using a simple optical setup [1,2]. In systems where the DAE exhibits Brownian motion, it is also possible to simultaneously extract information about the physical properties of the host material, such as the diffusion coefficient distribution of guest molecules, in addition to the microstructure. An example involving DAEs embedded in a polymer blend exhibiting micro-phase separation is shown in Fig. 1c[3]. In this presentation, we will also discuss real-space measurement of excitation energy transfer enabled by on upconverting excitation[4].

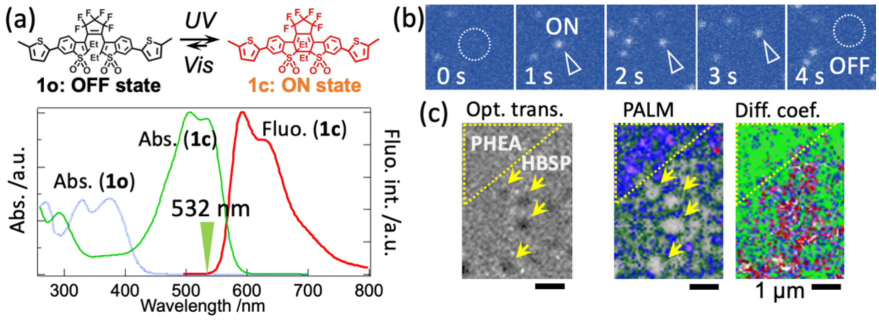

Figure 1. (a) Structures and steady state absorption and fluorescence spectra of **1o** and **1c**. (b) Fluorescence switching of the DAE under 532-nm excitation. (c) Optical transmission and PALM images of blended polymer film and corresponding 2D map of diffusion coefficient of the DAEs.

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References:

[1] Y. Arai, S. Ito, et al., *Chem. Commun.*, **2017**, *53*, 4066.
[2] R. Kashihara, M. Morimoto, S. Ito, H. Miyasaka, M. Irie, *J. Am. Chem. Soc.*, **2017**, *139*, 16498.
[3] S. Ito, M. Funaoka, I. Hanasaki, S. Takei, M. Morimoto, M. Irie, H. Miyasaka, *Polym. Chem.*, **2022**, *13*, 736.
[4] S. Ito, H. Kageyama, et al., to be submitted.

Molecular Engineering of Dithienylethene Photochromes: Toward Fully Optical Photo-Activatable Molecular Materials

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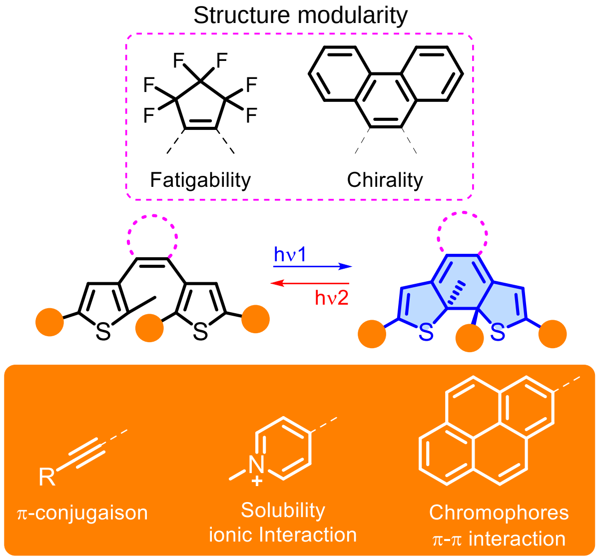
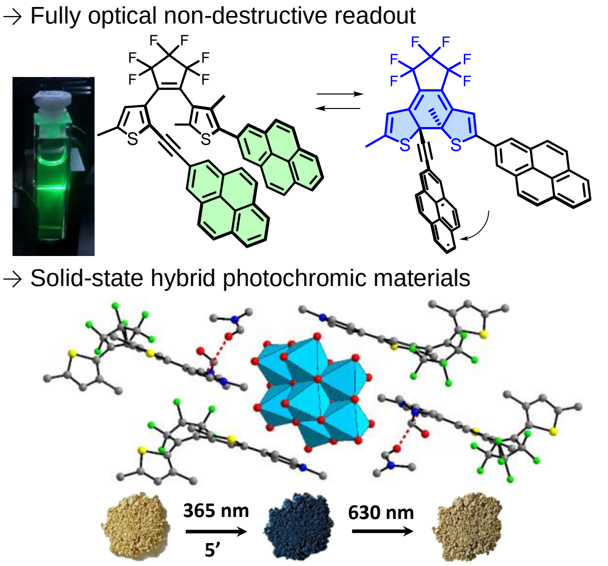
Photoactivatable materials, which can reversibly switch their solid-state optical properties in response to light stimuli, are essential components in the realm of advanced optical technologies.[1] These materials offer a broad spectrum of applications across diverse technological domains, including optoelectronics,[2] information processing and storage,[3] photocatalysis,[4] biomedical science,[5] energy conversion and storage,[6] as well as advanced defense and anti-counterfeiting technologies. In all these research areas, chemistry plays a pivotal role in enhancing and fine-tuning the unique optical properties of dynamic systems.





The integration of molecular photoswitches into more complex materials has long been a central strategy in the development of multifunctional molecular systems. Among these, dithienylethene-based compounds are particularly attractive due to their robust photochromic behavior. However, achieving precise photochemical control or modulation requires careful structural design tailored to the specific application. This level of control is essential for the development of next-generation, high-performance photoactivatable materials. Our contributions to this broad research field focus on several promising approaches:
i) the integration of photochromic organic molecules with inorganic polyoxometalates [7]
ii) the use of photo-triggered molecular geometrical changes to modulate specific excimeric luminescence, enabling fully optical, nondestructive readout systems [8]
iii) the introduction of chirality into the photoswitch backbone via atropisomerism.

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References:

[1] Luo, W.; Wang, G. *Adv. Opt. Mater.* **2020**, *8*, 2001362. [2] Zhao, J.-L.; Li, M.-H.; Cheng, Y.-M.; Zhao, X.-W.; Xu, Y.; Cao, Z.-Y.; You, M.-H.; Lin, M.-J. *Coord. Chem. Rev.* **2023**, *475*, 214918. [3] Yanling Zhuang; Xiuli Ren; Xueting Che; Shujuan Liu; Wei Huang; Qiang Zhao. *Adv. Photon.* **2020**, *3*, 014001. [4] Chen, X.; Niu, N.; Li, D.; Zhang, Z.; Zhuang, Z.; Yan, D.; Li, J.; Zhao, Z.; Wang, D.; Tang, B. Z. *Adv. Opt. Mater.* **2023**, *33*, 2211571. [5] Sun, J.; Li, H.; Gu, X.; Tang, B. Z. *Adv. Healthcare Mater.* **2021**, *10*, 2101177. [6] Wang, Z.; Hölzel, H.; Moth-Poulsen, K. *Chem. Soc. Rev.* **2022**, *51*, 7313. [7] a) Bolle, P.; Menet, C.; Puget, M.; Serier-Brault, H.; Katao, S.; Guerchais, V.; Boucher, F.; Kawai, T.; Boixel, J.; Dessapt, R. *J. Mater. Chem. C* **2021**, *9*, 13072. b) Stetsiuk, O.; Bolle, P.; Cordier, M.; Boixel, J.; Dessapt, R. *J. Mater. Chem. C* **2022**, *10*, 899. [8] a) Barale, M.; Escadeillas, M.; Taupier, G.; Molard, Y.; Orione, C.; Caytan, E.; Métivier, R.; Boixel, J. *J. Phys. Chem. Lett.* **2022**, *13*, 10936. b) Barale, M. ; Turcas, I. ; Gousseau, V. ; Escadeillas, M. ; Caytan, E. ; Taupier, G. ; Molard, Y. ; Fihey, A. ; Boixel, J. *Dyes and Pigments*, **2025**, *232*, 112473.

Optical Manipulation for Fabricating Protein-based Soft Matter

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We have demonstrated high potential of optical trapping at the solution interface for fabricating reconfigurable optical matter composed of nanoparticles (NPs).[1] Polystyrene and gold NPs are assembled and well-arranged by focusing a 1064 nm trapping laser at the glass/solution interface. These morphological structures expand from the focus to several tens of micrometers outward and can be controlled by tuning laser and microscope parameters. The constituent NPs exhibit fluctuations and migration within the assembly, reflecting their dynamic nature. Optical manipulation has also been applied to proteins at the air/solution interface,[2,3] which reveals new phases of protein such as highly concentrated solutions, droplets/concentrates, amorphous aggregates, and amyloid fibrils. Here, we report on their formation processes by examining their dependence on protein type, concentration, pD, additives, and laser parameters and consider the dynamics and mechanisms in view of protein-based soft matter.

Optical trapping of lysozyme under supersaturated concentration leads to the formation of a single disk-like assembly, reaching a sub-millimeter diameter along the air/solution interface. The concentration at the focus is increased by several folds; however, no droplet formation was observed. Protein molecules become further densely packed, their relative orientations rearranged, and multivalent interaction among them are rapidly enhanced quickly upon laser irradiation. This leaves neither time nor space for D_2O molecules solvated around the proteins to undergo liquid-liquid phase separation, thus, resulting in a further supersaturated phase.

When the lysozyme concentration is reduced by a factor of ten from the super saturated level and NaCl is present, protein clusters become sparsely dispersed in solution. Under these conditions, D_2O molecules can more readily associate with the proteins, allowing droplet formation during laser trapping. Observation combining fluorescence and Raman microscopy reveals the characteristic dynamics of nonlinearly evolving assembling. By changing pD, we confirm that an amorphous solid assembly is prepared inside the droplet.

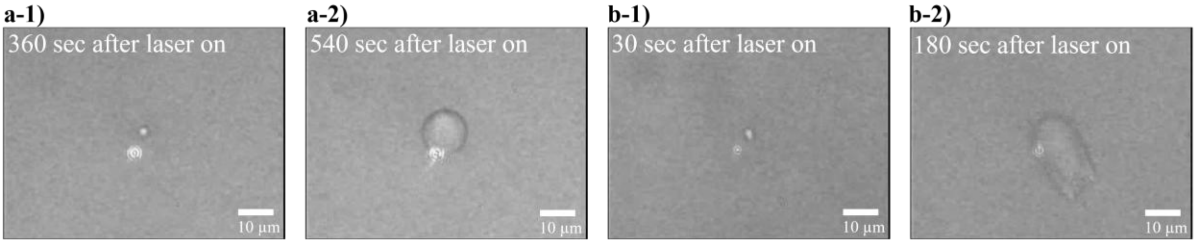

Figure 1. Representative transmission images of lysozyme (40 mg/mL with 4 wt% of NaCl) at air/D_2O solution interface; (a-1) initial stage and (a-2) droplet formation under pD 4.9, (b-1) initial stage and (b-2) aggregate formation under pD 7.3.

We have also demonstrated the formation of a single droplet of α-synuclein by adding polyethylene glycol as a crowding agent. Further laser irradiation induces partial solidification extending outward from the droplet, which can be interpreted as real-time observation of amyloid fibrillation originating from a single droplet. We will discuss these behaviors in context of optical manipulation for the fabrication of protein-based soft matter.

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References:

[1] Masuhara, Yuyama, *Annu. Rev. Phys. Chem.* 72, 565 (2021).
[2] Yi et al., *J. Phys. Chem. C* 125, 18988 (2021); *Appl. Phys. Express* 16, 025501 (2023).
[3] Yuzu et al., *Proc. Natl. Acad. Sci. U.S.A.* 121, e2402162121 (2024).

Mapping microscopic viscosity and macromolecular conformation using molecular rotors

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Viscosity is one of the main factors which influence diffusion in condensed media. In a cell viscosity can play a role in several diffusion mediated processes, such as drug delivery, signaling and mass transport. Previously, alterations in viscosity in cells and organs have been linked to malfunction; however, mapping viscosity on a single-cell scale remains a challenge.

We have imaged viscosity and crowding inside artificial model systems and in live cells using fluorescent probes, called molecular rotors.[1] In molecular rotors the speed of rotation about a sterically hindered bond is viscosity-dependent, which strongly affects fluorescence lifetime or spectra of rotors, allowing fluorescence imaging. This approach enabled us to measure both the microscopic viscosity and macromolecular conformation, *e.g.* the presence of unusual DNA topologies, G-quadruplexes (G4s),[2-5] and to monitor their temporal changes in real time. The talk will cover our recent developments, such as expanding the series of probes for DNA and RNA G4s [4, 5] and monitoring amyloid aggregation using rotors.[6]

References

[1] M. Paez-Perez, M. K. Kuimova, *Angew. Chem. Int. Ed*. 2024, 63, e20231123

[2] J. Robinson et al, *Angew. Chem. Int. Ed.* 2025, e202424931

[3] P. A. Summers, B. W. Lewis, et al *Nat. Commun*. 2021, 12, 162

[4] J. Robinson et al, *J. Amer. Chem. Soc.*, 2024, 146, 1, 1009

[5] T. Bradford et al, *Anal. Chem.* 2024, 96, 20223–20229.

[6] S. Allerton et al, *ACS Appl Mater Interfaces*, 2025, 17(7), 10499-10508

Small-molecule visible light photocatalytic water oxidation enables oxygen-independent ablation of cancer cells

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The power of light-driven catalysis in anticancer therapy is epitomized by the success of photodynamic therapy (PDT), which utilizes photosensitisers (PS) and light to convert molecular oxygen into cytotoxic reactive oxygen species (ROS). However, local hypoxia, a pervasive feature of solid tumours, dramatically impairs photocatalytic oxygen-dependent generation of ROS, leading to the failure of PDT.[1,2] How to effectively tackle hypoxia in PDT has spurred worldwide interest since most PSs act via oxygen-dependent mechanisms. One approach is to ensure an adequate oxygen supply during the illumination phase of PDT.[3] Photoredox catalysis has recently emerged as a more competent anticancer strategy for oxygen-poor environments.[4] Photocatalysts with an electron donor–acceptor type molecular structure can promote electron transfer to/from suitable acceptors/donors.[5] This molecular design has been explored as an effective strategy to obtain PSs with high oxidation/reduction potential that enables substrate oxidation/reduction from their excited state.[4-6] However, the success of this strategy relies on the close proximity of the PS and the biological substrates, which limits its efficacy to their local distribution and depletion. In contrast, water is the most abundant and ubiquitous molecule in cells and thus represents an ideal substrate for the efficient generation of ROS for PDT through photocatalytic oxidation process. Recently, a donor-acceptor molecular system capable of producing hydroxyl radicals *via* water oxidation through a double-electron transfer process has been reported.[7] We show in this work that it is possible to further streamline water photooxidization using a small molecule and visible-light to produce hydroxyl radicals in a single proton-coupled electron-transfer step. We further demonstrate that this photochemical strategy is effective for inducing cell death under extreme hypoxia conditions. Small molecule, single electron transfer photocatalytic water oxidation may become the next game changer in photodynamic therapy, freeing it at last from its long-standing oxygen dependence limitation.

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References:

[1] Y. Wan, L.-H. Fu, C. Li, J. Lin, P. Huang. *Adv. Mat.* **2021**, *33*, 2103978.
[2] Z. Chen, F. Han, Y. Du, H. Shi, W. Zhou., *Sig. Transduct. Target. Ther.* **2023**, *8*, 1.
[3] Z. Shen, Q. Ma, X. Zhou, *et al. NPG Asia Mater.* **2021**,*13*, 39.
[4] H. Huang, S. Banerjee, K. Qiu, P. Zhang, O. Blacque, T. Malcomson, M.J. Paterson, G.J. Clarkson, M. Staniforth, V.G. Stavros, G. Gasser, H. Chao, P. J. Sadler., *Nat. Chem.* **2019**, *11*, 1041.
[5] N.A. Romero, D.A. Nicewicz. *Chem. Rev.* **2016**, *116*, 10075.
[6] K.-X. Teng, L.-Y. Niu, N. Xie, Q.-Z. Yang. *Nat. Commun.* **2022**, *13*, 6179.
[7] C. Lee, M. Park, W.C.B. Wijesinghe, S. Na, C.G.Lee, , E. Hwang, G. Yoon, J.K. Lee, D.H. Roh, Y. H. Kwon, J. Yang, S.A. Hughes, J.E. Vince, J.K. Seo, D. Min, T.H. Kwon. *Nat. Commun.* **2024,***15*, 4025.

Lanthanide-based upconverting nanoparticles and black phosphorus quantum dots for deeper penetrating photodynamic therapy

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Photodynamic therapy (PDT) is an alternative cancer therapy that shows good promise due to the reduction in harmful side effects compared to systemic chemotherapies and radiotherapy. PDT works by generating light-induced oxidative stress, selectively localized in cancer cells. Current photosensitizers for PDT are limited in applications due to the use of visible light excitation and long retention and accumulation in tissue. Near infrared (NIR) light penetrates deeper into tissue however generally, there is not enough excitation energy to generate reactive oxygen species. We aim to extend the application of PDT to tumors by combining an upconverting nanoparticle (UCNP) with the two-dimensional (2D) nanomaterial Black Phosphorus (fig.1a).

UCNPs convert NIR light to visible light via a multiphoton absorption process. This so-called anti-Stokes luminescence is achieved by utilizing the long-lived 4f ladder-like energy states of lanthanide ions[1,2]. By incorporating UCNPs into our PDT system, we can access tumors by exploiting the biological transparency window in the NIR region but still generate visible light excitation locally. However, the upconversion efficiency of UCNPs can be very low owing to the inherent low molar absorption coefficient of the lanthanide ions as well as surface related quenching effects.

In this work, we outline our recent efforts to improve the efficiency of UCNPs and tune their emission by investigating the effects of the concentration of dopants, the composition of the host lattice and surface passivation. We then couple our optimized UCNPs to Black Phosphorus quantum dots (BPQDs), which are thermodynamically stable and highly efficient triplet state sensitizers for singlet oxygen, whilst also possessing superior biocompatibility, particularly in its degradation pathways. Finally, we study the intra-cellular behavior of our nanocomplexes of UCNPs and BPQDs, confirming excellent internalization in 2D (fig.1b) and 3D cancer cell models without cytotoxic effects in the dark. Most importantly, we demonstrate efficient singlet oxygen generation in vitro with NIR irradiation, leading to large amounts of cell death, proving our conjugate particle as a potential future alternative cancer treatment.

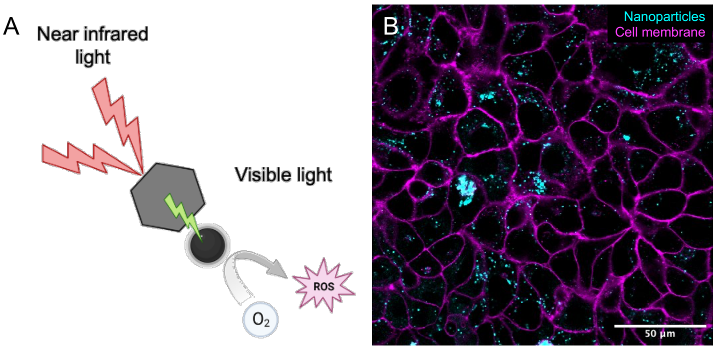

Figure 1: a) schematic diagram of PDT by the conjugate nanoparticle and b) its internalization in a monolayer of A549 lung cancer cells.

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References:

[1] DaCosta, M.; Doughan, S.; Han, Y.; Krull, U. Analytica Chimica Acta, **2014**, 832, 1-33.
[2] Hamblin, M. Dalton Transactions, **2018**, 47 (26), 8571-8580.

Fuels from the Sun: Understanding and controlling electron and energy transfer reactions in solar energy conversion materials

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Converting CO_2 into organic fuels or value-added products requires breaking the stable carbon-oxygen double bonds and calls for the use of electrochemical or catalytic routes to overcome the thermodynamic barrier. An attractive approach is to achieve this utilizing sunlight in a photocatalytic approach to CO_2 reduction, especially if mild conditions such as ambient temperature, aqueous conditions and benign materials can be used. We have long studied the necessary multielectron transfer reactions needed to achieve CO_2-to-CO reduction in model systems. However, we wanted to go further and try to design an something that would be sustainable from the beginning.

In this work, we used stable polymeric carbon nitrogen dots with good solubility in polar solvents and a wide absorption range (<650 nm) as photosensitizers. Their photophysical properties make them very interesting as light harvesters as well as catalytic materials. They dots are then combined with molecular catalysts based on Fe, for CO_2-to-CO reduction, see Figure 1. Mechanistic insight was gained through systematic variation of conditions, where an optimal catalyst concentration of 1.0 µM was found, yielding CO generation of ~200 µmol/h with high selectivity (~96 %) for 10h irradiation, resulting in a TON_{CO} of $\sim 10^5$ or TOF_{CO} of $\sim 12\ s^{-1}$. The mechanism for photo-induced CO_2 reduction using these types of catalysts is debated in the literature. Here, unexpectedly we observe a CO formation route via a reversible Fe(II)↔Fe(I) transformation pathway rather than the commonly invoked Fe0 state. This highlights the need for detailed understanding of the charge transfer processes underlying the CO_2-to-CO transformation.

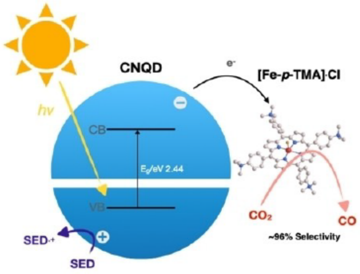

Figure 1. Schematic depiction of the photocatalytic assembly consisting of a carbon nitride dot, functionalized with EDTA and the Fe-porphyrin serving as the catalyst. The necessary steps, including light absorption by the carbon nitride dot and the subsequent electron transfer pathways are schematically shown in the figure.

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References:

L. Mistry, L. Le-Quang, G. Masdeu, W. Björkman, H. Härelind, M. Abrahamsson *ChemCatChem* **2022**, *14 (24)*, e202200897

Directional Magnetic Sensitivity in Immobilized Cryptochrome 4: Unraveling Nature's Photochemical Inclination Compass

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The physical basis of magnetoreception remains an open question in sensory biology. While it has been established that many species use the geomagnetic field to aid navigation, the underlying mechanism is still contested. For migratory songbirds, the leading hypothesis involves light-induced radical pairs formed in the flavoprotein cryptochrome, where quantum spin dynamics are thought to mediate the outcome of chemical reactions.[1] Behavioral experiments have established that European robins sense the direction of Earth-strength magnetic fields,[2] with the navigational ability dependent exclusively on blue and green light.[3] Disorientation of birds by oscillating radiofrequency fields, which perturb the spin sublevel populations, suggest the radical pair mechanism is operational in vivo.[4] In vitro, absorption-based spectroscopic studies have identified a range of light-induced radical intermediates in the cryptochrome photocycle, whose concentration depends on the strength of the applied magnetic field.[5] However, for a candidate compass molecule, the photochemistry should also necessarily respond to the magnetic field *direction*.

The recombination probability of a radical pair is subject to conservation of spin angular momentum and, hence, dependent on the overall spin state of the system. The magnetic momenta of the unpaired electron spins interact both with neighbouring nuclear spins (hyperfine interaction) and any applied external magnetic field (Zeeman interaction), with the anisotropy of the former giving rise to directional sensitivity. A persistent criticism of the cryptochrome hypothesis has been the presence of several hyperfine interactions in the radicals, whose opposing directionality could (in theory) destroy the inclination sensitivity. To address this concern, we have developed confocal microscopy for the study of spatially resolved anisotropic magnetic field effects.[6] Here we show that the fluorescence intensity of single crystals of *Columba livia* (common pigeon) cryptochrome 4 is modulated by the direction of an applied magnetic field of fixed magnitude (16 mT). This work constitutes the first report of anisotropic magnetic field effects in immobilised and aligned avian cryptochrome, which establishes that cryptochrome is fit for purpose as a photochemical inclination compass. Proteins immobilised in biological matrices, such as membranes or cytoskeletal environments, could exhibit similar anisotropic magnetosensitivity in vivo, and signal the magnetic field inclination to the bird.[1] Combining optical sectioning with knowledge of the crystal structure, we rationalise the observed trends in magnetic field effect anisotropy in terms of photoselection and the orientation of individual radical residues with respect to the applied magnetic field. The present study thus provides compelling evidence for the feasibility of cryptochrome-based radical pair-mediated magnetoreception.

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References:

[1] Hore and Mouritsen, *Annu. Rev. Biophys.*, **2016**, *45*, 39, 299-344.
[2] Wiltschko and Wiltschko, *Science*, **1972**, *176*, 4030, 62-64.
[3] Wiltschko, et al., *Nature*, **1993**, *364*, 525–527.
[4] Ritz, et al., *Nature*, **2004**, *429*, 6988, 177-180.
[5] Xu et al., *Nature*, **2021**, *594*, 7864, 535-540.
[6] Déjean et al., *Chem. Sci.,* **2020**, *11*, 7772-7781.

Selective Lower-Occupied Through-Bond Interactions for Efficient Organic Phosphorescence in Long Wavelength

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Organic room-temperature phosphorescence (RTP), which decays over a lifetime of 100 ms after the excitation light irradiation is stopped, is expected to be applied to high-resolution imaging independent of autofluorescence and high-speed two-dimensional oxygen concentration imaging[1]. Although organic RTP approaching 100% has been reported in the blue and green regions, the yield of organic RTP in the long-wavelength region remains low[2]. In this presentation, we report that the utilization of through-bond and through-space interactions between the 16th element and a fused ring group dramatically improves the yield of organic RTP in the long-wavelength region.

Chromophores in which multiple phenylthio substituents are directly substituted on dibenzo[*g,p*]chrysene (DBC) were synthesized. The 3p orbital of S and the 2p orbital of carbon of DBC form selective through-bonds in the highest occupied molecular orbital (HOMO)-X (X ≥ 1) [Fig. 1a; (i)], while no through-bonds were observed in the HOMO. The through-bonds in the selective HOMO-X (X ≥ 1) not only selectively increase the spin-orbit coupling between the higher singlet excited state (S_n) and the lowest triplet excited state (T_1) ($SOC_{S_n\text{-}T_1}$) [Fig. 1a; (ii)], but also maintain the magnitude of the transition dipole between S_n and the ground state (S_0) ($\mu_{S_n\text{-}S_0}$) [Fig. 1a; (iii)]. The expression of the cooperativity between $\mu_{S_n\text{-}S_0}$ and $SOC_{S_n\text{-}T_1}$ results in a selective increase in the emission rate (k_r^T) from T_1 in the long wavelength region [Fig. 1a; (iv)], increasing the red RTP quantum yield to 46%[3]. Afterglow emission was observed from a single nanocrystal using the π molecule as a guest [Fig. 1a; (v)]. Although previous afterglow emitters could not be used in the high-resolution region [Fig. 1b; (i)], the emergence of nanoparticles with highly efficient afterglow red RTP has made multicolor high-resolution afterglow imaging possible [Fig. 1b; (ii)]. The use of two-dimensional photodetectors with different afterglow times and colors allows a dramatic increase in the number of luminescent labels that can be distinguished simultaneously. Nanocrystals with such long-wavelength afterglow RTP are also suitable for application to two-dimensional high-speed oxygen mapping in *vivo*.

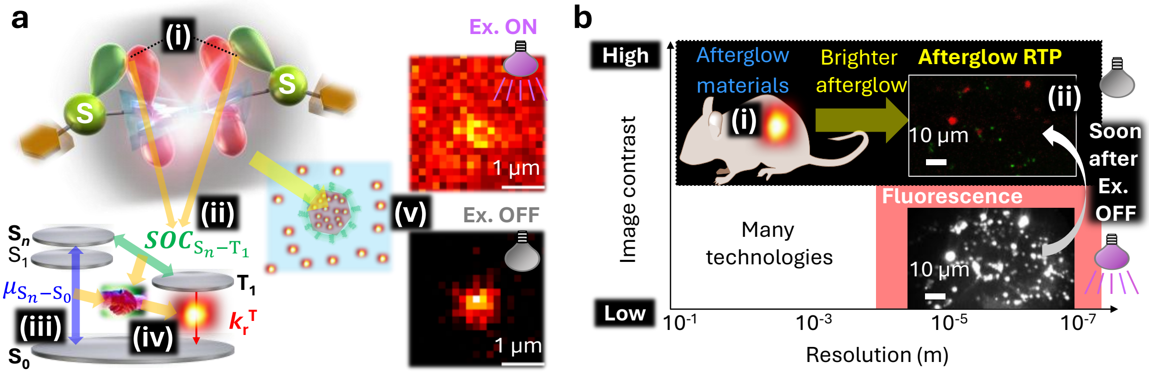

Figure 1. An explanation of the selective through-bonding of group 16 elements to the red phosphorescent π backbone to the HOMO-X, which leads to enhanced phosphorescence (a), and the high-resolution multicolor afterglow imaging region realized by the bright red afterglow nanoparticles (b).

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References:

[1] R. Shimura, K. Hayashi, S. Ueda, R. Tsuru, S. Hirata, *ACS Materials Lett.* **2025**, *7*, 2049-2055.

[2] B. Sk, S. Hirata, *Adv. Sci.* **2024**, *11*, 2308897.

[3] R. K. Mulimani et al., & S. Hirata, *Adv. Mater.* **2025**, *37*, 2502611.

Optical spin hyperpolarization for quantum sensing

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Enhanced spin polarization can significantly increase the sensitivity of magnetic resonance techniques such as EPR, NMR, and MRI. Furthermore, in the context of quantum information science (QIS), the generation of spin polarization is important for initialization and sensitivity enhancement in quantum computing and quantum sensing applications. When using electron spins in thermal equilibrium, high magnetic fields at very low temperatures are required to obtain large spin polarization. On the other hand, by using photoexcitation of chromophores, non-equilibrium large electron spin polarization can be obtained even at room temperature.

To control the assembly structure of the excited state and to make it responsive to external stimuli, we have used metal–organic frameworks (MOFs) as a platform.[1] Chromophores were introduced into the nanopores of MOFs as guest molecules or densely arranged in the MOF structures as ligands. For example, we propose a new quantum sensor design in which the coherence time changes in response to a variety of analytes at room temperature.[2] Furthermore, we have succeeded in efficiently generating triplet pairs by inducing singlet fission in MOFs and observing the quantum coherence of quintet state at room temperature for the first time.[3] We have also demonstrated the concept of light-harvesting spin polarization and effectively hyperpolarize radical electron spins by harvesting mobile excitons in MOFs.[4]

We have also developed chromophore dimers exhibiting singlet fission and quantum coherence of quintet triplet pair state at room temperature.[5] To selectively populate the specific sublevels of quintet triplet pair state, we arranged two pentacene chromophores in parallel and close proximity within a macrocycle. By making dynamic covalent Schiff-base bonds between aldehyde-modified pentacene derivatives, macrocyclic parallel dimer-1 (MPD-1) was selectively synthesized in high yield. MPD-1 exhibits fast sub-picosecond SF in polystyrene film and generates spin-polarized quintet multiexcitons. Furthermore, the coherence time T_2 of the MPD-1 quintet triplet pair is as long as 400 ns even at room temperature.

References:

[1] Akio Yamauchi et al., *Acc. Chem. Res.*, **2023**, *57*, 2963.
[2] Akio Yamauchi et al., *Nature Commun.*, **2024**, *15*, 7622.
[3] Akio Yamauchi et al., *Science Adv.*, **2024**, *10*, eadi3147.
[4] Tomoyuki Hamachi et al., *J. Am. Chem. Soc.*, **2025**, *147*, 4365.
[5] Wataru Ishii et al., *J. Am. Chem. Soc.*, **2024**, *146*, 25527.

Three-Coordinate Cu(I) Complexes of Anionic N-Heterocyclic Carbenes

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Three-coordinate Cu(I) complexes have garnered significant interest due to their unique photophysical properties, yet their potential as photosensitizers remains underexplored.[1,2] Here, we present a new class of neutral three-coordinate Cu(I) complexes featuring an anionic N-heterocyclic carbene ligand with a weakly coordinating tris(pentafluorophenyl)-borate moiety (WCA-NHC, see Fig. 1).[3,4] This design enhances solution stability and photophysical performance. A combination of steady-state and time-resolved spectroscopy, electrochemical analysis and quantum chemical calculations reveals that these complexes exhibit strong metal-to-ligand charge transfer (MLCT) absorption, thermally activated delayed fluorescence (TADF) and extended excited-state lifetimes (up to 8.6 μs). Their high excited-state energies (≈ 2.7 eV) enable efficient triplet energy transfer, as demonstrated in the norbornadiene-to-quadricyclane photoisomerization (see Figure 1). Additionally, temperature-dependent emission studies confirm a pseudo-Jahn-Teller distortion in the excited state, highlighting the role of structural relaxation in tuning emission properties. The long-lived excited states and high quantum yields (up to 11.5%) facilitate efficient energy transfer, making these complexes promising candidates for photoredox catalysis. These findings expand the applicability of three-coordinate Cu(I) photosensitizers and demonstrates that strategic ligand design can overcome previous limitations.

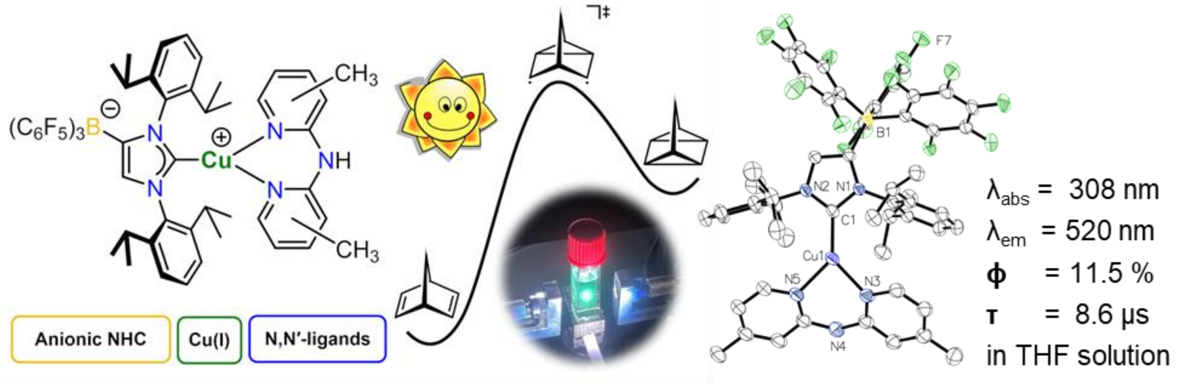

Figure 1. General structure of neutral [(WCA-NHC)Cu(N^N)] complexes (left) and a representative X-ray structure of complex C4 along with its main photophysical properties (right).

References:

[1] R. Marion, F. Sguerra, F. Di Meo, E. Sauvageot, J.-F. Lohier, R. Daniellou, J.-L. Renaud, M. Linares, M. Hamel, S. Gaillard, *Inorg. Chem*. **2014**, 53, 17, 9181-9191.

[2] P. Schmeinck, D. Sretenović, J. Guhl, R. Kühnemuth, C. A. M. Seidel, C. M. Marian, M. Suta, C. Ganter, *Eur. J. Inorg. Chem*. **2023**, 26, e202300416.

[3] S. Kronig, C. G. Daniliuc, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed*. **2012**, 51, 3240-3244.

[4] L. P. Ho, M. Tamm, *Chem. Eur. J*. **2022**, 28, e202200530.

Joint catalyst-surrogacy of a cobalt photocatalyst for carbonylation reactions in flow

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Amides and esters are key structural motifs in pharmaceutical and agrochemical compounds. Traditional strategies for amide and ester synthesis, such as carboxylic acid activation and transesterification, are well-established but often require forcing reaction conditions or generate undesirable waste. Palladium-catalysed carbonylation reactions offer an alternative but often require expensive ligands and catalyst precursors, elevated reaction pressures and temperatures; additionally, they are more technically challenging owing to the use of carbon monoxide gas.[1]

Recent advances in photocatalysis have demonstrated promising avenues for overcoming these challenges. Photocatalytic carbonylations using cost-efficient LEDs and cheaper transition metals such as cobalt have been investigated, and offer novel reactivity profiles and improved selectivity. [2] Although flow chemistry is now a recognized platform for safely scaling-up photochemical reactions due to enhanced light properties, existing flow-photocarbonylation methodologies are not widely adopted, and require a complex reactor set-up to handle CO gas.[3]

Herein, we report a technically simple and robust flow-photocatalysed carbonylation method using a cobalt catalyst that serves as both the photocatalyst and *in situ* CO surrogate (Fig. 1). This system eliminates the need for external CO gas, enabling efficient synthesis of amides and esters from aryl bromides under mild conditions. The reaction was optimized in flow, achieving yields up to 80% for various amides with high purities. The integration of an in-line membrane separator further streamlined the product isolation. While hydrodebromination side reactions currently limit maximum yields, the operational simplicity of this method makes it highly attractive for small-scale applications, with potential for further optimization via introduction of CO gas phase to enhance industrial relevance.

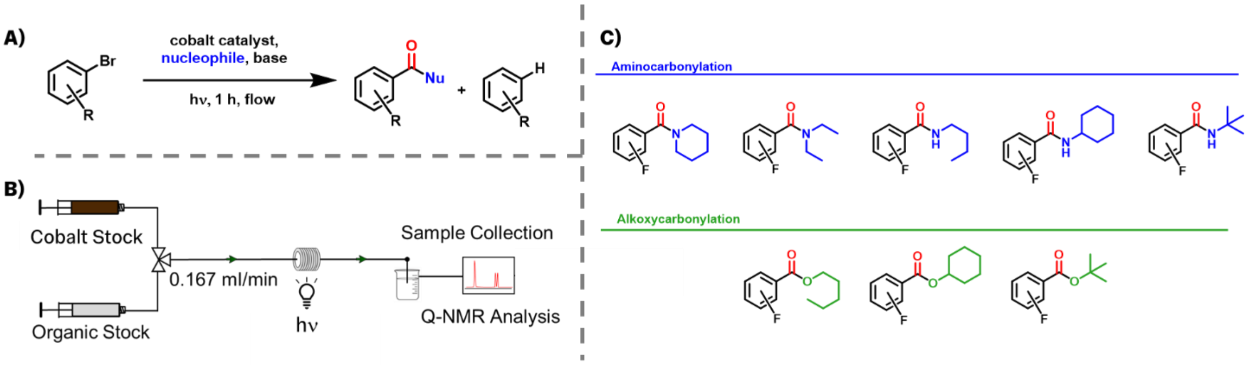

Figure 1 Photocarbonylation in flow: a) Reaction scheme, b) Reaction set-up in flow, c) Scope of the reaction.

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References:

[1] C. F. J. Barnard, *Organometallics* **2008**, *27*, *21*, 5402-5422.
[2] E. J. Alexanian et al., *Chem. Sci*. **2020**, *11*, 7210-7213.
[3] A. Polyzos et al., *Org. Lett.* **2018**, *20*, *15*, 4663-4666.

Ultrafast chiral spectroscopy for stereocontrolled photochemistry

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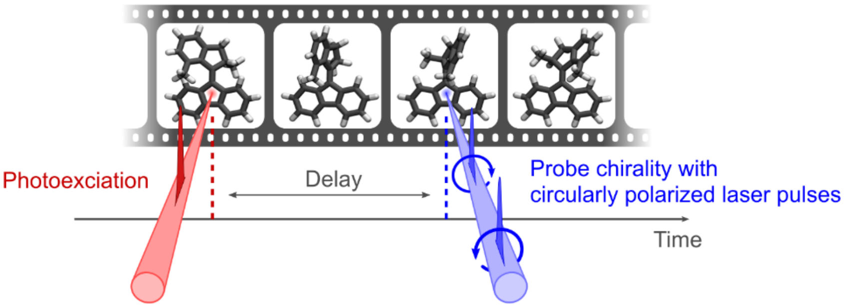

The incorporation of chiral structures into photochemical systems is a powerful strategy to control their functions [1]. For example, uni-directional molecular motors, chiral photocatalysts, and chiral metal nanostructures have achieved exceptional levels of stereocontrol over mechanical motion, energy transfer, and electric charge-carriers on the nanoscale. However, the direct characterization of the underlying chiral photoexcited states remains a formidable experimental challenge, due to a lack of analytical techniques that combine high chiral sensitivity in solution with ultrafast time resolution [2].

To address this challenge, we have developed an ultrafast circular dichroism technique that measures the absorption difference of left- and right-circularly polarized laser pulses in photoexcited chiral molecules [3]. Through an ultra-sensitive broadband detection scheme, we are thus able to capture ultrafast changes in molecular chirality and follow the stereochemical evolution of the associated excited states with sub-picosecond time resolution. On this basis we can now resolve chiral photochemical dynamics in real-time, which I will illustrate via two examples: 1) the identification and control of a chiral reaction coordinate in the spin-crossover dynamics of Fe(II) complexes [4], and 2) the resolution of the energy transfer and stereochemical dynamics in a chiral lanthanide-based OLED complex with circularly polarized luminescence (CPL) [5].

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References:

[1] J. R. Brandt, F. Salerno, and M. Fuchter, Nat. Rev. Chem. 1, 0045 (2017)
[2] M. Oppermann, CHIMIA 78, 45-49 (2024)
[3] M. Oppermann, B. Bauer, T. Rossi, F. Zinna, J. Helbing, J. Lacour, and M. Chergui, Optica 6, 56 (2019)
[4] M. Oppermann F. Zinna, J. Lacour, and M. Chergui., Nat. Chem. 14, 739-745 (2022)
[5] J. L. Lunkley, D. Shirotani, Y. Kazuaki, K. Sumio, and G. Muller, J. Am. Chem. Soc. 130, 13814-13815 (2008)

Photocatalytic reactions using metal complexes and non-planar porphyrins

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Photocatalytic reactions have gathered much attention due to the increasing importance of efficient utilization of photon energy in the production of useful chemicals and materials. In this presentation, I would like to highlight our progress in photochemical reactions using saddle-distorted porphyrins and transition-metal complexes based on photoinduced electron transfer. In this presentation, following three topics will be discussed.

1. We have been working on saddle-distorted dodecaphenylporphyrin (H_2DPP) and its derivatives as building blocks of supramolecular assemblies and photosensitizers in photocatalytic redox reactions.[1] In the photocatalytic oxidation of organic compounds in water, we have developed a supramolecular catalyst composed of a positively charged and diprotonated H_2DPP derivative as a photosensitizer (PS) and a ruthenium-substituted Keggin-type polyoxometalate as a catalyst with use of persulfate as an oxidant.[2] On the other hand, we have also developed photocatalytic hydrogen evolution using diprotonated H_4DPP^{2+} as a PS and Pt-nanoparticles as catalysts.[3]
2. Photocatalytic oxidation reactions have been developed using $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) as a PS. Among those, oxidation of organic substrates in water has been made using Ru^{II}-aqua complexes as catalysts in the presence of a weak oxidant [4] and water oxidation has been achieved using a bis-μ-hydroxo dinuclear Co^{III} complex as a catalyst and persulfate as an oxidant.[5] In addition, a Ru^{II} complex having a protonated π-expanded heteroaromatic ligand ($Htpphz^+$) has been found to perform photocatalytic oxidation of organic substrates in acidic water using O_2 as an oxidant: In the reaction, upon visible-light excitation, the S_2 state of the Ru^{II} complex can be used to oxidize aromatic substrates which interact with the $Htpphz^+$ ligand to form a supramolecular assembly.[6] This is a related strategy to that taken for gaseous alkane oxidation in aqueous medium to emphasize hydrophobic interaction in aqueous media.[7]
3. Inspired by the structure and function of Ni-containing carbon monoxide dehydrogenase (CODH), we have developed Ni complexes as catalysts for photocatalytic CO_2 reduction to produce CO in high efficiency and high selectivity in the presence of $[Ru(bpy)_3]^{2+}$ as a PS.[8] By using the same Ni^{II} complex in aqueous buffer solutions, photocatalytic H_2 evolution has been offered.[9] We also discovered that a dinuclear Ru^{II}-diimine complex can act as a self-photosensitizing catalyst to reduce CO_2 to CO almost stoichiometrically based on the reductant used.[10]

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References:

[1] T. Ishizuka, N. Grover, C. J. Kingsbury, H. Kotani, M. O. Senge, T. Kojima, *Chem. Soc. Rev.* **2022**, *51*, 7560.

[2] T. Ishizuka et al. and T. Kojima, *Green Chem.* **2018**, *20*, 1975.

[3] H. Kotani, T.Miyazaki, E. Aoki, H. Sakai, T. Hasobe, T. Kojima, *ACS Appl. Energy Mater.* **2020**, *3*, 3139.

[4] S. Ohzu, T. Ishizuka, Y. Hirai, S. Fukuzumi, T. Kojima, *Chem. Eur. J.* **2013**, *19*, 1563.

[5] T. Ishizuka et al. and T. Kojima, *Inorg. Chem.* **2016**, *55*, 1154.

[6] T. Ishizuka, T. Nishi, N. Namura, H. Kotani, Y. Osakada, M. Fujitsuka, Y. Shiota, K. Yoshizawa, *J. Am. Chem. Soc.* **2024**, *146*, 33022.

[7] H. Fujisaki, T. Ishizuka, H. Kotani, Y. Shiota, K. Yoshizawa, T. Kojima, *Nature* **2023**, *616*, 476.

[8] D. Hong et al. and T. Kojima, *Inorg. Chem.* **2018**, *57*, 7180.

[9] (a) D. Hong, Y. Tsukakoshi, H. Kotani, T. Ishizuka, T. Kojima, *J. Am. Chem. Soc.* **2017**, *139*, 6538. (b) D. Hong, T. Kawanishi, Y. Tsukakoshi, H. Kotani, T. Ishizuka, T. Kojima, *J. Am. Chem. Soc.* **2019**, *141*, 20309.

[10] T. Ishizuka, A. Hosokawa, T. Kawanishi, H. Kotani, Y. Zhi, T. Kojima, *J. Am. Chem. Soc.* **2023**, *145*, 23196.

Biophotonics. Decoding light signals from living organisms

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Biophotonics is the interdisciplinary science that deals with the interaction between light (photons) and biological materials. Our research is dedicated to exploring this interaction, aiming to extract meaningful information in a non-invasive, non-destructive manner from the biological tissues or organisms. Most of these systems share two challenging characteristics: a high concentration of light-absorbing molecules (chromophores) and strong light scattering. These features, while rich in information, often complicate conventional spectroscopic and photophysical analysis[1].

To address this, we develop and apply physical models that help us better understand these complex light-matter interactions. In this talk, I will present a selection of our contributions in this field, from theoretical approaches to practical applications. These include modeling chlorophyll fluorescence in leaves and plant canopies to support remote sensing technologies[2,3]; designing optical tools for assessing food quality[4,5]; and quantifying in vivo reflectance and fluorescence to explore their potential as biosignals in communication[6–7] (Fig. 1).

Figure 1. Some of the systems studied. From left to right: flowers, frogs, birds, fruits, individual leaves, plant canopies

Working at the interface of physics, chemistry, and biology, we aim to decipher how these interactions occur. We develop corrections to avoid distortions in the interpretation of recorded data, and also create tools for practical applications in environmental monitoring, crop monitoring, and post-harvest fruit condition assessment.

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References:

[1] H. Rodriguez, M. Mirenda, M. Lagorio, E. San Román, *Acc. Chem. Res.*, **2019,** 52, 1, 110-118.

[2] M. Lagorio, G. Cordon, J. Romero, I. López Valiño I, From space to cells. Physical models for light re-absorption and scattering. Chapter 6 in FLUORESCENCE OF LIVING PLANTS. Basics, Applications and Trends. Ed. Springer, **2025.**

[3] J. Romero, A. Otero, M. G. Lagorio, A. Berger, G. Cordon, *Rem. Sens. Env*., **2021**, 263, 112525.

[4] B. Ospina Calvo, T. Parapugna and M. Lagorio, *Photochem. Photobiol. Sci.*, **2017**, 16, 711-710.

[5] J. Novo, A. Iriel and M. Lagorio, *Photochem. Photobiol. Sci*., **2012**, 11, 724-730.

[6] A. Barreira, M. Lagorio, D. Lijtmaer, C. Lougheed, and P. Tubaro, *J. Zoology*, **2012,** 288, 135–142.

[7] C. Taboada, A. Brunetti, F. Pedron, F. Carnevale Neto, D. Estrin, S. Bari, L. Chemes, N. Peporine Lopes, M. Lagorio and J. Faivovich. *PNAS*, **2017**, 114, 3672–3677.

Excited-State Conformational and Electronic Responses of Fluorescent Charge-Transfer Molecules with Twisted Structural Skeleton

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A series of anthracene (A)-quinoxaline (Q) based organic fluorescent molecules composed of donor and acceptor subunits to exploring their photophysical properties were designed and synthesized. The geometries of these compounds (TAQ and TQA) were designed to display severe nonplanar distortions. Both TAQ and TQA exhibit prominent solvatofluorochromic properties with large Stokes shifts. The variable-temperature fluorescence spectra of TAQ and TQA in 2-methyltetrahydrofuran from 77 to 297 K revealed intriguing fluorescence responses. The fluorescence of TAQ is gradually red-shifted ongoing from the non-relaxed excited state (477 nm) to the full charge-transfer (CT) state (722 nm) upon increasing temperature until 197 K followed by a hypsochromic shift of emission to 577 nm upon further raising the temperature to 298 K. Obvious dual emissions were observed between 137-197 K. Large bathochromic shift (Δv = 7498 cm^{-1}) of TAQ fluorescence implies the presence of long-range CT or charge-separated state. A similar fluorescence response of TQA to that of TAQ is observed, albeit with a lesser degree of spectral shift. These unique photophysical behaviors are rationalized by structural relaxation via electronic configuration coupled conformational planarization in the excited state. Various spectroscopic measurements and computational studies were carried out to support the conclusions. Moreover, TAQ exhibits reversible stimuli-responsive fluorescent properties in the solid state due to the weak intermolecular interactions between the twisted molecular framework.

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Circularly Polarized Room Temperature Phosphorescence in Solution From Purely Organic Chiral Molecular Materials

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Room temperature phosphorescence (RTP) from purely organic compounds (*i.e.* without any metal), and related photophysical aspects linked to the management of triplet excited-states have become a crucial issue for several areas of research, ranging from optoelectronics, non-linear optics to photocatalysis, and bioimaging.[1] Recently, the possibility to obtain RT circularly polarized (CP) phosphorescence with chiral organic emitters has also attracted significant interest due to the potential access to different states of CP-light (either left or right).[2]

In this conference, I would like to present our recent results regarding this area of research, notably by illustrating how secondary interactions can stabilize triplet exciton and enable more efficient, and faster triplet-state emission from purely organic systems. More importantly, these secondary interactions stabilized chiral aggregates and give access to CP-RTP in solution, with a promising g_{lum} of up to 5 × 10^{-3}. These results provide one of the rare examples of (CP-)RTP in solution for purely organic systems, and offer new insights into the potential of ‘electric-dipole forbidden’ phosphorescence for achieving more intense CPL than classical allowed fluorescence of chiral emitters.[3]

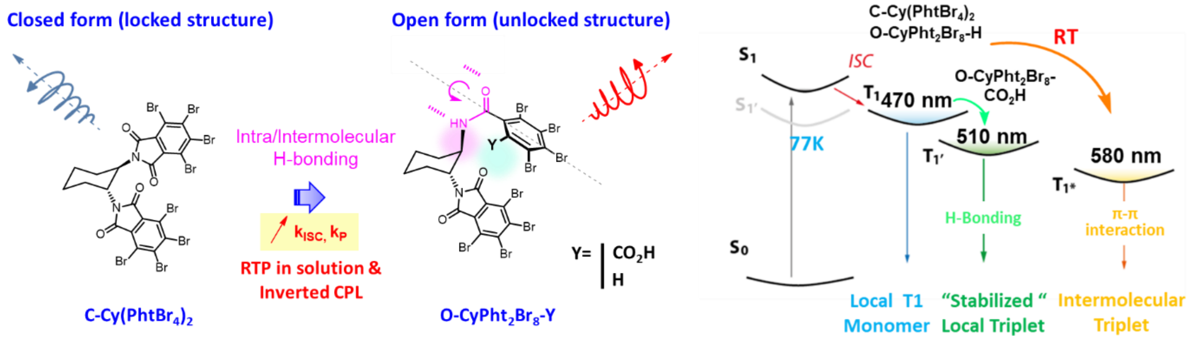

Figure: Chemical structures of the investigated chiral phthalimide derivatives with a proposed mechanism of RTP generation and the impact of hydrogen bond and π- π interactions on the emission wavelengths.

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References

[1] H. Ma, Q. Peng, Z. An, W. Huang and Z. Shuai, *J. Am. Chem. Soc.*, 2019, **141**, 1010-1015; D. Nidhankar, Goudappagouda, V. C. Wakchaure and S. S. Babu, *Chem. Sci.*, 2021, **12**, 4216-4236.; S. Hirata, *Applied Physics Reviews*, 2022, **9**, 011304.
[2] Z. An, C. Zheng, Y. Tao, R. Chen, H. Shi, T. Chen, Z. Wang, H. Li, R. Deng, X. Liu and W. Huang, *Nat Mater*, 2015, **14**, 685-690; L. Favereau, C. Quinton, C. Poriel, T. Roisnel, D. Jacquemin and J. Crassous, *J. Phys. Chem. Lett.*, 2020, **11**, 6426-6434; X. Wu, C.-Y. Huang, D.-G. Chen, D. Liu, C. Wu, K.-J. Chou, B. Zhang, Y. Wang, Y. Liu, E. Y. Li, W. Zhu and P.-T. Chou, *Nat. Commun.*, 2020, **11**, 2145.
[3] Y. Patil, C. Demangeat, L. Favereau, *Chirality*, 2023, **35**, 390.C. Demangeat, M. Remond, T. Roisnel, C. Quinton and L. Favereau, *Chem. Eur. J.*, 2024, **30**, e202401506.

Exploring bacteria-surface interactions with a fluorescent membrane tension probe

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The way bacteria interact with surfaces is crucial in various fields, including biofouling, biofilm formation, the infection of plants and animals, and the development of antimicrobial materials.[1] However, fundamental aspects of the physical interaction between live bacteria and surfaces are poorly understood. This is in part due to the challenges associated to the characterization of the interface in a biologically-relevant environment. New microscopy tools specifically tailored to the cell-material interface can have a real impact on guiding the development of new classes of materials that inhibit or promote bacterial growth.[2] We have explored bacterial-surface interactions in living cells with the fluorescent probe Flipper-TR, a mechanosensitive push-pull fluorophore that inserts into the membrane and whose lifetime reports on lateral forces.[3,4] One challenge with the use of Flipper-TR is that local changes in lipid composition, which in turn affect lipid packing, also alter its fluorescence lifetime. Therefore, we first establish its use in both Gram positive and negative bacteria in fluorescence lifetime imaging experiments, since Flipper has mostly been used in mammalian cells.[4] We show that this probe is suitable for model systems representing both bacterial types, and is sensitive enough to discriminate bacterial contact with different surfaces, including mechano-bactericidal nanofabricated topographies. Moreover, by using a probe that is environmentally sensitive but does not report on mechanical effects, we disentangle physical membrane tension from changes in lipid packing. Our work expands the fluorescence microscopy and spectroscopy toolbox to understand the interaction between cells and materials.

Funding: Ministerio de Ciencia e Innovación (PID2021-122231NB-I00), Comunidad de Madrid (TecNanoBio-CM)

References:

[1] H. H. Tuson, D. B. Weibel, *Soft Matter* **2013**, *9*, 4368.

[2] F. Viela, I. V. Ortega, J. J. Hernández, I. Rodríguez, S. Moreno-Da Silva, A. López-Moreno, E. M. Pérez, C. Flors, *Small Science* **2023**, 2300002

[3] A. Colom, E. Derivery, S. Soleimanpour, C. Tomba, M.D. Molin, N. Sakai, M. Gonzalez-Gaitan, S. Matile, A. Roux, *Nat Chem* **2018**, *10*, 1118.

[4] C. Roffay, J.M. Garcia-Arcos, P. Chapuis, J. Lopez-Andarias, F. Schneider, A. Colom, C. Tomba, I. Di Meglio, K. Barrett, V. Dunsing, S. Matile, A. Roux, V. Mercier, *Nat Protoc* **2024**, *19*, 3457

Illuminating Order: Optical Absorption Forces in Particle Assembly

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Optical trapping has emerged as an alternative method for controlling the assembly of nano- and microparticles at the microscale. This process normally involves the coupling between optical and non-optical (e.g. electrostatic, capillary, hydrodynamics) forces. Additionally, absorption forces also come into play for particles containing photoexcitable molecules.[1] Herein, we propose and experimentally demonstrate a model for photoexcitation-mediated particle assembling by single particle tracking analysis. The dispersed dye-doped microparticles are pushed toward the air/solution interface by absorption force, leading to their association and formation of hexagonal-close-packing (HCP) assemblies. Our observations indicate that the assembly is facilitated by coupling the absorption force with other non-optical forces.[2]

Optical absorption force can be amplified and controlled through chemical stimuli,[3] such as pH changes, allowing for precise modulation of particle interactions and assembly morphology. In the second part of the presentation, I will introduce pH-responsive particles that exhibit reversible optical transitions, paving the way for the development of adaptive materials that respond to chemical changes in their environment.

The results presented emphasize the potential of absorption forces in reversible controlling and modifying the structural order of particles over a large area. This applies to photoexcitation-mediated assemblies as well as the general (self)-assembly of various materials (e.g., polymers, proteins) at an interface. Such an approach is promising for the formation of highly ordered colloidal structures into new functional materials, such as metamaterials, which can exhibit unique optical properties such as high or conversely negative refractive index.

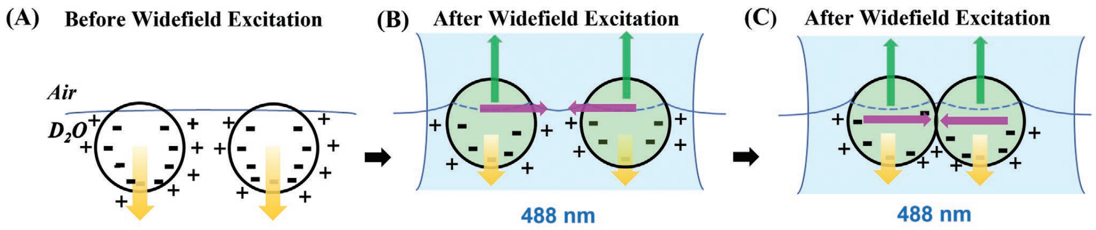

Figure 1. Illustration of (A–C) the 488 nm photoexcitation-induced association of two dye-dopped Polystyrene MPs at A/S interface. The orange arrow in (A–C) represents the dipole of the MPs, while the green and the violet arrows show absorption and capillary forces, respectively.

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References:

[1] Y.-C. Chang, et. al., *Adv. Optical Mater.* **2022**, *10*, 2200231.
[2] Q.Q. Wang, et al., *Adv. Optical Mater.* (Under revision).
[3] R. Bresolí-Obach, et al., *Adv. Optical Mater.* **2022**, *10*, 2200940.

Spectroscopic properties of chiral porphyrin self-assembled monolayers on thin ferromagnetic films

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Magnetism and organic chemistry have been viewed as largely unrelated fields. However, this perception has changed in recent years with the discovery that certain molecular materials can support spin transport — a phenomenon constituting the basis of spintronics, which underpins modern information processing and storage technologies.[1] Molecular spintronics takes advantage of the inorganic/organic interfaces (*spinterfaces*), where unique magnetic phenomena such as spin filtering emerge. Notably, chiral organic molecules themselves have demonstrated the ability to very efficiently act as spin filters.[2]

Here, we investigate how the magnetization of gold- capped Co/Ni ferromagnetic multilayers (FM), influences the spectroscopic properties of porphyrin molecules linked covalently to gold via chiral oligopeptide chain possessing C-terminal thiol group as anchor (Figure 1).

Porphyrin derivatives were designed and synthesized, incorporating a N-terminal 5-(4-carboxyphenyl)-10,15,20-(triphenyl)porphyrin chromophore linked via amide bond to short oligopeptide chain composed of alternating alanine (Ala) and 2-aminoisobutyric acid (Aib) residues in the form of $(\text{Ala-Aib})_n$ ($n = 8$). Both D- and L-enantiomers were synthesized and immobilized on the FM surfaces using wet chemistry to form self-assembled monolayers (SAMs). The resulting SAMs were investigated using a combination of steady-state and transient optical spectroscopy. While the D- and L-enantiomers exhibited nearly identical absorption spectra in both solution and solid state, the transient absorption measurements on solid samples revealed magnetization-dependent differences in bleach recovery kinetics. These effects were absent in control samples lacking the chiral SAMs, suggesting a direct molecular-level spin interaction between the chiral system and the ferromagnetic substrate.

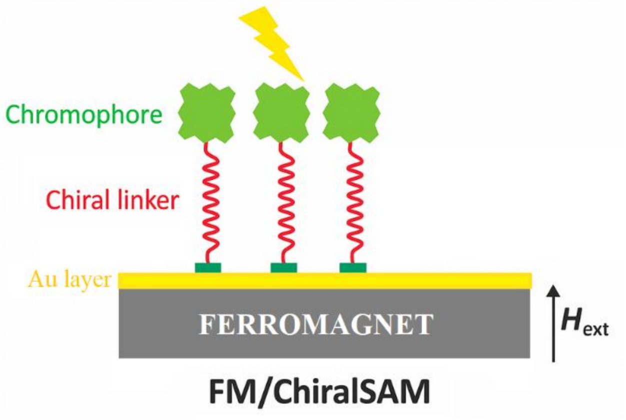

Figure 1. Schematic representation of FM/chiral self-assembled monolayer system.

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References:

[1] R. Naaman, D.H. Waldeck, *J. Phys. Chem. Lett* **2012**, 3, 2178
[2] B. P. Bloom, Y. Paltiel, R. Naaman and D. H. Waldeck, *Chemical Reviews*, **2024**, 124, 1950.

Triplet Energy Transfer of Monomer and Dimer of Rose Bengal in Methanol and in Polymer Films

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To further optimize current solar cell systems efficiency and advance the practical applications of triplet materials, study of dyes embedded in polymers is crucial.[1] Rose Bengal (RB), a classic dye with heavy atoms, is known for its efficient triplet state harvesting through intersystem crossing upon photoexcitation.[2] In this work, we use RB as a model compound to investigate the dynamics of its triplet states both in solution and embedded in various polymer films. The photophysical properties were detected by using step-scan Fourier-transform near infrared spectroscopy (FT-NIR). Based on time-dependent density functional theory (TD-DFT) calculations, the observed broad transient absorption bands at 6400 cm^{-1} and 9400 cm^{-1} are assigned to the $T_2 - T_1$ and $T_3 - T_1$ transition of RB, respectively after excitation at 355 nm and the cascading intersystem crossing (Fig. 1a). In solution, the decay lifetime of the triplet state is shortened from oxygen quenching. The self-quenching rate constant (k_{sq}) of triplet by RB itself is determined to be $3.2 \times 10^7\ \text{M}^{-1}\text{s}^{-1}$ in deaerated methanol at 296 K using a Stern-Volmer relation. When RB molecules are immobilized in polyvinyl alcohol (PVA) films, oxygen-quenching and self-quenching are eliminated, leading to a prolonged triplet lifetime upto 306 µs. RB can form dimers in solid polymer films for high weight%, and the dimer fractions are determined by the absorption intensity ratio of the 564 and 527 nm bands.[3] DFT simulation demonstrates that the structure of RB in film is a parallel pi stacking dimer combining with hydrogen bonding between RB and PVA (Fig. 1b). Additionally, the transmission electron microscope (TEM) image shows self-assembled RB embedded in PVA films of 10 wt% forming snowflake-like nano clusters (~30 nm). The distinct ~2 nm dots corresponding to an RB dimer, with intrinsic iodine atoms enhancing the TEM pattern contrast (Fig. 1c). As the excitation power or RB concentration in films increased, two distinct triplet state lifetimes were observed 20-30 µs and 200 µs. The long component, close to the observed lifetime of triplet in solution, is presumably attributed to the decay of the triplet. Decreased in concentrated RB film is explained to be quenched by the nearby RB with shortening distances. The short component is tentatively assigned to triplet-triplet annihilation leading to the depletion of excited state energy. This is the first time that the dynamics of RB triplets in film studied.

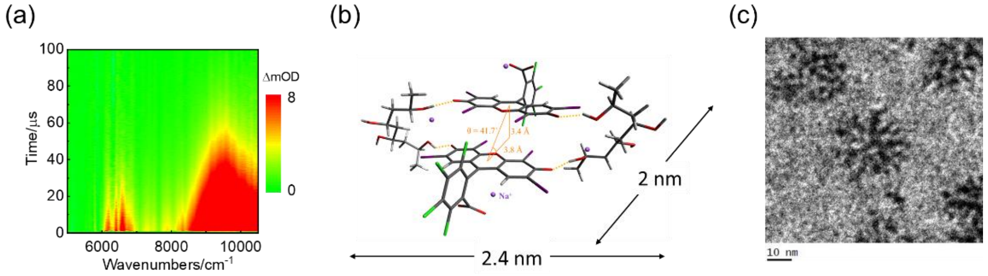

Figure 1. a) Transient absorption of RB in methanol. b) DFT simulation of an RB dimer with PVA. c) TEM image of RB in PVA film.

Funding: National Science and Technology Council of the Republic of China (NSTC 112-2628-M-007-005-MY3 and 113-2811-M-007-019).

Acknowledgement: We are grateful to the National Science and Technology Council, Taiwan for financial support and National Center for High-Performance Computing for computer time and facilities.

References:

[1] M. J. Bennison, A. R. Collins, B. Zhang, R. C. Evans, *Macromolecules* **2021**, *54*, 5287-5303.

[2] A. Penzkofer, M. Simmel, D. Riedl, *Journal of Luminescence* **2012**, *132*, 1055-1062.

[3] C. Alvarez-Lopez, D. Cavazos-Elizondo, B. Heyne, I. E. Kochevar, A. Aguirre-Soto, *Photochemistry and Photobiology* **2023**, *99*, 580-592.

Flux Synthesis of Sillén–Aurivillius Phase Oxyiodide Photocatalyst for Visible Light Water Splitting

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Sillén–Aurivillius layered perovskite oxyiodides, such as Bi_4NbO_8I (Fig. 1a), have recently emerged as a new class of materials for visible-light-driven water splitting photocatalysis, owing to their narrow band gaps and high photocatalytic activities.[1,2,3] However, their synthetic method has been limited to solid-state reaction (SSR), which restricts the material tunability and thus photocatalytic performance.

Here, we report a novel solution-based synthetic approach, the flux method, for the Sillén–Aurivillius oxyiodide Bi_4NbO_8I.[4] An appropriate choice of reaction conditions, including flux, precursor, and calcination atmosphere/temperature, is required for the single-phase formation. The provided plate-like particles are of excellent crystallinity (Fig. 1b) with size tunability. The superior charge carrier transport property of the flux sample, as shown by time-resolved microwave conductivity measurements (Fig. 1c), allows its higher photocatalytic water oxidation activity than the sample prepared via conventional SSR (Fig. 1d). The AQE for sacrificial O_2 evolution reached 8.8% at 405 nm, which is the best-reported performance for oxyiodides. Moreover, we demonstrated the visible-light Z-scheme water splitting using Bi_4NbO_8I as an O_2 evolution photocatalyst.

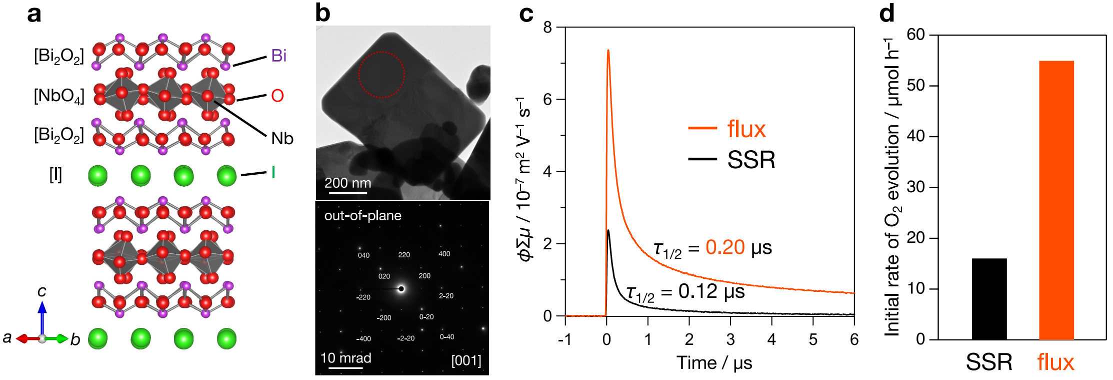

Figure 1. (a) Crystal structure of Bi_4NbO_8I. (b) TEM image and the corresponding SAED pattern of the flux sample. (c) TRMC transient decay profiles of pristine Bi_4NbO_8I samples prepared via the flux method and SSR method. (d) Initial rates of O_2 evolution over IrO_x-loaded Bi_4NbO_8I prepared via the flux method and SSR method in an aqueous $AgNO_3$ solution under visible light irradiation ($\lambda > 400$ nm).

We believe that the present flux synthesis approach is applicable to a variety of functional iodine-based materials, including other Sillén–Aurivillius phases, paving the way for oxyiodides as high-performance functional materials.

Funding: JSPS KAKENHI (JP20H00398, JP23H02061, and JP24KJ1470) and the JSPS Core-to-Core Program (JPJSCCA20200004).

References:

[1] K. Ogawa, H. Kageyama, R. Abe, et al., *J. Am. Chem. Soc.* **2021**, *143*, 8446−8453.
[2] M. Ogawa, R. Abe, et al., *Solid State Sci.* **2023**, *141*, 107221.
[3] K. Ogawa, A. Walsh, R. Abe, et al., *Chem. Mater.* **2023**, *35*, 5532−5540.
[4] M. Ogawa, R. Abe, et al., *Chem. Mater.* **2025**, *37*, 1123−1131.

Solid state solvation: a fresh view

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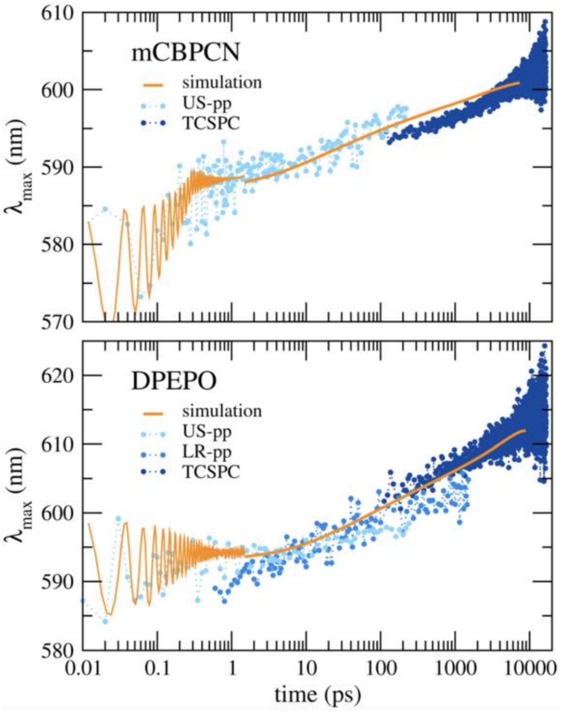
Abstract: The design of efficient organic electronic devices, including OLEDs, OPVs, luminescent solar concentrators, etc., relies on the optimization of relevant materials, often constituted by an active (functional) dye embedded in a matrix.[1] Understanding solid state solvation (SSS), i.e. how the properties of the active dye are affected by the matrix, is therefore an issue of fundamental and technological relevance[2,3]. Here[4] an extensive experimental and theoretical investigation of several matrices, typically adopted in OLED fabrication, addressing their dielectric properties and dynamical behavior is presented, shedding light on this, somewhat controversial, topic. The approach, relying on donor-acceptor dyes exploited as microscopic polarity sensors, is easily generalized to other types of matrices or media, offering a useful characterization tool to exploit SSS towards optimized optoelectronic devices.

The spectral properties of the dyes (Nile-Red and DCM) at equilibrium, i.e. absorption and Raman spectra, are not affected by the matrix dynamics. Reliable estimates of the matrix polarity are then obtained from an analysis of the micro-Raman spectra of polar dyes. Specifically, to establish a reliable polarity scale, the spectra of DCM or NR dispersed in amorphous matrices are compared with the spectra of the same dyes in liquid solvents with known polarity.

On the other hand, steady-state emission spectra obtained in solid matrices depend in a highly non-trivial way on the matrix polarity and its dynamics. An extensive experimental and theoretical analysis of the time-resolved emission spectra of NR in a very large time window (15 fs–15 ns) allows us to validate this dye as a good probe of the dielectric dynamics of the surrounding medium. We provide then a first assessment of the relaxation dynamics of two matrices (mCBPCN and DPEPO) of interest for OLED application, unambiguously demonstrating that the matrix readjusts for at least 15 ns after the dye photoexcitation.



Time evolution of the maximum of NR emission spectrum: bluish dots refer to experimental data collected with different techniques (as per the legend), and the orange line shows simulated results.

[1] *Ostroverkhova, Chem Rev. (2016), 116, 22, 13279–13412*
[2] *dos Santos et al., J. Phys. Chem. Lett. (2016), 7, 17, 3341–3346*
[3] Gillet et al., Nature Materials (2022), 21, 1150–1157
[4] *Bardi et al., Mater. Horiz., (2023),10, 4172-4182*

Acceleration of Excited-State Relaxation Dynamics via the Infrared Purcell Effect on Intermolecular Vibrations

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Strong light–matter interactions in the infrared (IR) regime have recently gained increasing attention as a route to manipulate nonradiative pathways in molecular systems. While polaritonic chemistry has primarily focused on modulating chemical reactivity through strong coupling between vibrational modes and optical cavities, the influence of cavity-induced modifications to vibrational relaxation pathways on excited-state dynamics remains less explored. In this study, we investigate how the infrared Purcell effect—achieved via spectral matching between molecular vibrational modes and an optical cavity resonance—can accelerate vibrational dephasing and energy relaxation, thereby modulating the dynamics of excited electronic states. Our goal is to elucidate how enhanced vibrational relaxation, induced by a tailored photonic environment, affects photophysical properties such as emission lifetime and quantum yield.

To this end, multilayer MoS_2 films were synthesized on silicon substrates using chemical vapor deposition (CVD). Intermolecular vibrational dynamics, particularly the interlayer breathing (B_1) mode of MoS_2, were probed via coherent vibrational measurements using a pump–probe setup based on a mode-locked Ti:sapphire laser (center wavelength: 800 nm; pulse duration: 17 fs; repetition rate: 80 MHz). The second harmonic (400 nm) served as the pump, while the fundamental was used as the probe. To assess the cavity resonance conditions, we constructed a terahertz time-domain spectroscopy (THz-TDS) system using a separate Ti:sapphire laser (center wavelength: 800 nm; pulse duration: 35 fs; repetition rate: 80 MHz) and a photoconductive antenna, allowing for precise determination of the resonance frequencies in silicon-based thin-film IR optical cavities. The experimental design enabled us to selectively compare MoS_2 films on resonant and non-resonant substrates.

Our measurements revealed that in bilayer MoS_2, coherent oscillations with a period of ~830 fs were superimposed on the carrier decay signals, confirming excitation of the B_1 vibrational mode. Systematic analysis with samples of varying thickness demonstrated a layer-dependent frequency shift, corroborating the assignment. THz-TDS data indicated that the cavity resonance spectrally overlaps with the B_1 mode. Notably, when the vibrational mode was in resonance with the IR cavity, both vibrational dephasing and carrier lifetimes were significantly reduced compared to non-resonant conditions. Photoluminescence measurements further showed suppressed emission intensity on the cavity substrate. These results collectively demonstrate that the infrared Purcell effect enhances the relaxation of vibrational modes, which in turn accelerates nonradiative decay from the excited state. This work highlights a new pathway to modulate excited-state lifetimes and photophysical behavior by engineering vibrational relaxation through optical cavities.

Opportunities and challenges in photochemically upcycling polymers

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Plastics are durable thanks to their chemical inertness, but this also severely limits their post-use recycling. To date, only ~1% of all plastic produced is chemically recycled, with the rest burned or landfilled. An alternative eco- and cost-friendly solution would be to use solar radiation to chemically upcycle polymers into value-added products that can be used elsewhere as feedstocks. We have focused on the photochemical conversion of polystyrene, a widely used polymer (ca. 20 million tons annually) that is especially resistant to chemical recycling. Recently, photocatalytic methods have shown potential in transforming polystyrene into valuable chemicals like benzoic acid. However, efficient C–H bond cleavage remains a major obstacle and the mechanistic details of this transformation remain unclear. [1]

In an effort to improve the upcycling process of polystyrene, we have investigated the mechanism of its oxidation under a variety of conditions (photoinduced electron transfer, hydrogen atom abstraction, production of reactive oxygen species). The results show that this apparently simple system harbors significant complexity and that that competing reactive pathways can be in part controlled using the environmental conditions. For example, the use of 9-mesityl-10-methylacridinium salts results in the oxidation of polystyrene through the generation of singlet oxygen whereas the use of anthraquinones proceeds through H atom abstraction. Overall quantum yields for the formation of benzoic acid of 1 – 5 % can be attained and the process can be powered using solar radiation (Fig. 1). [2]

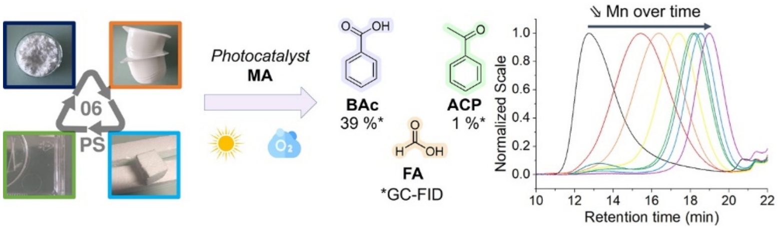

Figure 1. Example of chemical upcycling of polystyrene polymers or plastic wastes using an acridinium photocatalyst and solar radiation.

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References:

[1] K. Parkatzidis, H. S. Wang, A. Anastasaki, *Angew. Chem. Int. Ed.* **2024**, *63*, e202402436. https://doi.org/10.1002/anie.202402436.

[2] A.-L. De Abreu, D. Taton, D. M. Bassani, *Angew. Chem. Int. Ed.* ***2024***, *63*, e202418680. https://doi.org/10.1002/anie.202418680.

Design of Luminescent Transition Metal Complex Photocatalysts and Recyclable Immobilized Counterparts for Selective Activation

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By incorporating strongly π-accepting anionic isocyanoborate ligands into Re(I) diimine complexes, [1] we have developed a novel series of charge-neutral Re(I) complexes that exhibit intense blue phosphorescence, making them promising emissive materials for electroluminescent device applications.[1b,c] Beyond their luminescent properties, these anionic ligands significantly enhance the excited-state redox potentials of the complexes, enabling their photocatalytic applications for activating a wide range of substrates. To further improve stability and efficiency in photocatalytic applications, we have introduced a new class of phosphorescent Re(I) carbene complexes.[2] Unlike conventional tricarbonyl Re(I) diimine complexes, which require UV irradiation for photocatalytic CO_2 reduction, our Re(I) isocyanide and carbene complexes effectively harness visible light for this transformation. [2b-d]

In addition to CO_2 reduction, we will present our recent advances in photoredox catalysis for organic transformations, with a particular focus on the activation of fluorinated alkyl halides.[3] This work leverages the triplet emissive excited states of Re(I) and cyclometalated Ir(III) complexes to drive selective photoredox processes. To enhance the practical applicability of photoredox catalysis, we have also developed efficient and recyclable solid-supported photocatalysts by immobilizing transition metal complexes onto various solid-support materials. Emission quenching studies have been conducted to investigate bimolecular electron transfer between the excited states of these immobilized complexes and solution-phase substrates. We have established correlations between electron transfer efficiency and overall catalytic performance, providing significant insights into the design of efficient and reusable heterogeneous photoredox catalysts.[3c] Based on these findings, we have developed solid-supported photocatalysts for the selective photoactivation of the targeted substrates. Given the high efficiency of the solid-supported photocatalysts in heterogeneous photoredox catalysis, we will also discuss the successful application of photoredox catalysis in the chemical modification of materials to introduce functional properties.[4]

Funding: RGC GRF (Project Nos. CityU 11312222 and CityU 11309524)

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References:

[1] (a) C.-C. Ko, A. W.-Y. Cheung, L. T.-L. Lo, J. W.-K. Siu, C.-O. Ng, S.-M. Yiu, *Coord. Chem. Rev.* **2012**, *256*,1546; (b) W.-K. Chu, C.-C. Ko, K.-C. Chan, S.-M. Yiu, F.-L. Wong, C.-S. Lee, V. A. L. Roy, *Chem. Mater.* **2014**, *26*, 2544; (c) K.-C. Chan, K.-M. Tong, S.-C. Cheng, C.-O. Ng, S.-M. Yiu, C.-C. Ko, *Inorg. Chem.* **2018**, *57*, 13963.

[2] (a) C.-O. Ng, S.-C. Cheng, W.-K. Chu, K.-M. Tan, S.-M. Yiu, C.-C. Ko, *Inorg. Chem.* **2016**, *55*, 7969 ; (b) A. Maurin, C.-O. Ng, L.-J. Chen, T.-C. Lau, M. Robert, C.-C. Ko, *Dalton Trans.* **2016**, 14524; (c) Y. Feng, C.-O. Ng, K.-M. Tong, S.-C. Cheng, C.-C. Ko, *Energy Fuels* **2021**, 19170; (d) P.-Y. Ho, S.-C. Cheng, F. Yu, Y.-Y. Yeung, W.-X. Ni, C.-C. Ko, C.-F. Leung, T.-C. Lau, M. Robert, *ACS Catal.* **2023**, *13*, 5979.

[3] (a) Y.-L. Xiao, Y.-K. Chun, S.-C. Cheng, C.-O. Ng, M.-K. Tse, E. N.-Y. Lei, R.-Y. Liu, C.-C. Ko, *Catal. Sci. Technol.* **2021**, *11*, 556; (b) R. Liu, S.-C. Cheng, Y. Xiao, K.-C. Chan, K.-M. Tong, C.-C. Ko, *J. Catal.* **2022**, *407*, 206. (c) Y. Xiao, X. Lu, S.-C. Cheng, M.-K. Tse, J. Liang, H. Huang, W. Tu, C.-C. Ko, X. Zhu, L. Wang, Y. Zhou, Y. Yao, Z. Zou, *J. Catal.* **2023**, *426*, 52.

[4] (a) Y.-L. Xiao, S.-C. Cheng, Z. Shi, M.-K. Tse, Z. Huang, C. P. Tsui, C. M. Arava, V. A. L. Roy, C.-C. Ko, *Langmuir* **2021**, *37*, 11592. (b) C.-C. Ko, Y. Xiao, *US Pat.* Appl. No.:17/441,644.

Photoinitiated Synthesis of 1,1-Dicyanocyclopropanes as a Gateway to β-Aminocarbonyls from Olefins

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Cyclopropyl-1,1-diesters are the most studied class of electrophilic cyclopropanes, whereas their dicyano analogues – 1,1-dicyanocyclopropanes – remain largely underexplored, with only a few reports on their synthesis and reactivity, primarily focusing on cycloaddition reactions. Inspired by the potential reactivity of these systems and building on our work with alkylidene malononitriles,[1] we sought to harness photochemical strategies to access 1,1-dicyanocyclopropanes and use them as strained electrophiles, facilitating rapid access to β-aminocarbonyl derivatives, key scaffolds found in numerous bioactive molecules and pharmaceuticals.

To this end, we developed a visible-light-initiated atom-transfer radical addition–ring closure protocol that enables the efficient synthesis of previously inaccessible 1,1-dicyanocyclopropanes. The transformation proceeds under mild conditions using as little as 0.01 mol% *fac*-Ir(ppy)$_3$ or 4CzIPN as photocatalysts under blue LED irradiation (λ_{max} = 440–450 nm). The resulting cyclopropanes act as highly reactive strained electrophiles, undergoing nucleophilic ring-opening with amines to yield aminomalononitriles, which are directly converted in one pot to β-aminocarbonyl derivatives under aerobic conditions (Figure 1).

This photoinitiated strategy provides access to underutilized electrophilic cyclopropanes while showcasing the power of visible light to enable new reactivity pathways. The method offers a modular route from simple olefins to complex β-aminocarbonyl motifs, bypassing traditional aza-Michael and Mannich strategies.

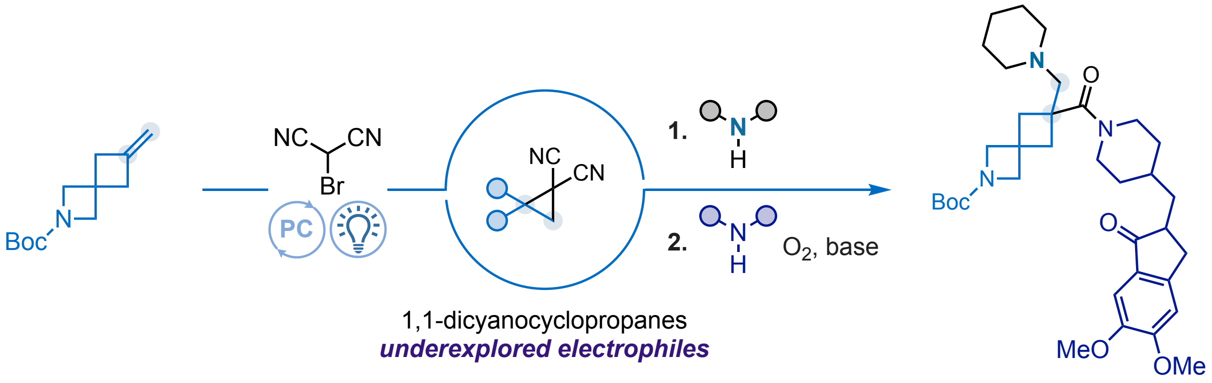

Figure 1. Modular synthesis of β-amino carbonyls via 1,1-dicyanocyclopropanes.

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References:

[1] (a) K. Anwar, F. J. A. Troyano, A. H. Abazid, O. El Yarroudi, I. Funes-Ardoiz, A. Gómez-Suárez, *Org. Lett.* **2023**, *25*, 3216; (b) K. Anwar, L. Capaldo, T. Wan, T. Noel, A. Gómez-Suárez, *Chem. Commun.* **2024**, *60*, 1456.

[2] (a) J. Li, M. J. Lear, Y. Hayashi, *Angew. Chem. Int. Ed.* **2016**, *55*, 9060; (b) Y. Hayashi, J. Li, H. Asano, D. Sakamoto, *Eur. J. Org. Chem.* **2018**, 675.

Thermochromic paraffin-based microcomposites for smart windows and greenhouses

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Buildings are responsible for ca. 40% of the global energy consumption in developed countries, half of which is associated to the increasing use of heating, ventilation and air-conditioning systems. In response, significant efforts are being directed towards the development of advanced, tunable materials for smart windows, capable of regulating light (and thus energy) transmission throughout the day and under varying weather conditions. Thermoresponsive materials, which undergo a phase transition from transparent to opaque above a specific temperature, offer substantial light modulation and strong resistance to photodegradation. These properties make them particularly attractive for energy-saving applications.[1,2] Among the most promising candidates there are hydrogels, ionogels, and liquid crystals, which have been widely explored for smart window technologies. However, these materials still face important challenges: high production costs, complex structural requirements to minimize solvent loss (particularly in hydrogels), and limitations in scalability.

In this study, we present a new class of scattering-based thermochromic composites, which offers light modulation performance comparable with well-established thermochromic materials, while also providing several additional advantages, including long-term stability, flexibility, low cost and a straighforward, scalable fabrication process. These composites are based on poly(vinyl alcohol) (PVA) films embedded with paraffin micro/nanoparticles. The thermoresponsive optical modulation exhibited by our films is driven by refractive index matching (transparent state) and mismatching (opaque state) between the matrix and the paraffin in its solid/liquid phases. By finely tuning the paraffin composition, particle size, and crystalline morphology, we achieved coatings with high luminous transmittance in the off-state (%T_{lum} = 77.3%), strong solar and near-infrared light modulation (ΔT_{solar} = 58.6%, ΔT_{NIR} = 40.0%), and effective thermal self-regulation. Furthermore, the incorporation of graphene oxide as a photothermal agent enables additional photoresponsive behavior. Several functional prototypes, such as energy-saving smart windows, light-modulating greenhouse films (Fig. 1), and adhesive coatings for train windows, illustrate their strong potential for real-world deployment in sustainable light and thermal management applications.

Figure 1. Pictures of a greenhouse prototype featuring a paraffin-based thermochromic coating.

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References:

[1] S. Tan, S. Guo, Y. Wu, T. Zhang, J. Tang, G. Ji, *Adv. Funct. Mater.* **2025**, *35*, 2415921.

[2] J. R. Otaegui, D. Ruiz-Molina, J. Hernando, C. Roscini, *Chem. Eng. J.* **2023**, 463, 142390.

Synergistic effect of light and acidity on glycerol acetalization over WO_3 catalysts

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Glycerol is an important platform chemical from biomass. Its acetalization with acetone can lead to the five-membered cyclic acetal known as solketal [(2,2-dimethyl-1,3-dioxolan-4-yl)methanol] which can be used as biosolvent or (bio)fuel additive, among other applications[1-2].

This study explores the potential of WO_3-based catalysts for the acetalization of glycerol with acetone under various illumination conditions. Two WO_3 catalysts (named WO_3-B and WO_3-Y where B and Y refers to its blue or yellow color, respectively) were synthesized using a solvothermal method, resulting in materials with differing degrees of surface reduction. The catalysts were thoroughly characterized and tested for glycerol acetalization both in the dark and under UV or simulated solar irradiation. WO_3-B demonstrated high catalytic activity, attributed to its Brønsted acidity and the presence of oxygen vacancies associated with W^{5+} species. Although WO_3-B was active under dark conditions due to acid catalysis, it deactivated after t=8h and its performance improved significantly under simulated solar light (Fig. 1a). This enhancement is attributed to a synergistic effect, possibly involving the formation of new photoinduced Brønsted acid sites or the regeneration of existing ones, thereby preventing catalyst deactivation. This behavior was especially evident in reuse experiments, where spent catalysts showed no activity in the dark but gradually regained performance when exposed to light (Fig. 1b).

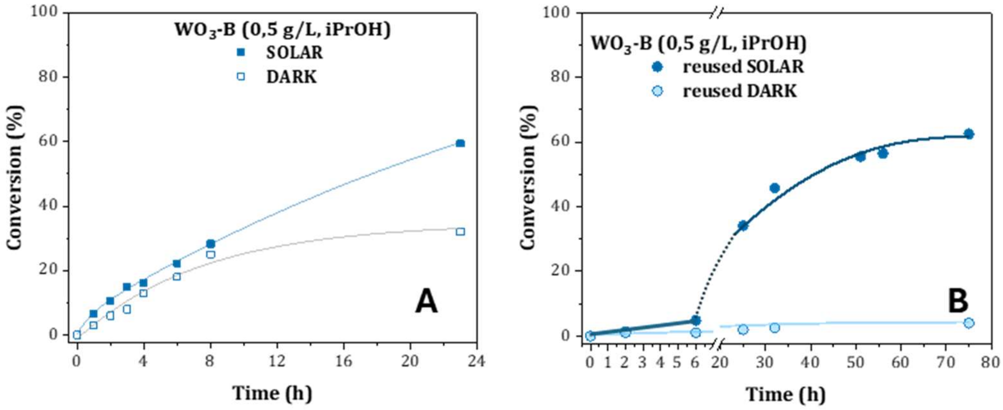

Figure 1. (Photo)catalytic activity of WO_3-B catalyst in the acetalization of acetone with glycerol: a) results for fresh catalyst in the dark (DARK) and under simulated solar illumination (SOLAR); b) reutilization of the catalyst in the dark and under simulated light. Reaction conditions were as follows: catalyst concentration, 0.5 g/L; total reaction volume, 15 mL; with propan-2-ol as solvent; glycerol:acetone:iPrOH ratio, 1:11:2; temperature, 20°C. Newport, Xe lamp, $1.9 \cdot 10^{-7}$ Einstein·s^{-1} as measured through ferrioxalate actinometry.

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References:

[1] I. Zahid, M. Ayoub, B.B. Abdullah, M.H. Nazir, M. Ameen, Zulqarnain, M.H. Mohd Yusoff, A. Inayat, M. Danish, *Ind Eng Chem Res*, **2020**, *59*, 20961–20978.

[2] A. Talebian-Kiakalaieh, N.A.S. Amin, N. Najaafi, S. Tarighi, *Front Chem*, **2008**, *6*,573.

Intra-band Exciton Dynamics of Quantum dot

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Mid-infrared (mid-IR) absorbing colloidal quantum dots (CQDs) were synthesized and their carrier dynamics probed with femtosecond mid-IR pump–probe (IRPP) spectroscopy. In dodecanethiol-ligated HgS CQDs we resolve three distinct kinetic components: (i) a pump-fluence-independent ultrafast decay of 1.2 ± 0.1 ps that we attribute to Auger-accelerated relaxation in biexcitonic states, (ii) a long-lived component exceeding 300 ps that reflects a phonon-bottleneck-limited single-exciton relaxation, and (iii) an intermediate 20–60 ps component whose microscopic origin, previously tentatively assigned to spin-orbit–induced inter-sublevel transitions, remains uncertain [1].

To clarify this intermediate process and to test the size-dependence of intraband Auger dynamics, we prepared three sizes of HgSe CQDs and monitored their intraband exciton evolution with IRPP spectroscopy. An oscillatory feature emerging at ~10 ps becomes markedly more pronounced with increasing dot diameter. Two-colour IRPP experiments—in which pump and probe pulses were tuned to each CQD's intraband absorption maximum (3.72 μm / 3000 cm^{-1}, 4.63 μm / 2600 cm^{-1}, and 7.23 μm / 2200 cm^{-1})—demonstrate that this oscillation arises from transient absorption rather than from bleach recovery caused by Auger-mediated carrier refilling. Hence, the conventional biexciton-driven intraband Auger model cannot account for the size-enhanced oscillatory response. We propose that coherent, collective carrier dynamics involving transitions among discrete intraband states govern the observed behaviour; ongoing work aims to quantify this contribution and thus establish a comprehensive, size-dependent picture of intraband electron dynamics in mid-IR CQDs.

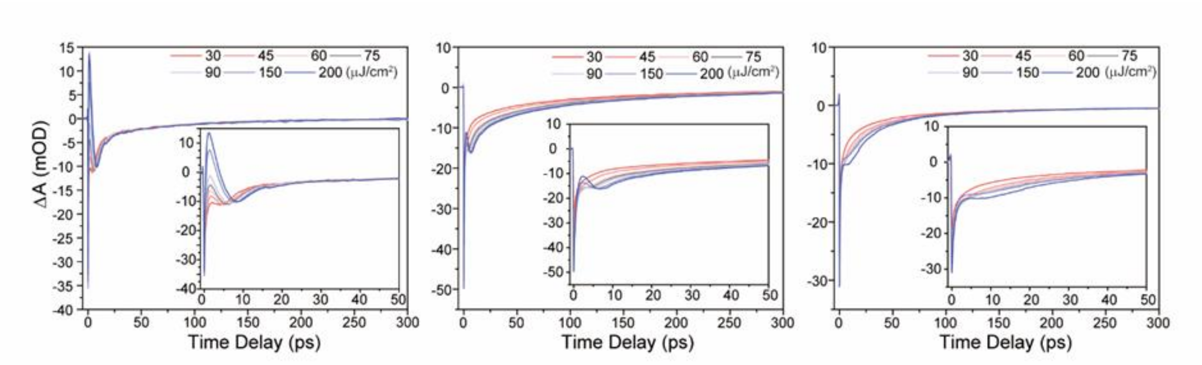

Figure 1. Pump-power dependent IR pump-probe signal of HgSe colloidal quantum dots with three different size (7.2, 4.7, and 3.6 nm). The inset magnifies the oscillation signal.

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References:

[1] J. Lim, Y. Choi, D. Choi, I. Chang, H. Kim K. Jeong,*, K. Kwak,*, and M. Cho,* *Matter*, 2021, *4*, 1072.

Carbon Nitride Thin Films for Artificial Photosynthesis

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Abstract

Two-dimensional materials in the carbon nitride family have recently garnered attention for their ability to function as photocatalysts under visible light. However, their application as thin films have been limited due to poor coating homogeneity. We have developed an innovative chemical vapor deposition (CVD) method that enables the deposition of carbon nitride thin films with tunable thickness and high uniformity.[1] The conformal nature of these CVD-grown films allows integration into microfluidic reactors, where they demonstrate superior performance in the photocatalytic oxidation of benzylic alcohols under flow conditions.[2] Furthermore, the homogeneity of the films facilitates the use of advanced spectroscopic techniques—including NMR, XPS, and XAS—for in-operando analysis of photocatalytic reaction mechanisms.[3] Using in-operando XPS and XAS, we explored the mechanism of photocatalytic water splitting, uncovering the crucial role of surface interactions, particularly the formation of hydrogen bonds with water, in activating the carbon nitride surface which is found critical in facilitating the otherwise difficult step of water oxidation (Fig. 1).

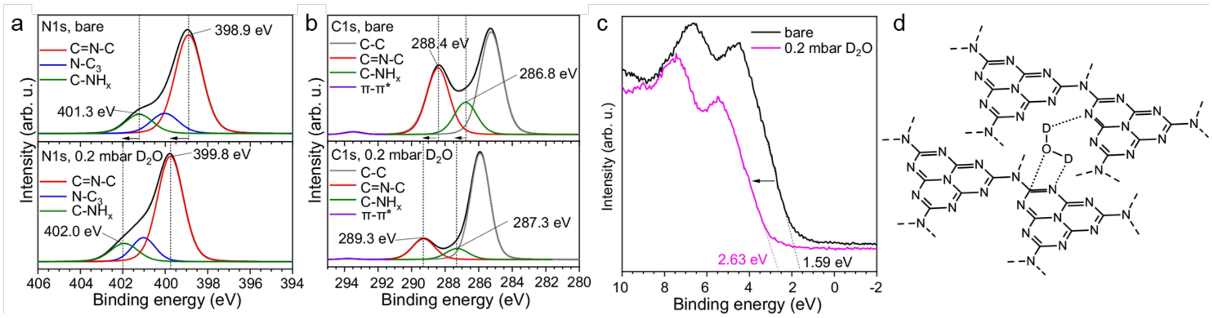

Figure 1. a, XPS, N1s spectra of carbon nitride thin film bare (upper panel) and after adsorption of heavy water (lower panel); arrows indicate spectral shift direction; b, XPS, C1s spectra of carbon nitride thin film bare (upper panel) and after adsorption of heavy water (lower panel); arrows indicate spectral shift direction; c, VB-XPS of the carbon nitride thin film bare (black line) and after adsorption of heavy water (magenta line) with relative valence band values, arrow indicates spectral change direction; d, schematic representation of the carbon nitride-heavy water structure after adsorption.[4]

Upon illumination we were able to confirm the evolution of hydrogen and oxygen while the spectroscopic features recorded support the proton-coupled electron transfer (PCET) mechanism. [4] These insights provide a fundamental understanding of one of the most extensively studied reactions of the past decade, both experimentally and theoretically. Although the use of thin films in energy conversion is still emerging, our work highlights their potential to drive significant progress in photocatalysis, photoelectrocatalysis, and beyond.

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References:

[1] P. Giusto, D. Cruz, T. Heil, H. Arazoe, P. Lova, T. Aida, D. Comoretto, M. Patrini, M. Antonietti, Shine Bright Like a Diamond: New Light on an Old Polymeric Semiconductor. Adv. Mater., 2020, 32, 1908140.

[2] S. Mazzanti, G. Manfredi, A. J. Barker, M. Antonietti, A. Savateev, P. Giusto, ACS Catalysis, 2021, 11, 11109.

[3] B. Dauth, P. Giusto, B. König, R. M. Gschwind, Angew. Chem. Int. Ed., 2024, 63, e202412972.

[4] D. Cruz, S. Żółtowska, O. Savateev, M. Antonietti, P. Giusto, Nature. Communications, 2025, 16, 374

Photocatalytic CO_2 Reduction Mediated by a Mo-Based Complex

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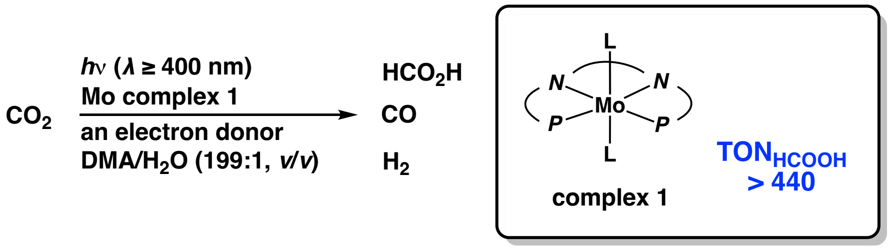
Photocatalytic carbon dioxide (CO_2) reduction has attracted attention, as it enables the conversion of CO_2 into energy-rich compounds under mild conditions without generating salt waste.[1] Among the potential products, formic acid (HCO_2H) is particularly valuable as a platform chemical and energy carrier, for instance, as a fuel in direct formic acid fuel cells (DFAFCs). However, because homogeneous photochemical CO_2 reduction remains challenging due to the difficulty in controlling multi-electron processes, typical approaches have relied on two-component systems consisting of a transition metal catalyst, a photosensitizer, and a sacrificial reductant. Our group has demonstrated that iridium (Ir),[2] ruthenium (Ru),[3] and osmium (Os)[4] complexes bearing PNNP-type tetradentate ligands function as efficient self-photosensitized catalysts, enabled by the robustness of the PNNP-metal framework. Nevertheless, reliance on precious metals remains a limitation. Herein, we present a new tetradentate PNNP-ligated molybdenum (Mo) complex (**1**) as the first Mo-based photocatalyst to reduce CO_2 to HCO_2H and hydrogen (H_2) without the need for an additional photosensitizer.

The photocatalytic CO_2 reduction was investigated using complex **1** in the presence of 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH) as an electron donor under photoirradiation ($\lambda \geq 400$ nm) at 1 atm of CO_2 (Scheme 1). The reaction proceeded selectively to produce HCO_2H without the need for an additional photosensitizer. Product yields increased with prolonged irradiation, achieving turnover numbers (TONs) of >440 for HCO_2H and 255 for H_2 over 168 hours. Control experiments confirmed that negligible amounts of products were formed in the absence of **1**, BIH, CO_2, or light. A labeling experiment using ^{13}C-labeled CO_2 ($^{13}CO_2$) in a $^{13}CO_2$-saturated DMF-d_7/H_2O mixture (199:1, *v*/*v*; 4.0 mL) verified that the carbon atoms in the generated HCO_2H originated from CO_2. Mechanistic insights into the excited-state behavior of the Mo complex were further elucidated by spectroscopic techniques, including transient absorption, electron paramagnetic resonance (EPR), and UV–vis spectroscopy.



Scheme 1. Photocatalytic reduction of CO_2 with a Mo complex as a photocatalyst under visible light irradiation ($\lambda \geq 400$ nm)

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References:

[1] M. Mikkelsen, M. Jorgensen, F. Krebs, *Energy Environ. Sci.* **2010**, *3*, 43.

[2] (a) K. Kamada, J. Jung, T. Wakabayashi, K. Sekizawa, S. Sato, T. Morikawa, S. Fukuzumi, S. Saito, *J. Am. Chem. Soc.* **2020**, *142*, 10261. (b) K. Kamada, J. Jung, Y. Kametani, T. Wakabayashi, Y. Shiota, K. Yoshizawa, S. H. Bae, M. Muraki, M. Naruto, K. Sekizawa, S. Sato, T. Morikawa, S. Saito, *Chem. Commun.* **2022**, *58*, 9218.

[3] K. Kamada, H. Okuwa, T. Wakabayashi, K. Sekizawa, S. Sato, T. Morikawa, J. Jung, S. Saito, *Synlett* **2022**, *33*, 1137.

[4] K. Kamada, J. Jung, C. Yamada, T. Wakabayashi, K. Sekizawa, S. Sato, T. Morikawa, S. Fukuzumi, S. Saito, *Angew. Chem. Int. Ed.* **2024**, *63*, e202403886.

Energy Management of Functional Molecular Materials

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The understanding of energy management, like energy harvesting, transformation, conversion, and storage, has been brought into focus, demanded by the search for new functional materials for various purposes, as research nowadays is driven by the need for more sustainable and alternative strategies for energy management. Herein, we present functional molecular materials and display the behavior and energy management in these systems as energy storage materials upon photoexcitation. Further, we discuss using this energy to employ conversion and storage in chemical bonds. We shortly dive into the preparation of the materials; however, focusing on the photophysical properties and requirements for efficient energy management. Moreover, we present a method of fast quantification of photophysical properties like half-lifetimes and quantum yields using a custom-built and semi-automated setup. As an extension and complement, proof-of-principle devices based on these molecular materials will be shown. Herein, the focus lies on molecular solar thermal energy storage systems (MOST). They attract increasing attention due to their possible and promising use regarding solar energy harvesting and, more significantly, storage.[1] Solar irradiation is used to excite the MOST material which then undergoes a chemical reaction to result in an energy-rich metastable isomer that can store the energy and release it on demand via triggered back-reaction, to restore the parent molecular state (Fig. 1a). Examples of their actual implementation into proof-of-principle devices have been shown to demonstrate their potential.[2] On the other hand, a novel technique, flow chemistry, takes on greater significance, especially due to several advantages over usual batch chemistry. Herein, we present materials for MOST and the use of flow techniques, both individually and in synergy (Fig. 1b), highlighting e.g., synthesis and optimization (Fig. 1d-e), and the investigation of MOST materials using standard analysis and emerging flow techniques (Fig. 1c-e).[3,4] Besides others, examples based on the norbornadiene (NBD)/quadricyclane (QC) photoisomerization pair will be on display.

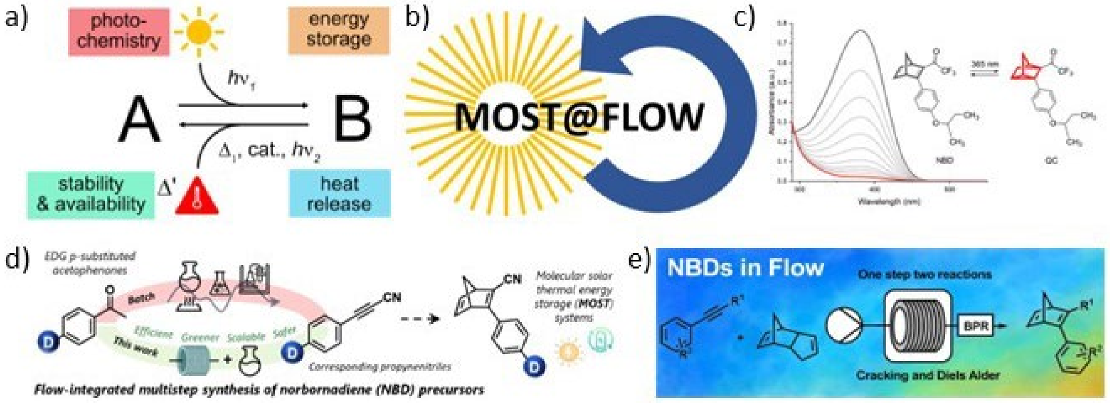

Figure 1. a) Principle and overview of MOST working principle; b) MOST@FLOW concept to investigate molecular properties using flow techniques; c) Conversion of an NBD by photoirradiation with 365nm to its QC form; d) flow-based precursor preparation for NBDs; e) Preparation of NBDs in flow by a one-step-two reaction approach.

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References:

[1] Z. Wang, P. Erhardt, T. Li, Z.-Y. Zhang, D. Sampedro, Z. Hu, H. A. Wegner, O. Brummel, J. Libuda, M. B. Nielsen, K. Moth-Poulsen, *Joule*, **2021**, *5*, 3316.

[2] Z. Wang, H. Hölzel, K. Moth-Poulsen, *Chem. Soc. Rev.* **2022**, *51*, 7313.

[3] J. Orrego-Hernández, H. Hölzel, M. Quant, Z. Wang, K. Moth-Poulsen, *Eur. J. Org. Chem.* **2021**, *2021*, 5337.

[4] N. Baggi, H. Hölzel, H. Schomaker, K. Moreno, K. Moth-Poulsen, *ChemSusChem* **2024**, *17*, e202301184.

Helical B–O–B Bridged Complexes: Molecular Design and Chiroptical Functions

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Helicenes possess intrinsic helical chirality and high aromaticity, making them promising candidates for next-generation chiral optoelectronic and photonic applications[1]. However, extending helicene frameworks for improved optical functions often complicates synthesis and restricts the tunability of small organic molecules, while simplified variants suffer from low racemization barriers and poor configurational stability. Overcoming this trade-off demands innovative helicene architectures.

Here, we report two families of B–O–B bridged helicene-like boron complexes with bipyridine (**1**) and phenanthroline (**2**) skeleton. These complexes were synthesized in facile one-pot reactions using dihydrazine precursors, acid chlorides and $BF_3 \cdot OEt_2$ (**Fig. 1.**). NMR, mass spectrometry, and single-crystal X-ray diffraction confirmed their B–O–B bridged structures and (*P*) / (*M*) chirality.

Complexes **1** exhibited yellow fluorescence (Φ_{PL} = 2–8 %), while dimethylaminobenzene-substituted analogue was non-emissive but displayed reversible ON/OFF switching upon TFA/TEA addition via photoinduced electron transfer (PET) inhibition. Upon TFA addition, CD and CPL measurements of **1c** revealed chiroptical OFF/ON switching**,** with maximum $|g_{abs}|$ and $|g_{lum}|$ values reached 1.2×10^{-2} and 5.0×10^{-3}, respectively[2]. Meanwhile, complexes **2** exhibited cyan to yellow emission in toluene (Φ_{PL} = 5–35%). The rigid phenanthroline framework enhanced emission efficiency and enabled emission color tuning by substitution changes. These complexes displayed great chiroptical properties,with maximum $|g_{abs}|$ and $|g_{lum}|$ values up to 6.7×10^{-3} and 2.0×10^{-3} respectively. Moreover, enantiopure **2** retained full CD intensity after heating at 100°C in toluene for 72 h, indicating a high racemization barrier.

This study offers a new molecular design strategy for helicenes, advancing the development of chiral small molecules for optoelectronic applications.

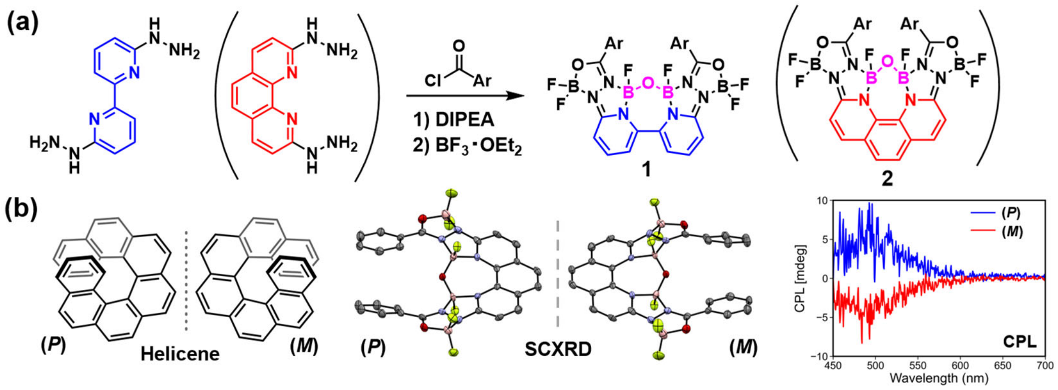

Figure 1. a) Synthesis of helicene-like B–O–B bridged complexes, b) Helical chirality and CPL spectra of complex **2**

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References:

[1] T. Mori, *Chem. Rev.* **2021**, *121*, 2373–2412.
[2] L. Cui, R. Furuta, T. Harada, T. Konta, Y. Hoshino, T. Ono, *Dalt. Trans.* **2024**, *53*, 9183–9191.

Modular assembly of polymer-based precision assemblies with microsecond charge separation

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The control of light-driven charge separation is of essential importance to utilize the transient energy in subsequent steps, *i.e.*, for charge accumulation or catalysis as well as molecular actuators. Detailed knowledge of the impact of structural and electronic properties were derived from sophisticated molecular donor-(photo)sensitizer-acceptor (D−P−A) assemblies. Nonetheless, the increasing complexity imposes a high synthetic burden to assemble future assemblies.

In this contribution, the progress for "chemistry-on-the-complex" as a versatile modular strategy will be presented,[1] which benefits from a late-stage diversification by, *e.g.*, efficient modern C-C coupling reactions (Figure 1a).[2] Importantly, the facile purification by modern automated re-cycling size exclusion chromatographywill be highlighted not only for discrete oligomeric redox-active multi-donors and multi-acceptors,[3] but also for the full assemblies including ionic Ruthenium sensitizer.

The charge separation within multiple redox-active units is demonstrated by transient absorption data (Figure 1b)[4] with lifetimes in the microsecond time-scale (Figure 1c).

The modularity of the approach will be presented for recent results, *e.g.*, to embed (block)copolymers with an intrinsic redox-cascade via modern controlled polymerization techniques, chemistry-on-the-complex and advanced separation techniques. The possibility to control forward and backward reactions can be tuned by (multiple) redox-innocent linkage patterns. Hence, the developed methodology is believed to be of high interest to circumvent synthetic restrictions, *e.g.*, to attach catalysts or to control charge separation and recombination at the polymer domain interfaces.

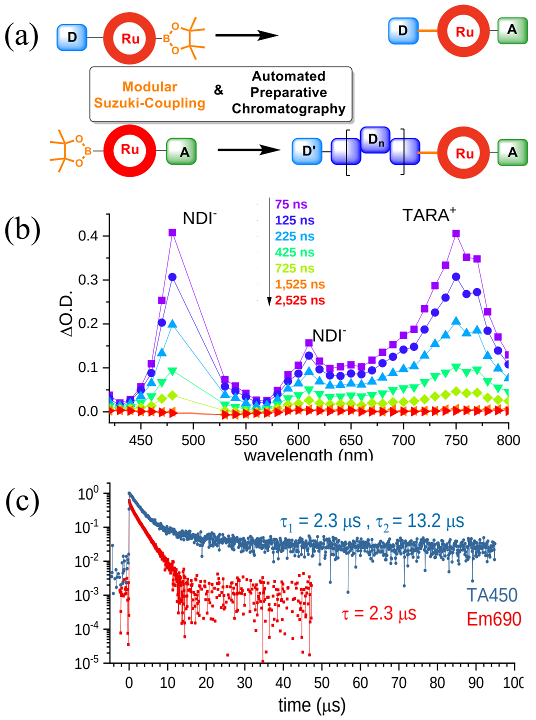

Figure 1. (a) Modular late-stage assembly of photo-redox-active assemblies. Transient absorption data illustrating the charge separation (b) in the microsecond timescale (c)

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References:

[1] T. Mede, M. Jager, U. S. Schubert, *Chem. Soc. Rev.* **2018**, *47*, 7577-627 10.1039/c8cs00096d.
[2] A. Kleine, U. S. Schubert, M. Jäger, *Inorganic Chemistry* **2024**, *63*, 4053-62 10.1021/acs.inorgchem.3c03380.
[3] A. Kleine, J. Kimmig, C. Mankel, U. S. Schubert, M. Jäger, *Macromolecules* **2024** 10.1021/acs.macromol.4c00448.
[4] R. Schroot, T. Schlotthauer, B. Dietzek, M. Jäger, U. S. Schubert, *Chem. Eur. J.* **2017**, *23*, 16484-90 10.1002/chem.201704180.

Photochemical Principles and Applications of Super-Resolution Fluorescence Imaging

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Super-resolution fluorescence microscopy (SRM) has advanced optical imaging by overcoming the diffraction limit, an achievement recognized by the 2014 Nobel Prize in Chemistry. The development and refinement of SRM techniques rely critically on the precise manipulation of photochemical processes at the molecular level. In this presentation, I will detail our investigations into the photochemical principles that govern SRM, including the control of fluorophore photophysics to achieve nanoscale resolution. Building upon these insights, I will further describe the application of SRM methodologies to a range of systems. These include the elucidation of extracellular vesicle biogenesis in Gram-positive bacteria and their direct interactions with human host cells, the super-resolution imaging of semiconductor nanopatterns, and single-molecule chemical sensing for probing phase separation in polymer blend films. Collectively, these studies demonstrate the potential of SRM to enable simultaneous nanoscale structural imaging and localized chemical analysis in both biological and materials science contexts.

All-organic Spin-State Photoswitches

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Digital data storage relies on the change of a material's electrical, magnetic, or optical properties between two states, indicating 1 and 0. Smaller units of information storage are an interesting research target, because they could lead to higher-density storage. Molecular organic switches are interesting in this context.[1] However, switching of spin states in all-organic molecules is challenging.

This contribution will focus on a helical photochemical spin-state switch.[2] Configurationally stable dimethyl[5]helicenes were used in the design of a photochemical magnetic switch with bistable spin states (Figure 1).[2] When introducing quinoidal 4,11-substituents, the helicene core undergoes rapid photochemical retro-electrocyclization which can be reversed using heat as stimulus. Upon photochemical ring opening at cryogenic temperatures, the helicene favors a diradical configuration with a triplet ground state and a stable EPR signal. The process is fully reversible and recovers the diamagnetic closed-shell form via thermal electrocylization. The system can be cycled without any significant degradation and represents a bistable photochromic spin switch that operates under chemical reactivity.

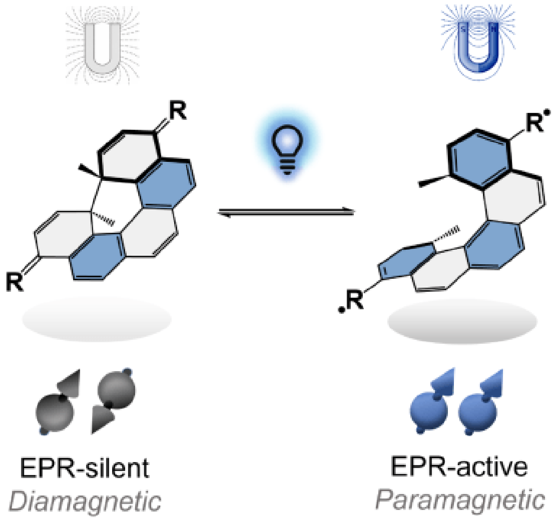

Figure 1. Dimethyl[5]helicene with various substituents (R) for photochemical spin-state switching.

References:

[1] For a full journal issue on molecular spintronics and quantum computing, see E. Coronado, A. J. Epsetin, *J. Mater. Chem.* **2009**, *19*, 1670−1671.

[2] K. Günther, N. Grabicki, B. Battistella, L. Grubert, O. Dumele, *J. Am. Chem. Soc.* **2022**, *144*, 8707–8716.

Reversing a unidirectional molecular motor: structural design and protocol for an electric-field driven control of the rotation direction

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Light-driven rotary motors allow direct transformation of light energy into unidirectional rotary motion at the nanoscale, giving rise to countless emerging applications in molecular engineering. The key feature enabling the unidirectional rotation and controlling its direction is the motor chirality, an inherently chemical factor, hard to modify postsynthetically [1-3].

Here we propose a new molecular rotary motor architecture, E-motor, in which the motor operation direction can be switched in situ, without the need for chemical modification of the system structure [4].This effect is achieved by the application of an external electric-field pulse and is intended to provide means for chirality control in motors deposited on a surface (Fig. 1a.). Our study relies on quantum-chemical calculations and nonadiabatic molecular dynamics simulations performed for a specifically tailored system, PFCN (Fig.1b.), designed to provide illustration for the proposed new motor type. We show that the model system's chirality and, hence, its operation direction, depends on orientation of a covalently bound polar switching unit, which can be controlled with an external electric field. At the same time, the proposed system manifests all characteristic photophysical properties of a unidirectional molecular motor, and its set chirality is preserved, i.e., it is thermally and optically stable during the regular motor operation in the absence of the electric field.

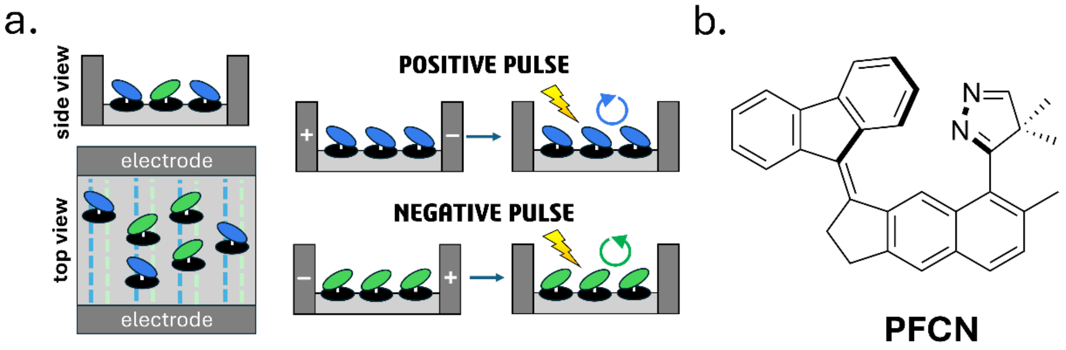

Figure 1. a) Working principle of an array of electric-field controlled molecular rotary motors, b) Electric-field switchable motor structure.

References:

[1] N. Ruangsupapichat, M. M. Pollard, S. R. Harutyunyan, B. L. Feringa, *Nat. Chem.* **2011**, *3*, 53.

[2] S. J. Wezenberg, B. L. Feringa, *Nat. Commun.* **2018**, *9*, 1984.

[3] V. García-López, D. Liu, J. M. Tour, *Chem. Rev.* **2020**, *120*, 79.

[4] K. Szychta, W. Danowski, J. Jankowska, *Sci. Adv.*, **2025**, *11,* eadt8008.

Ultrafast Excited-State Dynamics and Inter-Chromophore Interactions in Self-Assembled Coordination Complexes

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Chromophore-decorated self-assembled coordination complexes (SCCs) potentially provide a synthetic analogue to the organization of pigments in the light harvesting antenna systems of photosynthetic organisms. A clear understanding of the impact of coordination on inter-chromophore interactions, as well as of the energy and exciton/charge transfer mechanisms between decorating chromophores and their interaction with the metal ions at the coordination points, is needed for further development of artificial photosynthetic systems. To shed more light on these interactions [1, 2], we performed a series of ultrafast optical spectroscopy experiments on M_2L_4 and $M_{12}L_{24}$ SCCs decorated with different ratios of BODIPY and anthracene moieties in the exo-positions.

Time-resolved photoluminescence experiments showed a slowdown of the BODIPY emission upon increasing anthracene/BODIPY ratio when exciting the anthracene chromophore, demonstrating a chromophore-chromophore interaction leading to a unidirectional energy transfer from the anthracene to the BODIPY chromophores. Ultrafast transient absorption experiments on SSCs decorated with BODIPY, evidenced novel optically induced transitions substantially below the energy of the first excited singlet states of the corresponding chromophores. Since this type of excited state dynamics is not observed for free-floating chromophore-functionalized ligands, this observation indicates strong interactions between the BODIPY chromophores and the scaffold of the complexes.

The ultrafast experiments show that the coordination complex serves as an effective scaffold to mediate inter-chromophore interactions. At the same time, they show that the coordination complex is more than just a passive structure and plays an active role in the photophysics of the complexes. The present work provides initial steps to obtain an understanding of the photophysics of chromophore-decorated SCCs, which contribute to the overall goal to realize artificial photosynthetic systems.

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References:

[1] A. J. Musser, P. P. Neelakandan, J. M. Richter, H. Mori, R. H. Friend, and J. R. Nitschke, *Journal of the American Chemical Society* **2017**, *139*, 12050.

[2] E. Maligaspe, T. Kumpulainen, H. Lemmetyinen, N. V. Tkachenko, N. K. Subbaiyan, M. E. Zandler, and F. D'Souza, *The Journal of Physical Chemistry A* **2010**, *114*, 268.

Light-Harvesting Organic Nanomaterials for Efficient Energy Transfer and Amplified Biosensing

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Dye-loaded fluorescent polymeric nanoparticles (NPs) are among the brightest organic nanomaterials developed so far.[1] To ensure their high brightness, aggregation-caused quenching (ACQ) of encapsulated dyes needs to be suppressed. To this end, we developed a concept of dye insulation by bulky hydrophobic counterions (Figure 1A), which serve as spacers between dyes and favor dye encapsulation inside NPs.[2] As a result, we obtained NPs that are ~100-fold brighter than reference quantum dots of similar size.[3] Assembling dyes inside polymeric NPs resulted in a giant light-harvesting nanoantenna, where ~10000 encapsulated dyes undergo efficient Förster resonance energy transfer (FRET) to a single acceptor (Figure 1B), providing >1000-fold signal amplification (antenna effect).[4] Blank hydrophobic salts could further enhance its performance, with antenna effect reaching record breaking value of 4800.[5] Ultrafast time-resolved measurements and exciton annihilation studies revealed exciton migration at sub-ps time scale with diffusion length reaching 70 nm.[6] The light-harvesting concept was applied to amplify phosphorescence of porphyrins for ratiometric sensing of oxygen.[7] Functionalization of these nanoatennas with nucleic acids yielded ultrabright FRET-based nanoprobes for amplified detection of nucleic acids.[8] Recently, we also found that the energy transfer between two NPs connected by DNA duplexes can go far beyond the Förster law (~20 nm), which is important for amplified biosensing.[9]

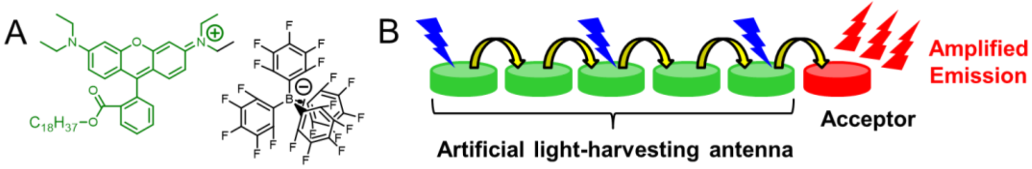

Figure 1. (A) Cationic dye (green) with it bulky counterion (black) used for building light-harvesting nanoantennas. (B) Schematic presentation of light-harvesting nanoantenna based on dyes for signal amplification.

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References:

[1] A. H. Ashoka, I. O. Aparin, A. Reisch, A. S. Klymchenko, *Chemical Society Reviews* **2023**, *52*, 4525.
[2] a) A. Reisch, P. Didier, L. Richert, S. Oncul, Y. Arntz, Y. Mely, A. S. Klymchenko, *Nature Commun.* **2014**, *5*; b) B. Andreiuk, A. Reisch, E. Bernhardt, A. S. Klymchenko, *Chem. Asian J.* **2019**, *14*, 836.
[3] A. Reisch, K. Trofymchuk, A. Runser, G. Fleith, M. Rawiso, A. S. Klymchenko, *ACS Appl. Mater. Interfaces* **2017**, *9*, 43030.
[4] K. Trofymchuk, A. Reisch, P. Didier, F. Fras, P. Gilliot, Y. Mely, A. S. Klymchenko, *Nature Photonics* **2017**, *11*, 657.
[5] D. S. Biswas, N. Melnychuk, C. Severi, P. Didier, A. S. Klymchenko, *Advanced Optical Materials* **2024**, *12*, 2301671.
[6] A. M. Gharbi, D. S. Biswas, O. Crégut, P. Malý, P. Didier, A. Klymchenko, J. Léonard, *Nanoscale* **2024**, *16*, 11550.
[7] P. Ashokkumar, N. Adarsh, A. S. Klymchenko, *Small* **2020**, *16*, 2002494.
[8] N. Melnychuk, S. Egloff, A. Runser, A. Reisch, A. S. Klymchenko, *Angewandte Chemie International Edition* **2020**, *59*, 6811.
[9] D. S. Biswas, P. Gaki, E. Cruz Da Silva, A. Combes, A. Reisch, P. Didier, A. S. Klymchenko, *Advanced Materials* **2023**, *35*, 2301402.

Stimuli-Responsive Photoluminescence and Photomechanical Effects in Pentiptycene-Based Molecular Crystals

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Materials with stimuli-responsive photoluminescence and photomechanical properties hold great potential for applications in machinery and sensory devices. However, designing molecular systems that exhibit such dynamic behaviors remains challenging. We recently demonstrated that the rigid, H-shaped pentiptycene scaffold can enhance solid-state molecular mobility while preventing aggregation-caused quenching. This unique combination enables the formation of molecular crystals with promising dynamic and photoluminescent properties. Specifically, attaching a pentiptycene unit to various functional groups—such as an anthracene moiety,[1-4] a cyclometalated Pt(II) center,[5] or an Au(I) isocyanide complex[6]—via an acetylene linker gives rise to molecular solids exhibiting luminescence mechanochromism, vapochromism, thermochromism, photochromism, and/or photomechanochromism (Figure 1). Additionally, certain pentiptycene-derived π-conjugated systems display photomechanical effects, including bending, twisting, elongation, cracking, and jumping[2,3] This presentation will highlight recent progress in pentiptycene-based photomechanical and stimuli-responsive luminescent molecular crystals, with a particular focus on the underlying (supra)molecular motion mechanisms.

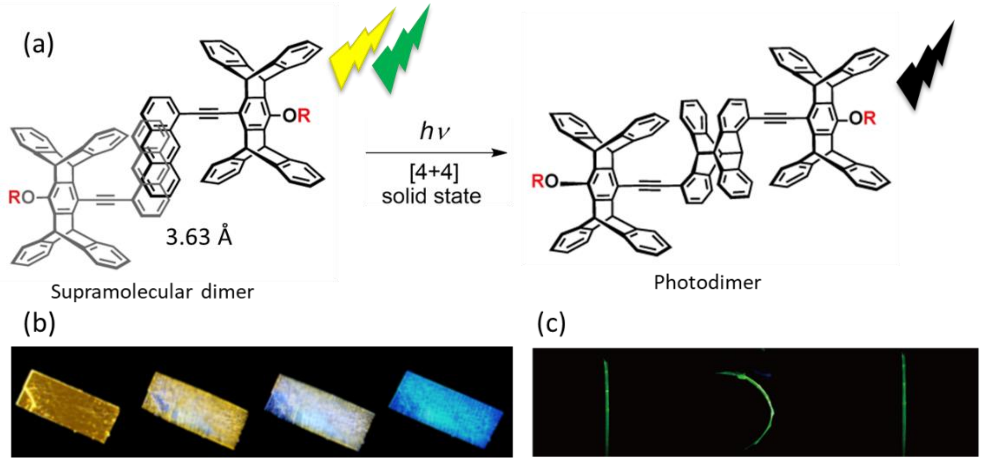

Figure 1. Example of stimuli-responsive photoluminescence of pentiptycene-based molecular crystals: (a) [4+4] photodimerization of the anthracene-pentiptycene system, (b) luminescence photomechanochromism, and (c) photomechanical bending.

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References:

[1] L.-Y. Hsu et al., & J.-S. Yang, *Chem. Sci.* **2018**, *9*, 8990-9001.
[2] C.-Z. Kuo et al., & J.-S. Yang, *Chem. Eur. J.* **2020**, *26*, 11511-11521.
[3] Y.-S. Chen, C.-H. Wang, Y.-H. Hu, C.-Y. D. Lu, J.-S. Yang, *J. Am. Chem. Soc.* **2023**, *145*, 6024-6028.
[4] Y.-H. Yang, Y.-S. Chen, W.-T. Chuang, J.-S. Yang, *J. Am. Chem. Soc.* **2024**, *146*, 8131-8141.
[5] C.-Y. Lien et al., & J.-S. Yang, *Inorg. Chem.* **2020**, *59*, 11584-11594.
[6] Y.-F. Hsu et al., & J.-S. Yang, *Inorg. Chem.* **2022**, *61*, 11981-11991.

Modulating the Single- and Two-Photon Emission Dynamics in Semiconductor Nanocrystals

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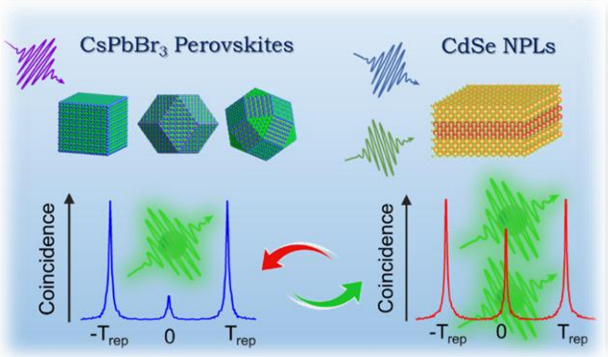

Quantum materials capable of emitting single- and two-photons have garnered significant attention from the research community due to their applications in optoelectronics and quantum communication.[1,2] This poster presents the modulation of single- and two-photon emission dynamics in nanocrystals via facet engineering and varying the excitation energy. These aspects are investigated at the single-nanocrystal level using time-resolved single-particle photoluminescence spectroscopy. Understanding the dynamics in $CsPbBr_3$ perovskite nanocrystals by facet engineering forms the first part of the poster. Here, we have observed that the biexcitonic quantum efficiency increases with the increase in the number of facets on perovskite nanocrystals, progressing from cube to rhombic dodecahedron to rhombicuboctahedron nanostructures. The observed enhancement is attributed mainly to an increase in their surface polarity as the number of facets increases, which reduces the Coulomb interaction of charge carriers, thereby suppressing Auger recombination. These findings underscore the significance of facet engineering in modulating the biexciton emission.[2] The second part of the poster presents the use of excitation energy to tune biexciton dynamics in CdSe-based nanoplatelets (NPLs). Upon varying the excitation energy from 3.1 eV (405 nm) to 2.1 eV (593 nm), the biexciton to single exciton quantum yield increases from 36 to 75%. Delving into the mechanism, we conclude that the non-radiative Auger recombination process is independent of the excitation energy. Experiments conducted by maintaining the photogenerated excitons constant have suggested that the increase in the quantum yield of biexcitons is due to a trap-assisted process.[3] In short, exciton and biexciton generation in semiconductor quantum materials can be tuned by facet engineering and varying the excitation energy.

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References:

[1] Panfil, Y. E.; Oded, M.; and Banin, U., *Angew. Chem. Int. Ed.* **2018**, *57*, 4274 – 4295.
[2] Nguyen, H. A.; Dixon, G.; Dou, F. Y.; Gallagher, S.; Gibbs, S.; Ladd, D. M.; Marino, E.; Ondry, J. C.; Shanahan, J. P.; Vasileiadou, E. S.; *et al., Chem. Rev.* **2023**, *123*, 7890-7952.
[3] Titus, T.; Vishnu, E. K.; Garai, A.; Dutta, S. K.; Sandeep, K.; Shelke, A.; Ajithkumar, T. G.; Shaji, A.; Pradhan, N.; Thomas, K. G., *Nano. Lett.* **2024,** *24*, 10434-10442.
[4] Titus, T. *et al.*, (*manuscript under preparation*).

Simulating the Full Spin Manifold of Triplet Pairs in Singlet Fission

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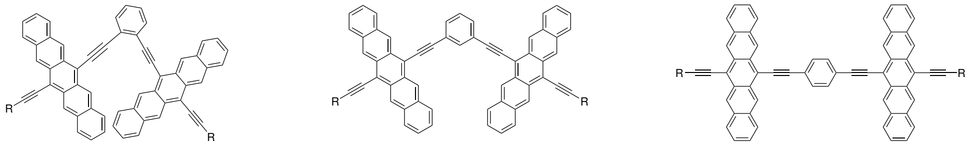
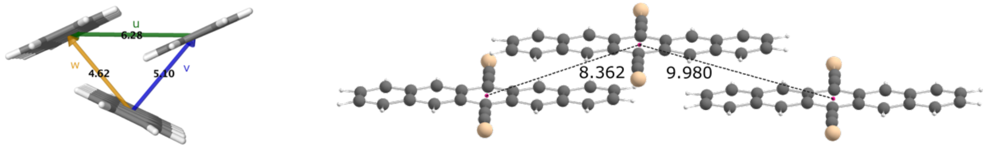
Singlet fission (SF) is a spin-allowed process in which one photon is converted into two triplet excitons on very short time scales and can thus address wavelength regions of the solar radiation spectrum which are otherwise unusable for generating electric current in photovoltaic devices. While there is consensus that the antiferromagnetically coupled triplet-pair state ^{1}(TT) represents an essential gateway state for SF, the participation of its ferromagnetically coupled congener ^{5}(TT) in the disentanglement of the triplet excitons is a matter of debate. Obviously, the computational exploration of alternative SF pathways calls for the reliable description of the energetic positions and possible couplings in the full spin manifold of the triplet-pair states. As these states are doubly excited with respect to the ground state, this poses a major challenge for computational methods. The density functional theory based multi-reference configuration interaction (DFT/MRCI) method[1,2] serves as a good basis for this endeavor, because it provides a balanced description of locally excited (LE) and charge-transfer (CT) states as well as double excitations. Furthermore, it is one of the few methods that allows the calculation of electronic spin–spin and spin–orbit coupling matrix elements between states of different multiplicity.



a) *ortho, o*-2　b) *meta, m*-2　c) *para, p*-2



d) pentacene crystal　e) TIPS-pentacene crystal

Figure 1. a) - c) Chemical structures of 6,6'-linked pentacene dimers studied in this work (R = methyl (Me) or triisopropylsilyl (TIPS)), d) u, v, and w stacking patterns in the herringbone structure of pentacene crystals, e) large and small overlap patterns in the brickwork structure of TIPS-pentacene

After a brief introduction of the computational methods, I will present our theoretical findings[3] on the SF mechanisms of covalently tethered TIPS-pentacene dimers (Fig. 1 a-c) and compare them with experimental reference data[4]. For studying the SF mechanisms in bulk pentacene[5] and TIPS-pentacene[6], combined quantum mechanical and molecular mechanics methods were employed. Apparently, the geometrical arrangement of the monomer units is a key factor in determining the SF mechanism of pentacene derivatives in the solid state, favoring either a direct or CT-mediated pathway.

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References:

[1] C. M. Marian, A. Heil, M. Kleinschmidt, *WIREs Comput. Mol. Sci.* **2019**, *9*, e1394.

[2] D. Dombrowski, T. Schulz, M. Kleinschmidt, C. M. Marian, *J. Phys. Chem. A*, **2023**, *127*, 2011.

[3] T. Schulz, C. M. Marian, *J. Comput. Chem.* **2024**, *45*, 2727.

[4] J. Zirzlmeier, D. Lehnherr, P. B. Coto, E. T. Chernick, R. Casillas, B. S. Basel, M. Thoss, R. R. Tykwinski, D. M. Guldi, *Proc. Natl. Acad. Sci.* **2015**, *112*, 5325.

[5] T. Schulz, S. Hédé, O. Weingart, C. M. Marian, *J. Chem. Phys.* **2024**, *160,* 144114.

[6] T. Schulz, S. Hédé, C. M. Marian, *J. Phys. Chem. Lett.* **2025**, *16*, 2887.

Welcome to the Dark Side: Photoactive Iron Complexes with Microsecond Excited-State Lifetimes

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In recent years, photosensitizer development based on earth-abundant metals or organic dyes as a replacement for precious metal complexes in photoredox catalysis has obtained significant attention.[1] Iron-based complexes are very attractive for this due to its high abundance in the Earth crust, low toxicity and environmental impact.[2,3] Up to now, the limited excited-state lifetimes up to a few nanoseconds represent a limiting factor to their widespread use.

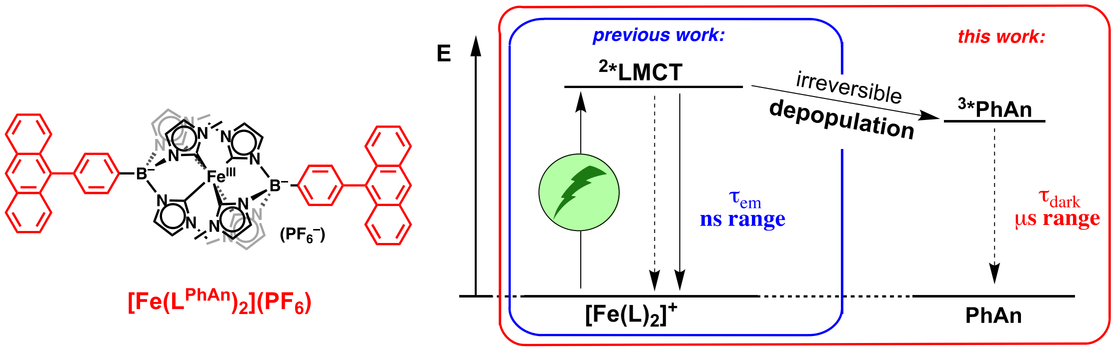

Figure 1. Structure of the investigated molecular dyad (left) and energy scheme comparing the established iron-based complex[4] with an emissive ligand-to-metal charge transfer (^{2*}LMCT) excited state (blue box) and the newly designed dyad with an energy acceptor (PhAn) attached (red box).

One possibility to tackle this issue is the design of molecular dyads composed of a photosensitizer and an energy acceptor. Up to now, the development of dyads mostly focused on excited-state equilibrium to repopulate the iron-based emissive state exploiting a so-called reservoir effect.[5,6] In contrast, we designed a molecular dyad composed of an energy acceptor attached to an iron-based photosensitizer that exhibited a microsecond-living non-luminescent excited state without repopulation of the iron-centered emissive state (Fig. 1).[7] Photophysical characterization and comparison to the unmodified iron photosensitizer highlighted the benefit of the energy acceptor present in the dyad. In addition to an improved excited-state lifetime, the energy acceptor also changed the excited-state character to triplet. This enables singlet oxygen photosensitization and led to a tenfold increase in cage escape yield for bimolecular electron transfer, in comparison to the unmodified complex. More detailed photophysical analyses uncovered that the mechanism to populate the triplet excited state is more complex than a direct doublet-triplet energy transfer. Our results clearly highlight the advantages of molecular dyads based on iron-based complexes with previously short excited-state lifetimes. This is expected to have significant impact on the use of these complexes in photoredox catalysis in the future.

References:

[1] C. Förster, K. Heinze, *Chem. Soc. Rev.* **2020**, *49*, 1057–1070.
[2] O. S. Wenger, *Chem. Eur. J.* **2019**, *25*, 6043–6052.
[3] F. Glaser, A. Aydogan, B. Elias, L. Troian-Gautier, *Coord. Chem. Rev.* **2024**, *500*, 215522.
[4] K. S. Kjær, N. Kaul, O. Prakash, P. Chábera, N. W. Rosemann, A. Honarfar, O. Gordivska, L. A. Fredin, K.-E. Bergquist, L. Häggström, T. Ericsson, L. Lindh, A. Yartsev, S. Styring, P. Huang, J. Uhlig, J. Bendix, D. Strand, V. Sundström, P. Persson, R. Lomoth, K. Wärnmark, *Science* **2019**, *363*, 249–253.
[5] S. Campagna, S. Genovese, A. Cancelliere, A. Arrigo, F. Puntoriero *Res. Square* **2024**, DOI: 10.21203/rs.3.rs-4002627/v1.
[6] J. Wellauer, J., B. Pfund, I. Becker, F. Meyer, A. Prescimone, O. S. Wenger, *J. Am. Chem. Soc.* **2025**, 147 (10), 8760–8768.
[7] F. Glaser, S. De Kreijger, L. Troian-Gautier, *J. Am. Chem. Soc.* **2025**, 147 (10), 8559–8567.

Organic photoreactions utilizing boron, silicon, and tin elements

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Photoinduced reactions have received much attention as a powerful tool to access kinetically or thermodynamically prohibited reactions on the ground state, affording complex molecules useful in material science and medicinal chemistry. These photoreactions have been based mainly on using main-group elements with high electronegativity such as carbon (C), oxygen (O), nitrogen (N), halogens (F, Cl, Br, and I) as well as transition-metals. On the other hand, we have been interested in the characteristics of main-group elements with low electronegativity, such as boron (B),[1,4] silicon (Si),[3] and tin (Sn),[2] in the excited state, enabling the highly reactive and/or selective photoinduced reactions (borylation, silylation, stannylation, and so on) shown in Fig. 1. These photoreactions can expand the chemical space of complex organic compounds and provide potentially useful and important molecules in material science and medicinal chemistry.

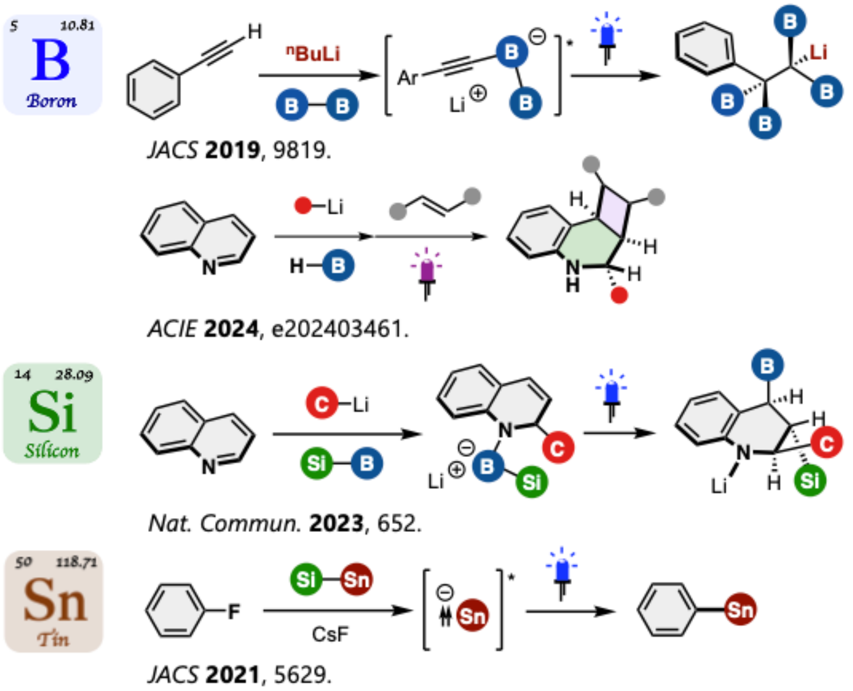

Figure 1. Organic photoreactions utilizing boron, silicon, and tin elements

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References:

[1] Y, Nagashima et al., & M. Uchiyama, *J. Am. Chem. Soc.* **2019**, *141*, 9819.
[2] Y, Nagashima et al., & M. Uchiyama, *J. Am. Chem. Soc.* **2021**, *143*, 5629.
[3] Y, Nagashima et al., & M. Uchiyama, *Nat. Commun.* **2023**, *14*, 652.
[4] Y, Nagashima et al., *Angew. Chem. Int. Ed.* **2024**, *63*, e202403461.

Gold Nanoarchitectures for Plasmon-Enhanced Reactions

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Au nanostructures and their hybridizations have garnered considerable interest due to their unique optical and physicochemical properties.[1-3] Trimetallic systems incorporating Au are particularly powerful because they harness the distinctive attributes of different metals, which—when combined—generate synergistic effects that surpass those of monometallic and bimetallic systems. The strategic design of trimetallic nanoparticles (NPs) allows for the fine-tuning of electronic and geometric structures, unlocking exceptional catalytic activity and durability. However, the precise synthesis of these complex NPs remains challenging due to the diverse physicochemical properties of constituent metals, including differences in deposition potentials. Achieving controlled morphology and spatial arrangement of each metal in trimetallic systems continues to be a significant obstacle.

Trimetallic systems have attracted growing interest in (electro)catalysis, largely due to their synergistic benefits. Yet, precise control over metal positioning and a deep understanding of the structure–performance relationship remain elusive. Here we introduce a synthetic strategy for Pd@Pt@Au mesoporous nanoparticles (MNPs), featuring a distinct core–shell Pd@Pt configuration with well-dispersed, isolated Au islands anchored on the outer shell to enhance plasmonic effects.[4] As a proof of concept, the electrocatalytic performance of Pd@Pt@Au MNPs for the methanol oxidation reaction (MOR) is evaluated under both light-induced and dark conditions. The results demonstrate significantly enhanced activity relative to commercial Pt black, with the catalytic performance increasing approximately 7.5-fold under light irradiation. The placement of Au on the outer shell offers superior plasmonic enhancement, contributing to the elevated catalytic activity observed under illumination. This investigation provides insights into the controlled synthesis of trimetallic MNPs and highlights their catalytic potential. It underscores the crucial role of precise Au positioning in optimizing performance for plasmon-enhanced electrocatalysis. Today’s presentation will present a range of Au-related topics and ongoing updates.

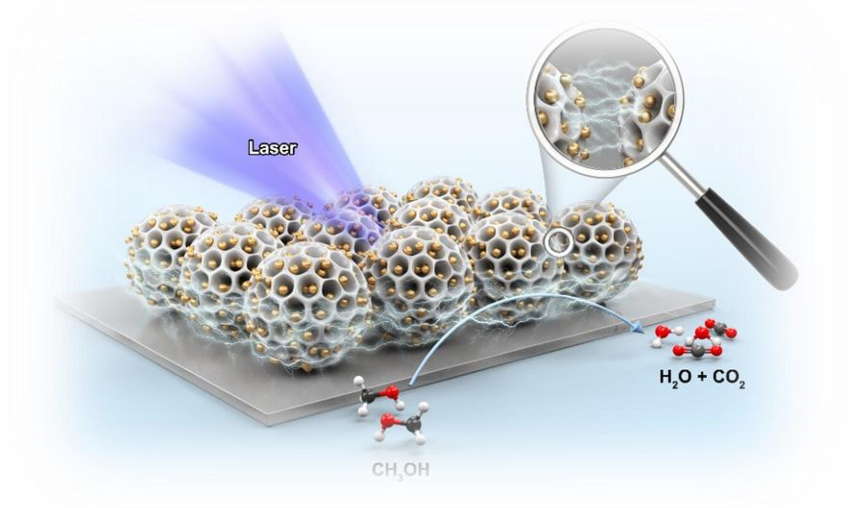

Figure 1 Pd@Pt@Au mesoporous nanoparticles (MNPs) for plasmon-enhanced electrochemical reactions

References:

[1] M. Eguchi *et. al.*, Langmuir, 28, 9021 (2012).
[2] M. Eguchi *et. al.*, Chem. Lett., 43, 140 (2014).
[3] M. Eguchi *et. al.*, Angew. Chem. Int. Ed., 62, e202307615 (2023).
[4] L. Zhu, Y. Kang, M. Eguchi* *et. al.*, Chem. Sci. In press (2025) DOI: 10.1039/D4SC07345B

Multiphoton-Driven Photocatalytic Defluorination of Persistent Perfluoroalkyl Substances and Polymers by Visible Light

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Perfluoroalkyl substances (PFASs) and fluorinated polymers have been extensively used due to their exceptional thermal stability, chemical resistance, and surface properties. However, their extreme persistence and bioaccumulation pose serious environmental and health concerns. Conventional methods for PFAS decomposition rely on harsh treatments such as high-temperature incineration or UVC irradiation, which are energy-intensive and often impractical for large-scale applications.

Here, we report a photocatalytic method capable of efficiently decomposing perfluorooctane sulfonate (PFOS), a representative persistent PFAS, and Nafion, a widely used sulfonated polymer, under ambient conditions using visible LED light and semiconductor nanocrystals (NCs) [1]. By irradiating aqueous dispersions of CdS or Cu-doped CdS NCs with 405-nm LED light, PFOS was completely decomposed within 8 hours, achieving a turnover number of 17,200 C–F bonds per NC. Nafion also underwent 81% defluorination after 24 hours. Decomposition of PTFE powders was much slower than those of PFOS and Nafion. On the other hand, hydrophobic PTFE powders became hydrophilic, and were precipitated in the water solution, demonstrating the potential of the decomposition.

Spectroscopic analyses and control experiments revealed that this reaction proceeds through a cooperative multiphoton process involving photoinduced ligand desorption, enhanced PFAS adsorption, and Auger-induced generation of hydrated electrons and high-energy excited states. These reactive species exhibit reduction potentials sufficient to break even the C–F bonds. The process is further facilitated by nanoscale confinement and surface dynamics of NCs. Notably, this system operates in water at room temperature and atmospheric pressure and toxic CdS can be easily replaced with other compound semiconductor NCs, highlighting its practicality and environmental compatibility.

Our findings demonstrate a sustainable photochemical route for PFAS degradation using visible light, offering new insights into advanced photocatalytic mechanisms and contributing to the development of a fluorine-recycling society.

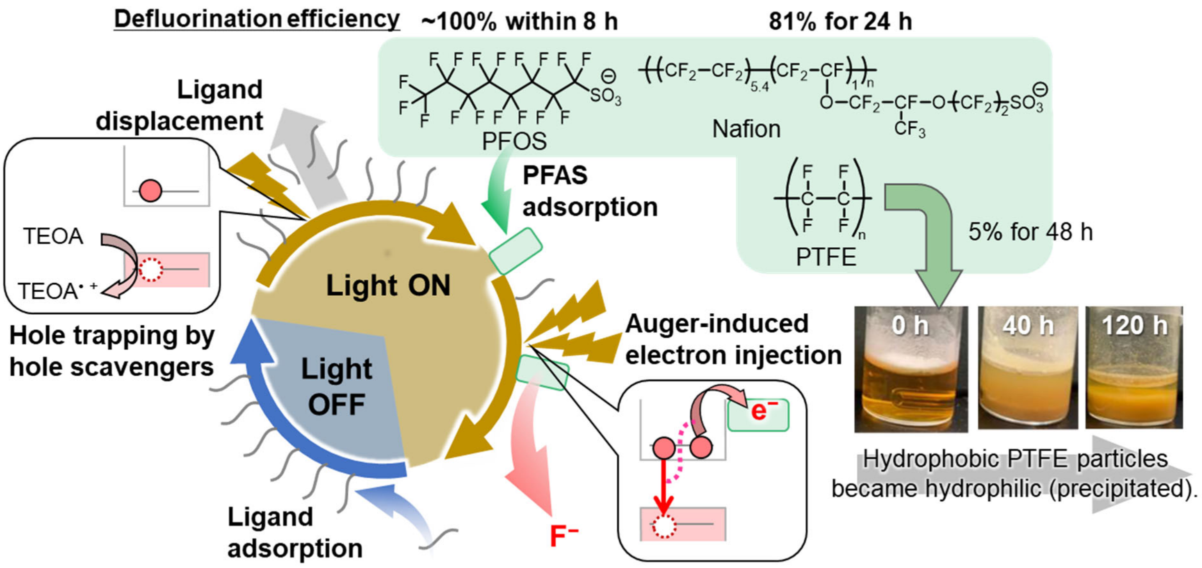

Figure 1. Plausible reaction mechanism for multiphoton-driven photocatalytic defluorination by semiconductor NCs [1].

Reference:

[1] Y. Arima, Y. Okayasu, D. Yoshioka, Y. Nagai, Y. Kobayashi. *Angew. Chem. Int. Ed.* **2024**, *63*, e202408687.

Structure-Dependent Performance of Cu_2O Photocatalysts for Solar-Driven CO_2 Conversion

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Abstract

Climate change, driven by increasing carbon dioxide (CO_2) emissions, presents a significant global threat, affecting economic, social, and environmental sustainability. As CO_2 emissions continue to rise-, particularly in nations where fossil fuel dependence is prevalent, there is an urgent need to develop technologies that not only capture CO_2 but also convert it into useful products. Meanwhile, Cu-based photocatalysts have emerged as promising materials for catalytic CO_2 reduction to multi-carbon products. There are reports on the selective production of Methanol, an important platform chemical and energy carrier, using Cu_2O. This study reports the structure- and size-dependent photocatalytic performance of bare Cu_2O catalysts from the perspective of the selective production of methanol. A series of Cu_2O catalysts with varied morphologies was prepared via reductive precipitation with glucose and hydroxides and characterized for their physicochemical properties. The results revealed that morphology and particle size play critical roles in product selectivity. Cu_2O photocatalyst with less-defined morphologies and smaller particles exhibited higher methanol production compared to the well-defined polyhedral structures, while smaller particles enhanced activity. This is attributed to exposed crystal facets, increased surface areas, and improved photogenerated charge separation. The study highlights the structure-selective relationships and their potential as tunable photocatalysts for producing liquid solar fuels. The results contribute to the rational design of the Cu_2O system for efficient and selective CO_2-to-solar fuel conversion.

Funding: Alexander von Humboldt Foundation

Illuminating Insights – how well plate material influences light stimulation efficiency

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Investigations into photosensory receptors and other light-dependent research domains demand rigorous attention to the optical properties of experimental apparatuses, including multiwell plates.

Our study critically evaluates the transmittance characteristics of a variety of multiwell plates, which are pivotal in light-based experiments, mapping their combined absorption and scattering traits across the UV-VIS spectrum.

We demonstrate that although transmittance remains comparably high above 450 nm, considerable differences are observed at lower wavelengths. Some plates show exceptionally high transmittance, making them suitable for sensitive applications, whereas other plates show significant light loss at lower wavelengths. Importantly, micro-structured well plates can decrease transmittance across the whole UV-Vis spectrum by up to 50%.

In response to these findings, we have integrated the transmittance data into an innovative illumination platform that ensures consistent and even illumination across different well plate types. This platform, complemented by a computational tool, enables researchers to adapt light dosages to accommodate the unique optical properties of each plate. This advance is crucial for researchers across diverse disciplines where light plays a pivotal role, ensuring that experimental conditions are reproducible and results are reliable.

The study emphasizes the need for meticulous recalibration of lighting when altering well plate types and sets a foundation for further research on the impact of various experimental media on light transmittance, thereby enhancing the precision of light-based research methodologies.

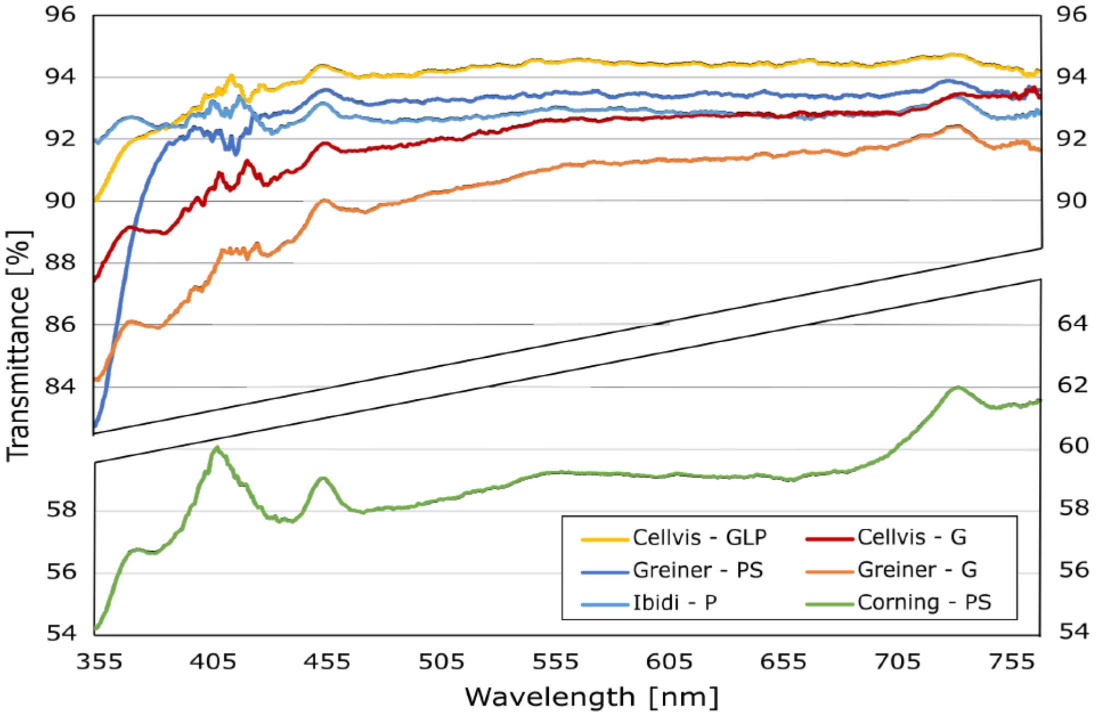

Figure 6. Transmittance through the well plate bottom from 350 nm to 770 nm for different well plate types, averaged from three independent experiments.

Abstract ICP 2025

Highthroughput screening of lead-free halide perovskites using Bayesian optimization for photocatalysis

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The global need for sustainable energy solutions demands the rapid discovery of lead-free, stable, and efficient catalytic materials. Addressing this, we present a one-dimensional (1D) binary combinatorial library of lead-free halide perovskites fabricated via an automated pipetting highthroughput robotic system. Through Gaussian process-based Bayesian optimization (BO) integrated with high-throughput screening, we systematically interrogate the optoelectronic properties across 96 distinct compositions within one library. Surface photovoltage (SPV) measurements emerge as a decisive probe, offering a major factor into charge carriers at the surface critical for photocatalytic performance.

Our data-driven strategy identifies a standout composition which showcases the highest SPV response, superior ambient and water stability, and complete organic dye degradation within 15 minutes under white light illumination. We found iodine vacancy-driven defect engineering, while cathodoluminescence (CL) and photoluminescence (PL) analyses confirm the presence of shallow defect states that suppress carrier recombination.

We establish a proof-of-concept for accelerated catalyst discovery within a 1D compositional space, blending experimental prowess with machine learning agility. The insights guide to design novel lead-free perovskites for water splitting and greenhouse gas mitigation, setting a new benchmark for next-gen sustainable material platforms.

Reaction Engineering as Key to Transfer Photoreactions To Application

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Photochemical reactions are emerging as transformative tools for sustainable chemical manufacturing, offering energy-efficient pathways to synthesize fine chemicals, pharmaceuticals, and renewable fuels while minimizing waste and fossil fuel dependence. However, their industrial adoption hinges on overcoming critical scalability challenges tied to photon and mass transport and eventually reactor design. Due to the complex interaction of the different transport processes, the transfer of photochemical processes from laboratory to industrial scale remains a considerable challenge.

A critical limitation in the scaling-up of photochemical processes is light attenuation, which can either limit reactor performance or lead to inefficiencies, such as byproduct formation. Conventional scale-up strategies that rely on reactor volume enlargement (sizing up) frequently prove ineffective, thus necessitating alternative approaches. These include numbering up microstructured reactors or integrating mesostructured designs (e.g., translucent monoliths or packed beds) to maintain short optical paths while enhancing throughput.

This contribution will discuss recent results on the effect of mass transport on the overall performance of photoreactors. It will be shown how static mixers can be used to enhance the mass transport in the modular, industrial scalable, continuously operated photoreactor (MISCOP, s. Figure 1, left), which was developed together with Peschl Ultraviolet.[1] Theoretical and experimental studies showed that reactive performance can be increased, eventually leading to an increase in photonic efficiency by a factor of 2.4.[2,3] Furthermore, the effect of mass transport limitations between irradiated and shadowed regions in intensified capillary photoreactors for gas/liquid photoreactions, such as photooxidations, will be analyzed.[4]

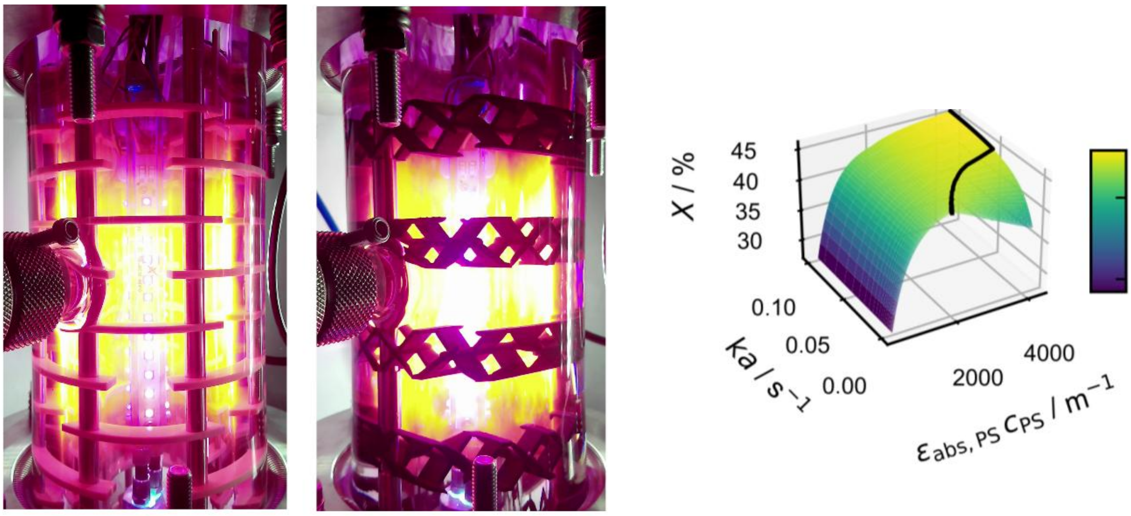

Figure 1. **Left:** Pictures of the modular, industrial scalable, continuously operated photoreactor (MISCOP) during operation with different static mixers.[2] **Right:** Effect of the mass transport rate (*ka*) and the linear absorption coefficient on the conversion of a gas/liquid photoreaction.[4]

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References:

[1] F. Gaulhofer, M. Metzger, A. Peschl, D. Ziegenbalg, *Industrial & Engineering Chemistry Research* **2023**, *62*, 11456–11469.

[2] F. Gaulhofer, H. Becker, A. Peschl, D. Ziegenbalg, *Reaction Chemistry & Engineering* **2024**, *9*, 3231–3247.

[3] F. Gaulhofer, M. Metzger, A. Peschl, D. Ziegenbalg, *Reaction Chemistry & Engineering* **2024**, *9*, 1845–1858.

[4] B. Wiedemann, K. M. Carogher, S. Kuhn, D. Ziegenbalg, *Chemical Engineering Journal* **2025**, *503*, 157987.

Reconfigurable Photoflow Reactor for Accelerated Process Development

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In this study, we investigate the influence of eight distinct configurations of a flat-plate Photoflow reactor from Redeem Solar Technologies, each demonstrating unique photonic and mixing characteristics that affect light distribution and fluid dynamics within the reactor, Figure.1.

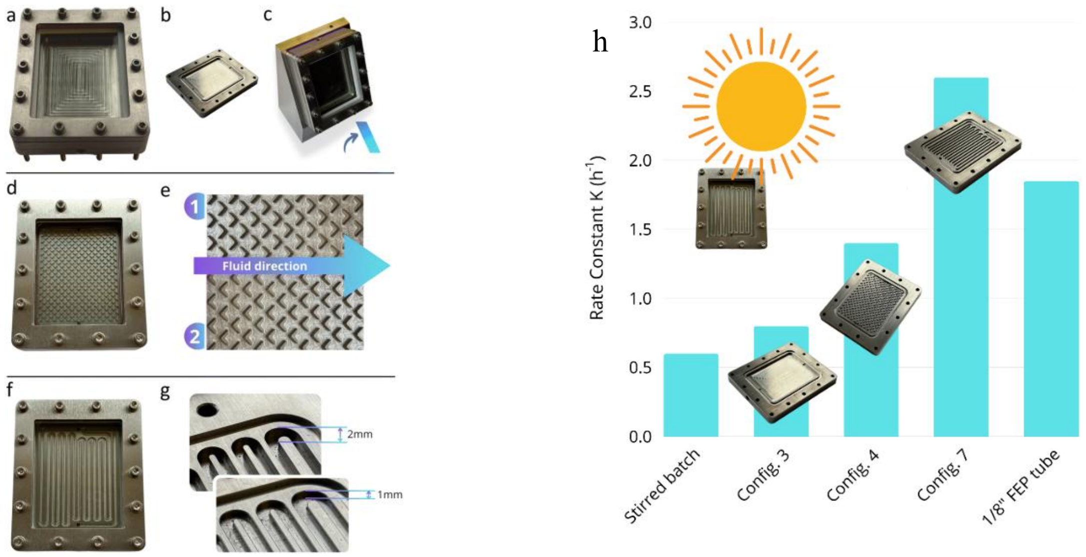

Figure 1. Fig. 1 Illustration of the photoflow reactor configurations. (a) Assembled reactor featuring a thin flowing film with a 2 mm depth (Config. 1), (b) the reactor bottom part that is replaced to switch to 0.5 mm depth reactor (Config. 2), (c) the 2 mm deep reactor position at 60 degree angle from the ground (Config. 3), (d) assembled reactor featuring a repeated open arrow head mixing structure, (e) illustration of the switch between having the arrow head pointing towards the direction of low (Config. 4) or the opposite (Config. 5), (f) assembled reactor featuring a serpentine channel with 2 mm depth, (g) the reactor bottom part that is replaced to switch between channels with 1, 2, and 3 mm depth corresponding to (Config. 6), (Config. 7), and (Config. 8), (h) comparison of the rate constant resulting from different reactor configurations.

The configurations vary in several ways: a wide rectangular channel design with differing depths and angles of inclination, two distinct static mixing structures, and three serpentine-like channels with variable depths. Each configuration demonstrated significant differences in how light interacts with the flow, impacting the photonic absorption and mixing efficiency. These differences lead to varying degrees of rate acceleration compared to a conventional stirred batch photoreactor. Notably, the serpentine configuration with a 2 mm deep channel exhibited the highest rate acceleration. By optimizing these configurations, we observed a dramatic reduction in reaction time, from 6 hours in a batch reactor to less than 1.25 hours. The apparent rate constant (K) increased by over four times. This acceleration could be correlated with the inverse product of the flow cross-sectional area and the light penetration depth, underscoring the importance of reactor geometry in enhancing light-matter interactions and mixing efficiency. The optimized Photoflow reactor achieved the desired product at room temperature, without the need for harmful or wasteful terminal oxidants, while maintaining both high reaction rates and excellent product selectivity.[1, 2, 3]

Funding: Die Österreichische Forschungsförderungsgesellschaft (FFG)

References:

[1] F. Ehrlich-Sommer et al., & M. Y.S. Ibrahim, *React. Chem. Eng.* **2025**, Advanced Article
[2] A. Reisenhofer, et al., & N.C. Mösch-Zanetti, *Appl Organomet Chem,* **2025** *39: e70129*
[3] S. Batool et al., & M. Y.S. Ibrahim, *Sustainable Energy Fuels,* **2025**,*9,* 555-564

Transient Absorption Microscopy of Carbon Nitride Photocatalyst Particles

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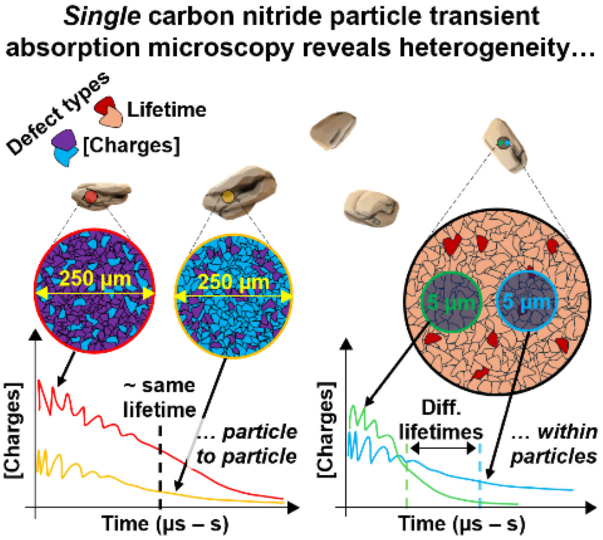
Polymeric photocatalysts made of Earth-abundant elements have been extensively developed over the past decade to take advantage of their synthetic tunability.[1] Within this family, carbon nitrides (CN_x) are emerging as leading photocatalysts because of their high photocatalytic performance combined with good stability and facile synthesis.[2] However, significant gaps remain in our knowledge of the photophysical properties of these organic polymeric materials. Determining the pathways and mechanism of photoinduced processes will greatly aid our efforts to engineer better CN_x photocatalysts for solar fuel production, environmental remediation, and synthetic photochemistry.[3]

We have developed a first-of-its-kind transient absorption microscopy (TAM) system that can monitor charge carrier dynamics on the microsecond – second timescales together with spatial resolution on the micron scale. Spatial mapping of the charge carrier dynamics with this system provides novel insights into the particle-to-particle heterogeneity and heterogeneity within individual CN_x particles.[4] Our observations point to the presence of at least two different types of trap states that dictate the density of trapped charges and the charge carrier lifetime, respectively (Fig. 1).



Single **carbon nitride particle transient absorption microscopy reveals heterogeneity…**

Figure 1. Schematic representation of the particle-to-particle variations and spatial heterogeneity observed in the charge carrier dynamics of CN_x.

Photocatalysts are often surface-modified with cocatalysts to enhance their photocatalytic activity and drive specific chemical transformations. Using pixel-wise comparison of CN_x particles before and after Pt deposition, our TAM investigation points to a preferential effect of electron extraction by Pt for areas that have initially shorter charge carrier lifetimes. We also make use of transient absorption spectroscopy (TAS) on other CN_x/cocatalyst heterojunctions where Ni and Co are added onto the surface of CN_x.[5,6] We can observe the impact of these surface modifications on the charge carrier dynamics and glean information on charge transfer pathways and reaction mechanisms.These new insights into the charge carrier dynamics of CN_x are key to elucidating the factors that control interfacial charge transfer in defect-rich organic semiconductors such as CN_x.

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References:

[1] Y. Wang, A. Vogel, M. Sachs, R. S. Sprick, L. Wilbraham, S. J. A. Moniz, R. Godin, M. A. Zwijnenburg, J. R. Durrant, A. I. Cooper, J. Tang, *Nat. Energy* **2019**, *4*, 746–760.
[2] P. O. Ohemeng, R. Godin, *Sustainable Energy Fuels* **2023**, *7*, 3250–3265.
[3] R. Godin, J. R. Durrant, *Chem. Soc. Rev.* **2021**, *50*, 13372–13409.
[4] S. Khasnabis, R. Godin, *Small* **2024**, 2406652.
[5] C. Liu, J. Liu, R. Godin, *ACS Catal.* **2023**, *13*, 573–586.
[6] M. Beckedorf, J. Holland, R. Godin, *Artif. Photosynth.* **2025**, *1*, 50–62.

New Tools for Photochemical Reaction Development and Optimization

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In the pursuit of greener and more sustainable chemical synthesis methods, photocatalysis has emerged as a transformative technology. By harnessing the power of light, this approach offers unprecedented opportunities to revolutionize chemical processes, reduce waste, and minimize the environmental footprint of chemical production. This talk will highlight the development of synthetic strategies involving organic free radicals generated through photocatalysis, emphasizing both practicality and mechanistic insight, with demonstrated applications in complex molecular systems. In addition, I will describe a new high-throughput platform for performing photocatalytic reactions in nanoliter-scale droplets, enabling rapid reaction discovery and optimization through massively parallel experimentation.

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References:

[1] E. A. Noten, C. H. Ng, R. M. Wolesensky, C. R. J. Stephenson. *Nat. Chem.* **2024**, *16*, 599

[2] M. Glossbrenner, S. Gonzalez-Granda, O. Nayal, L. Farmer, E. A. Noten, C. Balintfy, D. A. Pratt, and C. R. J. Stephenson ChemRxiv DOI: 10.26434/chemrxiv-2023-gw0xb

[3] A. C. Sun, D. J. Steyer, R. I. Robinson, C. Ginsburg-Moraff, S. Plummer, J. Gao, J. W. Tucker, D. Alpers, C. R. J. Stephenson, R. T. Kennedy, *Angew. Chem. Int. Ed.* **2023**, *62*, e202301664.