ADAM MICKIEWICZ
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Molecules & Light 2025

VI Autumn Meeting of the Polish Photochemistry Group

Book of Abstracts

Poznań, 14-17 September 2025

molecules_light2025.web.amu.edu.pl

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The Polish Section of the European Photochemistry Association (EPA) warmly welcomes participants to the sixth edition of the conference *Molecules & Light*. Following the tradition of previous meetings, the event will bring together researchers in photophysics, photochemistry, photocatalysis, and molecular spectroscopy.

As in the previous editions, ML2025 will review current research activities in these areas and provide an opportunity to establish and strengthen scientific and personal contacts within our community.

This year's edition hosts 7 invited lectures, 1 discussion panel, 50 oral communications, and 53 poster presentations, with the participation of 120 researchers from 11 countries. We are greatly encouraged by such an excellent turnout, which highlights the importance of this conference as a platform for scientific exchange. We are also delighted to continue the tradition of vibrant discussions and fruitful collaborations within an international setting.

Welcome to Poznań !

Scientific Committee

Conference Chairman

Marek Sikorski

Faculty of Chemistry, Adam Mickiewicz University in Poznań

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Jerzy Karpiuk,

Institute of Physics, Polish Academy of Sciences, Warsaw

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Faculty of Chemistry, Jagiellonian University, Kraków

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Katarzyna Taras-Goślińska

Anna Golczak

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Naisargi Varma

The conference is co-organized by:

Institute of Physics, Polish Academy of Sciences, Warsaw

Jagiellonian University, Kraków

Maria Curie-Sklodowska University, Lublin

University of Gdańsk, Gdańsk

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The Center for Advanced Technologies — A Model for Knowledge Transfer and Multidisciplinary Innovation

Dawid Frąckowiak

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The Center for Advanced Technologies (CZT UAM) in Poznań represents a pioneering model of knowledge transfer that bridges science, research, and industry. Established within the framework of the Wielkopolska Centre for Advanced Technologies (WCZT) consortium — bringing together five public universities, four institutes of the Polish Academy of Sciences, one research institute, and the Poznań Science and Technology Park — the Centre provides a unique platform for collaboration across disciplines and sectors.

Launched in 2015 on the Morasko Campus of Adam Mickiewicz University, the Centre builds upon the vision of its founder, Prof. Bogdan Marciniec, to create a space where fundamental research, applied studies, and business innovation converge. Its research focus lies in the development of novel, selective synthetic routes to advanced chemicals, biochemicals, and agrochemicals, as well as new generations of bio- and nanomaterials. The Centre also emphasizes the characterization of their properties and the design of advanced technologies and biotechnologies for use in medicine, pharmacy, agriculture, optoelectronics, ceramics, and high-tech industries. Beyond generating groundbreaking scientific results, CZT UAM offers a proven model of innovation transfer — ensuring a seamless progression from basic research to applied solutions and business-driven implementation. This approach has been recognized through multiple awards, including the *EuroSymbol of Synergy between Science and Business*.

Today, the Center for Advanced Technologies invites researchers, industry partners, and innovators to collaborate in building transformative solutions that address global challenges. With cutting-edge infrastructure, a strong interdisciplinary network, and a mission rooted in bridging science with practice, CZT UAM provides an open and dynamic environment for impactful research and sustainable innovation.

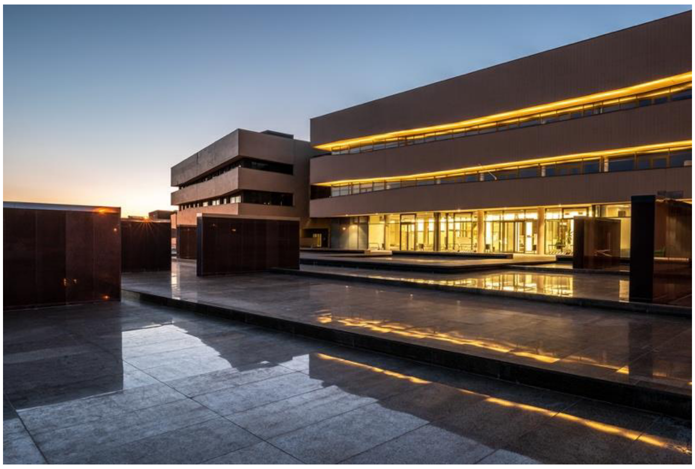

Figure 1. Center for Advanced Technologies building at AMU Morasko Campus in Poznań.

Invited Speakers

Daniel Gryko

Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland

Johan Hofkens

Single molecule Laboratory, Division of Molecular Imaging and Photonics, Heverlee, Belgium

Max Planck Institute for Polymer Research, Mainz, Germany

Maria Vittoria Dozzi

Dipartimento di Chimica, Università degli Studi di Milano, Milano, Italy

Burkhard König

Faculty of Chemistry and Pharmacy, University of Regensburg, Regensburg, Germany

Petr Slavicek

Department of Physical Chemistry, University f Chemistry and Technology, Prague, Czech Republic

Michel Sliwa

LOB, CNRS, INSERM, École Polytechnique, Institut Polytechnique de Paris, Palaiseau - France

LASIRE - UMR 8516, Université de Lille, Campus scientifique, Villeneuve d'Ascq Cedex - France

Prashant Kamat

Department of Chemistry and Biochemistry and Radiation Laboratory, University of Notre Dame, Notre Dame, IN, USA

Conference Program

SUNDAY 14.09.2025

Venue: Faculty of Chemistry, Uniwersytetu Poznańskiego 8, Poznań			
15:00–17:00			***Registration***
Aula 2.64			*Chairman: Marek Sikorski and Anna Lewandowska-Andrałojć*
17:00–17.15			***Opening Ceremony***
17:15–18:00	**IL1**	***Daniel Gryko***	**1,4-Dihydropyrrolo[3,2-*b*]pyrrole and Dipyrrolonaphthyridinedione – Novel Building Blocks for Optoelectronics**
18:00–18:15	O1	*Christoph Kerzig*	Combining the best of organic and inorganic photochemistry with molecular and coulombic dyads
18:15–18:30	O2	*Adam Zuba*	New TADF emitters based on strong boracyclic acceptors
18:30–18:45	O3	*Jerzy Karpiuk*	Rydberg states and electron capture. Mechanism of ultrafast photoinduced intramolecular electron transfer processes in spirocyclic D–A dyads
18:45–19:00	O4	*Sebastian Mackowski*	Remote control of photoswitching of DTE-py2 molecules with plasmonically active silver nanowires
19:00–21:00			***Welcome Reception***

MONDAY 15.09.2025

Venue: Faculty of Chemistry, Uniwersytetu Poznańskiego 8, Poznań			
8:00			***Registration***
Aula 2.64			*Chairman: Jerzy Karpiuk*
9:00–9:45	**IL2**	***Johan Hofkens***	**Labels and Linkers for Microscopy: from Improved Imaging to Applications**
9:45–9:50	***(time to move between lecture halls)***		
Aula 2.64			*Chairman: Gotard Burdziński*
9:50–10:05	O5	*Hubert Piwonski*	Nanotube-scaffolded cyanine J-aggregates and Stokes-shift controlled emission: dual innovations for plant bio-imaging
10:05–10:20	O6	*Anna Zieleniewska*	Microenvironmental modulation of photothermal behavior in photoacid-doped soft coatings
10:20–10:35	O7	*Katarzyna Choroba*	Ir(III) and Re(I) Imidazo[4,5-f][1,10]phenanthroline Systems as Effective Emitters and Photosensitizers
10:35–10:50	O8	*Małgorzata Bayda-Smykaj*	Organosilicon Compounds in Coloured Emission

Aula 2.61			*Chairman: Sebastian Mackowski*
9:50–10:05	O9	*Joanna Jankowska*	Internally polarized Covalent Organic Frameworks: a new material concept for molecular photovoltaics
10:05–10:20	O10	*Rafał Szabla*	Breakdown and salvation of statistical rate theory in photoinduced electron transfer
10:20–10:35	O11	*Vitali Stsiapura*	Computational studies of non-radiative decay pathway for TICT state in Thioflavin T
10:35–10:50	O12	*Anna Kaczmarek-Kędziera*	Predictive power of quantum chemistry for fluorescence quantum yield: Are we there yet?
10:55–11:30			***Coffee Break***
Aula 2.64			*Chairman: Aleksandra Lindner*
11:30–12:15	**IL3**	***Maria Vittoria Dozzi***	**BiVO$_4$ and CuWO$_4$-based Photoanodes for Solar Energy Conversion**
12:15–12:20	***(time to move between lecture halls)***		
Aula 2.64			*Chairman: Janusz Dąbrowski*
12:20–12:35	O13	*Adam Kubiak*	A scalable IoT-controlled LED photocatalytic system for the removal of pharmaceuticals from real wastewater
12:35–12:50	O14	*Marcin Kobielusz*	Tuning Strontium Titanate for Enhanced Photocatalytic Reduction of Nitroaromatic Compounds
12:50–13:05	O15	*Kasidid Yaemsunthorn*	Old material in a new light: TiO$_2$-mediated free-radical photopolymerization
13:05–13:20	O16	*Joanna Zams*	Theoretical insight into the low-lying excited states of a Cu(I) photosensitizer
Aula 2.61			*Chairman: Christoph Kerzig*
12:20–12:35	O17	*Joanna Palion-Gazda*	Controlling photoinduced intramolecular charge transfer processes in Re(I) and Ir(III) complexes.
12:35–12:50	O18	*Adam Glinka*	Probing ultrafast charge transfer in Fe/Co dyad complex using UV-VIS and mid-IR time resolved absorption spectroscopy.
12:50–13:05	O19	*Gerald Hörner*	Spin-State dependent Emission of 3d-Metal Complexes
13:05–13:20	O20	*Naisargi Varma*	Novel flavin derivatives: synthesis, Photo-redox Catalysis, and photophysical insights
13:20–13:30			***Conference Photo***
13:30–14:30			***Lunch***
Aula 2.64			*Chairman: Radek Cibulka*
14:30–15:15	**IL4**	***Burkhard König***	**Better Organic Synthesis with Light!**

15:15–15:25		*Dawid Frąckowiak*	The Center for Advanced Technologies — A Model for Knowledge Transfer and Multidisciplinary Innovation
15:25–15:30	***(time to move between lecture halls)***		
Aula 2.64			*Chairman: Borys Ośmiałowski*
15:30–15:40	O21	*Patryk Pyrcz*	Impact of Spatial Confinement on Probing Single-Molecule Surface-Enhanced Raman Scattering in Plasmonic Nanocavity
15:40–15:50	O22	*Vishnu Vijayakumar-Syamala*	Pressure-Induced Red-to-NIR Luminescence Switching in Square-Planar Rh(I) Complexes
15:50–16:00	O23	*Farwa Khalid*	Kinetics and High Field NMR study of the photodegradation of Retinyl Acetate under Ultraviolet Irradiation
16:00–16:10	O24	*Wiktoria Zacheja*	Impact of the localized surface plasmon resonance in gold nanorods on molecular photoswitching
16:10–16:20	O25	*Jacek Baranowski*	Charge transport material influence on photoinduced ion segregation in perovskite solar cells
16:20–16:30	O26	*Marina Smirnova*	Enhancing stability and photoinduced charge transfer in porphyrin – MXene nanohybrids for light-driven applications
Aula 2.61			*Chairman: Agata Blacha-Grzechnik*
15:30–15:40	O27	*Anna LąGowska*	Distinct effects of progesterone and cholesterol on the properties of lipid membranes: Insights from Biophysical Experiments and Molecular Dynamics Simulations
15:40–15:50	O28	*Marta Warszyńska*	Synergistic Activation of Antitumor Immunity via Bacteriochlorin-Based Photodynamic Therapy and Immune Checkpoint Blockade
15:50–16:00	O29	*Jacek Łyskawa*	Probing cell membranes under dehydration using fluorescence lifetime measurements
16:00–16:10	O30	*Kamil Pulit*	Development of Organic Ligands for Theranostic Iridium(III) Complexes: Synthetic Strategies and Spectroscopic Characterization
16:10–16:20	O31	*Patrycja Piękoś*	Experimental and Computational Investigation of Novel BODIPY-3-Serotonin Dye
16:20–16:30	O32	*Paweł Repetowski*	Modified Sulfonyl Phthalocyanines for Effective Photodynamic Therapy and Prospects for Combination with Immunotherapy
16:30–17:00			***Coffee Break***
17:00–19:00			***Poster Session***

TUESDAY 16.09.2025

Venue: Faculty of Chemistry, Uniwersytetu Poznańskiego 8, Poznań			
8:00			***Registration***
Aula 2.64			*Chairman: Grażyna Stochel*
9:00–9:45	**IL5**	***Petr Slavicek***	**Closing the Gap Between Computational Photodynamics and Photochemistry**
9:45–10:00	O33	*Wojciech Macyk*	When the fate of photogenerated charges matters—classification of heterojunctions in photocatalysis
10:00–10:15	O34	*Gotard Burdziński*	Photoresponse of xanthophylls in flowers
10:15–10:30	O35	*Radek Cibulka*	Photoredox catalysis with scandium(III) as a photoactive species
10:30–10:45	O36	*Joanna Olesiak-Banska*	Atomically precise noble metal nanoclusters as NIR luminescent markers
10:45–11:00	O37	*Aleksandra Lindner*	Organic chromophores on ferromagnets illuminated: a photochemical and magnetic study
11:00-11:30			***Coffee Break***
Aula 2.64			*Chairman: Gerald Hörner*
11:30–12:15	***Discussion panel: Prashant Kamat***		**How to Compose a Scientifically Effective Article**
12:15–12:30	O38	*Janusz Dąbrowski*	Shaping Light-Driven Therapies: Smart Photosensitizers and Molecular Materials for Enhanced Photodynamic Efficiency
12:30–12:45	O39	*Saif Eddine Cherif*	Positional Effects of Methoxy Substituents on the Photoacidity and Photovoltaic Properties of Merocyanine Photoacids
12:45–13:00	O40	*Joanna Ortyl*	Advancements in Cationic Photopolymerization: Composite Materials and Novel Photoinitiators for Specialized Applications
13:0–13:15	O41	*Mateusz Brzeziński*	Light in the Dark: Aminal-linked COFs for Efficient Light Upconversion
13:15-13:30	O42	*Suzanne Fery-Forgues*	Switching from phototherapeutically-active molecules to red-emitting photoluminescent materials with tricarbonylrhenium(I) complexes
13:30–14:30			***Lunch***
16:00–19:00			***Excursions***
19:30–23:00			***Gala dinner: Brovaria***

WEDNESDAY 17.09.2025

Venue: Faculty of Chemistry, Uniwersytetu Poznańskiego 8, Poznań			
Aula 2.64			*Chairman: Marek Sikorski and Anna Lewandowska-Andralojc*
9:00–9:15			**Opening of the session of the occasion of 75th birthday of Professor Bronisław Marciniak**
9:15–10:00	**IL6**	**Michel Sliwa**	**Toward the Design of Fast Red Reversible Photoswitchable Fluorescent Proteins using Multi-timescale Transient Absorption Spectroscopy.**
10:00–10:15	O43	*Krzysztof Bobrowski*	Radiation Chemistry and Photochemistry: Complementary Approaches for the Study of Free Radicals
10:15–10:30	O44	*Chantal Houée-Levin*	Methionine oxidation still brings surprises
10:30–10:45	O45	*Chryssostomos Chatgilialoglu*	An assortment of sulfur-centered radicals in chemistry and biology
10:45–11:00	O46	*Tomasz Pędziński*	Oxidation Pathways of Model Disulfides
11:00-11:45			***Coffee Break***
Aula 2.64			*Chairman: Wojciech Macyk*
11:45–12:30	**IL7**	***Prashant Kamat***	**Steering Energy and Electron Transfer in Semiconductor-Molecular Hybrids**
12:30–12:45	O47	*Sylwester Gawinkowski*	Wavelength-Dependent Enhancement Studies for Optimizing Excitation in SERS Spectroscopy
12:45–13:00	O48	*Olaf Morawski*	Photochemistry of quinoxaline derivatives in methanol and hydrogenation of aza-arenes
13:00–13:15	O49	*Caterina Bellatreccia*	Towards Better TADF Photocatalysts: Mechanistic insights and Practical Tools For Understanding Electron Transfer dynamics
13:15-13:30	O50	*Stefanie Tschierlei*	Three-Coordinate Cu(I) Complexes of Anionic N-Heterocyclic Carbenes
13:30–14:30			***Lunch***
14:30–15:00			***Closing Ceremony***

List of oral presentations

O1	**Christoph Kerzig** Combining the best of organic and inorganic photochemistry with molecular and coulombic dyads
O2	**Adam Zuba** New TADF emitters based on strong boracyclic acceptors
O3	**Jerzy Karpiuk** Rydberg states and electron capture. Mechanism of ultrafast photoinduced intramolecular electron transfer processes in spirocyclic D–A dyads
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O5	**Hubert Piwonski** Nanotube-scaffolded cyanine J-aggregates and Stokes-shift controlled emission: dual innovations for plant bio-imaging
O6	**Anna Zieleniewska** Microenvironmental modulation of photothermal behavior in photoacid-doped soft coatings
O7	**Katarzyna Choroba** Ir(III) and Re(I) Imidazo[4,5-f][1,10]phenanthroline systems as effective emitters and photosensitizers
O8	**Małgorzata Bayda-Smykaj** Organosilicon compounds in coloured emission
O9	**Joanna Jankowska** Internally polarized Covalent Organic Frameworks: a new material concept for molecular photovoltaics
O10	**Rafał Szabla** Breakdown and salvation of statistical rate theory in photoinduced electron transfer
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O22	**Vishnu Vijayakumar-Syamala** Pressure-induced red-to-NIR luminescence switching in square-planar Rh(I) complexes
O23	**Farwa Khalid** Kinetics and high field NMR study of the photodegradation of Retinyl Acetate under ultraviolet irradiation
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O27	**Anna Lągowska** Distinct effects of progesterone and cholesterol on the properties of lipid membranes: insights from biophysical experiments and molecular dynamics simulations
O28	**Marta Warszyńska** Synergistic activation of antitumor immunity via bacteriochlorin-based photodynamic therapy and immune checkpoint blockade
O29	**Jacek Łyskawa** Probing cell membranes under dehydration using fluorescence lifetime measurements
O30	**Kamil Pulit** Development of organic ligands for theranostic iridium(III) complexes: synthetic strategies and spectroscopic characterization
O31	**Patrycja Piękoś** Experimental and computational investigation of novel BODIPY-3-serotonin dye
O32	**Paweł Repetowski** Modified sulfonyl phthalocyanines for effective photodynamic therapy and prospects for combination with immunotherapy
O33	**Wojciech Macyk** When the fate of photogenerated charges matters —classification of heterojunctions in photocatalysis
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O49	**Caterina Bellatreccia** Towards Better TADF Photocatalysts: Mechanistic insights and Practical Tools For Understanding Electron Transfer dynamics
O50	**Stefanie Tschierlei** Three-Coordinate Cu(I) Complexes of Anionic N-Heterocyclic Carbenes

List of posters presentations

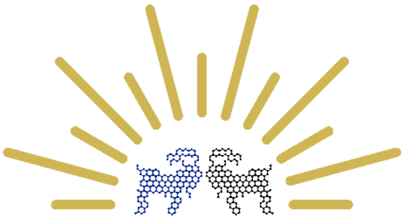
P1	**Jesús Aguilar Morgado** AMIBO dyes: a yet unexplored family of boronic acid derivatives.
P2	**Marcin Andrzejak** Theoretical modeling of D-sp3-A type donor-acceptor systems with exotic excited states
P3	**Dominik Barczyk** Modification of Tetrapyrrolic Photosensitizers to Enhance Photodynamic Therapy Efficiency
P4	**Debika Barman** Structural Isomer Engineering for Tunable TADF/RTP Emission and Improved Photodynamic Therapy Outcomes
P5	**Monika Borkowska** Reactivity by design: oxidation pathways of structurally varied disulfides
P6	**Patryk Borowski** Crystallographic and spectroscopic insights into metal-metal interactions in square-planar Pd(II) and Pt(II) complexes
P7	**Šimon Budzák** Theoretical Insights into the Photochemistry of Triarylhydrazone Photoswitches
P8	**Michał Budziałowski** Determining The Flexoelectric Response of Strontium Titanate Cantilevers by Nanoindentation Instrumentation
P9	**Magdalena Duszka** Computational quest for new organic molecules with excited-state singlet-triplet inversion and high oscillator strength
P10	**Sebastian Egner** Back to nature – A small Mg(II)-complex as a chlorophyll analogue
P11	**Michał Gil** Spectroscopy and photophysics of nitro-substituted porphycenes.

P12	**Karol Hauza** Photochemistry of chiral porphyrin assemblies on thin ferromagnetic films
P13	**Magdalena Jankowska** Precision at the Nanoscale: 3D Printing Functional Nanocomposites with DLP Technology
P14	**Marta Jaruga** Three-dimensional TiO_2-based photocatalytic matrices for selective pharmaceutical removal from aqueous solutions
P15	**Adem Karakuzu** Impact of Device Architecture on Recombination Dynamics in Bifacial Perovskite Solar Cells
P16	**Manjot Kaur** Investigating Nonlinear Optical Properties of Crown Ether Au_{25} Nanoclusters for Multiphoton Microscopy.
P17	**Joanna Kisała** Semiconductor photocatalysis in Advanced Reduction Processes
P18	**Wiktoria Kluba** Solar Energy Efficiency in Poland and Its Potential in Hydrogen Photocatalysis
P19	**Aleksander Kolman** Spectroscopic Characterization of Dual-Function *m*-THPC/Pluronic P123/Graphene Oxide Systems for Potential Application in Photodynamic and Photothermal Therapy
P20	**Dominika Krok-Janiszewska** New Photoinitiating Systems for Radical Photopolymerization: Multifunctional Tools for Advanced 3D Printed Materials
P21	**Anna Kryczka** Effect of the remote amine groups in bis-cyclometalated iridium(III) complexes
P22	**Ewa Krystkowiak** Emission properties of solute-solvent hydrogen-bonded complexes
P23	**Jacek Kubicki** Scientific Opportunities for Polish researchers at the European XFEL

P24	**Waldemar Kujawski** Spectroscopic studies of the intermolecular interactions between genistein and methyl-β-cyclodextrins
P25	**Anđela Lalatović** Polydopamine-Coated Gold Nanorods as Photothermal Agents for NIR Photopolymerization
P26	**Daria Larowska-Zarych** To See or Not to See? That is the Method. Single-molecule Surface-Enhanced Raman Spectroscopy (SM-SERS) for Dye Molecules
P27	**Aleksandra Leśniewicz** Spectroscopic and Structural Insights into TPPS-GO/rGO Interactions: Toward Photostable Hybrid Nanomaterials
P28	**Kamila Łępicka** Raman and UV-vis spectroelectrochemical studies to follow donor-acceptor interactions in ambipolar semiconductor layers
P29	**Zuzanna Łukasiewicz** Innovative Large-Scale PDA/rGO Free-standing Nanofilms: Potential Applications in Photoelectronics
P30	**Marta Miotke-Wasilczyk** Molecular factors controlling the photo-induced isomerization of 4-hydroxyazobenzene derivatives
P31	**Chinmai Mysorekar** Unraveling Ultrafast Dynamics in Co-Sensitized DSSC
P32	**Jela Nociarová** Early stages of carbon dots formation: the presence of molecular fluorophores
P33	**Joanna Nowak-Karnowska** Fluorescence Quenching of Luminarosine Nucleoside and Its Derivatives by G-Quadruplexes
P34	**Małgorzata Noworyta** Development of Zirconium Oxide-Enhanced Polymer Composites Using Vat Photopolymerization in Additive Technologies

P35	**Filip Petko** New Advanced Iodonium Salts as One-Component Cationic Polymerization Photoinitiators for Cationic Vat 3D Printing
P36	**Anna Piec** Positional and Electronic Effects of Substituents on Photophysical Properties of BF_2-Based Dyes
P37	**Jakub Pietraszewski** Optimization of 3D Printing Settings for Enhanced Print Quality in Dental Applications
P38	**Michał Rode** Competition between Photoswitching and Fluorescence in Hemiindigos and Hemithioindigos
P39	**Patryk Rybczyński** BisBF_2 pyridoins: a new strong electron accepting platform for use in multi-photon applications - substitution and extension of conjugation influencing the photophysical properties
P40	**Aleksander Smolarkiewicz-Wyczachowski** Magnetic nanoparticles coated with hemoglobin - influence on the binding capacity of photosensitive drug and photodynamic effect
P41	**Karolina Socha** Donor–acceptor photosensitizers based on a perylene core: synthesis and photochemical characterization
P42	**Aleksandra Stec** Research on the synthesis of new pyridylcoumarins derivatives as photosensitizers for initiating photopolymerisation processes in 3D printing technology
P43	**Vitali Stsiapura** Photoluminescence of Pt-containing NCN-pincer compounds in solutions and single crystals
P44	**Szymon Sułkowski** Light-driven strategies for vitamin B_{12} analogues: photooxygenolysis, transmetalation and rhodamine conjugation

P45	**Karolina Sulowska** Chiroptical Responses of Gold and Silver Nanoclusters
P46	**Patryk Szymaszek** Photophysical Properties and Photoreactivity of Novel Iridium(III) Complexes for Light-Activated Applications
P47	**Katarzyna Taras-Goślińska** The application of photodynamic inactivation to microorganisms
P48	**Vladimir Tomin** Influence of the solvent polarity on the slow kinetics of Pyrene time-resolved fluorescence
P49	**Karolina Urbanowicz** Hydrophilic BODIPY complexes based on organoboron scaffolds as photosensitizers for antimicrobial photodynamic therapy
P50	**Dzmitryi Ushakou** The origin of the excitation wavelength dependence of fluorescence anisotropy in ESIPT-active compounds
P51	**Sidharth Walia** Photoresponsive Self-Assembled Pd (II) Double-Walled Triangle: Metal Ion Mediated Instant *cis* → *trans* Isomerization in the Absence of Light
P52	**Karolina Wrochna** Coumarin-BODIPY Dyad Selectively Localizing in the Endoplasmic Reticulum for Application in Photodynamic Therapy
P53	**Kacper Piskorz** Perylene Derivatives as Efficient Photochemical Sensitizers for Light-Induced Polymerization and 3D Printing Applications



Invited lecture abstracts

1,4-Dihydropyrrolo[3,2-*b*]pyrrole and Dipyrrolonaphthyridinedione – Novel Building Blocks for Optoelectronics

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Recently we have discovered and optimized the first practical synthesis of non-fused pyrrole[3,2-*b*]pyrroles *via* domino reaction of aldehydes, primary amines, and butane-2,3-dione.[1] Six bonds are formed in heretofore unknown tandem process, which gives rise to substituted pyrrole[3,2-*b*]pyrroles – the 'missing link' on the map of aromatic heterocycles. Unparalleled simplicity and versatility of this one-pot reaction, non-chromatographic purification and superb optical properties (including strong violet, blue or green fluorescence both in solution as well as in the solid state), brought these molecules from virtual non-existence to the intensively investigated area functional π-systems. The parent 1,4-dihydro-pyrrolo[3,2-*b*]pyrroles served as building block to construct various π-expanded analogs including nitrogen-embedded buckybowl with inverse Stone–Thrower–Wales topology[2,3] and diindolo[2,3-*b*:2′,3′-*f*]pyrrolo[3,2-*b*]pyrroles. These compounds constitute the most electron-rich ladder-type heteroacenes known to date - E_{HOMO} was located at ca. −4.6 eV. Recently, we have proved that the dipyrrolonaphthyridinedione (DPND) core constitutes an excellent scaffold for the design of strongly fluorescent dyes or quadrupolar-type materials with large two-photon absorption (TPA) cross-sections (up to 5,180 GM).[3] These properties result from an unusual arrangement of donor (pyrrole ring) and acceptor (carbonyl group) moieties within the DPND core.

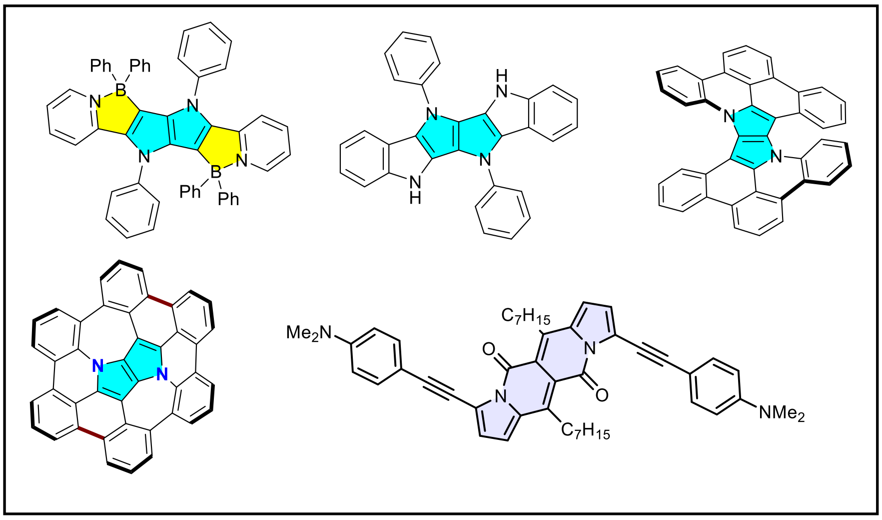

Figure 1. Exemplary architectures based on pyrrolo[3,2-*b*]pyrrole and DPND cores.

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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

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$BiVO_4$ and $CuWO_4$-based Photoanodes for Solar Energy Conversion

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Among the most promising photocatalysts for solar energy conversion into hydrogen as a clean fuel via photoelectrochemical (PEC) water splitting, two ternary metal oxides able to absorb a relatively large portion of the solar spectrum, *i.e.*, $BiVO_4$ and $CuWO_4$, represent good candidates to be employed as photoanodes in the demanding water oxidation reaction [1].

In particular, $BiVO_4$, having a 2.4 eV band gap energy, has emerged as the leading photocatalyst for this application despite its poor electron transfer ability and slow water oxidation kinetics. Two main strategies have thus been pursued to improve the PEC performance of $BiVO_4$, consisting in either i) coupling it with another suitable semiconductor oxide in a heterojunction, or ii) doping it with hexavalent metal ions such as Mo^{6+}.

Indeed, significantly higher values of Incident Photon to Current Efficiency (IPCE) have been attained at wavelengths shorter than 500 nm when $BiVO_4$ was coupled with WO_3 in a $WO_3/BiVO_4$ heterojunction, by exploiting the excellent visible light harvesting properties of $BiVO_4$ combined with the superior conductivity of photoexcited electrons, typical of WO_3. Due to the favourable band alignment between the two oxides, photopromoted electrons in $BiVO_4$ are expected to migrate into WO_3 and then rapidly to the external circuit, while photoproduced holes may accumulate in $BiVO_4$. Selected case studies dealing with the performances exhibited under different irradiation configurations by home-made thin coupled electrodes, prepared through variable deposition techniques, will be presented [2-4]. At the same time, the multifaceted role of Mo^{6+} doping onto both the bulk and surface properties of $BiVO_4$ will be clarified by means of a unique combination of morphological and PEC analyses [5, 6].

On the other hand, an efficient use of $CuWO_4$ as photoanode material requires to overcome its severe internal charge recombination due to intra-gap states, acting as electron traps, as revealed through a PEC investigation coupled with ultrafast transient absorption analyses [7]. This issue has been mitigated by the 50 at.% molybdenum for tungsten substitution [8], with the development of $CuW_{0.5}Mo_{0.5}O_4$ photoanodes, exhibiting a 4-fold increase of the bulk charge carrier separation efficiency compared to pristine $CuWO_4$, as clearly evidenced by intensity modulated photocurrent spectroscopy (IMPS) analysis [9], in full agreement with the results of PEC measurements performed in the presence of sacrificial agents or cocatalysts [10]. Optimized $CuW_{0.5}Mo_{0.5}O_4$ combined with $BiVO_4$ in a heterojunction finally exhibited a definitely superior PEC performance compared to the individual components, with a synergistic charge separation improvement in the 350-480 nm range under frontside irradiation through a $BiVO_4$ layer thick enough to absorb most of the incident light [9].

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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 crucial organic synthesis reactions in both industry and academia. We will examine how photochemistry can enhance the performance of this class of reactions. The 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.

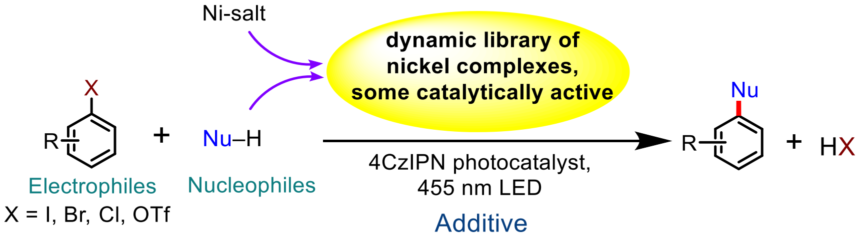

Figure 1. Fast and predictable cross-coupling with adaptive dynamic homogeneous catalysis (AD-HoC).

Acknowledgments
We thank the Deutsche Forschungsgemeinschaft (DFG) for financial support.

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Closing the Gap Between Computational Photodynamics and Photochemistry

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On-the-fly non-adiabatic molecular-dynamics (NAMD) simulations have emerged over the past two decades as an almost routine tool for desecribing light-matter interactions in small- and medium-sized systems on ultrafast time scales. Yet their true predictive power remains contested. Drawing on insights from the recent Computational Photodynamics Predictive Challenge [1], I will critically evaluate where current methods succeed, where they fail, and why.

Next part of the talk surveys the state of the art in simulating femtosecond phenomena probed by advanced light sources - including X-ray scattering, ultrafast electron diffraction, and time-resolved X-ray photoelectron spectroscopy [2,3]. I will highlight the key determinants of simulation quality,[4,5,6] with special emphasis on nuclear-quantum effects [7].

Despite all the succeses of comuptational photodynamics, there is a clear gap between the present day theory and the need of the practioning photochemist, designing new molecules. First, the dynamics of interest often extend far beyond accessible simulation windows, I will demonstrate this on the example of our effort to understand the dynamics of cyanine dyes [8]. Second, solvent environments can reshape excited-state landscapes in non-trivial ways [9], espcially e.g. for charge transfer reactions. Third, intersystem crossing remains underrepresented in routine simulations, leaving photophysical yields difficult to anticipate [10]. The role of spin-vibronic coulling will ve emphasize in this context.

I will conclude by outlining strategies for extending computational photodynamics to higher-energy regimes and longer time scales, and by suggesting benchmarks that could accelerate its adoption by practicing photochemists.

Acknowledgments

The support of Czech Science Foundation (grants number 23-07066S and 24-11466S) is gratefully acknowledged.

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Toward the Design of Fast Red Reversible Photoswitchable Fluorescent Proteins using Multi-timescale Transient Absorption Spectroscopy.

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In recent years, reversible switchable fluorescent proteins (RSFPs) have gained attention due to their ability to undergo a reversible, photo-induced transition using two different lights between a fluorescent (On) state and a non-fluorescent (Off) state. Their significance lies in their application in super-resolution fluorescence microscopy (nanoscopy), enabling nanometric spatial resolution—a breakthrough that was recognized with the Nobel Prize in Chemistry in 2014. The development of novel RSFPs that work in the red/NIR domain is one of recent challenges in nanoscopy as this domain is highly advantageous for live-cell imaging due to its reduced phototoxicity, lower autofluorescence, greater penetration depth in vivo, and expanded spectral multiplexing capabilities. Another key challenge is also the need for fast RSFPs with millisecond thermal back recovery of the Off/On state, such RSFPs would enable super-resolved imaging with only one light.

Here, we present the development of fast red RSFPs based on (i) a derivative of the wild-type bacteriophytochrome from Deinococcus radiodurans [1] and (ii) a charge-transfer (CT) complex composed of a flavin cofactor and a substrate-analogue inhibitor from the monomeric sarcosine oxidase flavoprotein family (MSOX) [2]. To characterise key intermediates that govern switching quantum yield and thermal back recovery we investigated their photodynamics using a unique instrument that allows multi-timescale transient absorption experiments [3]. We applied Arbitrary Detuning Asynchronous Optical Sampling (ADASOPS) to enable precise, multi-timescale control of pump-probe delays, spanning sub-picoseconds to milliseconds time with the same instrument [4]. This approach allowed us to reveal nanosecond-scale dynamics with unprecedented accuracy. We will discuss our findings and their implications for the design of novel red/NIR RSFPs optimized for nanoscopy applications.

Acknowledgments

Ultrafast platform *PEPR LUMA* – French Agence Nationale de la Recherche (ANR), (ANR-23-CE29-0010 - PhotoCT)

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Steering Energy and Electron Transfer in Semiconductor-Molecular Hybrids

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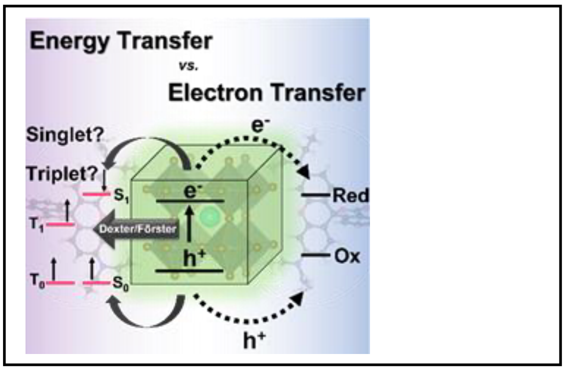
Semiconductor nanocrystals that absorb in the visible and near infrared, serve as building blocks to harvest photons and initiate energy or electron transfer to surface bound chromophores. The multifunctional properties of semiconductor nanocrystals make it challenging to steer the energy and or electron transfer pathway selectively (Scheme 1). Proper selection of the semiconductor nanocrystal donor requires consideration of the nanocrystal bandgap, along with the alignment of valence and conduction band energies relative to that of the acceptor, in order to achieve desired output of energy or electron transfer.

Singlet vs. Triplet Energy Transfer. By employing halide perovskite nanocrystals as a model donor, we have obtained mechanistic insights into singlet or triplet energy transfer processes. The singlet and triplet characteristics of the semiconductor nanoparticle enable tuning of energy transfer pathways through its bandgap engineering. The alignment of energy levels between the semiconductor donor and the singlet/triplet energy levels of the acceptor dye, plays integral role in directing energy transfer.

Forward and Back Electron Transfer. By employing methyl viologen as electron acceptor and p-phenylene diamine (PPD) as hole acceptor, we have validated the relationship between hole transfer and electron transfer rate constant and –ΔG, using Marcus-electron transfer theory. Fundamental understanding of electron and hole transfer, and back electron transfer processes in semiconductor nanocrystals will allow us to maximize the efficiency of photocatalytic reduction/oxidation processes.



Acknowledgments

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How to Compose a Scientifically Effective Article

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Sharing scientific knowledge through publications is an integral part of research career. Since more and more organizations evaluate scientific productivity by scholarly publication rates, the impact of published work becomes an important issue.[1-3] New researchers face the challenge of mastering the art of scientific publication to draw attention to their new scientific findings. Whether or not we want to describe science in such terms, scientific publishing is competitive in nature, and thus younger scientists must vie with their more experienced peers for recognition. While the electronic age has made the publication process easier and quicker, optimizing the structure of a scientific paper requires a certain degree of skill and proficiency.[4] It is important to realize that a well-composed manuscript with a compelling scientific story that can appeal to the journal's readership sees a higher rate of success

The lecture will address following questions.

- What are common practices in publishing scientific work?
- What are common misconceptions?
- What are the key steps that are necessary to compose an effective paper?
- How to (and how not to) use AI tools?
- How to respond to reviewers' comments?

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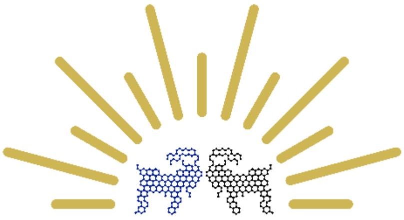

Oral presentation abstracts

Combining the best of organic and inorganic photochemistry with molecular and coulombic dyads

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Dyads or bichromophores can be designed such that unique properties for photochemical energy and electron transfer reactions result. These properties are based on the interplay of an inorganic chromophore, enabling quantitative intersystem crossing as well as visible light absorption, and a covalently linked organic moiety with a long-lived triplet state. We synthesized ruthenium complex-based molecular dyads decorated with a covalently attached pyrene chromophore and used them for efficient photooxygenations in water, which is a challenging solvent for such reactions.[1] The long-lived pyrene triplets in these dyads are relatively redox-inert compared to the MLCT triplets of the parent metal complexes. Hence, these dyads provide an efficient access to acceptor triplet states that are otherwise very tricky to obtain, which allowed us to establish a triplet quenching pathway control approach with molecular dyads.[2] Guided by our recent study on coulomb effects on the energy transfer kinetics,[3] we have developed a novel strategy for obtaining the advantages of molecular dyads without the time- and resource-consuming synthesis of these tailored photocatalysts. Simply by mixing a cationic ruthenium complex with an anionic pyrene derivative in water, a salt bichromophore is produced owing to electrostatic interactions (Fig. 1). We exploited this so-called coulombic dyad for several photoreactions in the context of light-to-energy conversion with outstanding reaction quantum yields and turnover numbers.[4] Currently, we are about to establish that the coulombic dyad strategy can be used for versatile applications following a toolbox approach.

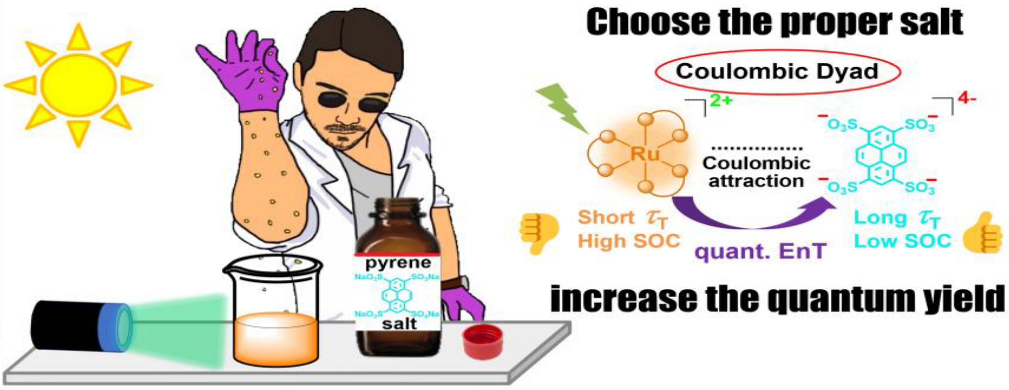

Figure 1. Straightforward preparation of a coulombic dyad for more efficient photocatalytic reactions.

Acknowledgments

Financial support from the DFG (KE 2313/7-1) and the FCI (Ph.D. fellowship) is acknowledged.

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New TADF emitters based on strong boracyclic acceptors

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Thermally activated delayed fluorescence (TADF) emitters currently play a crucial role in the advancement of OLED technology. One of the main challenges, however, is the limited number of efficient blue emitters. To adress this issue, a promising strategy involves designing molecules that incorporate strongly electron-accepting moieties in combination with relatively weakly electron-donating groups.

The aim of this research was the synthesis and characterization of a series of novel TADF emitters based on 10*H*-dibenzo[*b,e*][1,4]thiaborinine 5,5-dioxide (**SO2B**) and its C-substituted derivatives. To date, **SO2B** is one of the strongest acceptor units used in the design of TADF emitters.[1]

At the initial stage of the study, **SO2B** was paired with a conventional donor, carbazole, as well as with a selection of weak, nitrogen-free donor units derived from anisole, thiophene and methoxy group. Experimental results demonstrated that, despite the use of these simple and weak donor components, efficient TADF emission was retained. In the next step, a series of **SO2B** derivatives substituted with fluorine and methoxy groups was synthesized and subsequently combined with carbazole as a donor unit. All of the obtained systems exhibited TADF in solution and in Zeonex film, with emission lifetimes up to 16 μs, highlighting the robustness of the **SO2B** acceptor in enabling efficient delayed fluorescence.

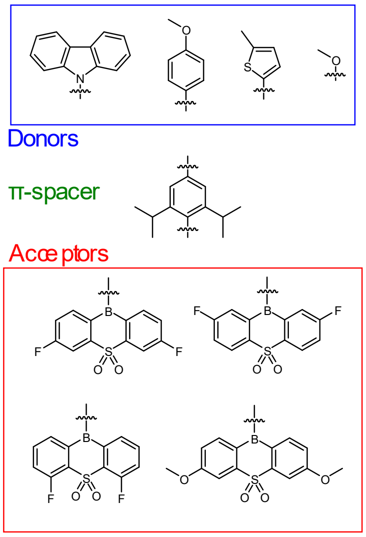

Figure 1. Building blocks of studied TADF emitters

Acknowledgments

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Rydberg states and electron capture. Mechanism of ultrafast photoinduced intramolecular electron transfer processes in spirocyclic D–A dyads

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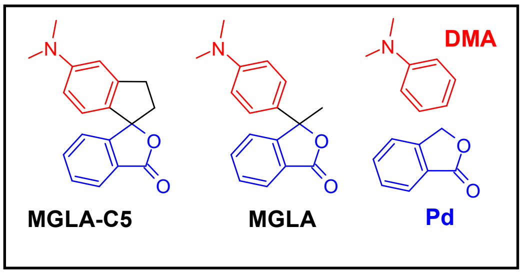
The electron spin is an essential factor in molecular processes and research into the mechanisms enabling spin flip and triplet state generation in heavy atom-free organic molecules is of fundamental importance for many physical, chemical or biological processes. Controlled generation of triplet states requires deeper insights into structure-property-relationship in the intersystem crossing (ISC) processes and exploration of suitable molecular structures.

Triplet states of organic molecules can be populated from intramolecular charge transfer (CT) states by charge recombination and the rate and efficiency of the process can be controlled by structural factors. Multiple phosphorescence of sp^3-C-linked N,N-dimethylaniline-phthalide (DMA–Pd) donor–acceptor dyads (D–A) demonstrates the presence of different simultaneous intersystem crossing (ISC) processes, which are initiated by ultrafast photoinduced electron transfer (ET) in rigid environment and start from a vibrationally non-relaxed state. [1]

The primary ET ($\tau \leq 250$ fs) to the $\mathbf{^{1}[D^{\bullet+}–A^{\bullet-}]}$ state in DMA–Pd dyads is related to the early excited state dynamics within the DMA moiety involving the interplay of the S_1 ($\pi\pi^*$) state with the closely lying Rydberg S_2(3s, $\pi\sigma^*$) state, [2] wherein the driving force for ultrafast ET in rigid medium is provided by the high dipole moment of Pd moiety (4.9 D) acting as a dipole trap for electron capture via the shape resonance which rapidly relaxes to the Pd molecular anion. The complex successive photophysics of DMA–Pd dyads, and in particular the ISC processes, can be rationalized by taking into account that the resulting phthalide anion can exist in two stable structures: one short-lived with the bicyclic geometry of the neutral molecule, and another long-lived with the five-membered lactone ring open by cleavage of the C–O bond. [3]

The three phosphorescent states observed in DMA–Pd emission at 77 K are generated from the photoinduced $\mathbf{^{1}[D^{\bullet+}–A^{\bullet-}]}$ state relaxing via three independent and kinetically non-correlated ISC mechanisms to (i) a locally excited $\mathbf{[^{3}D^{*}–A]}$, (ii) charge transfer $\mathbf{^{3}[D^{\bullet+}–A^{\bullet-}]}$, and (iii) zwitterion biradical $\mathbf{^{3}[D^{\bullet}{}_{+}–A^{\bullet}{}_{-}]}$ triplets. In methylcyclohexane glass, the $\mathbf{[^{3}D^{*}–A]}$ state is formed in a rapid spin-orbit charge transfer ISC (SOCT-ISC, $k_{\mathrm{ISC}} \geq 2.3 \cdot 10^{11}\,\mathrm{s}^{-1}$) from the non-relaxed $\mathbf{^{1}[D^{\bullet+}–A^{\bullet-}]}$ state, while in polar solvent glasses, the $\mathbf{[^{3}D^{*}–A]}$ and $\mathbf{^{3}[D^{\bullet+}–A^{\bullet-}]}$ states are populated from $\mathbf{^{1}[D^{\bullet+}–A^{\bullet-}]}$ and the $\mathbf{^{3}[D^{\bullet}{}_{+}–A^{\bullet}{}_{-}]}$ state forms in the dissociation of the C–O bond in Pd moiety.



Scheme 1. DMA–Pd dyads.

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Remote control of photoswitching of DTE-py2 molecules with plasmonically active silver nanowires

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Silver nanowires (AgNWs), nanostructures that facilitate both localized and propagating plasmon resonance, can be used in a unique way for manipulating and controlling the optical properties of emitters. While the plasmon resonance in AgNWs covers the whole visible spectral range, their elongated shapes allow for efficient light propagation over tens of microns via surface plasmon polaritons. On the other hand, fluorescent photochromic DTE-py2 (of 1,2-bis[2-methyl-5-(4-pyridyl)-3-thienyl]perfluorocyclopentene) molecules are applicable in sensing or bioimaging due to sensitivity, good thermal stability, and reversibility of the photoswitching process. The photoswitching of DTE-py2 is reversible and can be triggered to the ON state by illuminating with visible light. Conversely, UV illumination results in complete disappearance of fluorescence emission (OFF state).

In this work we fabricate a hybrid nanostructure composed of a microdroplet of DTE-py2 molecules deposited on one end of an AgNW. Using wide-field illumination with UV radiation the photochromic molecules are first converted to the OFF state. Subsequently, with a focused laser we illuminate a free AgNW end of the hybrid nanostructure. The emergence of remote photoactivation of DTE-py2 molecules is evidenced by observation of strong fluorescence emission from the microdroplet containing photochromic molecules deposited on the other end of the AgNW. Reversibility and reproducibility of this process is demonstrated.

The influence of the localized plasmon resonance in AgNWs on the photoswitching of DTE-py2 molecules can be studied by tuning the wavelength of light used to activate the fluorescent form thereof. By triggering photoactivation cycles as a function of the illumination wavelength, illumination time, and the number of photocycles, clear and strong effect of the plasmonic interactions on the DTE-py2 photoswitching is demonstrated. Namely, the efficiency of this process is the highest for the illumination wavelengths resonant with the plasmon resonance in AgNWs, i.e. 480 nm and 535 nm. In contrast, illumination with 405 nm light results in no difference in behavior between molecules deposited on AgNWs and on a glass substrate.

In summary, the results of advanced fluorescence microscopy studies of hybrid nanostructures composed of photoswitching DTE-py2 molecules coupled with AgNWs confirm strong influence of the localized plasmon resonance on the photoswitching process. Not only it is possible to enhance the efficiency of the molecular photoswitching by the localized plasmon resonance in AgNWs, but also propagating plasmon resonance can trigger remote photoactivation of fluorescence emission of DTE-py2 molecules. Both plasmonic enhancement and wavelength selectivity of the photochromic reaction can be invaluable for light manipulation and remote optical sensing in such hybrid nanostructures.

Nanotube-scaffolded cyanine J-aggregates and Stokes-shift controlled emission: dual innovations for plant bio-imaging

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Understanding the uptake, transport, and localization of nanomaterials in plants is essential for advancing nano-enabled precision agriculture [1]. Genetic engineering plays a pivotal role in meeting rising global demands for food and crops. Nanoparticle-mediated gene delivery, particularly using carbon nanotubes (CNTs), has been shown to bypass species- and tissue-specific barriers and enable transgene-free gene editing [2]. This method allows delivery of functional genetic cargo into mature plants with minimal species constraints. Although CNT-based gene delivery is feasible, its molecular mechanism remains poorly understood. To clarify this debated mechanism, direct visualization and characterization of individual nanotubes within plant tissues are needed. However, plant tissues pose major challenges for fluorescence imaging due to strong autofluorescence from pigments like chlorophyll and high light scattering from structural and biochemical heterogeneity. CNTs are well-known optical probes due to their broad absorption (visible to NIR) and narrow shortwave infrared (SWIR) emission, which reduces spectral overlap with tissue autofluorescence. Yet, their low photoluminescence quantum yield limits detectability in intact leaves, especially at the single-particle level. To address this, we explored photosensitization of CNTs via slip-stacked cyanine dye J-aggregates assembled on their surface, enabling excitation energy transfer (EET) to enhance CNT brightness. While promising in concept, this strategy resulted in only marginal photoluminescence enhancement [3]. We thus transitioned to boron nitride nanotubes (BNNTs), which are structurally similar to CNTs but optically transparent across the visible and NIR spectrum. Instead of relying on nanotube emission, we used BNNTs as scaffolds for J-aggregate assembly and exploited their superradiant emission. The resulting CyJ-BNNT nanocomposites displayed ultra-narrow spectral bands, improved brightness, and high photostability, key features for single-particle fluorescence imaging in plant tissues.

A significant limitation in exploiting J-aggregates as fluorescence probes lies in their inherently small Stokes shift, which complicates excitation-emission separation. To address this, we investigated how the spatial packing of various cyanine dyes could be modulated by tuning their assembly conditions. This strategy leads to increased Stokes shift while maintaining J-type exciton coupling, allowing for efficient excitation at the J-aggregate absorption maximum and full utilization of the emitted spectrum. Thus, through concurrent optimization of photophysical interaction, dye architecture, and mode of assembly, we developed fluorescence probes with photophysical properties that could overcome key limitations of traditional plant imaging: insufficient single-particle brightness and limited spectral separation. By introducing Stokes shift engineering as a tunable photophysical parameter, we propose a viable strategy to unlock the full potential of J-aggregates as bioimaging probes.

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Microenvironmental modulation of photothermal behavior in photoacid-doped soft coatings

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Water plays a critical, yet underexplored, role in modulating the photothermal behavior of light-to-heat converting materials, especially within soft, water-processable polymer matrices. Drawing inspiration from biological systems that harness hydration to regulate energy dissipation, we present a framework to examine how water affects dielectric loss heating and photothermal efficiency in polymer-based coatings doped with molecular photoacids and photoswitches.[1]

Our strategy combines electrochemical impedance spectroscopy (EIS), temperature-resolved optical spectroscopy, and calorimetry to investigate water's microenvironmental effects on key parameters such as proton conductivity, molecular aggregation, and heat dissipation. We propose model systems based on polyvinyl alcohol (PVA), hydroxypropyl cellulose (HPC), and chitosan, selected for their adjustable hydration profiles and relevance to sustainable materials design.[2]

This approach offers foundational insights into how hydration influences thermal behavior in soft materials and guides the development of humidity-responsive coatings for solar energy harvesting, smart textiles, and biomedical interfaces. By elucidating structure–property–environment relationships at the nanoscale, we establish a platform for the rational design of next-generation photothermal systems.[3]

Acknowledgments This work was supported by the Liebig Fellowship from the Fonds der Chemischen Industrie and by the TUM Junior Fellow Funds at TU Munich.

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Ir(III) and Re(I) Imidazo[4,5-f][1,10]phenanthroline Systems as Effective Emitters and Photosensitizers

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The bichromophoric approach, meaning the incorporation of the organic chromophore with a long-lived triplet excited state into the transition metal complex molecule, is one of the most efficient strategies for developing luminophores with long-lived excited states. Depending on the energies of ^{3}MLCT (metal-to-ligand charge transfer) and ^{3}IL (intraligand) triplet excited states, three scenarios are possible (Figure 1a). I: the ^{3}MLCT is lower in energy than the ^{3}IL localized on the organic chromophore; II: both states are close in energy, establishing an equilibrium where the ^{3}IL repopulates the luminescent ^{3}MLCT, acting as an energy "reservoir"; III: the ^{3}IL is lower in energy than ^{3}MLCT. Complexes in category III are expected to extend triplet excited state lifetimes compared to ^{3}MLCT emitters, but they are usually non-emissive at r.t. A perpendicular arrangement of the substituent and the organic ligand core minimizes mixing of their orbitals, maintaining the independence of the two units, while reducing the dihedral angle results in partial mixing of the orbitals (Figure 1b) [1].

Transition metal complexes with long lifetimes of triplet excited states are particularly desirable as photosensitizers in applications including light-emitting materials, sensors, photoredox catalysis, photodynamic therapy (PDT), triplet-triplet annihilation upconversion (TTA-UC), and time-resolved bioimaging [2]. Developing efficient photosensitizers is a challenge, and rational design of photoactive materials requires a full understanding of the photoinduced processes. Within the presentation, key strategies in designing triplet-emissive Ir(III) and Re(I) complexes with imidazo[4,5-f][1,10]phenanthrolines by the bichromophoric approach will be demonstrated. Characteristics of the ^{3}MLCT and ^{3}IL states along with their formation mechanism and deactivation kinetics will be discussed in view of their potential application for triplet-triplet energy transfer processes (i.e. $^1O_2$ generation or TTA-UC).

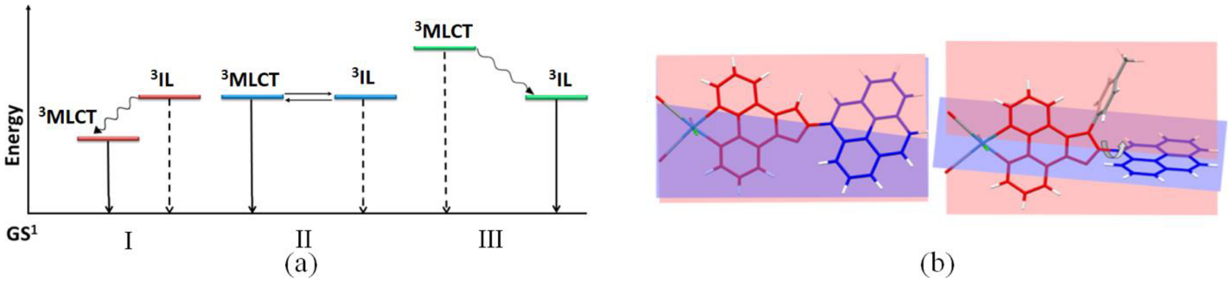

Figure 1. Three possible scenarios of ^{3}MLCT and ^{3}IL energy arrangements (a), the dihedral angle change in the representative bichromophore Re(I) compounds from the introduction of steric hindrance (b).

Acknowledgments

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Organosilicon Compounds in Coloured Emission

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The general concept of **Donor-Spacer-Acceptor** type of compounds for new light-emitting materials is to design attractive emitters by stitching together simple block elements with well-known photophysical properties. An extraordinary emission, e.g. emission of a desired colour, is expected to emerge due to intramolecular excited-state processes between the Donor and Acceptor moieties (e.g. energy/charge/electron/hole transfer). In other words, although the emission from linked chromophores may not be very attractive, the compound can still display remarkable emission due to excited-state processes between the linked chromophores. This idea can be realized within silicon-based compounds. The flexible silylene bridge seems to be a great choice for a linker because (i) it opens up possibility of fairly easy synthesis of any Donor-Spacer-Acceptor compounds, (ii) it can facilitate the observed processes. A deeper insight into the mechanisms of the excited-state processes of Donor-Spacer-Acceptor compounds is the target on the way of obtaining new light-emitting materials.

In the presentation: come and see what kind of compounds we designed as single-molecule emitters of tailored colour of emission (blue and white).

Figure 1 The general concept of Donor-Spacer-Acceptor type of compounds for coloured emission

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Internally polarized Covalent Organic Frameworks: a new material concept for molecular photovoltaics

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Covalent Organic Frameworks (COFs) are an emerging class of crystalline, porous materials with tunable optoelectronic properties, making them promising candidates for next-generation photovoltaic technologies. Their modular design enables precise control over light absorption, charge transport, and energy-level alignment, opening pathways to lightweight, flexible, and sustainable solar energy devices [1]. However, key challenges such as limited charge-carrier mobility and lifetimes, material stability under operational conditions, and scalable fabrication methods must be addressed to fully realize their photovoltaic potential [2].

In this contribution [3], we propose a novel design for photovoltaic COFs which is predicted to strongly enhance the photo-generated charge carriers lifetimes: even by several orders of magnitude. This effect, probed and modeled by means of quantum-chemical calculations, relies on incorporating electrically polarized light-absorbing units into the donor-acceptor 2D-COF systems, leading to formation of – what we call – a COF-Pol material, whose structure and general working principle have been schematically shown in Figure 1 below. The proposed design facilitates dissocation of the initially formed photo-exciton, as well as prevents the separated charges from radiative or nonaradiative recombinaton afterwards. Eventually, the boost of the total photovoltaic efficency is expected, which should be measurable as increased photogenerated current intensity.

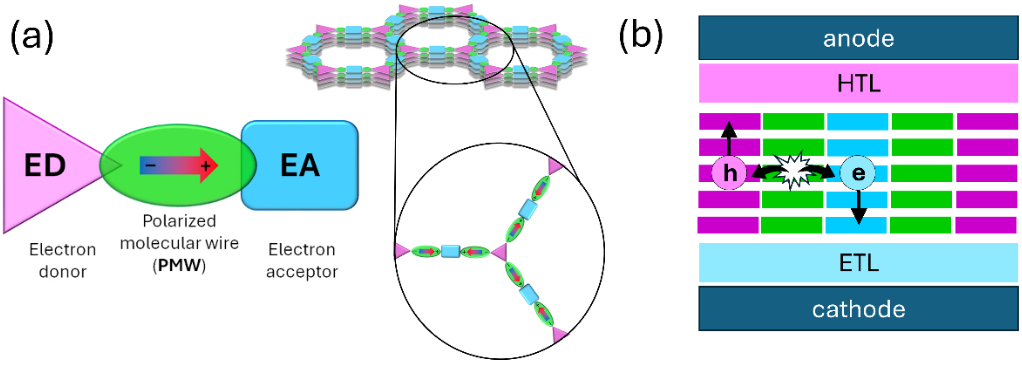

Figure 1. Conceptual design (a) and general working principle (b) of the proposed COF-Pol material.

Acknowledgments

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Breakdown and salvation of statistical rate theory in photoinduced electron transfer

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Electron transfer is one of the most fundamental processes that sustain the key functions of living organisms. It drives essential metabolic redox reactions, photoinduced CO_2 fixation, signalling between proteins and DNA repair processes. Several approaches were proposed for the evaluation of equilibrium electron transfer processes, including the ever-present Marcus Theory and Fermi's Golden Rule. However, the aforementioned approaches do not offer even qualitatively correct rate predictions for non-equilibrium (*e.g.* photoinduced) electron transfer, which still poses notorious computational challenges. In this talk, I will discuss the key aspects controlling photoinduced electron transfer in biological and organic chromophores [1-4]. In particular, I will discuss how different components of electron transfer rate equations are affected by molecular structure, including base stacking. I will also show how to accurately quantify rates and/or time-scales of nonequilibrium electron transfer processes with surface hopping excited-state dynamics and our new tool which employs the advantages of nonadiabatic transition state theory.

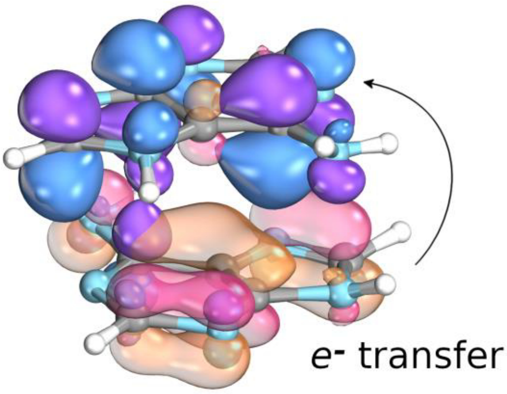

Figure 1. Molecular orbitals associated with the excited state that is responsible for photoinduced electron transfer between two stacked adenine nucleobases.

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Computational studies of non-radiative decay pathway for TICT state in Thioflavin T

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Photophysical properties of Thioflavin T (ThT) have received much attention due to extensive use of this fluorescent probe for detection of amyloid fibrils – insoluble protein aggregates - related to several neurodegenerative disorders. Earlier it has been found that after ThT photoexcitation an efficient twisted intramolecular charge transfer (TICT) process takes place in the excited state (Fig.1) resulting in viscosity-dependent fluorescence intensity of this dye (changes up to ~3 orders of magnitude) [1]. Effects of molecular environment on photoinduced processes and fluorescence of ThT in different media (solutions, polymers, aggregates, etc.) have been studied in details, however, decay mechanism of the intermediate non-emissive TICT-state was not investigated earlier.

We used state-averaged complete active space SCF (SA-CASSCF) calculations to study forward (LE →TICT) and backward (TICT→S_0) intramolecular charge transfer processes in the excited state of ThT. Calculations were carried out using OpenMOLCAS package for several active spaces of molecular orbitals (MO) using ANO-S and 6-31G* basis sets. We found that a considerably large active space (14 electrons in 14 MO) is needed for qualitatively correct description of electronic structure evolution in the excited state of ThT molecule during twisting process. SA-CASSCF calculations showed that deactivation of TICT-state in ThT can proceed via energetically accessible S_1/S_0 conical intersection. ThT conformation that corresponds to S_1/S_0 minimum energy crossing point on the excited state PES has twisted benzothiazole and dimethylaniline fragments, non-planar distortions in benzothiazole ring, and is bent along the longer molecular axis. This energetically accessible S_0/S_1 conical intersection can be related to fast and viscosity-dependent decay channel of the dark ICT state in ThT molecule.

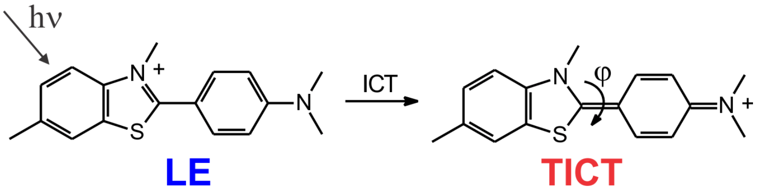

Figure 1. Scheme of intramolecular charge transfer reaction between the emissive locally-excited (LE) and dark TICT states of ThT molecule

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Predictive power of quantum chemistry for fluorescence quantum yield: Are we there yet?

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Rational design of fluorophores is increasingly supported by advanced quantum chemical methods. While theoretical approaches can reliably predict absorption and emission wavelengths – obtained primarily through appropriate tuning of electron-donating or electron-withdrawing substituents on π-conjugated systems — the accurate prediction of fluorescence quantum yield remains a significant challenge. This is due to the complexity of excited-state deactivation pathways, including intersystem crossing, non-radiative decay, and environment-induced effects.

In this study, we investigate a series of benzothiazole-based fluorophores exhibiting intramolecular and intermolecular charge transfer, structure rigidification, and supramolecular interactions in solution, aggregate, and solid-state forms. Using these examples, we assess the capabilities and limitations of common computational protocols in predicting fluorescence quantum yields and photophysical trends relevant to applications in bioimaging, optoelectronics, and singlet fission.

We discuss the practical barriers encountered at the interface of theory and experiment, particularly those related to system size, which often preclude the use of state-of-the-art methods and necessitate the development or adoption of more efficient and scalable alternatives.

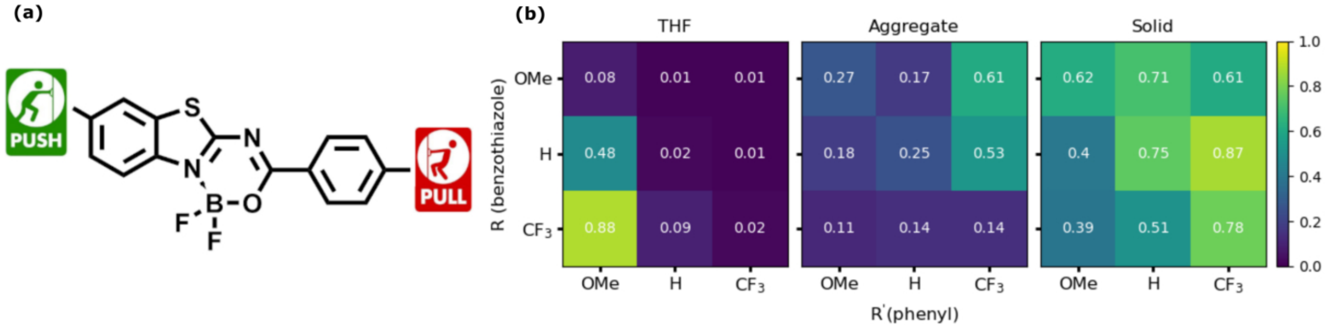

Figure 1. (a) Investigated benzothiazole fluorophores (b) Heatmaps of experimental fluorescence quantum yield for the analyzed derivatives of benzothiazole

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A scalable IoT-controlled LED photocatalytic system for the removal of pharmaceuticals from real wastewater

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The growing presence of pharmaceutical residues in aquatic environments poses a serious challenge to conventional wastewater treatment systems. Among emerging micropollutants, non-steroidal anti-inflammatory drugs (e.g., naproxen) and antibiotics (e.g., amoxicillin) are of particular concern due to their persistence, poor biodegradability, and capacity to induce toxic or antibiotic-resistant effects even at low concentrations [1,2]. Conventional biological processes in municipal wastewater treatment plants (WWTPs) are largely ineffective in removing such compounds, and their transformation products may exhibit enhanced toxicity compared to the parent molecules. Although heterogeneous photocatalysis—particularly TiO_2-based systems—has demonstrated significant potential for the degradation of persistent organic micropollutants under mild conditions, most existing studies remain confined to laboratory-scale settings. Current reactor designs are frequently based on batch systems, lacking dynamic process control, automation, or adaptability to varying environmental and matrix conditions. Furthermore, few implementations address long-term material stability, light distribution uniformity, or oxygen limitations that emerge during scale-up [3].

To overcome these limitations, a novel pilot-scale photocatalytic reactor was developed, featuring TiO_2-coated Luffa cylindrica scaffolds illuminated by high-CRI LED modules. The system integrates a fully IoT-based control platform, enabling real-time monitoring and regulation of light intensity, pH, temperature, dissolved oxygen (DO), oxidation-reduction potential (ORP), and total dissolved solids (TDS). The applied architecture allows for continuous, unattended operation with adaptive lighting control and automatic response to matrix fluctuations.

Significant reductions in chemical oxygen demand (COD) were observed (up to 54%), accompanied by an increase in the BOD_5/COD ratio from <0.1 to as high as 0.31, indicating a substantial improvement in the biodegradability of the treated effluent. Degradation intermediates were identified using electrospray ionization mass spectrometry (ESI-MS), and toxicity assessments using the ECOSAR model revealed a clear reduction in predicted chronic toxicity of final products [4]. Importantly, the system operated continuously over extended periods, with a total annual energy consumption estimated at ~824 kWh, corresponding to ~144 EUR/year in electricity costs—highlighting its energy efficiency and economic feasibility.

Acknowledgments

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Tuning Strontium Titanate for Enhanced Photocatalytic Reduction of Nitroaromatic Compounds

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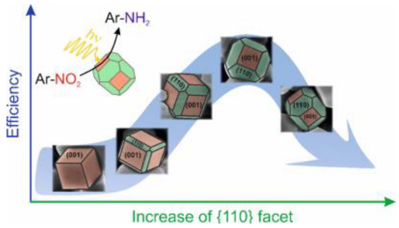
Photocatalysts such as TiO_2 are widely used in applications like surface cleaning, disinfection, and environmental remediation. However, with relatively minor adjustments, such as the use of appropriate solvents, these materials can also facilitate selective organic transformations, including the photocatalytic reduction of nitroaromatic compounds [1]. This approach offers significant advantages in terms of selectivity, particularly in the presence of other functional groups that are sensitive to reduction, as is often the case in pharmaceutical synthesis. For photocatalysis to become a viable alternative to conventional methods, it is essential to develop materials with sufficiently high quantum efficiencies. In this regard, strontium titanate ($SrTiO_3$) emerges as a promising candidate. Compared to TiO_2, $SrTiO_3$ is a milder oxidising agent and has been reported to achieve near-unity quantum efficiencies in photocatalytic water splitting [2].

In this work, we report the synthesis of well-faceted crystals of strontium titanate [3]. The high uniformity of the obtained samples allowed us to investigate how the presence of energetically distinct crystal facets influences charge separation. Our study reveals facet-dependent charge separation within the $SrTiO_3$ crystals, leading to the accumulation of electrons on the {001} facets, identified as the reduction sites, and holes on the {110} facets, serving as oxidation sites. Building on this understanding, we further demonstrated that photocatalytic activity can be enhanced by decorating the crystals with metal nanoparticles. We examined both the effect of metal type on activity and the role of selective deposition on specific crystal facets. We will present how tuning the crystal facets and controlling the spatial distribution of metal nanoparticles can significantly enhance the photocatalytic efficiency of $SrTiO_3$.



Scheme 1. Effect of tailored $SrTiO_3$ crystal on the efficiency of photocatalytic reduction of nitroaromatics**.**

Acknowledgments
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Old material in a new light: TiO_2-mediated free-radical photopolymerization

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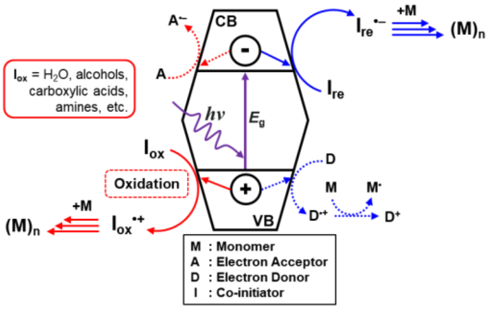
TiO_2 has become one of the most widely studied materials in heterogeneous photocatalysis, particularly in environmental applications. These systems often rely on non-selective processes and do not require precise control over reaction pathways. In this work, we explore a completely different and underutilized potential of heterogeneous photocatalysts by applying it to the field of free-radical photopolymerization (FRP), where pathway selectivity, functional monomer compatibility, and reaction control are essential. We use it as a tunable platform to initiate polymerization through both oxidative and reductive pathways. This approach addresses key limitations of conventional homogeneous FRP systems, which often depend on expensive and toxic organic photoinitiators, by introducing TiO_2 as a green, reusable, and cost-effective alternative [1]. Unlike traditional systems, TiO_2 enables polymerization in oxygen-rich and aqueous environments, two major challenges in the field, while also offering advantages such as reusability and smart composite materials.

By carefully selecting the active catalyst and simultaneously controlling the appropriate reaction conditions [2], FRP can be steered toward the desired mechanism [1]. Our experiments show that both intrinsic material properties (such as crystal phase and particle size) and extrinsic reaction parameters (including scavenger type, solvent, and catalyst loading) strongly influence whether oxidative or reductive radicals govern the initiation step as well as the polymerization profiles [2]. These findings represent one of the first systematic efforts to link semiconductor photocatalysis with radical polymerization mechanisms, redefining the role of a well-known material and opening a promising, sustainable frontier in polymer chemistry.



Scheme 1. Schematic of TiO_2-mediated FRP pathways [1]. Oxidative (red) and reductive (blue) routes depend on photocatalyst, reaction conditions, and monomer properties. Dashed lines show complementary redox steps. I_{re} and I_{ox} represent electrophilic and nucleophilic co-initiators, respectively.

Acknowledgments
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Theoretical insight into the low-lying excited states of a Cu(I) photosensitizer

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Heteroleptic Cu(N^N)(P^P) complexes have gained attention as effective photosensitizers in a range of applications, such as dye-sensitized solar cells[1], organic light-emitting diodes[2], and, notably, in photocatalytic processes like the reduction of CO_2 to CO. In this context, these copper-based systems are considered attractive candidates to replace traditional noble-metal photosensitizers—typically centered on metals like ruthenium, rhenium, or iridium—offering advantages in sustainability and practicality. Although the synthesis and photocatalytic performance of these copper complexes have been established[3], the underlying mechanisms governing their photosensitizing behavior remain insufficiently explored.

To address this gap, computational chemistry—particularly quantum chemical modeling—provides valuable insights. However, the considerable molecular size of Cu(I)-diimine-diphosphine complexes restricts computational studies to DFT-based techniques. Their extensive π-conjugation and significant charge-transfer characteristics in low-energy excited states present notable challenges for accurate DFT modeling. Consequently, a comprehensive methodological assessment was undertaken to determine an appropriate computational strategy. The selected protocol was validated through comparisons with experimental observations and alternative computational methods applied to simplified model systems.

We present a systematic investigation of a series of Cu(I)-diimine-diphosphine complexes, each incorporating different diimine ligands. Special focus is given to the energetics and nature of the lowest singlet and triplet excited states, which are central to the photosensitization process. We examine how these states are influenced by the conformation of the copper center, and we provide a detailed analysis of their electronic structure using both difference density plots and the one-electron transition density matrix approach as implemented in the TheoDORE software[4].

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Controlling photoinduced intramolecular charge transfer processes in Re(I) and Ir(III) complexes.

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For nearly a century, 2,2′:6′,2″-terpyridine (terpy) derivatives have been extensively studied for their unique optical, electrochemical and biological properties. Among these, donor–π–acceptor (D–π–A) fluorophores incorporating terpy within the conjugated system take a special position due to the photoinduced intramolecular charge transfer (ICT) from the strongly donating substituent (D) to the accepting unit (terpy). The efficiency of ICT in D–π–terpy systems depends on numerous factors including the electron-donating and withdrawing strengths of the building blocks, the degree of electronic communication between donor and acceptor units, and external factors such as solvent polarity, pH environment and viscosity.[1]

The introduction of D–π–terpy ligands into the heavy metal coordination sphere invokes an increase complexity in photoinduced processes occurring in resulting complexes, as well as may have a key role in controlling their photophysical parameters such as an emission wavelength, quantum yield and excited-state lifetime. In particular, triplet state equilibria between the ^{3}MLCT (metal-to-ligand charge transfer) and ^{3}ILCT/^{3}IL (intraligand charge transfer/intraligand) states or complete switching of the emissive state from ^{3}MLCT to ^{3}ILCT may dramatically change the emission energy and triplet excited-state lifetimes.[1,2]

This presentation provides a comprehensive analysis of structure–property relationships in view of potential applications of Re(I) and Ir(III) complexes with amine-functionalized D–C_6H_4–terpy ligands. A particular emphasis would be paid on the role of the structural modifications of D–π–terpy, coordination mode (terpy-κ^2N vs. terpy-κ^3N) and the nature of ancillary ligands (X/L) in controlling the photophysical behavior of $[\mathrm{IrCl(C^\frown N)(R\text{-}C_6H_4\text{-}terpy\text{-}\kappa^3N)]PF_6}$, $[\mathrm{Ir(C^\frown N)_2(R\text{-}C_6H_4\text{-}terpy\text{-}\kappa^2N)]PF_6}$, $[\mathrm{Ir(R\text{-}C_6H_4\text{-}terpy\text{-}\kappa^2N)_2](PF_6)_3}$ and $[\mathrm{ReCl(CO)_3(R\text{-}C_6H_4\text{-}terpy\text{-}\kappa^2N)}]$.[1,3]

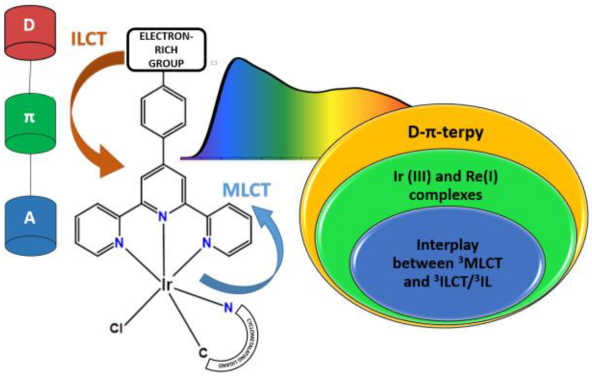

Figure 1. Scheme showing the main research topics.

Acknowledgments

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Probing ultrafast charge transfer in Fe/Co dyad complex using UV-VIS and mid-IR time resolved absorption spectroscopy.

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Transition metal (TM) complexes are especially interesting in terms of their versatile applications in solarenergy conversion and other fields ranging from molecular electronics and photocatalysts to light-emitting devices and biolabels. Such compounds frequently provide access to unique chemical processes thanks to the specific metal centers interactions and cooperation. It is, thus, of great importance to sensibly control optical and magnetic properties of such materials at the molecular level, so as to apply this knowledge to generate materials with particular properties across all the size scales from single molecules to bulk materials, relevant for specific applications. Despite numerous efforts, this very challenging target remains far from being achieved. In this respect, information on structural and charge transfer dynamics associated with charge transfer (CT) that occur upon electronic excitation is essential for rational design of new materials. Many of the industrial applications of photoactive compounds are based on the heavier (and more expensive) elements like Ru, Ir or Pt. Many complexes of these metals are well-known to provide very good efficiency towards the energy storage or conversion. However, application of molecular materials based on Earth-abundant metals, such as Fe, Co, Cu etc., is an attractive alternative.

In this contribution, a study on the photophysics of Iron (III) Cobalt (II) diad will be presented, including time resolved transient absorption spectroscopy in UV-VIS range as well as mid-IR range covering frequencies associated with cyano moieties vibration. This approach was aimed to use the cyano group as a spectator of the charge transfer process occuring between the cores of the bimetallic complex.

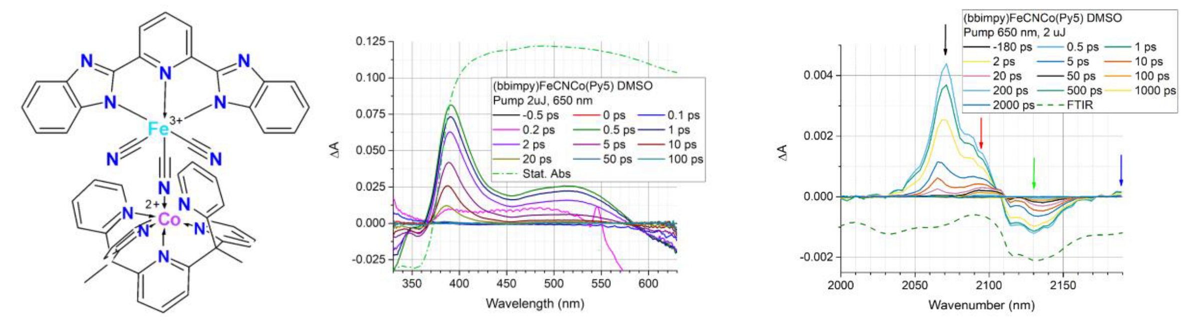

Figure 1 The structure of the studied Fe(III) Co(II) diad, UV-VIS transient absorption spectra, mid-IR time resolved absorption specta

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Spin-State dependent Emission of 3d-Metal Complexes

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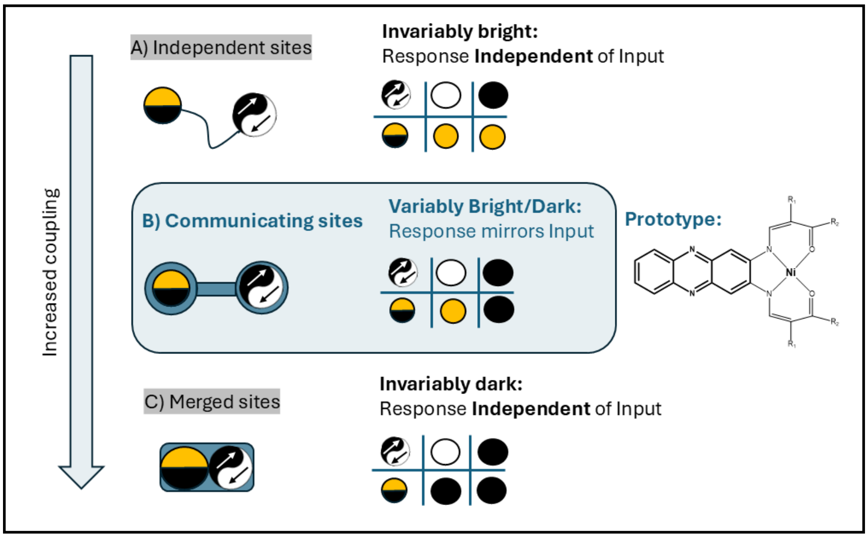
For a long time, the photochemistry of 3d metal complexes has been dictated by the short lifetimes and the dissociative nature of the lowest excited states. Only very recently, the invention of extremely strong σ-donating C-borne ligands helped to invert the state diagram, rendering charge-transfer competetive for several 3d metals. As a consequence of the strong ligand fields, low-spin configurations dominate and spin-state equilibria are essentially blocked. Emission from such states has been reported in several cases. [1,2] Complementary to the 'strong-field approach', we recently devised a coordination chemical platform to probe the spin state of nickel(II) complexes via spin-state dependent readout of ligand-borne fluorescence. [3]

In this contribution we will arrange results from steady-state and time-resolved spectroscopies with post-DFT theoretical approaches to rationalize the peculiar excited-state landscape and give an outlook to a broader application of our approach (Scheme 1).



Scheme 1. Structure-imposed Actor (☯) – Reporter (◒) coupling; ☯ denotes a two-state spin switch (actor), with white and black referring to different spin states; ◒ denotes a fluorophore (reporter), which may be bright (yellow circles) or dark (black circles).

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Novel flavin derivatives: synthesis, Photo-redox Catalysis, and photophysical insights

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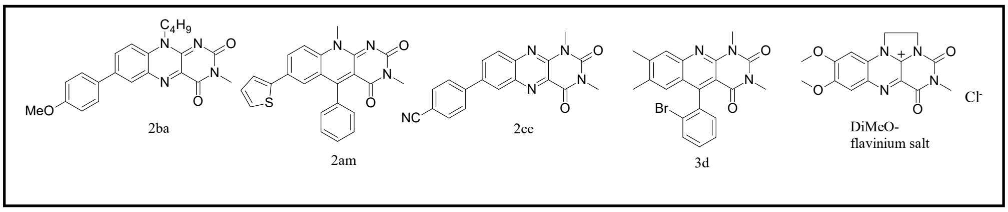
A versatile synthetic strategy to flavin derivatives has been established through palladium-catalysed Suzuki cross-coupling of brominated flavins - 5-deazaflavins (DIAll), alloxazines (All), and isoalloxazines (IsoAll) - with boronic acids and esters under mild conditions[1]. In parallel, a one-pot, three-component condensation of *N, N*-dimethylbarbituric acid, aromatic aldehydes, and anilines enabled access to deazaalloxazine (DAll) analogues[2]. These complementary methods allow rapid diversification of flavin scaffolds bearing electron-withdrawing, electron-donating and halogen substituents. The photophysical behaviour of the resulting derivatives was thoroughly investigated in various solvents, including fluorescence quantum yields, excited-state lifetimes, radiative and nonradiative decay rates, intersystem crossing efficiencies, and singlet oxygen quantum yields (Φ_Δ). The Φ_Δ values span a broad range from 0.01–0.34 for DIAll and DAll (Φ_Δ value for 2ae, 2aa, 3d, 4b, 4i is 0.24, 0.32, 0.26, 0.34 and 0.23, respectively), 0.054–0.29 for IsoAll (2be = 0.17), 0.10–0.98 for All (Φ_Δ value for 2ce, 2ea, 3b = 0.87,0.63,0.90 respectively), and 0.46 for diMeO-flavinium salts[3], with a subset (2ak, 2bk, 2ck) showing negligible sensitisation. These findings underscore the strong influence of substituents on singlet oxygen generation and excited-state dynamics, establishing these flavin derivatives as a tunable platform of photoredox catalysts for organic synthesis and oxidative transformations.



Scheme 1. Selected *novel flavin derivatives.*

Acknowledgments:

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Impact of Spatial Confinement on Probing Single-Molecule Surface-Enhanced Raman Scattering in Plasmonic Nanocavity

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Raman spectroscopy provides valuable insights into a molecule's structure and its interactions with the surrounding environment. Although Raman scattering is inherently inefficient, the use of carefully engineered noble metal nanoparticles can enhance the Raman signal by more than ten orders of magnitude. This substantial enhancement enables the acquisition of surface-enhanced Raman scattering (SERS) spectra from single molecules [1]. The application of supramolecular host–guest chemistry, with cucurbit[7]uril (CB[7]) as host molecule [2], in single-molecule SERS (SM-SERS) spectroscopy [3] represents a powerful approach for isolating the target molecule from its nanoenvironment, such as surrounding gas or solvent molecules. Encapsulation of the guest molecule within a host macrocyclic molecule is expected to influence SM-SERS signal fluctuations, particularly by restricting the translational and rotational motion of the guest within the plasmonic nanocavity. In this study, we address a gap in SM-SERS research concerning host–guest complexes. Specifically, we investigate three key aspects that have not been thoroughly explored: (i) the effect of thionine encapsulation by CB[7] on the SERS spectrum in both dry and aqueous environments, (ii) the photostability of the host–guest complex under plasmonic excitation conditions, and (iii) the detection and temporal evolution of SM-SERS spectra for both the host–guest complex and free dye molecules at room temperature.

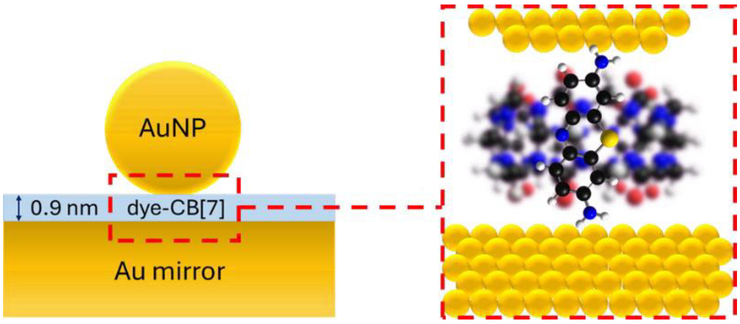

Figure 1. Schematic of the nanoparticle-on-mirror (NPoM) geometry featuring CB[7] as a macrocyclic nanocontainer and thionine as the guest molecule, used in our study as a plasmonic substrate for SM-SERS measurements.

Acknowledgments

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Pressure-Induced Red-to-NIR Luminescence Switching in Square-Planar Rh(I) Complexes

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Crystalline materials that reversibly change optical properties under external stimuli have broad optoelectronic applications [1–2]. Here, we investigate two square-planar Rh(I) complexes (*Rh4X*; **Figure 1a**), featuring metallophilic Rh···Rh interactions forming nearly linear 1D chains along the crystallographic *c*-axis (**Figure 1b**). These interactions significantly influence their photophysical properties [3], and tuning them under pressure provides valuable insights into their structure–property relationships.

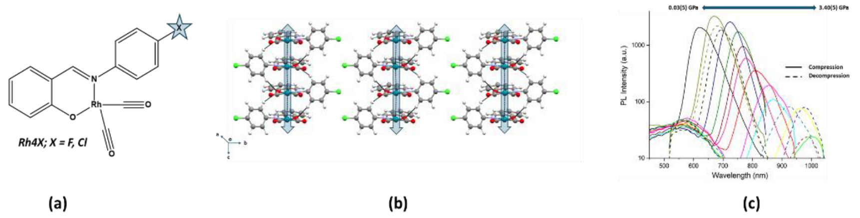

Figure 1. (a) Molecular structure of *Rh4X* (X= F, Cl), (b) 1D chains formed via Rh···Rh metallophilic interaction in *Rh4Cl*, and (c) piezochromic shift (luminescence spectra) seen in *Rh4F* from 0.03(5) to 3.40(5) GPa.

High-pressure single-crystal X-ray diffraction (0-4 GPa) revealed anisotropic unit cell compression in both complexes, with ~0.4 Å reduction of the Rh···Rh distances. Electronic analysis based on the QTAIM framework revealed an increasing degree of partial covalency in the Rh···Rh interactions with pressure. Remarkably, both complexes exhibited giant, reversible piezochromism with emission maxima shifting from red (~620 nm) to NIR (~1000 nm) region (**Figure 1c**). Additionally, these complexes are dichroic and also show significant emission enhancement upon lowering the temperature. TD-DFT calculations were performed to rationalize the origin of their luminescence, and the experimental findings were further corroborated by theoretical studies. Overall, this study demonstrates how metallophilic interactions can be leveraged to fine-tune the photophysical properties of square-planar Rh(I) complexes in the solid state, enabling pronounced piezochromic effects.

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Kinetics and High Field NMR study of the photodegradation of Retinyl Acetate under Ultraviolet Irradiation

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Retinyl Acetate, an active form of vitamin A, is widely used in skincare and the food industry. However, photochemical degradation significantly compromises its stability upon exposure to ultraviolet (UV) light. This degradation involves isomerization, bond cleavage, and molecular rearrangement, initiated by the absorption of UV energy that excites the molecule and alters its chemical structure. These transformations lead to the formation of many products and reduced the effectiveness of Retinyl acetate [1].

In this study, advanced high-field nuclear magnetic resonance (NMR) spectroscopy (300 MHz) was employed to investigate the photodegradation behavior of Retinyl Acetate under controlled Ultraviolet irradiation. We used in-situ illumination setup using an optical fiber to deliver UV light directly to the sample, enabling real-time observation with minimal disturbance in sample. Two-dimensional NMR techniques were used to identify the resulting degradation products, while time-resolved non-uniform sampling (TR-NUS) and diffusion-ordered spectroscopy (TR-DOSY) provided insights into molecular changes and dynamic behavior over time [2]. We have managed to assign the peaks from the HSQC spectra of the main reagents of the reaction and follow the process with high temporal resolution. The information from TR-DOSY was used to calculate the average mass of the reacting mixture and was used to avoid the ambiguity in the assignment of the HSQC peaks.

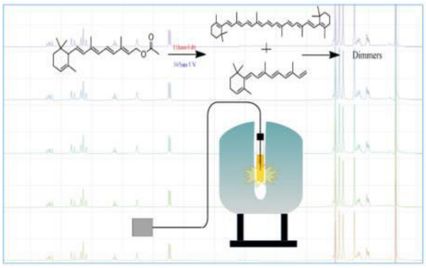

Figure 1: UV Induced photodegradation of Retinyl Acetate in Ethanol-D6

Acknowledgment
The financial support from the National Science Centre, Poland, in the form of a grant SONATA (project no. 2022/47/D/ST4/00846) is acknowledged.

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Impact of the localized surface plasmon resonance in gold nanorods on molecular photoswitching

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Metallic nanoparticles made of gold or silver exhibit unique optical properties that enable efficient absorption and scattering of electromagnetic radiation. When such metallic nanoparticles are illuminated with light at frequencies resonant with the oscillation frequency of free electrons on their surface, they induce collective electron oscillations known as localized surface plasmon resonance (LSPR)[1]. The features of LSPR are closely tied to the morphology of the nanoparticles; in particular for elongated nanostructures two distinct resonance modes are expected, whose energies can be tuned by adjusting their dimensions.

On the other hand, certain molecules - referred to as photoswitchable molecules2 - can undergo reversible transitions between two states upon exposure to light. Several factors, including the wavelength of the light, temperature, and environmental conditions, influence the efficacy of this photoinduced switching process.

This study aims to investigate how the morphology of gold nanostructures affects the photoswitching dynamics of 1,2-bis[2-methyl-5-(4-pyridyl)-3-thienyl]perfluorocyclopentene (DTE-py_2) molecules. These molecules can switch between fluorescent and non-fluorescent states using UV and visible light, which opens and close the ring. Fluorescence imaging of samples containing DTE-py2 molecules deposited on gold nanorods (Au NRs) indicate strong influence of the LSPR in Au NRs on the photoswitching performance of DTE-py2, with notable enhancements for excitation wavelengths corresponding to the plasmon resonance. Additionally, we found that Au NRs featuring identical spectral characteristics despite differences in their morphology have distinct effects on the photoswitching behavior of DTE-py_2 molecules. These findings demonstrate that molecular photoswitching can be tuned and controls via interactions with plasmonic resonances in metallic nanoparticles.

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Charge transport material influence on photoinduced ion segregation in perovskite solar cells

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Perovskites are a class of materials which is under extensive research due to their application in photovoltaic devices [1]. However, their commercialisation is hindered by a couple of issues, primarily with their stability. An interesting phenomenon occuring in mixed-halide perovskites is a reversible segregation of halide (iodide and bromide) anions into separate phases which takes place when the sample is illuminated. The details of this effect's mechanism are still not fully explained [2,3]. Here, we present the results of our newest studies regarding the influence of charge (electron/hole) transport material (ETL/HTL) on ion segregation. It was previously reported that TiO_2 as ETL promotes this effect, but Spiro-OMeTAD (as HTL) was thought to suppress this effect by hole extraction [4]. In numerous experiments performed for the benchmark *triple-cation* perovskite composition ($(Cs_{0.05}FA_{0.81}MA_{0.14})Pb(I_{0.85}Br_{0.15})_3$, where FA is formamidinium and MA is methylammonium), we show that the presence of HTL also contributes to ion segregation. Furthermore, thanks to the use of a transient absorption (TA) setup of tunable wavelength, we are able to track the influence of a contact material at both sides of a thin film separately (in the vicinity of this material and at some distance). TA also allows us to determine ultrafast charge cooling and charge recomination dynamics in perovskites upon excitation and compare its characteristic time constants in the mixed and segregated phases. These findings shed new light on our understanding of photoinduced ion segregation, challenging previous explanations and calling for a deeper scientific reflection on the nature of this process.

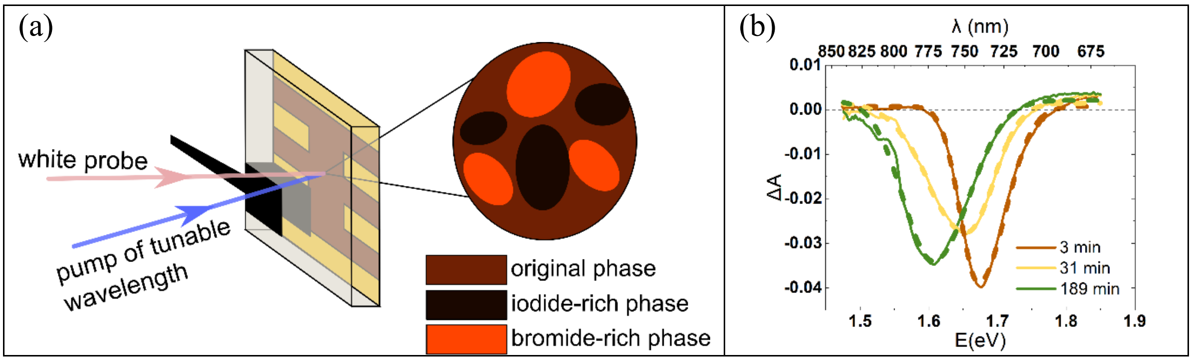

Figure 1: (a) A scheme of ion segregation measurement using the TA setup. **(b)** Exemplary shift of TA spectrum resulting from ion segregation. The signal shifts as the low-bandgap iodide-rich phase is formed.

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Enhancing stability and photoinduced charge transfer in porphyrin – MXene nanohybrids for light-driven applications

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Two-dimensional transition metal carbides and nitrides known as MXenes, particularly $Ti_3C_2T_x$, have emerged as promising materials for light-driven applications due to their high electrical conductivity, tunable structure, and large surface area. However, their practical use is hindered by limited ambient stability and a tendency for oxidation. In this work, we report the fabrication and photophysical characterization of a novel hybrid material composed of $Ti_3C_2T_x$ MXene nanosheets and meso-(p-hydroxyphenyl)porphyrin (TPPH), coupled via non-covalent interactions [1].

Spectroscopic studies (UV – Vis, fluorescence, and femtosecond transient absorption) confirmed the formation of a ground-state complex, evidenced by a 40 nm red-shift in the Soret band (Figure 1). The data revealed efficient photoinduced electron transfer from the singlet excited state of TPPH to the MXene surface as evidenced by the formation of a porphyrin radical cation.

Importantly, the hybrid material demonstrated enhanced ambient stability, with the lifetime of colloidal dispersion more than four times longer than that of pristine MXene. These results suggest that non-covalent porphyrin functionalization is a viable strategy for both prolonging MXene stability and improving its performance in solar energy conversion systems.

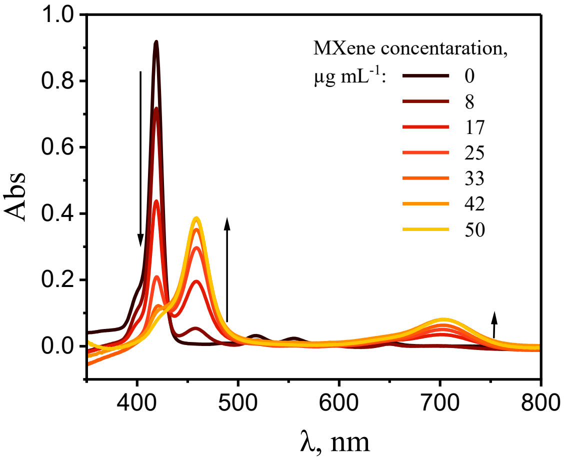

Figure 1. Absorption spectra recorded during the process of titration of TPPH solution EtOH–H_2O (1 : 2 v/v) with of $Ti_3C_2T_x$ dispersion.

Acknowledgments
This work was supported by the NCN (Grant Number: UMO-2021/43/O/ST5/00137).

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Distinct effects of progesterone and cholesterol on the properties of lipid membranes: Insights from Biophysical Experiments and Molecular Dynamics Simulations

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The function of steroid hormones is intrinsically linked to their interaction with cell membranes. The direct interaction of steroids with signalling receptors inside the cell leads to changes in gene expression. Literature reports indicate that steroids can induce cellular responses in a non-genomic manner through interaction with intracellular signalling receptors [1] and in a non-specific manner, for example by actively altering the physicochemical properties of the membrane [2]. The investigation of the molecular mechanisms underlying these interactions has the potential to facilitate our understanding of the genesis of pathological conditions associated with hormonal imbalance.

The studies presented here focus on analysing the effects of the female sex hormone, progesterone, on the physicochemical properties of model lipid membranes. The structural and dynamic properties of biomimetic lipid membranes composed of unsaturated phosphatidylcholine, sphingomyelin and a selected steroid are analysed using a combination of fluorescence confocal microscopy, probes sensitive to changes in the local environment and a fluorescence recovery technique after photobleaching. The present study demonstrates that, in contrast to cholesterol, progesterone facilitates lipid diffusion and hinders the phase separation process in the membrane. Nevertheless, its effect on the degree of lipid ordering is more subtle than that observed for cholesterol. These observations were further corroborated by molecular dynamics simulations, which indicated divergent mechanisms of interaction between the two steroid molecules and the lipid membrane. The results of this study suggest that progesterone, by modulating the organisation of domains in the cell membrane, accelerating diffusion and gently influencing lipid ordering, may induce rapid cellular responses, essential for the non-genomic mode of interaction of steroid hormones with cells.

Acknowledgments
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Synergistic Activation of Antitumor Immunity via Bacteriochlorin-Based Photodynamic Therapy and Immune Checkpoint Blockade

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Photodynamic therapy (PDT) is a minimally invasive cancer treatment that relies on the combined action of a photosensitizer, visible or near-infrared light, and molecular oxygen to produce reactive oxygen species. These ROS exert cytotoxic effects on tumor cells, leading to localized tumor destruction. Importantly, beyond its direct tumoricidal activity, PDT also modulates the immune system and can contribute to systemic antitumor responses, making it a valuable tool in cancer immunotherapy .

Recent research has highlighted the ability of PDT to induce immunogenic cell death (ICD) - a form of cell death that stimulates dendritic cell maturation and promotes durable antitumor immune memory. The efficiency of ICD appears to depend on factors such as the subcellular localization of the PS and its formulation (e.g., micellar encapsulation), both of which can influence the activation of antigen-presenting cells (APCs), including macrophages [2].

Despite its immunostimulatory potential, tumors often evade immune detection by upregulating immune checkpoint proteins like PD-L1, leading to T cell suppression. To counteract this, combining PDT with immune checkpoint inhibitors (e.g., anti-PD-1 or anti-PD-L1 antibodies) has emerged as a compelling strategy. This combination not only enhances tumor clearance but also supports the development of systemic, long-lasting immunity, potentially reducing the risk of metastasis and recurrence.

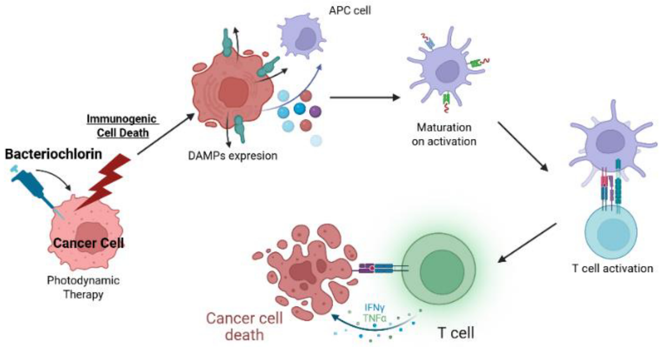

Figure 1. Induction of immunogenic cell death leading to T cell activation by bacteriochlorin-based photodynamic therapy

Acknowledgments
This research has been funded by the program "Excellence Initiative – Research University" at the Jagiellonian University and National Science Center (NCN, Opus project no 2020/37/B/NZ7/04157).

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Probing cell membranes under dehydration using fluorescence lifetime measurements

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Cell membrane structures are not only complex in their chemical composition and spatial organization but also exhibit a remarkable capacity for adaptation, rapidly adjusting their properties in response to both internal and external stimuli, such as hydration levels or environmental pH.

In this study, we worked with lipid bilayers supported on a solid substrate, which naturally tended to undergo phase separation into disordered (Ld phase) and ordered (Lo phase) regions. Using fluorescence lifetime imaging microscopy (FLIM), we investigated the fluorescence lifetimes of several probes: DOPE-Atto 633 in the Ld phase, and TopFluor (TF) attached to either sphingomyelin (SM) or cholesterol, under varying hydration conditions and in both membrane phases.

Our findings reveal that the behaviour of TF is influenced by the molecule to which it is bound: in fully hydrated membranes, TF-SM exhibited a shorter fluorescence lifetime, while TF-cholesterol showed a longer one. Additionally, FLIM successfully distinguished between membrane phases: lifetimes were shorter in the Ld phase and longer in the more tightly packed Lo phase. Upon dehydration, the lifetime maxima shifted: TF-cholesterol and Atto 633 lifetimes decreased, whereas the effect was less pronounced for TF-SM.

This study demonstrates that FLIM can effectivly detect changes in the physico-chemical environment even for fluorescent probes that are not classified as traditional solvatochromic dyes, i.e. those typically used for sensing environmental polarity. Beyond providing quantitative data, this technique enables precise spatial mapping of changes in biomimetic membranes, offering deeper insight into the behaviour of native cellular membranes.

Acknowledgments

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Development of Organic Ligands for Theranostic Iridium(III) Complexes: Synthetic Strategies and Spectroscopic Characterization

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Modern treatment strategies for cancers, especially those located in the skin, increasingly include photodynamic therapy (PDT). This method involves the selective photo-oxidation of altered biological tissues[1] and requires two key elements: a photosensitiser and an appropriate light source. The photosensitising substance applied to the tumour area, is activated by specific-wavelength light and produces ROS that destroy cancer cells via photo-oxidation[2]. PDT is minimally invasive, allows repeated use, and targets diseased tissue selectively. However, limited light penetration reduces its effectiveness for deeper skin lesions.

In recent years, the concept of theranostics - an approach that combines therapy and diagnostics in a single molecular system - has become increasingly important. Thanks to their fluorescent properties, some photosensitisers can have a dual function: therapeutic (destruction of tumour cells) and diagnostic (visualisation of the location of tumour lesions). This enables precise tracking of treatment and monitoring the body's response to therapy[3].

The aim of this study was to synthesise new ligands based on the structure of 3-pyridylcoumarin, which can be used to obtain iridium(III) complexes[4] – compounds that are characterised by strong absorption of radiation in the UV-Vis range and a high potential to generate ROS. The obtained iridium(III) complexes were analyzed using UV–Vis spectroscopy, offering insights into their potential applications in biomedical settings.

Acknowledgments

Research funded under competition No. 2024/ABM/03/KPO/ project No. KPOD.07.07-IW.07-0125/24 entitled: “Project title: Luminescent theranostic compounds with anticancer activity, i.e., the combination of photodynamic therapy and diagnostics through imaging in a single molecule, and the development of 3D-printed local microneedle systems to ensure precise, individualized cancer therapy” from the National Plan for Recovery and Resilience, which is part of Investment D3.1.1 Comprehensive development of research in medical and health sciences, a project financed by the Medical Research Agency.

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Experimental and Computational Investigation of Novel BODIPY-3-Serotonin Dye

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BODIPY derivatives are widely recognized for their excellent photophysical properties, including high fluorescence efficiency, sharp absorption bands, and chemical stability.[1,2] In this study, we present the synthesis and characterization of a novel BODIPY-3-Serotonin dye, combining the fluorescent properties of BODIPY with the chemically sensitive Serotonin. The compound was characterized using NMR as well as UV-Vis spectroscopy in a range of solvents with varying polarity, revealing pronounced solvatochromic effects and highlighting its potential as an environment-sensitive probe. pH titration experiments demonstrated that the dye exhibits a strong spectral response to changes in proton concentration over a broad pH range, indicating its potential application as a pH sensor. Complementary DFT and TD-DFT calculations were carried out to explore the electronic structure and photophysical behavior of the dye. The theoretical data align well with experimental findings, supporting the observed absorption and emission properties and providing insight into the electronic transitions and solvent-dependent effects. This combined spectroscopic and theoretical approach confirms the potential of BODIPY-3-Serotonin as a versatile pH-sensitive fluorescent dye with tunable optical properties. These results demonstrate the potential of BODIPY-3-Serotonin as a promising platform for the design of responsive fluorescent probes in chemical and biological sensing applications.[3]

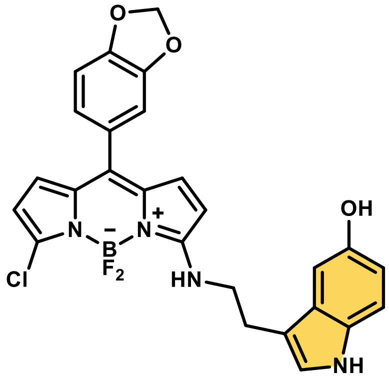

Figure 1. Structure of the studied BODIPY-3-Serotonin dye.

Acknowledgments

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Modified Sulfonyl Phthalocyanines for Effective Photodynamic Therapy and Prospects for Combination with Immunotherapy

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Photodynamic therapy (PDT) offers a minimally invasive strategy for cancer treatment by generating reactive oxygen species (ROS) that induce localized tumor cell death and vascular damage while also stimulating immune responses [1]. Our recent work has focused on the development of modified Zn(II) and Pt(II) sulfonyl phthalocyanines with improved photophysical properties, high singlet oxygen generation, and effective incorporation into Pluronic-based micelles to enhance their bioavailability and cellular uptake. These systems demonstrated potent phototoxicity *in vitro* and significant antitumor efficacy in CT26 tumor-bearing mice, with vascular-targeted PDT (V-PDT) resulting in high rates of complete tumor eradication and no recurrence [2]. Building upon these promising results, we are currently exploring the integration of these phthalocyanine-based systems with immune checkpoint inhibition strategies to enhance systemic antitumor immunity, aiming to combine the localized effects of PDT with systemic immune activation. This approach holds the potential to expand the therapeutic scope of PDT beyond local tumor control, offering a pathway toward durable responses in cancer treatment [3].

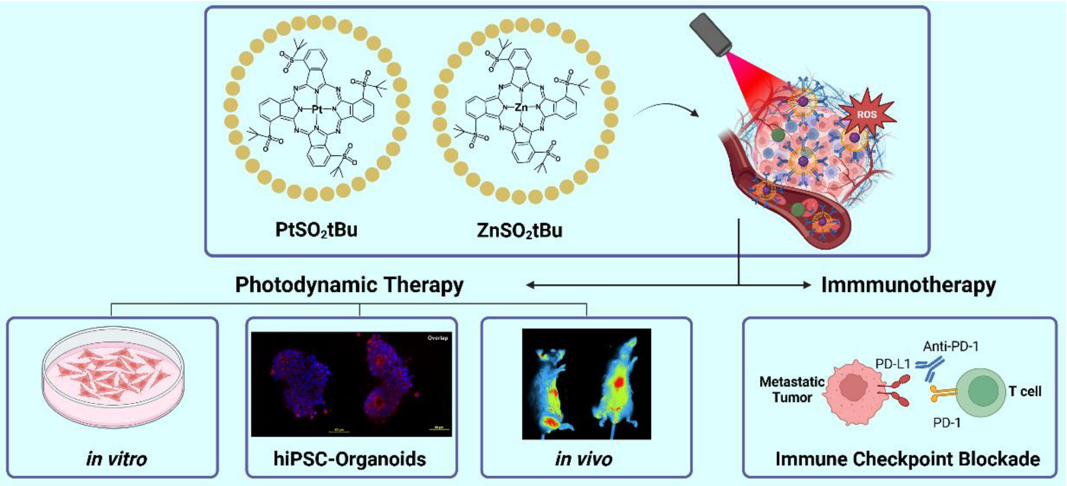

Figure 1. Schematic representation of photodynamic therapy (PDT) with modified phthalocyanines and its planned integration with immune checkpoint inhibition to enhance systemic antitumor immunity.

Acknowledgments
This work has been funded by the program "Excellence Initiative – Research University" at the Jagiellonian University and NCN grant No. 2020/37/B/NZ7/04157.

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When the fate of photogenerated charges matters — classification of heterojunctions in photocatalysis

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Photocatalytic systems designed for various applications often comprise two or more semiconductor components. Such composites are used to achieve an efficient charge separation, more reactive holes or electrons or other additional functionalities. However, the proper classification of various heterojunctions formed of semiconductors is often difficult. We have proposed a strategy for correctly elucidating the heterojunction type [1]. It comprises three main steps: (I) the determination of band alignment, (II) the thermodynamic analysis of the interface, and (III) the verification of charge fate and charge transfer kinetics under irradiation (Figure). The experimental techniques appropriate for particular steps, including novel approaches, will be presented, together with their limitations. Following this strategy and methods of spectroscopic [2] and redox [3] characterization of semiconductors, it is possible to conduct the analysis, which explores the intricate dynamics of photoinduced charges within correctly classified heterojunctions. Such a strategy gives a more reliable picture than the often presented, oversimplified study.

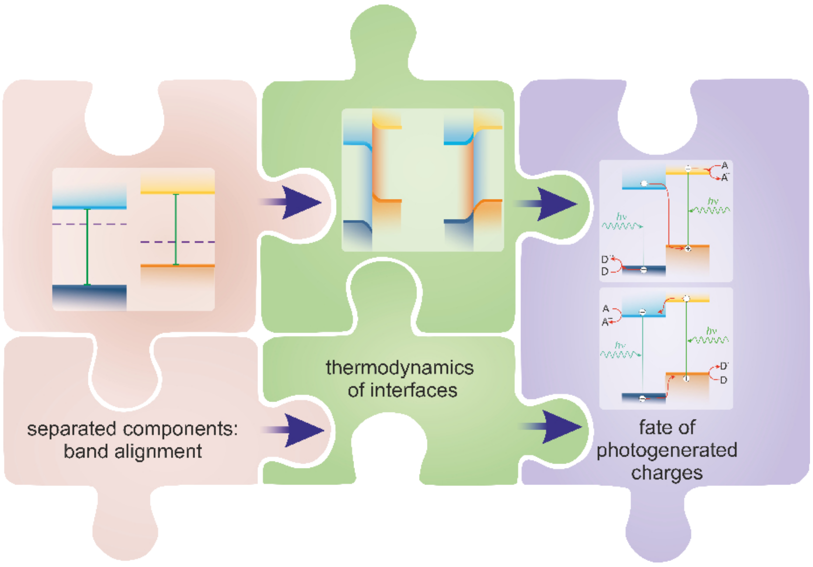

Figure. Determining the type of heterojunction in three consecutive steps: (I) the analysis of band alignment and Fermi levels; (II) the investigation of thermodynamic properties of the interface; (III) the verification of charge fate and charge transfer kinetics under irradiation.

Acknowledgments

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Photoresponse of xanthophylls in flowers

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Natural dyes developed by nature show diverse functionality and optimized properties. The bright coloration of floral inflorescences plays a key role in attracting pollinators. The optimal temperature of inflorescence for pollinator visits can be reached in sunny morning, since the absorbed light energy is effectively converted to heat. Yellow and orange colors are commonly attributed to the presence of xanthophylls and xanthophyll esters localized in chromoplasts [1,2]. These pigments can be identified using analytical techniques such as high-performance liquid chromatography–mass spectrometry (HPLC-MS) and nuclear magnetic resonance (NMR). While the photophysical properties of xanthophylls have been extensively investigated [3], significantly less is known about their behavior in extract solutions containing solubilized chromoplasts, and even fewer studies have addressed intact, isolated chromoplasts [4]. Yellow inflorescences of dandelion (*Taraxacum officinale*) contain major xanthophyll as all-*E*-lutein epoxide [5]. Here, we present recent results obtained using femtosecond UV-vis transient absorption spectroscopy on xanthophylls extracted from petals of dandelion. Upon blue-light excitation (λ = 465 nm, Figure 1), the xanthophylls undergo a full photocycle, characterized by singlet excited-state deactivation and recovery of the ground state (S_0) population in 240 ps time window, accompanied by non-radiative dissipation of energy as heat. In chromoplasts a more complex deactivation pattern is expected [4] since a singlet fission process can occur in aggregated xanthophylls, leading to formation of two triplet states from one excited singlet state.

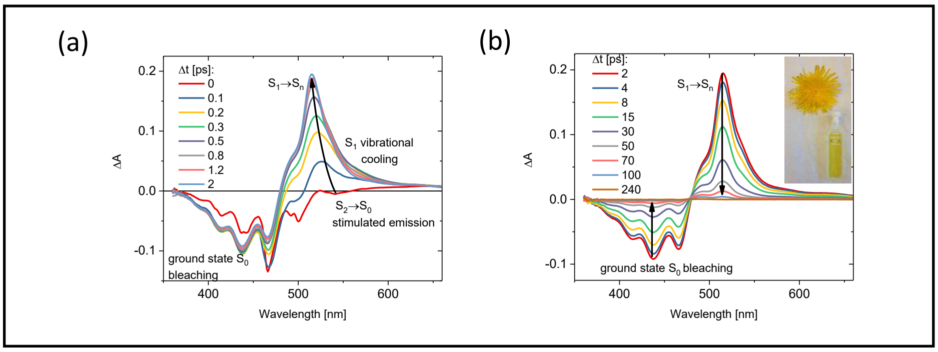

Figure 1. Transient UV-vis absorption spectra recorded for methanolic exctract from petals of dandelion after laser pulse excitation at 465 nm for delays in time windows 0 – 2 ps (a) and 2 – 240 ps (b).

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Photoredox catalysis with scandium(III) as a photoactive species

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Photoredox catalysis has already become a full-fledged alternative to traditional methods in organic synthesis.[1] Through the use of light-excited dyes, photoredox catalysis allows the mild construction of challenging chemical bonds or even enables otherwise unattainable chemical transformations. Ruthenium and iridium polypyridyl complexes stand out among the photocatalysts used so far. Unfortunately, the large-scale use of Ru and Ir catalysts is limited due to the extreme price of ruthenium and especially iridium.

Scandium is a relatively abundant metal and its trivalent salts are extensively used as Lewis acids.[2] However, Sc(III) salts are considered to be redox inactive and therefore no one use them in photoredox catalysis as a stand-alone excitable photocatalyst. In our presentation, we demonstrate the unprecedented activity of $Sc(OTf)_3$ catalysing, upon excitation with visible light, the aerobic oxidation of benzylic C-H bonds and the direct oxidative cyanation of arenes as examples of C-H activation and C-C coupling reactions, which are key synthetic transformations.[3] These unprecedented procedures dispel the usual notion of Sc(III) salts as redox-inactive and photo-inactive species that are generally used as Lewis acids and expand their possible application as simple, readily available photocatalysts. In addition, the photocatalytic procedures based on scandium triflate are simple and selective, use low amounts of catalyst and worked without any additive.[4]

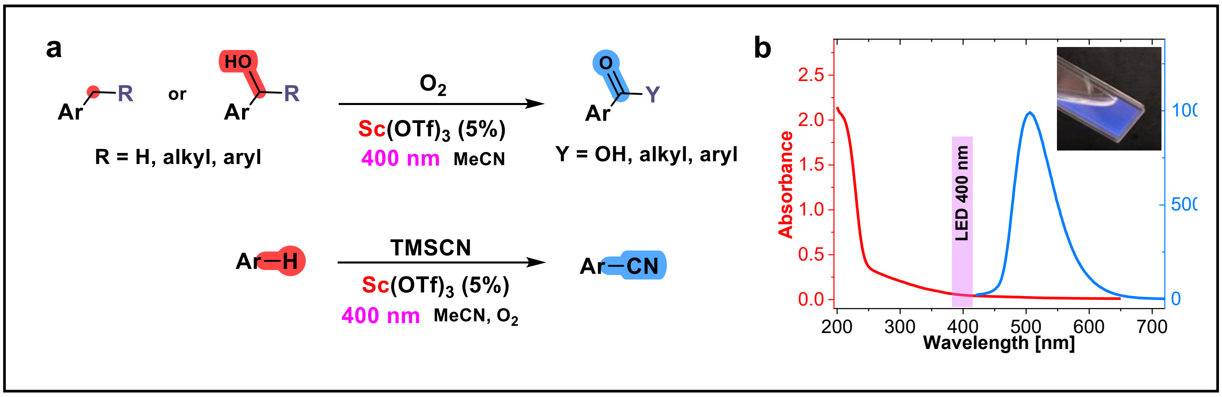

Figure 1. Examples of applications of $Sc(OTf)_3$ as a sole photoredox catalyst (a), UV-Vis and fluorescence spectrum of $Sc(OTf)_3$ solution in acetonitrile (c = 0.05 M) (b).

Acknowledgments

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Atomically precise noble metal nanoclusters as NIR luminescent markers

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Noble metal nanoclusters (NCs) are a group of ultra-small luminescent nano-materials with unique physicochemical and optical properties, which combines properties of molecules and nanoparticles. They present unique linear and non-linear optical properties: tunable photoluminescence (from UV to NIR), large Stokes shifts (that can easily exceed 0.5 eV), high photostability, high two-photon absorption cross-sections.[1, 2] Moreover, NCs are sensitive to a single atom change as their one-photon (1PA) and two-photon absorption (2PA) spectra may be easily tuned by the cluster size and core composition. Thus, they serve as a perfect platform for elucidation of structure- physicochemical property relations and broad potential applications in catalysis, bioimaging or sensing.

Here, we study linear and nonlinear optical properties of gold and silver nanoclusters and discuss the compositional and structural impact on the photoluminescence (PL) excited under 1P and 2P excitation, which is easily tunable in the near-infrared (NIR) range of wavelengths [3, 4, 5] We investigate a range of nanoclusters: thiol-stabilized Au25 in aqueous solutions and organic solvents, Ag25 nanoclusters and their alloys with replaced one or multiple gold atom i.e. Ag25-xAux (x=0, 1, 5-10) as well as DNA-stabilized atomically-precise silver nanoclusetrs. Strong nonlinear response of fluorescent nanoclusters in the near infrared range of wavelengths indicates great potential of nanoclusters in multiphoton bio-imaging, enhanced in case of Au doping to Ag nanoclusters.

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Organic chromophores on ferromagnets illuminated: a photochemical and magnetic study

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Within recent years the so called *spinterface*—the interface between ferromagnetic and molecular materials—gained a lot of attention as an ideal platform for creating new spin-related effects [1]. Even though molecular spintronics, where the *spinterface* plays a central role, is a vividly developing field, surprisingly little has been done to explore the potential of inorganic/organic interfaces in combination with advantages offered by the light-induced processes in organic chromophores.[2]

Porphyrin chromophores were covalently anchored to thin gold-capped ferromagnetic films (FM/Au) through chiral oligopeptide chains, forming a self-assembled monolayer (SAM). Properties of such FM/Au/SAM inorganic/organic interfaces were studied in parallel via (***i***) photochemical methods (*steady-state and transient absorption spectroscopy*) allowing detailed characterization of the behavior of the photoexcited molecular layer in the proximity of the FM, and (***ii***) *ferromagnetic resonance spectroscopy* (FMR) being an exceptionally sensitive method for detecting changes in the magnetic properties of the FM, here induced by the molecules in their ground and photoexcited states.

The transient absorption spectroscopy of the FM/Au/SAM stack demonstrated a pronounced sensitivity of the excited-state dynamics in the molecular layer to the out-of-plane magnetization polarization (UP or DOWN) in the FM layer, confirming a substantial role of the *spinterface* in photoexcitation characteristics of SAM. Moreover, slight changes were also observed depending on the chirality of the oligopeptide linker. At the same time, FMR measurements without light irradiation did not show any remarkable changes in the magnetization dynamics of the FM upon adsorption of the molecules. Currently the influence of light on the magnetization dynamics in the FM/Au/SAM is studied.

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Shaping Light-Driven Therapies: Smart Photosensitizers and Molecular Materials for Enhanced Photodynamic Efficiency

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The development of light-responsive molecular systems offers exciting opportunities to address pressing medical challenges, including drug-resistant infections and cancers. Photodynamic therapy (PDT), which relies on photosensitizer activation by light to generate reactive oxygen species (ROS), is a versatile and minimally invasive modality for both oncological and antimicrobial applications. This work focuses on the design and photochemical evaluation of smart photosesnitizers based on porphyrins and phthalocyanines, aiming to enhance the photodynamic efficiency through precise structural tuning.[1-2]

A diverse series of novel porphyrins and phthalocyanines (Fig. 1) were synthesized and subjected to comprehensive photophysical and photochemical studies, including transient absorption spectroscopy and time-resolved singlet oxygen phosphorescence. By systematically modifying the macrocyclic core, axial ligands, and peripheral substituents, we established clear structure–activity relationships governing key parameters such as singlet oxygen quantum yield (Φ_Δ up to 0.93), triplet-state lifetime, and photostability under physiological conditions. Selected compounds were further integrated into nanocarriers or immobilized on functionalized TiO_2 surfaces, yielding hybrid systems with enhanced selectivity and tissue penetration.[3-4]

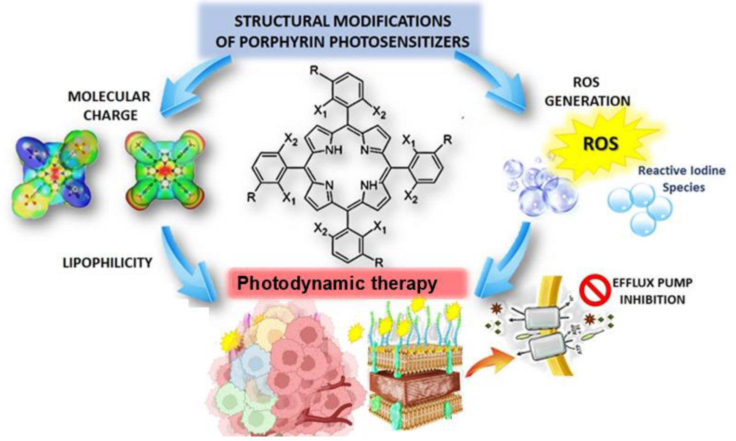

Figure 1 . Schematic representation of discussed studies on the novel families of photosensitizers for PDT.

Biological validation of the optimized photosensitizers was carried out in both *in vitro* 2D/3D cellular and *in vivo* murine models. These findings confirm that rationally engineered molecular photosensitizers can be tailored for dual antimicrobial and anticancer photodynamic applications, offering a flexible platform for next-generation light-driven therapies.

Acknowledgments
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Positional Effects of Methoxy Substituents on the Photoacidity and Photovoltaic Properties of Merocyanine Photoacids

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In nature, light-induced proton gradients are fundamental to biological energy transduction, enabling the remarkably efficient conversion of solar energy into chemical potential. This mechanism, central to processes such as photosynthesis, exemplifies how living systems harness photonic energy to drive essential biochemical transformations.[1-3]

In this work, we investigated the influence of methoxy group positioning on the photoacidity, stability, quantum yield and solubility of merocyanine photoacids.[4] Among the synthesized compounds, the most promising photoacid exhibited a significant pH jump in a water–methanol solvent mixture. This study demonstrated that introducing a methoxy group on the indolium moiety, as well as another methoxy group in the ortho position relative to the ene-iminium core in the opposite side, significantly enhanced the compound's performance. When this merocyanine was placed between two glass slides equipped with electrodes and exposed to asymmetric sunlight, it generated an open-circuit voltage.[5] These findings highlight the potential of positionally modified merocyanine photoacids for light-driven electrochemical applications.

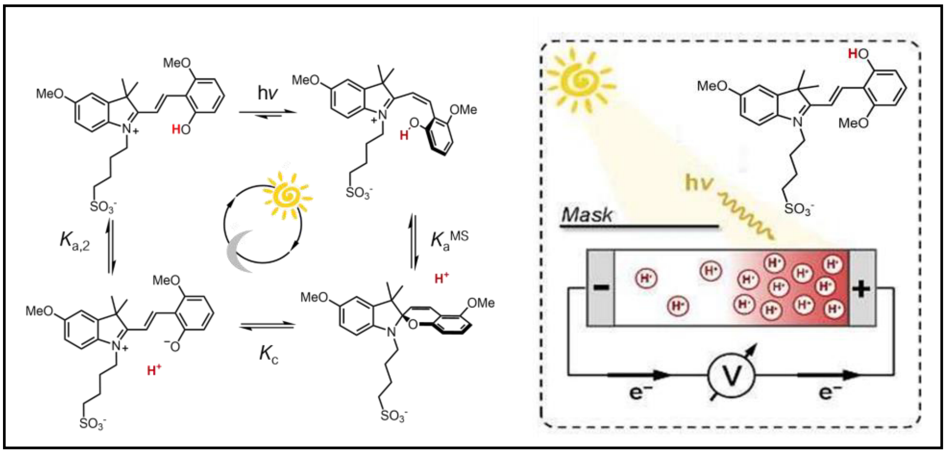

Figure 1 (a) Four-state model describing MCHs' operation in aqueous environments: visible light-triggered isomerization (upper-right path) contrasts with thermal relaxation (bottom-left path), where the SP ring-opening is the rate-determining step. (b) Working principle of the energy harvesting device used in this study: asymmetric light irradiation of two glass slides enclosing merocyanine induces the formation of a persistent proton concentration gradient.

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Advancements in Cationic Photopolymerization: Composite Materials and Novel Photoinitiators for Specialized Applications

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This presentation focuses on the recent advancements in cationic photopolymerization techniques specifically applied to composite materials. We will explore the development of novel photoinitiators tailored for specialized applications, particularly in frontal photopolymerization processes. Cationic photopolymerization has gained substantial attention due to its unique advantages, including high reactivity and the ability to cure in the presence of moisture, making it ideal for a range of materials.

In this context, we report on the synthesis and characterization of innovative photoinitiators that enhance the efficiency and performance of cationic photopolymerization. The application of these initiators in frontal photopolymerization demonstrates potential for creating complex, high-performance composite materials with superior properties such as increased mechanical strength, thermal stability, and reduced curing times.

Furthermore, we discuss the implications of these advancements for various industries, including coatings, adhesives, and biomedical applications, where tailored materials are essential. This research aims to contribute to the evolution of cationic photopolymerization methodologies and the development of materials that meet the growing demands of specialized applications.

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Light in the Dark: Aminal-linked COFs for Efficient Light Upconversion

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Photon upconversion, particularly through sensitized triplet-triplet annihilation (sTTA) mechanisms, offers an elegant solution to overcome fundamental limitations of emission efficiency in photonic systems by converting abundant low-energy radiation into valuable high-energy photons even under low photon flux. This makes it attractive for various applications ranging from solar energy harvesting to biological imaging [1], [2]. However, the translation of upconversion from solution-based molecular systems to robust solid-state architectures has long been hindered by the tendency of organic chromophores to aggregate and quench their luminescent properties [3], [4]. Covalent organic frameworks (COFs) present an elegant solution to this persistent problem, offering precise structural control of photoactive components while maintaining permanent porosity and high surface areas.

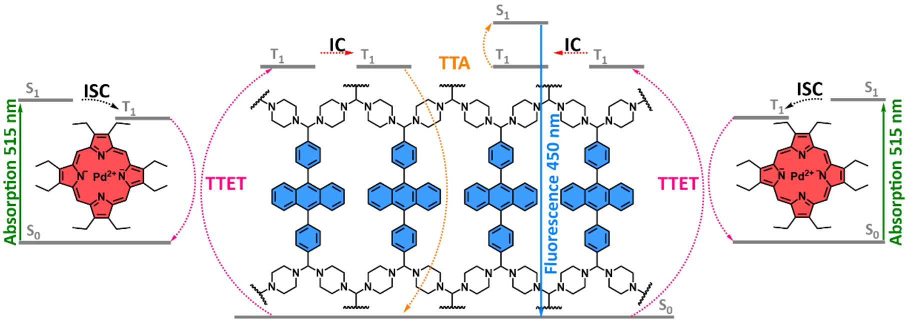

Figure 1. Upconversion mechanism in Ant-COF-H&PdOEP system.

Our investigation focuses on aminal-linked covalent organic frameworks: Ant-COF-H and Ant-COF-OH, incorporating diphenylanthracene units as upconverting emitters. Both materials were successfully synthesized, and their structural integrity was validated through Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy, whereas powder X-ray diffraction (PXRD) proved their high crystallinity. Density Functional Theory (DFT) geometry optimization of the periodic systems revealed plausible structures of those materials as 2D-type polymers with relatively large interlayer spacing, which resulted in high photoluminescence quantum yields of ~ 15%, with energetic characteristics closely resembling those of the parent diphenylanthracenes. Both COFs, when paired with a palladium porphyrin complex, facilitate efficient excited-state energy transfer and sustain strong emission not limited by the molecules' diffusion rate, scoring upconversion quantum yields of ~ 4%.

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Switching from phototherapeutically-active molecules to red-emitting photoluminescent materials with tricarbonylrhenium(I) complexes

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The development of compounds with red-shifted absorption and/or emission is essential to improve the performance of materials designed for bio-imaging techniques, and to facilitate the use of phototherapeutically-active molecules *in vivo*. Recently, tricarbonylrhenium(I) complexes have attracted much attention because of their unique photophysical and photochemical properties, including solid state photoluminescence [1−3] and the ability to generate CO and reactive oxygen species under light irradiation [4, 5]. However, obtaining efficient red emitters in this series of compounds is very difficult, and moving the absorption of photosensitizers sufficiently towards long wavelengths while keeping good photochemical performance is another major challenge.

In the present work, we started by developing complexes based on (3-(2-pyridyl)-1,2,4-triazole) (pyta) ligands, until obtaining compounds that emit a yellow-green light very efficiently in solid state [2]. A modification of the ancillary ligand Y endowed the complexes with good photoreactivity [5]. Then, simple chemical modifications inspired by theoretical calculations resulted in a set of photoreactive molecules that absorb at long wavelengths [6]. Some of them emit in the red in the solid state with excellent efficiency (PLQY > 43%) (Fig. 1). However, the development of red emitters is at the expense of the CO-photoreleasing activity, which is prevented above a limiting absorption wavelength. This study shows how to move from one compound category to another. It provides new information on the optimization of either photoluminescence or photochemistry in tricarbonylrhenium complexes, with a view to developing two original families of materials.

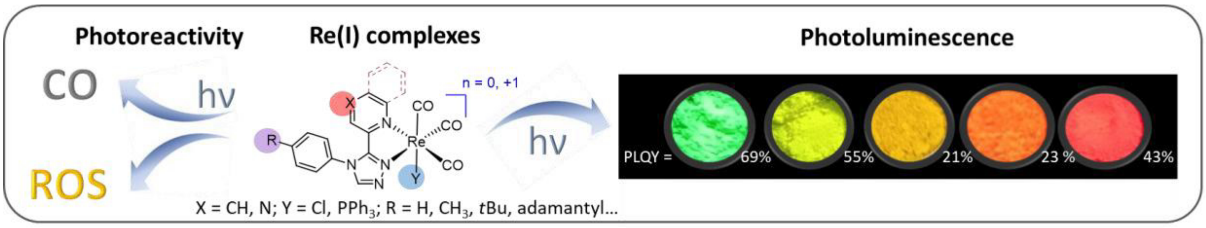

Figure 1. Versatile chemical structure and photoactivity of some tricarbonylrhenium complexes.

Acknowledgments
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Radiation Chemistry and Photochemistry: Complementary Approaches for the Study of Free Radicals

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Radiation Chemistry is concerned with the interactions of ionizing radiation, such as high-energy photons (γ-radiation and X-rays) and charged particles (electrons, protons) with matter. Photochemistry, on the other hand, has been associated with the interaction of matter with lower energy photons (UV and visible light). Differences in the basic physical phenomena describing the interaction of low- and high-energy radiation with matter in photochemical and radiation-chemical methods result in differences in the primary processes leading to the formation of reactive species (radicals, radical ions and excited states). During the past century, the fields of radiation chemistry and photochemistry developed in parallel, but each as its own pace. Their power as individual techniques is manifest. However, where they are combined, experimental difficulties of a single method can be evaded and more results and new insights can be obtained from the chemical system under study. Radiolysis and photolysis have played a substantial role in providing a substantial knowledge for our understanding of radical reactivity mechanisms including electron transfer, particularly on fast time scales. Despite the complementary nature of these two branches of chemistry crossover between them occures far less frequently than it should. Therefore, the key differences between these two experimental approaches, along with examples of their strengths and weaknesses, will be briefly outlined. The advantages of using both methods will be presented, using sulfur radicals as an example. Application of complementary radiation and photochemical techniques allowed to compare in detail the one-electron oxidation mechanisms of sulfides initiated either by $^{\bullet}$OH radicals and the excited triplet state of the sensitizer (CB*).

Acknowledgments

I am very grateful to Bronislaw Marciniak from Adam Mickiewicz University and Gordon L. Hug from the Notre Dame Radiation Laboratory (USA) for their long-lasting fruitful collaboration and friendship. Special acknowledgements are extended to all co-authors of our joint papers from Warsaw Team (IChTJ), Poznań Team (AMU) and Teams from Abroad for the insightful comments and helpful suggestion and fruitful exchange of ideas.

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Methionine oxidation still brings surprises

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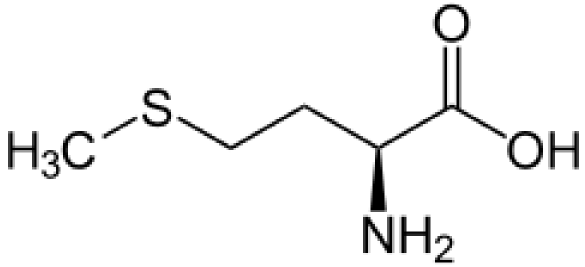
Methionine is an amino acid which has many important roles in biology, in particular in the course of oxidative stress.



The story of its oxidation began a very long time ago, with Prof D. Asmus' team, and then with two Polish teams, those of Prof. K. Bobrowski in Warsaw and Prof. B. Marciniak in Poznan.

Thanks to these teams, we know that the first step of oxidation by OH radicals is the formation of various free radicals with a two-center three electron bond, whose absorption spectra have been characterized by pulse radiolysis. In our group, we characterized the finals compounds by Mass Spectrometry and Infra-red coupled to it (IRMPD). It allowed us to show that methionine sulfoxide was one of them even in the absence of oxygen, but many other compounds could be formed such as decarboxylated methionine.

Recently, we were interested by some form of competition between oxidation of methionine and a DNA base, adenosine, in the compound S-adenosyl methionine. This compound has a great importance in biology since it triggers DNA modifications, among other processes. The mechanism of its oxidation was quite unexpected. Thus it brought new knowledge about methionine oxidation and most importantly about oxidative stress. The story of methionine oxidation is not finished.

An assortment of sulfur-centered radicals in chemistry and biology

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Sulfur-centered radicals play a crucial role in various disciplines, including chemistry, biology, and medicine. The most impressive aspect is the variety of structures that can be built around the sulfur atom, which contains the unpaired electron. Figure 1 shows the most representative sulfur-centered radicals. The nature of substituents exerts a dramatic influence on the structure and reactivity of the species, e.g., the sulfuranyl radical ($R_3S^\bullet$) may exist in σ-, σ*-, or π-type structures. An overview of our experience in this research area will be presented.

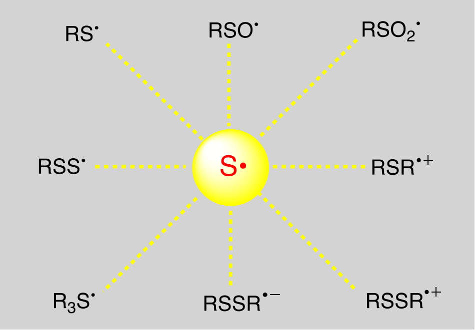

Figure 1. A variety of free radicals in which the unpaired electron is located on a sulfur atom.

Oxidation Pathways of Model Disulfides

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Disulfide bonds are critical structural elements in some biologically relevant peptides and proteins as they stabilize folded structures. Oxidative modifications of these linkages may be associated with a loss of structure and function. In this work we investigated the oxidation of a series of model disulfides with singlet oxygen ($^1O_2$), a key intermediate in photo-oxidation reactions. The kinetics of disulfide-mediated $^1O_2$ removal were monitored using the time-resolved 1270 nm phosphorescence of $^1O_2$. The experiments were carried out using a home-made, time-resolved emission spectrophotometer based on TCSPC/MCS method. Stern-Volmer plots of these data showed a large variation in the quenching rate constants k_q (from 2×10^7 for α-lipoic acid to 3.6×10^4 $M^{-1}s^{-1}$ for cystamine). It was found that ring disulfides (lipoic acid, lipoamide) react more rapid than linear disulfides. LC-MS analyses show formation of mono- (thiosulfinate) and di-oxygenated (thiosulfonate) products. The variation in quenching rates and product formation are ascribed to zwitterion stabilization by neighboring, or remote, lone pairs of electrons. These data suggest that some disulfides, including some present within or attached to proteins (e.g., α-lipoic acid), may be selectively modified, and undergo subsequent cleavage, with adverse effects on protein structure and function.

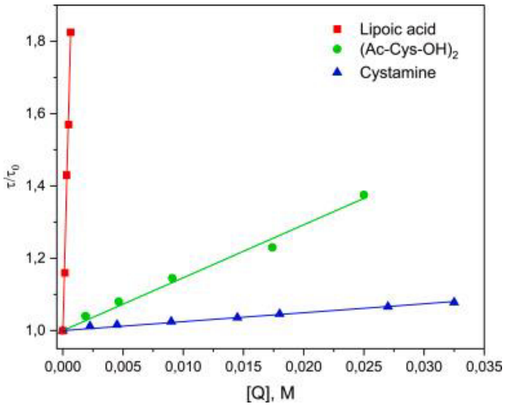

Figure 1. This Stern-Volmer plots for the quenching of $^1O_2$ by selected disulfides in D_2O-based 0.1 M phosphate buffer solutions (pD = 7.8 = pH + 0.4): α-lipoic acid (red squares), $(N\text{-}Ac\text{-}Cys)_2$ (green circles), and cystamine (blue triangles).

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Wavelength-Dependent Enhancement Studies for Optimizing Excitation in SERS Spectroscopy

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Surface-enhanced Raman scattering (SERS) achieves extraordinary analytical sensitivity through electromagnetic field amplification by plasmonic nanostructures, enabling single-molecule detection with enhancement factors exceeding ten orders of magnitude. Beyond electromagnetic enhancement, complex physical and chemical processes—including charge transfer and molecular chemisorption—significantly influence spectral characteristics and detection capabilities.

Excitation wavelength selection determines both signal intensity and spectral band distributions, reflecting the interplay between plasmonic resonances and molecular electronic transitions. Our systematic investigation of wavelength tuning effects on detection sensitivity reveals that even minimal deviations from optimal electronic transition energies substantially reduce resonant Raman contributions, directly impacting detection limits.

Using porphyrin derivatives on gold nanorods, we demonstrate how excitation profile analysis provides insights into molecule-nanostructure interactions and electronic structure modifications upon adsorption. [1] Observed spectral shifts indicate that maximizing SERS enhancement requires understanding and compensating for surface-induced changes in molecular electronic properties.

This methodology establishes a framework for wavelength optimization in analytical SERS applications while advancing fundamental understanding of molecule-nanostructure interactions and the underlying physicochemical processes governing surface-enhanced spectroscopic phenomena.

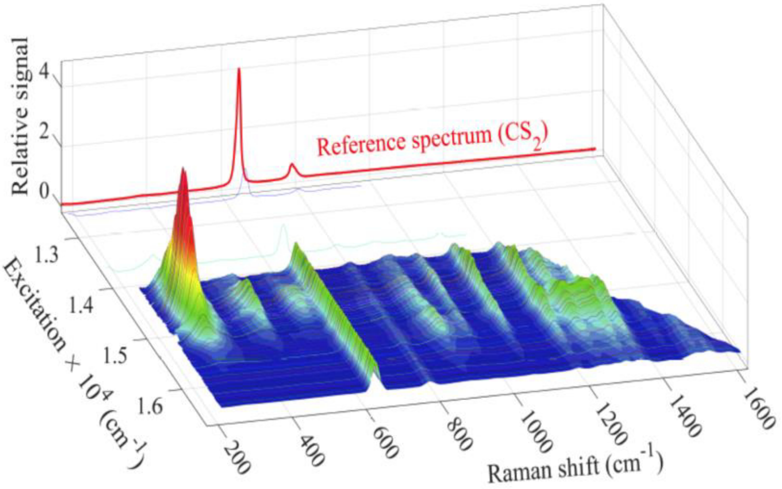

Figure 1. SERS excitation dependence of meso-dicyclopentyl-porphycene.

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Photochemistry of quinoxaline derivatives in methanol and hydrogenation of aza-arenes

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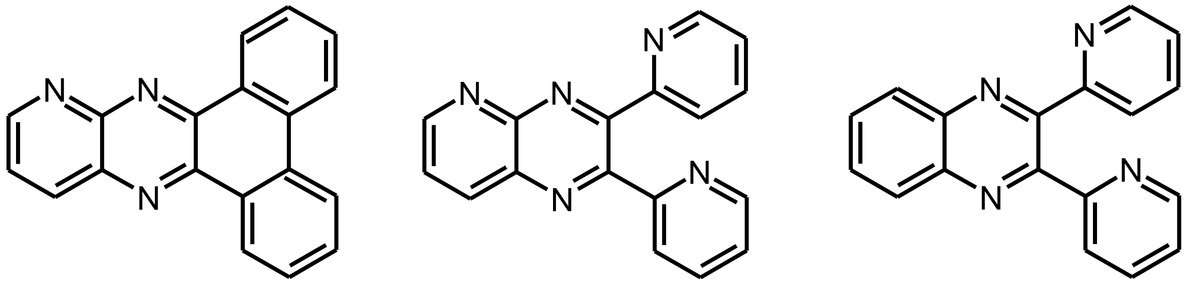
Three quinoxaline derivatives (Scheme 1) were investigated experimentally and explored theoretically to check their ability to photocatalitic alcohol splitting [1]. Theory predics the structures form hydrogen bond complexes with protic solvents' molecules. In electronic excited state of the complex electron and proton are transferred from solvent's molecule onto the photocatalyst *(Proton Coupled Electron Transfer* - PCET). This results in hydrogenation of the catalyst that may serve as hydrogen store. Optical study of these molecules fully confirms theoretical predictions. In all quinoxaline derivatives studied the lowest excited singlet state has the nπ* character whereas the second excited singlet has the ππ* character. Photochemical reactivity of the S_1(nπ*) and hydrogenation of photocatalyst was evidenced by changes in absorption spectra as well as in NMR and high resolution mass spectra. The introduction of oxygen into the solvent with hydrogenated molecules leads to the dehydrogenation of the photocatalyst. However, cyclic hydrogen attachement and detachement is only partially reversible, since in parallel to the photocatalytic hydrogenation of the molecules, their methoxylation and methylation occur in methanol. For PQ2Py and Q2Py, loss of the pyridine ring and rapid degradation were observed. In contrast, PQPhen having a more compact structure, can survive several cycles of hydrogenation and dehydrogenation. This observation is an important clue for the search for new and stable photocatalysts for the splitting of alcohols or water, which could have applications in the practical production of hydrogen gas.



PQPhen **PQ2Py** **Q2Py**

Scheme 1. Structures of the studied molecules.

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Towards Better TADF Photocatalysts: Mechanistic insights and Practical Tools For Understanding Electron Transfer dynamics

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Chromophores displaying Thermally Activated Delayed Fluorescence (TADF) have gained significant importance in the field of photocatalysis owing to their peculiar photophysical properties and to their easy and cost-effective synthesis. Particularly, the class of TADF chromophores based on the isophtalonitrile core with carbazolyl or diphenyl amine substituents (Figure 1) collects some of the most used photocatalysts in modern photocatalytic synthesis.[1] These compounds show a very low ΔE_{S1-T1}, which allows to observe intersystem crossing ($S_1 \rightarrow T_1$, isc) and consequent reverse intersystem crossing ($T_1 \rightarrow S_1$, risc) at ambient temperature. During a photocatalytic process, this peculiar behaviour allows access to both S_1 and T_1 in the same molecule, depending on the combination of kinetic constants and quencher concentration. While being a significant advantage in terms of product yield, this aspect complicates the mechanistic investigation of a photochemical reaction involving a TADF photocatalyst.[2] Our research aimed at validating the methods used for more conventional photocatalysis in the case of TADF photocatalysts. In particular, by the use of a kinetic simulation we defined the validity limits of the Stern-Volmer analysis based on emission lifetimes and intensities. In addition to that, we analysed a simplified scheme of a photocatalytic reaction and we determined how the combination of kinetic constants and quencher concentration influence the consumption of the quencher during the reaction evolution. These information not only allow a deeper comprehension of the photocatalytic mechanism, but also enable targeted modifications to the TADF photocatalyst to improve product yield in the overall photoreaction.

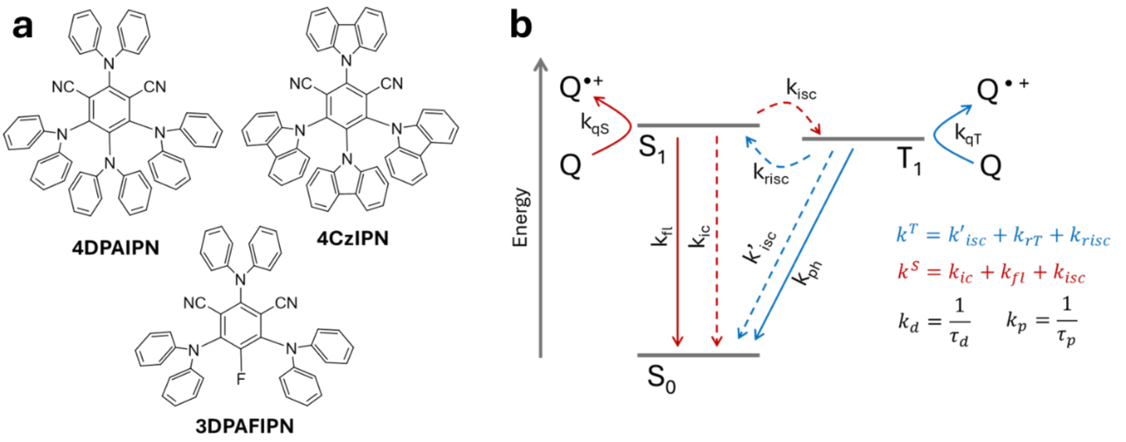

Figure 1: a) Chemical structure of some exponents of isophtalonitrile-based photocatalysts commonly used in literature. b) Jablonski diagram of TADF chromophores in the presence of a quencher.

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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).[3,4,5] 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.

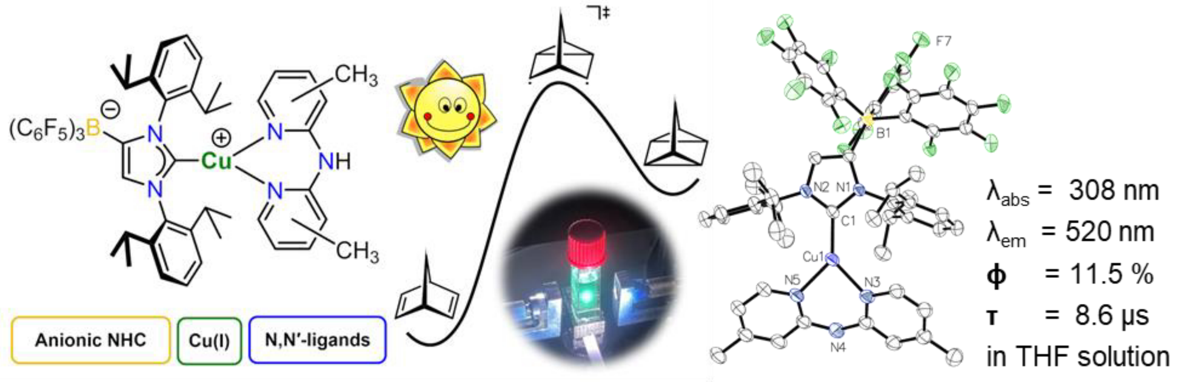

Figure 1. General structure of neutral [(WCA-NHC)Cu(N^N)] complexes (left) and a representative X-ray structure of complex C4 along with its main photophysical properties (right).

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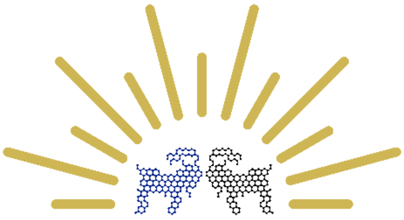

Poster presentation abstracts

AMIBO dyes: a yet unexplored family of boronic acid derivatives.

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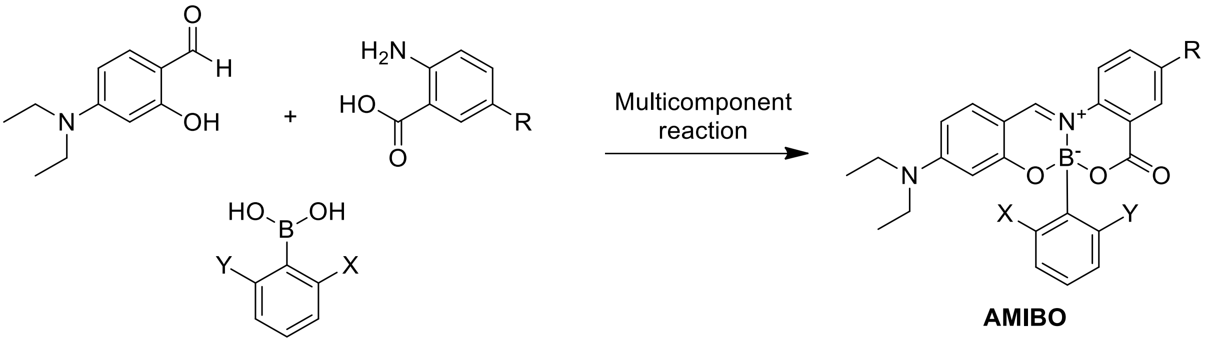
Organoboron chromophores are found among the most widely studied organic cromophores, due to their high structural versatility. Including boron-containig heterocycles with aromatic polycyclic architectures can taylor the photophysical properties of the systems and ultimately enable the fine-tuning of fluorescence [1,2].

In this contribution, we describe the design, synthesis, and caracterization of a boronic acid-containing molecular scaffold: AMIBO (2-**AM**inobenzoic acid derived **I**mino**BO**ronates) dyes. This molecular architecture, despite its synthetic ease and interesting properties, remains largely underexplored in the chemical literature. The basic structure presents an aromatic polycyclic core, with a central tetrahedral boron atom, as part of an iminoboronate complex.

We have studied a set of AMIBO dyes bearing a diethylamino electron donor group, and a variety of electron withdrawing groups located on opposite distal position of the structure, to understand the effect of the *push-pull* charge-transfer excited state on the photophysics and photochemistry of the systems. In an attemp to deepen our knowledge of this architecture we have also made alternative approaches[3,4] towards the structural and functional diversification of the systems. This includes the improvement of hydrolytic stability and of the photosensitization of singlet oxygen formation.



Scheme 1. General synthesis and structure of the AMIBO dyes studied in this work.

Acknowledgments

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Theoretical modeling of D-sp3-A type donor-acceptor systems with exotic excited states

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Donor-acceptor systems (D/A) are widely used in optoelectronics. Among the properties of the D/A systems that determine their potential applicability one of the most prominent is the nature of the low-energy electronic states: what are their relative energies, are they optically accessible, how fast are the transitions between them (especially the inter system-crossings), and how large are the charge transfer (CT) contributions. The most common DA systems are those with the D and A moieties linked by a single bond. Much less studied are system in which there is a spiro connection between the two fragments. Interesting examples of the latter systems are analogues of the malachite green lactone: MGLA and MGLA-C5. These two rather small molecules possess surprisingly diverse low-energy excited states, showing complex photophysical behavior.

In this work we model their experimental absorption spectra by means of the (TD)DFT calculations, employing several exchange-correlation functionals, as well as the *ab initio* approach. It turns out that the dominating band in the absorption spectra is mostly due to the local excitation on the donor moiety, whereas the low energy smaller band is composed of two transitions, a local and a predominantly CT one. After geometry relaxation, the latter is strongly red shifted, becoming the lowest excited singlet state. We then focus on its character and changes introduced by the influence of different solvents, their impact on the dipole moment of the two lactones in this state, and on the shifts of the fluorescence band. The extremely strong solvatofluorochromism reported for the studied lactones [1,2] is especially interesting, as it provides an excellent playground for testing the performance of different quantum-chemistry methods and different approaches to treating the solute-solvent interactions. We demonstrate that the most commonly used approach to describing excited states in solutions (LR-PCM/TDDFT) utterly fails in capturing the solvent induced fluorescence shifts.

It requires self-consistent treatment of the excited state electronic density and solvent polarization to approach the experimental values. In order to avoid the notorious sensitivity of TDDFT to the choice of functional, however, one must either employ the *ab initio* methods, or use the Restricted Open-shell Kohn Sham (ROKS) approach, in which the lowest excited singles state is calculated in the same manner as the ground state. The ROKS results are thus far less functional-dependent than TDDFT, while approaching or even surpassing the accuracy of *ab initio* methods in capturing the experimentally observed solvatofluorochromism. Eventually we observe that the calculated dipole moment in the S_1 excited state significantly changes with the solvent polarity, which raises the question regarding the applicability of approaches that estimate the excited state dipole moments assuming their constant values, such as those based on the Lippert Mataga equation.

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Modification of Tetrapyrrolic Photosensitizers to Enhance Photodynamic Therapy Efficiency

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Photodynamic therapy (PDT) is an emerging anticancer approach that relies on light-activated photosensitizers (PSs) to generate reactive oxygen species (ROS). The generated ROS disrupt tumor cells via oxidative stress, impair vasculature, and stimulate immune mechanisms within the tumor microenvironment (TME).

In this study, several structurally modified PSs were investigated to improve photodynamic performance. Metalation with Zn^{2+} or Pd^{2+} was used to enhance spin-orbit coupling and promote triplet formation, while macrocycle reduction from porphyrin to bacteriochlorin enabled red-shifted absorption into the near-infrared (NIR), crucial for deeper tissue penetration. These modifications improved photophysical and biological properties.

The compounds were evaluated for light absorption, photostability, ROS generation, lipophilicity (log P), and triplet-state lifetime, a key parameter affecting therapeutic efficiency. *In vitro* studies included cellular uptake, dark toxicity, and phototoxic response in cancer cells. Importantly, *in vivo* results demonstrated that a selected bacteriochlorin derivative preferentially accumulates in tumor tissue and remains there for an extended period, ensuring sustained therapeutic potential. These findings support the rational design of next-generation PSs for more effective PDT.

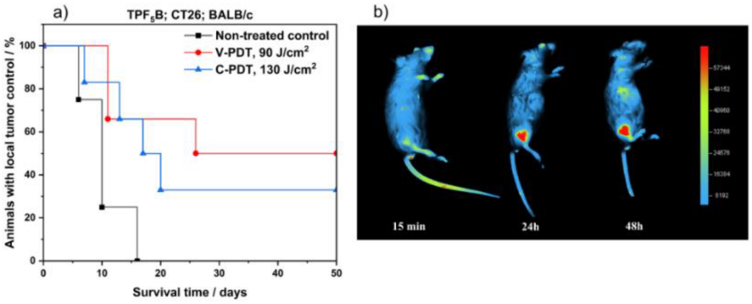

Figure 1. (a) Antitumor efficacy of TPF_5B formulated in Pluronic P123 micelles against CT26 tumors in the BALB/c mouse model, evaluated at DLI = 15 min (V-PDT) and DLI = 24 h (C-PDT). (b) Whole-body fluorescence imaging of BALB/c mice bearing CT26 tumors in the right leg, captured at 15 minutes, 24 hours, and 48 hours after intravenous injection of 1.5 mg/kg TPF_5B-P123.

Acknowledgments

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Structural Isomer Engineering for Tunable TADF/RTP Emission and Improved Photodynamic Therapy Outcomes

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Image-guided photodynamic therapy (PDT) has emerged as a powerful, minimally invasive technique for cancer treatment. Although organic luminogens exhibiting thermally activated delayed fluorescence (TADF) and room-temperature phosphorescence (RTP) have shown promise in PDT applications, a direct comparative investigation of their photophysical behavior and therapeutic efficacy remains underexplored.[1-3] In this study, two aggregation-induced emission (AIE)-active positional isomers, 4-CBT2 and 3-CBT2, were rationally designed and synthesized by altering the position of carbazole units on a phenyl core. This positional modulation led to distinct variations in molecular conformation, which in turn influenced crucial photophysical parameters, including the singlet–triplet energy gap (ΔE_{ST}), rates of reverse intersystem crossing (RISC) and intersystem crossing (ISC), spin–orbit coupling (SOC), radiative decay rates (k_r) and the nature of the triplet states. These changes effectively tuned the emission channels from TADF to RTP in their condensed state. Both isomers were subsequently employed as photosensitizers for image-guided PDT, offering a direct, systematic comparison of ROS generation efficiency and therapeutic performance between TADF and RTP-active systems. This study not only elucidates the mechanistic influence of emission pathways on ROS production but also provides valuable guidelines for the rational design of next-generation organic photosensitizers for advanced phototherapeutic applications.

Acknowledgments

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Reactivity by design: oxidation pathways of structurally varied disulfides

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Sulfur–sulfur bonds, specifically disulfide linkages, are fundamental structural components within proteins, playing a critical role in stabilizing their three-dimensional conformation and directly influencing their biological activity. Disulfide bonds, due to their high reactivity and structural importance, are also prime targets for oxidative modification.[1] Disruption or alteration of these bonds typically results in the destabilization of the protein's folded state. These modifications often lead to impaired function or irreversible damage in proteins, resulting in numerous pathological conditions including neurodegenerative diseases, cardiovascular disorders, and various protein aggregation-related dysfunction.[2] Previous investigations have demonstrated significant variability in the susceptibility of disulfide bonds to oxidative agents, depending on their conformations and the rigidity associated with them.[3]

The present study explores the possible mechanisms photooxidation of differing in terms of structure disulfide models, mediated by 3-carboxy benzophenone (3CB) under anaerobic conditions. Through this work, the aim is to identify and characterize the stable products formed from disulfide models, exposed to the photosensitizer and evaluate the structural and functional consequences of such modifications. The findings of this study are expected to enhance our understanding of protein oxidative stability and contribute to the broader understanding of oxidative stress-related pathologies.

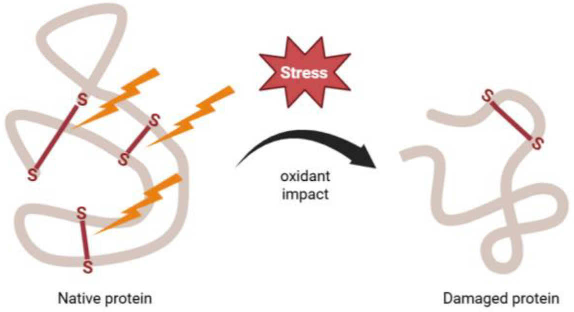

Figure 1 Conceptual representation of the oxidative damage to a protein structure, resulting in its dysfunction

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Crystallographic and spectroscopic insights into metal-metal interactions in square-planar Pd(II) and Pt(II) complexes

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This study reports a comparative crystallographic study of two coordination complexes featuring 2-isocyano-1,3-dimethylbenzene ligands with palladium(II) and platinum(II) centers. The compounds were synthesized via a modified literature protocol[1] and crystallised from hexanes. Single-crystal X-ray diffraction experiments revealed both compounds form a triclinic crystal structures (P -1 space group) and exhibit square-planar geometry around the metallic centres. A key structural feature observed in both complexes is the formation of dimeric units stabilized by close metal–metal contacts. Metal-metal distances reached 4.1885(4) Å (Pt) and 4.1751(4) Å (Pd) at room temperature. Moreover, cooling the experiment temperature down to 100 K results in a noticeable (ca. 5%) decrease of the metal-metal distance, suggesting a thermally responsive behaviour.

Further studies involve spectroscopic and theoretical investigations aimed at understanding how dimeric metal-metal interactions influence the physicochemical properties of studied compounds. Additionally, we plan to explore how factors such as temperature and pressure affects the crystal structure and complex optical properties.

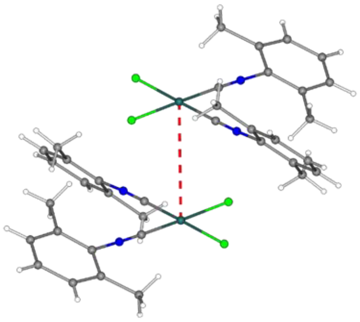

Figure 1 Characteristic dimeric motif with metal-metal interactions marked with red thick line

Acknowledgments

The authors thank the SONATA BIS grant (2020/38/E/ST4/00400) of the National Science Centre in Poland for financial support. The Wrocław Centre for Networking and Supercomputing (grant No. 285) is gratefully acknowledged for providing computational facilities. The in-house X-ray diffraction experiments were carried out at the Department of Physics, University of Warsaw, on a Rigaku Oxford Diffraction SuperNova diffractometer, which was co-financed by the European Union within the European Regional Development Fund (POIG.02.01.00-14.122/09)

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Theoretical Insights into the Photochemistry of Triarylhydrazone Photoswitches

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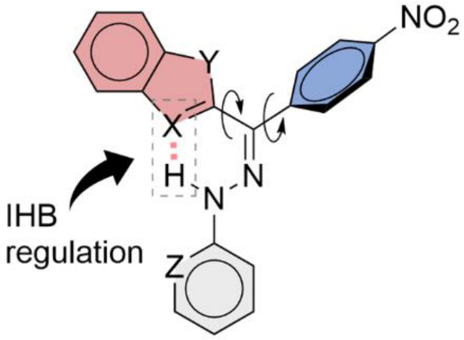
Triarylhydrazones (TAHZs) complement the growing family of recently discovered diarylhydrazone photoswitches. They typically exhibit higher molar absorptivities and operate under longer-wavelength light, while retaining the appealing features of diarylhydrazones—such as excellent addressability and high thermal stability of both isomers. However, TAHZs often suffer from low quantum yields for *Z*-to-*E* photoisomerization due to relatively strong excited-state intramolecular hydrogen bonding (IHB) in the *Z* isomer. While IHB contributes to a large separation between absorption maxima, it also promotes competing deactivation pathways that reduce the efficiency of photoisomerization. In this contribution, we present a strategy to weaken IHB through judicious selection of heteroaryl substituents. This approach not only significantly enhances the *Z*-to-*E* photoisomerization quantum yield but also preserves molecular addressability. This is achieved by decreasing the intensity of the S_0–S_1 transition and enabling the appearance of bright higher excited states in the *E* isomer. While in solution the excited-state intermolecular proton transfer (ESIPT) limits photoswitching efficiency, we demonstrate that in the solid state it may give rise to a novel type of photochromism in hydrazones.



Scheme 1. General structure of the studied molecules, with X, Y, and Z representing variable heteroatoms.

Acknowledgments
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Determining The Flexoelectric Response of Strontium Titanate Cantilevers by Nanoindentation Instrumentation

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Flexoelectric effect is a phenomenon where an electric polarization is induced in a material due to a non-uniform strain gradient. Compared to similar phenomena like piezoelectricity and ferroelectricity, this effect is not limited by specific geometries or crystalline structures, which makes it significant in energy harvesting. The effect is currently characterized by methods such as Dynamic Mechanical Analyzer or techniques based on Scanning Probe Microscopy. The main drawbacks of those methods are the limited achievable oscillation amplitude of a contact tip and the relatively large size of the sample. This work presents a novel and unique characterization method based on the Nanoindentation Instrumentation. Here, using direct mechanical excitation on free-standing cantilever beams, the flexoelectric response of a single strontium titanate crystal (STO) can be experimentally obtained by sub-micrometre oscillations. See **Figure 1**. Contrary to the common methods, the presented method allows access to a relatively small strain field and proves effective for investigating the responses of significantly smaller materials. Additionally, a scientific model is presented using COMSOL Multiphysics software. The model simulates the cantilever strain gradient and the flexoelectric potential.

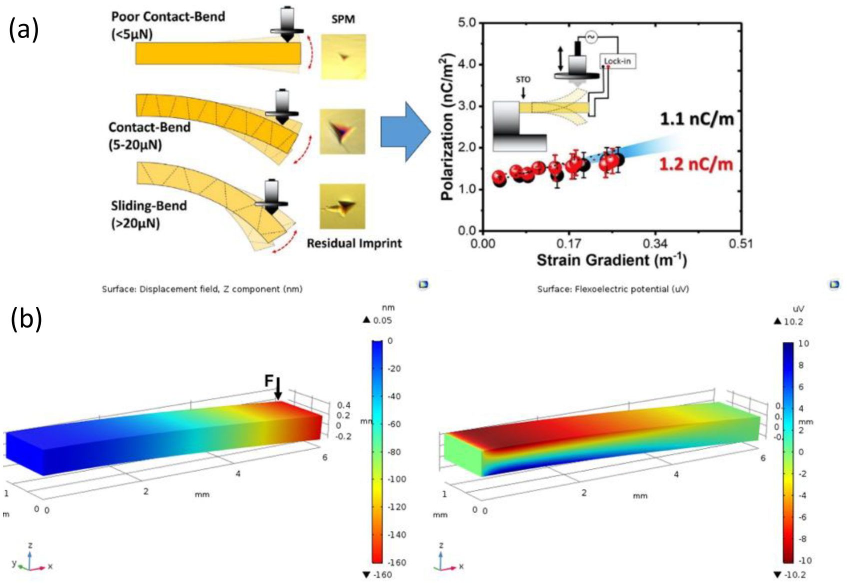

Figure 1: (a) Schematic illustration of the contact bending at a different load and the corresponding residual imprint. Flexoelectric Polarization was measured from both sides of the cantilever, in agreement with the reported values for STO [1]. (b) COMSOL model of the cantilever showing the displacement and the corresponding flexoelectric potential.

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Computational quest for new organic molecules with excited-state singlet-triplet inversion and high oscillator strength

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The discovery of metal-free organic chromophores that can serve as efficient emitters in organic light emitting diodes (OLEDs) has transformed the materials science of optoelectronic devices in recent years. In OLED emitters, the lowest singlet (S_1) and triplet (T_1) excited electronic states are populated by the recombination of injected electrons and holes in a 1:3 ratio according to spin statistics. The high population of the "dark" T_1 state is unfavorable for achieving high fluorescence quantum yields. The common solution is to maintain a sufficiently small, positive S_1-T_1 energy gap, enabling reverse intersystem crossing (RISC) at room temperature. This process populates the S1 state from the T_1 state, as observed in thermally activated delayed fluorescence (TADF) materials. Recent studies,[1,2] however, have shown that certain closed-shell, nitrogen- and boron-doped organic molecules deviate from Hund's rule, exhibiting an inverted singlet-triplet (IST) ordering where the lowest excited singlet state (S_1) has lower energy than the lowest triplet state (T_1). This reversal of energy levels enables down-conversion from the triplet to the singlet state, a process that should be more efficient than in the typical TADF emitters.

The primary challenge in designing suitable IST molecules for use as OLED emitters stems from their low fluorescence rate. In our recent theoretical investigation, we propose a novel class of IST molecules that exhibit high oscillator strength while retaining inversion or near degeneracy of the first singlet and triplet excited states.[3]

Acknowledgments

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Back to nature – A small Mg(II)-complex as a chlorophyll analogue

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Jäger-type ligands with dianionic tetradentate N_2O_2 coordination sites are well suited for imparting interesting functionality towards 3d transition metals, especially iron(II) ions. [1, 2] They are far less well suited to coordinate the harder main group ions, e.g. Mg(II), Al(III), which require the ligands to be adapted regarding their "hardness", e.g. by integrating electron withdrawing groups into the ligand backbone. As a promising candidate in this direction we identified a nitrile-appended ligand which opened the path to coordination dependent, ligand-based photophysical properties with the respective Zn(II) complexes. [3, 4] Here the metal centre acts as a "rigidity anchor", a role reminescent of Mg(II) ions in chlorophyll, which ridify and anchor the chlorine macrocycle to the membrane. Indeed, our electron-poor ligand system coordinates readily to Mg(II) ions, giving highly photoactive Mg(II) complexes, which can act as a functional chlorophyll model system. Attractive features subsume its ready synthetic access from feedstock chemicals and small molecular size: Structural complexity is reduced to its minimum while function is retained.

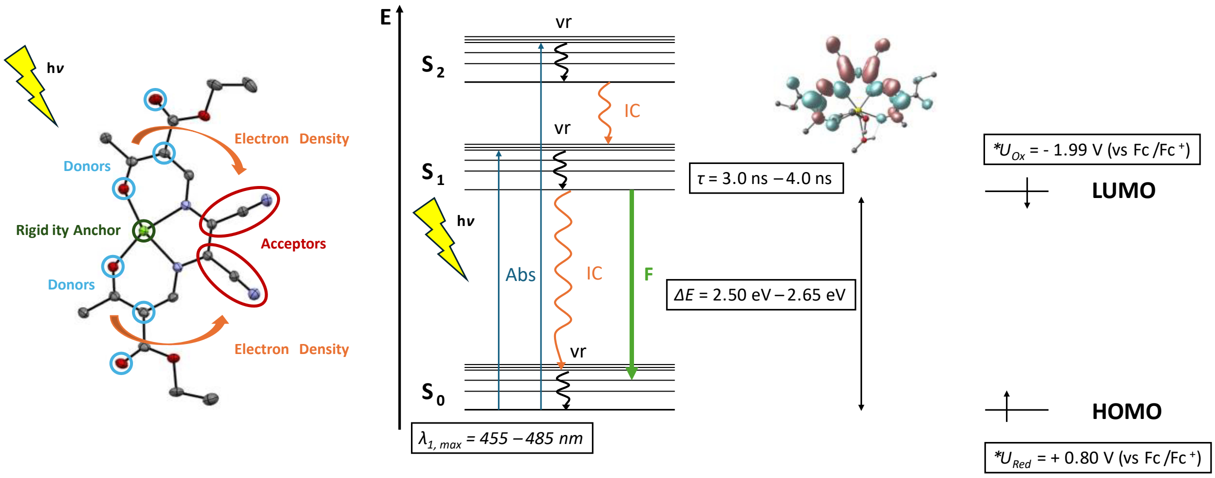

Figure 1: Functional roles of complex moietiesin light triggered electronic transitions and concise overview of important photophysical data.

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Spectroscopy and photophysics of nitro-substituted porphycenes.

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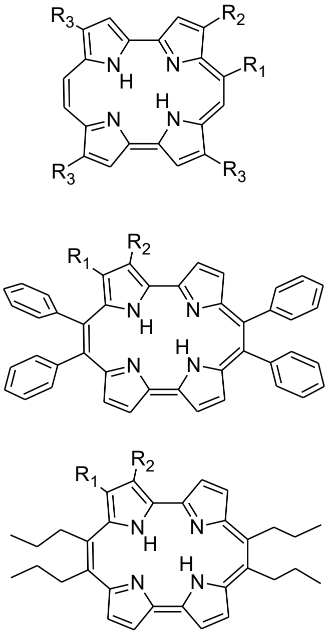
Porphycenes, structural isomers of porphyrins, attract interest regarding fundamental research (as models of intramolecular hydrogen bonds and single/double hydrogen transfers) and applications (as photosensitizers in photodynamic therapy and photoinactivation of bacteria). In this work, spectroscopy, photophysics, and singlet oxygen generation efficiency were measured for a series of novel porphycenes (Figure 1), singly substituted with a nitro group at all three possible locations on the macrocycle periphery (*meso*, *β*, *β'*).

Porphycenes belong to the group of hard chromophores, for which the absorption characteristics do not change much upon substitution. Photophysical parameters, however, change drastically across the series, depending on the position of the nitro group and the proximity of another substituent: *n*-propyl or *t*-butyl moiety. In addition, tautomeric equilibria also depend on the substitution pattern [1]. The results should allow rational design of porphycenes depending on the specific problem to be tackled.



$R_1 = R_2 = R_3 = H$
$R_1 = H$; $R_2 = R_3 = n$-Pr
$R_1 = H$; $R_2 = R_3 = {}^t$Bu
$R_1 = NO_2$; $R_2 = R_3 = H$
$R_1 = NO_2$; $R_2 = R_3 = n$-Pr
$R_1 = NO_2$; $R_2 = R_3 = {}^t$Bu
$R_1 = H$; $R_2 = NO_2$; $R_3 = {}^t$Bu

$R_1 = R_2 = H$
$R_1 = NO_2$; $R_2 = H$
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$R_1 = R_2 = H$
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$R_1 = H$; $R_2 = NO_2$

Figure 1. Derivatives of porphycene substituted with a nitro group.

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Photochemistry of chiral porphyrin assemblies on thin ferromagnetic films

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Magnetic inorganic–organic hybrid materials have become a hot topic in science, partly due to the discovery of the chiral-induced spin selectivity effect (CISS) [1]. This effect, occurring in chiral organic layers, can be utilized for storing, transferring [2], and processing information in future molecular spintronics devices. In this study, we used spectroscopic methods to examine how the magnetization of Co/Ni ferromagnetic layers, covered with a thin gold layer, influences porphyrin molecules adsorbed on their surface (Fig. 1A). The porphyrins used were 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrins with polypeptide chains in L- and D-enantiomeric forms. Adsorption from solution onto FM-coated substrates led to the formation of self-assembled monolayers (SAMs).We compared the optical properties of the porphyrins in solution with those in SAM form, using both steady-state and time-resolved spectroscopic techniques. While the two enantiomers behaved identically in solution, femtosecond transient absorption experiments on the solid samples revealed differences in their bleach decay, depending on the magnetization of the FM layer. These differences were not observed in samples without the ferromagnetic layer, indicating a molecular-level interaction between the chiral system and the FM layer.

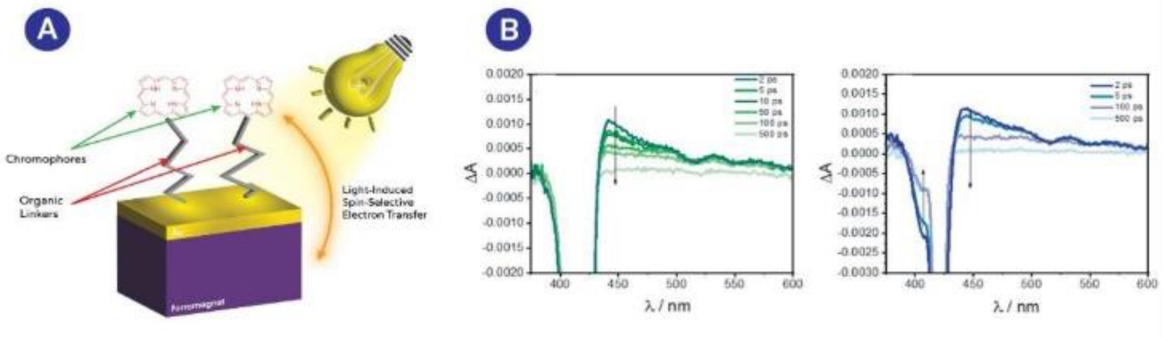

Figure 1. (A) Schematic representation of the FM/chiral self-assembled monolayer system. **(B)** Transient absorption spectra of FM/organic samples under a modulated magnetic field.

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Precision at the Nanoscale: 3D Printing Functional Nanocomposites with DLP Technology

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Photoinduced polymerization is growing in popularity as an environmentally friendly and safe method of manufacturing polymeric protective coatings on various surfaces. The main advantage of photopolymerization over other methods of preparing polymer coatings is its speed. Currently, photopolymerization techniques have found wide application in the microelectronics industry, in stereolithography, in medicine - for obtaining polymer hydrogels used for wound healing), and in dentistry for making photocurable fillings. [1] 3D printing is an additive manufacturing method that is considered one of the most advanced methods of creating materials. This is mainly due to the lack of need for mechanical processing of the resulting objects. 3D printing techniques based on photopolymerization, such as stereolithography (SLA) and digital light processing (DLP), are currently attracting a lot of attention due to their versatility and ability to be customized. They are characterized by a number of advantages, which include: producing materials with well-defined geometries. [2] Composite materials are a class of multifunctional materials that are very popular due to their favourable properties. Especially worthy of attention are nanocomposite materials, in which the addition of nanofiller changes the final properties of the product, for example improves its thermomechanical properties, increases heat resistance, and provides conductive properties. The final properties depend on selecting an appropriate nanofiller, among which carbon nanotubes, silica and natural and polymer fibres are widely used additives. [3].

The present work is concerned with the application of new high-performance terphenyl derivatives to the role of photosensitizers of the diphenyliodonium salt IOD for initiating radical, cationic and hybrid photopolymerization under UV-Vis light. Subsequently, the possibility of employing two-component initiating systems in DLP 3D printing to obtain polymer nanocomposites was investigated. According to a series of studies, the most effective initiator system was selected, which was further used for 3D printing application studies.

Acknowledgments
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Three-dimensional TiO_2-based photocatalytic matrices for selective pharmaceutical removal from aqueous solutions

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Titanium dioxide (TiO_2) is a pivotal material in photocatalysis due to its chemical stability, non-toxicity, and strong oxidative properties. However, its powdered form faces practical limitations, such as recovery difficulties, agglomeration, and restricted active surface area, which hinder broader applications [1]. To address these issues, designing TiO_2 in 3D structures, such as sponges, offers significant advantages. Three-dimensional architectures not only facilitate better handling and recovery but also provide enhanced light penetration, increased mass transfer, and a larger effective surface area [2,3]. The sponge-like matrices mimic natural systems, ensuring a more uniform distribution of active sites and improved interaction with target pollutants, making them particularly promising for environmental and energy applications. To overcome these challenges, research has focused on modifying the structural and morphological properties of TiO_2 [4,5]. This study proposes the use of biomimetic sponge matrices as templates for TiO_2 deposition. Inspired by the hierarchical and porous architectures found in nature, these structures enable precise control over TiO_2 crystallization. While sponges have been previously utilized for TiO_2 deposition, no comprehensive study has directly compared different sponge matrices within a single investigation. Moreover, the influence of the sponge structure itself on the deposition process and resulting material properties remains largely unexplored. The resulting three-dimensional (3D) materials, developed in this study, feature uniform TiO_2 coverage, enhanced active surface area, improved light absorption, and more efficient charge separation, all contributing to superior photocatalytic performance. The development process involved careful selection of sponge matrices and advanced deposition techniques such as sol-gel processes and hydrothermal synthesis. Material characterization using SEM, XRD, and UV-Vis spectroscopy provided a detailed understanding of the relationship between structure and photocatalytic activity. The effectiveness of these innovative 3D TiO_2 materials was demonstrated in the degradation of pharmaceutical contaminants like ketoprofen in wastewater. These materials significantly outperformed conventional TiO_2 powders and also showed promise in hydrogen generation under solar irradiation. In conclusion, biomimetic sponge matrices offer a transformative approach to designing next-generation photocatalysts, addressing the limitations of conventional TiO_2 and paving the way for more efficient and sustainable systems for water purification, environmental remediation, and energy production.

Acknowledgments

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Impact of Device Architecture on Recombination Dynamics in Bifacial Perovskite Solar Cells

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Metal halide perovskites have emerged as one of the most promising materials in the field of photovoltaics due to their exceptional optoelectronic properties, ease of fabrication, and tunable band gap. Their unique crystal structure facilitates high absorption coefficients, long carrier diffusion lengths, and low exciton binding energies [1]. These characteristics have enabled perovskite solar cells (PSCs) to achieve rapid efficiency improvements, now reaching 27% in laboratory-scale devices, approaching the performance of crystalline silicon while benefiting from lower processing temperatures and compatibility with flexible substrates [2]. Furthermore, perovskites can be easily processed through solution-based methods, allowing for scalable and cost-effective manufacturing. Their compositional versatility also opens the door to various tandem and hybrid configurations. Despite these advantages, stability, hysteresis, and interfacial losses, particularly those arising from non-radiative recombination, remain significant challenges that limit the commercialization of perovskite technologies.

Bifacial design plays a significant role in enhancing photocurrent efficiency and power output, with the ability to absorb direct and reflective sunlight radiation without significantly increasing the cost of PSCs [3]. Designs with quasi-2D perovskite layers are well suited for bifacial devices thanks to excellent optoelectronic properties, including long charge carrier diffusion lengths, tunable bandgap, and high absorption coefficient. However, the design of the bifacial PSCs includes some challenges. One of the critical challenges is the recombination of charge carriers at the interfaces, which limits the performance of bifacial PSCs [4].

In this study, we fabricated guanidinium (GA)-based quasi-2D PSCs using transparent gold (10 nm layer thickness) as a back electrode material, and two electron transport layers (ETLs): TiO_2 and SnO_2. Open-circuit voltage decay transient measurements were performed to quantitatively analyze the dominant recombination mechanisms in these devices. PSCs employing SnO_2 as the ETL demonstrated superior performance compared to those with TiO_2, showing enhanced bifaciality and reduced recombination losses. These results offer valuable insights into light-matter interactions and contribute to the advancement of high-performance, stable, and flexible optoelectronic devices.

Acknowledgments

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Investigating Nonlinear Optical Properties of Crown Ether Au_{25} Nanoclusters for Multiphoton Microscopy.

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Metal nanoclusters have a size of less than 3 nm, exhibit quantum confinement effect, possess nonlinear optical properties, biocompatible, and are also photostable[1]. Also, nanoclusters show both linear and nonlinear optical properties. These properties make nanoclusters a promising fluorescence probe for bio-imaging, such as multiphoton-excited fluorescence microscopy. Advantages of using these NLO properties include deeper penetration in biological entities, significantly reduced biological tissue light dispersion, and reduced autofluorescence[2].

But before that, it will be important to investigate the optical properties of the NCs, especially the two-photon cross-section area and brightness. For our studies we are using crown ether Au_{25} nanocluters[3] and for the measurements of NLO properties, we are using custom-built multiphoton microscope consisting of a femtosecond mode locked Ti: Sapphire laser (~100 fs, 80 MHz, Chameleon, Coherent Inc.) with incident wavelength range tunable within λ = 690-1080 nm and an optical parametric oscillator Chameleon OPO (Coherent Inc.) with an output signal tunable at λ = 1000-1600 nm.

Additionally, we are examining both linear and non-linear properties in relation to various environmental conditions, for example, the polarity of solvents. To support these measurements, we are utilizing the amphiphilic nature of the crown ether[4], which allows our clusters to dissolve in different solvents, like water, DCM, and toluene.

This study can contribute to a better understanding of nanoclusters' behaviour in different environments, i.e., solvents, in terms of their optical properties, including nonlinear properties. Such work is needed as NCs can be utilized as functional probes for multiphoton imaging of biological samples like amyloid aggregates easpically spherulities.

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Semiconductor photocatalysis in Advanced Reduction Processes

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Advanced Reduction Processes (ARPs) include techniques able to achieve degradation of contaminants by producing highly reactive reducing species such as, electron, or $CO_2^{\bullet-}$[1]. Semiconductor photocatalysis is a highly effective and sustainable process leverages the unique redox properties of semiconductor materials under light irradiation to break strong carbon-halogen bonds, leading to detoxification and mineralization of these compounds. Semiconductor photocatalysts include metal oxides (TiO_2, ZnO, SnO_2, etc.) [1], metal chalcogenides (CdS, ZnS, MoS_2) [2, 3], spinel ferrites ($CoFe_2O_4$, $ZnFe_2O_4$, $FeFe_2O_4$, etc.) [4], perovskites ($BiFeO_3$, $SrTiO_3$) [5, 6]. The photocatalytic dehalogenation reaction can proceed through two pathways: (a) direct pathway - in which the photogenerated electrons are separated and captured by the contaminant molecules; and (b) the indirect path, in which photogenerated holes are used to produce reducing radicals by reaction with molecules such as $HCOO^-$, $C_2O_4^{2-}$ [7]. The overall efficiency of a semiconductor is dictated by three key intrinsic characteristics of the material: (i) small band gap allowing harvesting visible light (Fig. 1 a), (ii) absolute potentials of the E_{CB} and E_{VB} (Fig. 1 b), (iii) the rate of charge recombination. A small bandgap is desirable regarding a broad light absorption band. The band-edge positions play crucial role in conducting the corresponding oxidation and reduction reactions. However, when redox ability is considered, the catalyst should have a high CB position and a low VB position, resulting in a large bandgap. These two prerequisites are not compatible. To achieve higher light absorption and appropriate band potentials, the materials design strategies are used such as introducing point defects in semiconductors, or forming heterostructures with multiple semiconductors and other materials.

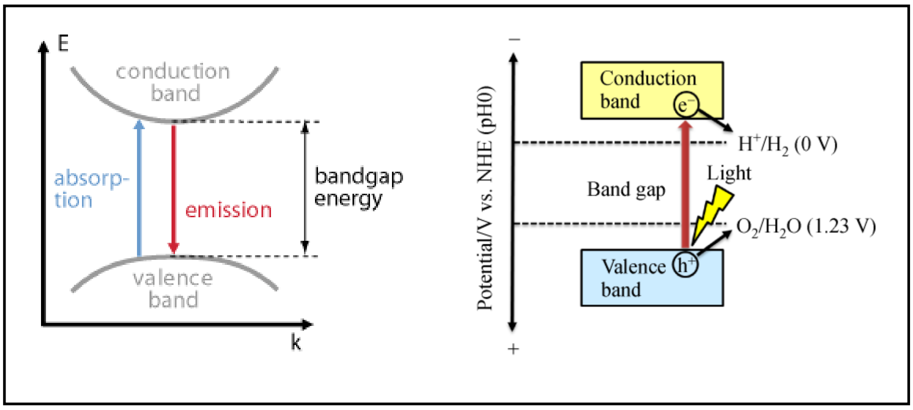

Figure 1. The band gap energy of semiconductoer (a) [8]; the minimum of the conduction band and the maximum of the valence band potential vs NHE.

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Solar Energy Efficiency in Poland and Its Potential in Hydrogen Photocatalysis

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The transition to clean energy sources is essential to mitigating climate changes and reducing greenhouse gas emissions. Hydrogen is a particularly promising zero-emission fuel, as its combustion produces only water. However, its common production methods – such as steam methane reforming – are enviromentally unsustainable [1]. In contrast, photocatalytic hydrogen production, which harnesses solar radiation, presents a promising solution. It relies solely on renewable inputs – water and sunlight – making it far more eco-friendly alternative.

To evaluate the real-world potential of photocatalytic hydrogen production, this research applied a system previously tested under laboratory irradiation using LED light sources [2]. The system consisted of eosin Y as the photosensitizer, cobalt(II) ions as the catalyst, triethanolamine as the electron donor, and graphene oxide as a 2D material enhancing electron transport. The aim was to compare the efficiency of hydrogen production under controlled laboratory conditions (LED irradiation) and in an environmental setup using natural sunlight (Figure 1).

Preliminary results indicate significant differences in hydrogen production efficiency depending on the testing conditions. Outdoor experiments showed approximately three times lower hydrogen production under cloudy skies, but about twice the yield on sunny days compared to laboratory results, confirming a strong dependence on light intensity and highlighting the potential of natural sunlight for practical applications.

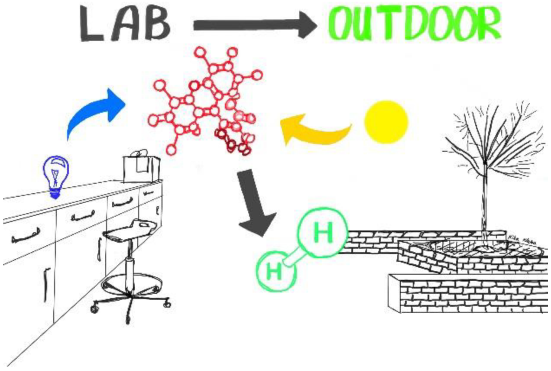

Figure 1. Schematic representation of the project concept

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Spectroscopic Characterization of Dual-Function *m*-THPC/Pluronic P123/Graphene Oxide Systems for Potential Application in Photodynamic and Photothermal Therapy

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The development of multifunctional therapeutic platforms that integrate photodynamic therapy (PDT)[1] and photothermal therapy (PTT)[2] offers a promising strategy for enhancing cancer treatment efficacy. In this study, we examined the spectroscopic characteristics and functional performance of a ternary hybrid system consisting of the photosensitizer *m*-THPC, Pluronic P123 micelles, and graphene oxide (GO). Encapsulation of *m*-THPC within P123 micelles improved its solubility, maintained its monomeric state in PBS, and enabled efficient singlet oxygen generation ($^1O_2$)—an essential component for PDT[3]. Incorporation of GO led to fluorescence quenching and suppression of triplet-state formation via ultrafast photoinduced electron transfer, thereby reducing PDT activity. However, GO also imparted notable photothermal conversion capability under near-infrared (NIR) irradiation. At optimized GO concentrations, partial retention of photodynamic activity was achieved alongside an effective photothermal response, suggesting a potential for synergistic therapeutic effects. These findings underscore the potential of carefully engineered *m*-THPC/P123/GO nanoplatforms as advanced multifunctional agents for combined PDT/PTT cancer therapy.

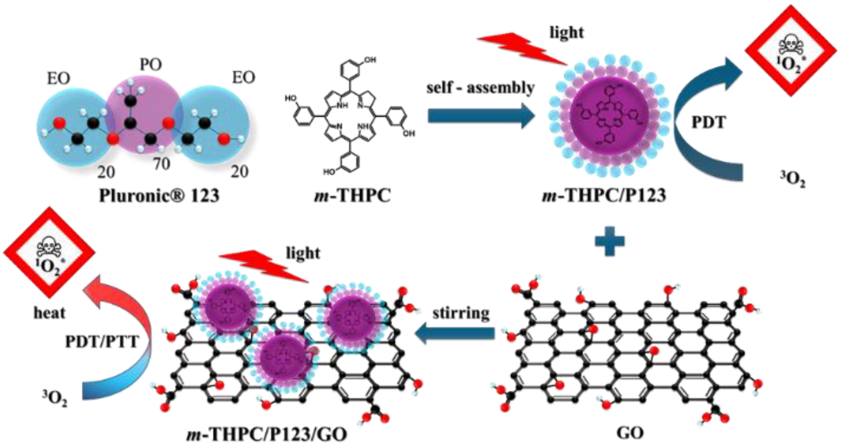

Figure 1. Schematic illustration of the ternary *m*-THPC/Pluronic P123/GO hybrid system for combined PDT/PTT therapy. Encapsulation of *m*-THPC in P123 micelles enables $^1O_2$ generation upon light irradiation. Upon integration with GO, partial quenching of PDT activity occurs via photoinduced electron transfer, while photothermal conversion under NIR light is introduced, supporting a dual PDT/PTT therapeutic effect.

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New Photoinitiating Systems for Radical Photopolymerization: Multifunctional Tools for Advanced 3D Printed Materials

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Radical photopolymerization is a versatile and rapidly evolving technology for the fabrication and curing of polymeric materials under light irradiation. Its excellent spatial and temporal control has led to broad applications in 3D printing, coatings, adhesives, electronics, and biomedical engineering. The efficiency of this process is critically dependent on the nature of the photoinitiating system, which is responsible for generating reactive radicals upon light exposure. However, conventional photoinitiators often face significant limitations, including poor solubility, narrow absorption spectra, and the lack of additional material functionalities [1],[2].

This study presents the design, synthesis, and comprehensive evaluation of novel ionic photoinitiating systems specifically engineered for radical photopolymerization. These systems combine light-triggered radical generation with the advantageous features of ionic compounds, such as enhanced solubility, tunable polarity, and intrinsic ionic conductivity. Both multicomponent (initiator/co-initiator) and single-component systems were developed, incorporating diverse ionic moieties (e.g., imidazolium, pyridinium, phosphonium) and chromophores responsive to UV and visible light. The integration of ionic functionality into the molecular architecture imparts a dual role—ensuring efficient photoinitiation and enabling the functional modification of the resulting polymer network.

A broad range of analytical techniques, including UV-Vis spectroscopy, fluorescence analysis, photo-DSC, and real-time FTIR spectroscopy, were employed to assess the photophysical, electrochemical, and kinetic behavior of the synthesized systems. Selected formulations demonstrated outstanding initiation efficiency and facilitated the formation of polymer networks with enhanced ionic transport properties and mechanical robustness. Their applicability in light-based additive manufacturing, particularly digital light processing (DLP), was validated through the successful fabrication of ion-conductive and electroactive polymeric structures.

These findings underscore the potential of ionic photoinitiating systems as multifunctional and high-performance alternatives to traditional photoinitiators, offering a promising platform for the development of next-generation photopolymer materials with precisely tunable physicochemical and functional properties.

Acknowledgments

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Effect of the remote amine groups in bis-cyclometalated iridium(III) complexes

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2,2′:6′,2″-Terpyridine (terpy) derivatives represent a versatile class of donor ligands known for their strong coordination ability with a wide range of transition metal ions. Structural modifications of the terpy core, particularly through the introduction of electron-donating substituents via phenylene linkers, enable the development of donor–π–acceptor (D–π–A) systems that reveal efficient Intramolecular Charge Transfer (ICT). These modifications significantly affect the photophysical properties of the resulting metal complexes by modulating the nature of their excited states. In Ir(III)-based systems, remote amine functionalities have been shown to markedly lower the HOMO–LUMO gap and stabilize ILCT-type (Intraligand Charge Transfer) excited states, which frequently manifest in pronounced bathochromic shifts in absorption abilities, deep-red phosphorescence and elongated photoluminescence lifetimes. These properties make terpy-based Ir(III) complexes highly attractive candidates for photofunctional applications, including OLEDs, photocatalysis, and photodynamic therapy [1, 2].

The current presentation is focused on the photophysics of a series of novel $[Ir(py\text{-}bzth)_2(R\text{-}C_5H_4\text{-}terpy)]PF_6$ complexes, where py-bzth denotes the 2-(pyridin-2-yl)benzothiophenato ligand ($C^\frown N$) and $R\text{-}C_6H_4$-terpy represents C_6H_5-terpy or 2,2':6',2''-terpyridines functionalized with electron-rich acyclic and cyclic amine groups (Figure 1). The role of the remote amine group in controlling of ground- and excited-state properties of $[Ir(py\text{-}bzth)_2(R\text{-}C_5H_4\text{-}terpy)]PF_6$ complexes has been evidenced by applying a wide range of techniques, including UV-Vis, static and time-resolved photoluminescence spectroscopy, and femtosecond ultrafast transient absorption spectroscopies.

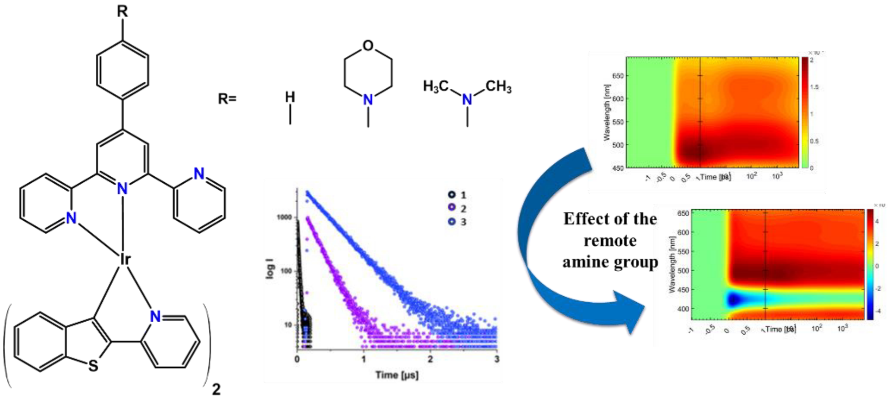

Figure 1. Schematic presentation of the discussed Ir(III) complexes.

Acknowledgments

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Emission properties of solute-solvent hydrogen-bonded complexes

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2-amino-7-nitrofluorene (ANF), an aromatic compound with donor-acceptor properties, is often used as a probe for solvatochromic studies [1,2]. It can form complexes with protic solvents through hydrogen bonds of two types, A and B, and with aprotic solvents through C-type hydrogen bonds (Fig. 1).

The project concerns spectral emission studies of ANF in two-component solvents consisting of a solvent that interacts only non-specifically with the addition of a solvent that forms donor or acceptor hydrogen bonds [3]. Based on the absorption data [4], the amount of added solvent was limited so that ANF-solvent complexes with 1:1 stoichiometry were formed, and their fluorescence spectra were determined. The results show that the position of the band maximum in the fluorescence spectra of ANF-solvent complexes is characteristic of complexes formed by a given type of hydrogen bonds. ANF-solvent complexes of type B or C emit in a longer wavelength range than ANF in S_1-ICT state, and the Stokes' shift values for them are smaller than for ANF. The maximum of the fluorescence band of ANF-solvent complexes formed by a B-type hydrogen bond is shifted to longer wavelengths and is characterized by smaller Stokes' shift values than the complexes formed by a C-type hydrogen bond. The shift of the band maximum to longer wavelengths compared to the fluorescence spectrum of ANF is due to an increase in the energy of B-type and C-type hydrogen bonds in the S_1-ICT excited state. The emission of ANF-solvent complexes of type A, clearly identified in absorption spectra, was not observed. The reason for this must be the weakening of the hydrogen bonds of type A in the S_1-ICT state as the ANF-solvent complexes break down [5].

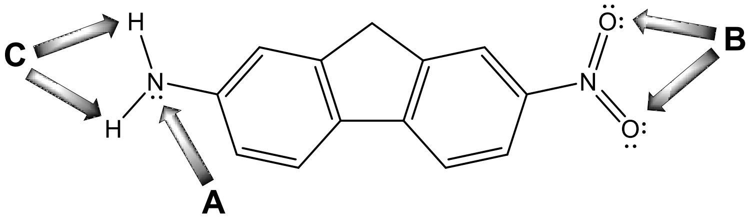

Figure 1. 2-amino-7-nitrofluorene (ANF) molecule structure with A, B and C type hydrogen bonding sites.

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Scientific Opportunities for Polish researchers at the European XFEL

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The European X-ray Free Electron Laser (EuXFEL) is an international laboratory where intense ultrashort pulses X-rays are generated and applied in scientific research. It contributes to the significant expansion of our knowledge in many scientific disciplines (m.in. medicine, pharmacology, chemistry, materials science, nanotechnology, energy and electronics) and the emergence of new technologies affecting our daily lives [1]. During the presentation, a Project financed by the Ministry of Science and Higher Education to support the Polish scientific community in the use of new research opportunities offered by EuXFEL will be presented [2]. The project includes the following activities:

1. training in basic knowledge of XFEL applications and research techniques used, including several months of internships for young researchers at institutions participating in XFEL research and a lecture on XFEL for undergraduate and doctoral students;
2. funding the participation of Polish scientists in conferences and workshops on XFEL research;
3. assistance in establishing or expanding scientific contacts with EuXFEL employees and/or research groups carrying out similar research in Poland and abroad;
4. assistance in the preparation of research projects in competitions for measurement time on XFEL sources, also by performing pilot and complementary studies.

The lecture will end with a presentation by the Network of Centres of Excellence in the field of research using XFEL (CD XFEL), in which the above program is implemented.

Acknowledgments: This project was financed by the Ministry of Science and Higher Education program "*Support for the participation of Polish research teams in international research infrastructure projects*", based on contract No. 2022/WK/13.

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Spectroscopic studies of the intermolecular interactions between genistein and methyl-β-cyclodextrins

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Genistein, a natural isoflavone, is an active compound based on which promising drugs can be synthesized to inhibit Huntington's and Alzheimer's disease [1]. Macrocyclic compounds such as cyclodextrins, cucurbit[n]uriles and calixarenes play a key role in the construction of drug carriers in the form of macrocyclic host-guest assemblies, as their self-organization enables the formation of an inclusion complex. Cyclodextrins are well known as excipients that improve the stability, solubility and also enhance the efficacy of encapsulated drugs [2]. However, effectiveness of pharmacological therapy is directly determined by the kinetics of the drug release from the carrier [3]. Therefore, it is of great importance for therapeutic applications to understand the molecular mechanisms underlying host-guest relationships and their interactions with the microenvironment.

In our work steady-state spectroscopic methods have been used to study solvent dependent ground- and excited-state photophysical and photochemical properties of genistein molecule exhibiting Excited-State Intramolecular Proton Transfer (ESIPT) behaviour [4]. The influence of the spatial structure of the macrocyclic compound methyl-β-cyclodextrin (mβ-CD), i.e. the cavity size and shape, on the stability and activity of the encapsulated drug and the supramolecular structure of the resulting complexes (the way the drug is oriented in the carrier cavity) was determined. The ground- and excited-state inclusion complexes between GEN and mβ-CD has been investigated at different temperatures in DMSO solution by UV-vis absorption and fluorescence spectroscopy, ^{1}H NMR spectroscopic technique, and quantum-chemical calculations. Performed studies provided insights into the factors influencing the driving force behind complex formation and the location of GEN inside mβ-CD.

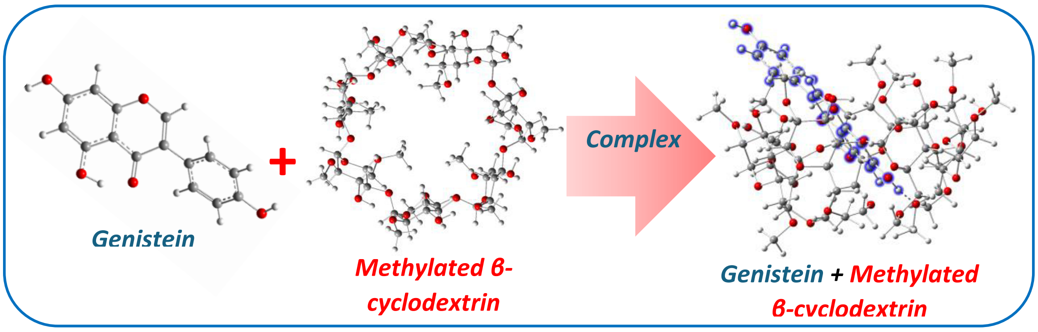

Figure 1. Schematic representation of the host-guest complex between genistein and methylated β-cyclodextrin.

Acknowledgments
The quantum-chemical calculations have been carried out using resources provided by Wroclaw Centre for Networking and Supercomputing (http://wcss.pl).

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Polydopamine-Coated Gold Nanorods as Photothermal Agents for NIR Photopolymerization

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The application of NIR light-based thermal vat photopolymerization in additive manufacturing is a new field still in its initial stages. Effective photothermal agents that can transform near-infrared (NIR) light into localized heat are required to advance this new approach further. It has previously been demonstrated that polydopamine-coated gold nanorods (AuNRs@PDA) have superior photothermal characteristics. This study examines their ability to facilitate thermal polymerization in (meth)acrylate-based resin systems triggered by NIR light.

The main objective of this work is to utilize Raman spectroscopy for monitoring polymerization facilitated by AuNRs@PDA to understand their role in initiating and controlling the spatial distribution of polymerization. To verify the Raman results, transmission electron microscopy (TEM) is employed to assess the degree of localization of polymerization around the nanoparticles and structural stability of AuNRs@PDA after NIR irradiation.

This research aims to further the development of advanced materials and methods for controlled photopolymerization, with prospective applications in additive manufacturing, biomedical devices, and functional nanocomposites.

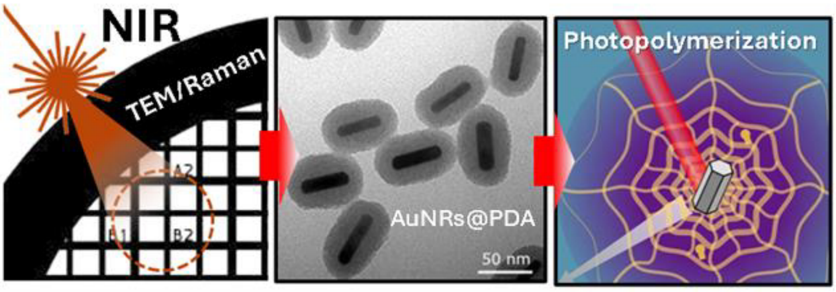

Figure 1 Proposed method to study photopolymerization around AuNRs@PDA using NIR light, thermal initiators, Raman spectroscopy, and TEM.

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To See or Not to See? That is the Method. Single-molecule Surface-Enhanced Raman Spectroscopy (SM-SERS) for Dye Molecules

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It has been nearly two decades since the first single-molecule detection using surface-enhanced Raman spectroscopy (SERS) was demonstrated [1], marking a significant milestone in the method's evolution. The SERS signal enhancement arises from a combination of electromagnetic and chemical mechanisms, with a significant contribution from local surface plasmon resonances and molecule–surface interactions. Importantly, the single-molecule SERS (SM-SERS) signal depends on various factors, such as temperature, excitation intensity, and molecular orientation. [2]

This study explores the SERS response of thionine (TA), a phenothiazine-based dye, immobilized on gold nanorod substrates. Special attention was given to the impact of molecular orientation on the Raman signal. To achieve spatial control, we utilized a supramolecular host–guest strategy by incorporating dye molecules into the cavity of water-soluble macrocyclic host, pillar[6]arene (P6A). Complex was formed via electrostatic and π–π interactions between the cationic dye and the anionic, symmetric macrocyclic host.

The use of pillar[n]arenes as a platform for SERS-active supramolecular systems is promising their structural symmetry and synthetic accessibility. The inclusion of dye molecules within the macrocyclic cavity is hypothesized to restrict their orientation and enhance specific vibrational modes. Our findings underline the potential of using supramolecular chemistry to tune SERS performance and offer insight into structure–signal relationships in surface-confined dye molecules.

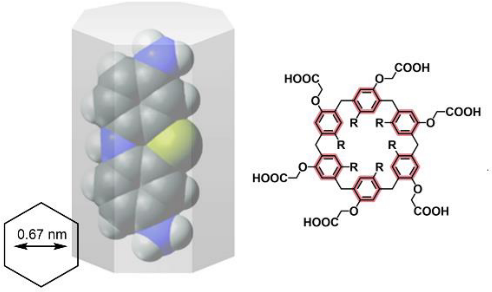

Figure 1. Schematic representation of TA-P6A complex and molecular structure of carboxylated P6A.

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Spectroscopic and Structural Insights into TPPS-GO/rGO Interactions: Toward Photostable Hybrid Nanomaterials

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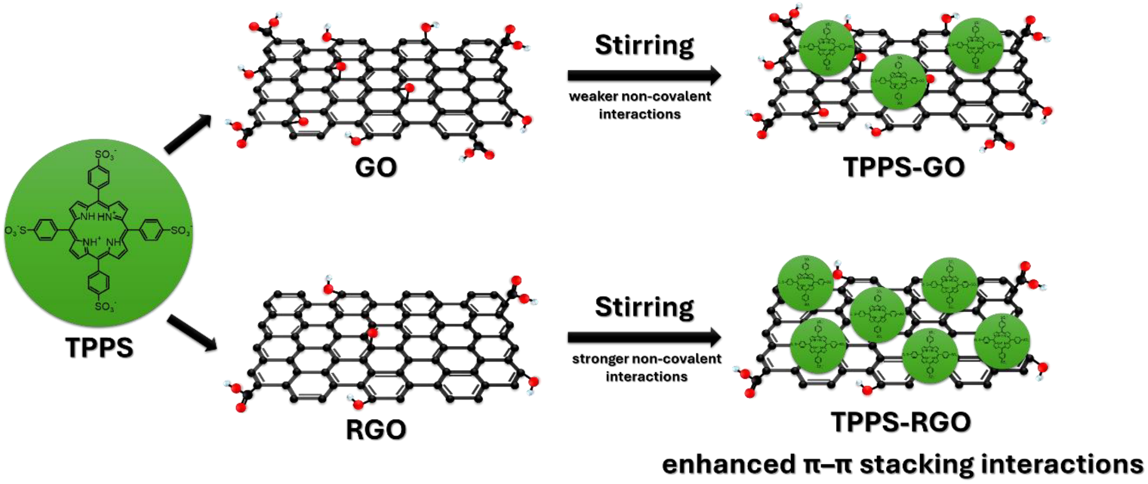
The development of hybrid nanostructures combining porphyrins and graphene-based materials has attracted significant attention due to their unique optoelectronic properties and potential biomedical applications [1-3]. In this work, we systematically investigate the non-covalent interactions between meso-tetra(4-sulfonatophenyl)porphyrin (TPPS) and various graphene derivatives, including graphene oxide (GO), reduced graphene oxide (RGO) (Scheme 1), and RGO functionalized with Pluronic 123 (RGO-P-123). Using absorption, emission, femtosecond and nanosecond transient absorption spectroscopy, complemented by structural analyses, we reveal that TPPS interacts more strongly with RGO than with GO. This enhanced interaction is primarily driven by π–π stacking between the porphyrin macrocycle and the highly conjugated surface of RGO. Moreover, the presence of Pluronic 123 improves the dispersion stability of the TPPS-RGO system, which is crucial for maintaining the long-term functionality of these materials. Our findings provide fundamental insights into the non-covalent binding mechanisms within porphyrin–graphene hybrids and highlight their promising potential for designing advanced materials tailored for photocatalysis and cancer therapy applications.



Scheme 1. GO/RGO functionalization scheme

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

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Raman and UV-vis spectroelectrochemical studies to follow donor-acceptor interactions in ambipolar semiconductor layers

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A new alternated donor-acceptor-donor (DAD type polymer semiconductor layers, revealing ambipolar properties, i.e., electrochemical activity in both the positive and negative potential ranges should afford the conductivity extending over a very wide voltage range, highly desirable for devising and fabricating materials capable of energy transducing and storage.

Energy transport in polymer semiconductors is triggered by current or voltage. It can be considered efficient if it forms recognizable isoenergetic states throughout the active polymer layer. However, this conduction process is usually interrupted by the presence of so-called defects, i.e., conjugation breaks, short conjugation ranges, and chemically altered polymer units. Notably, the limited ability of electrons and holes to transport is directly connected to the semiconductor stability problem, caused by charges trapped in the bulk or on the surface without being sufficiently released.

The scientific problem aimed to be solved by our research consists of improving the charge transport in the bulk and surface conductivity of ambipolar polymer semiconductor layers by the targeted tuning of their molecular structure, and by this, donor-acceptor interactions for application in energy storage and transducing devices.

With that respect, we combined the in situ/operando UV-vis-NIR and Raman spectroelectrochemical studies supplemented by Kelvin Probe Force Microscopy working in amplitude modulation mode (KPFM-AM) to distinguish the most stable and conducting molecular structures of ambipolar semiconductor layers. Significantly, the crucial differences in electronic and vibrational states belonging to distinctly prepared molecular structures of the ambipolar semiconductor were visualized by in situ/operando spectroelectrochemical UV-vis-NIR and Raman. While the KPFM-AM surface potential measurements were used for probing the differences in electronic states locally on the surface. Hence, we recognized the charge-trapping features characteristic of the distinct and specific molecular structures of the same DAD-type polymer semiconductor layers prepared under different electropolymerization conditions.

Acknowledgments

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Innovative Large-Scale PDA/rGO Free-standing Nanofilms: Potential Applications in Photoelectronics

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Polydopamine (PDA) free-standing films can self-assemble at the air/water interface, forming transferable, nanometer-thick films [1]. In this study, PDA was combined with reduced Graphene Oxide (rGO) to create a nanocomposite film that can be transferred onto nearly any surface. This hybrid material exhibits unique electronic and photonic properties, highlighting its potential for advanced photoelectronic applications.

The nanocomposite was synthesized via a one-pot synthesis method using boric acid, which acts as both a reducing agent for GO [2] and a mechanical stabilizer for PDA [3]. The film's structure and composition were characterized using XRD, SEM, AFM, XPS, IR, and Raman spectroscopy.

Electrical conductivity, measured using 4-point probe techniques, showed a reversible decrease under UV and white LED illumination (8 mW/cm^2). This light-responsive behavior is attributed to structural and morphological changes triggered by irradiation. Time-resolved reflectivity confirmed rapid, reversible actuation mainly driven by thermal expansion—unlike pure PDA [4], which responds more slowly via water adsorption. Conductive AFM revealed a heterogeneous electronic structure with distinct high- and low-conductivity domains, underscoring the material's complex and tunable properties.

Although these results are initial, they suggest strong potential for use in devices such as photosensors, phototransistors, and memory storage systems. Moreover, the study provides important understanding of how to modulate intermolecular interactions of PDA within composite materials.

Acknowledgments

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Molecular factors controlling the photo-induced isomerization of 4-hydroxyazobenzene derivatives

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Photoresponsive hydrogels provide an effective strategy for local drug delivery, especially in the treatment of wound surfaces, where poor vascularisation can render systemic antibiotics ineffective [1-2]. The performance of such materials depends primarily on the respond to light stimuli of molecular photoswitches incorporated in their structure [3]. The mechanism of action of such systems is based on the *trans-cis* isomerization phenomenon. In this process, the photoreactive molecule changes its geometry, which ultimately leads to the controlled release of the drug from the matrix [4]. However, in order to achieve the desired material properties, the structural elements of the system must first be thoroughly examined.

In this work, we investigated a series of 4-hydroxyazobenzene derivatives (containing various substituents with electron donor and acceptor properties), which represent the functional core of designed light-sensitive hydrogel systems. A synergistic approach, combining experimental photoisomerization studies (365 nm irradiation) and quantum chemical calculations, has been utilised to reveal a complex photoisomerization pathway. The results obtained in this study provide clear evidence for the formation of transient tautomeric (*hydrazone*) species, thus redirecting the conventional understanding of the direct *trans-to-cis* transition. Furthermore, solvatochromic analysis and theoretical modelling indicate that specific derivatives may exist as a tautomer, fundamentally altering their photophysical behaviour. Kinetic studies also demonstrate that isomerization is significantly inhibited in viscous media. This observation highlights the key role of steric hindrances in regulating the photoswitching efficiency in the polymer matrix.

Our results contribute to the understanding of the photochemistry and photophysics of azobenzene and provide new fundaments for the effective design of highly efficient photoresponsive drug delivery systems.

Acknowledgments

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Unraveling Ultrafast Dynamics in Co-Sensitized DSSC

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Dye-sensitized solar cells (DSSCs) represent a promising class of photovoltaic technology, offering a cost-effective and flexible approach to solar energy conversion [1-2]. A key strategy to enhance their performance is co-sensitization, which involves using multiple dyes with complementary properties to broaden light absorption, minimize dye aggregation, and improve charge separation [3-4]. This study investigates the photophysical processes in a co-sensitized DSSC system incorporating two triphenylamine-based dyes, XY1b and L1, selected for their complementary absorption spectra and distinct electronic properties. We employ stationary absorption and ultrafast transient absorption (TA) spectroscopies to analyze their behavior when adsorbed onto TiO_2 surfaces.

Absorption measurements show that the dye ratio in solution differs from their adsorption ratio on TiO_2. TA spectroscopy provides rate constants of charge transfer processes (desired electron injection to TiO_2 and unwanted electron recombination) and critical insights into electronic coupling between the co-adsorbed dyes. The electron recombination in one dye is unexpectedly enhanced in the presence of another co-adsorbed dye. Our results also demonstrate that the oxidized state and excited state of one dye can be quenched by the presence of the other, indicating strong inter-dye interactions and mediation of lower-bandgap dye in charge separation of higher-bandgap dye (Figure 1). Notably, the co-sensitized system shows higher sunlight power conversion efficiency than single-dye systems, proving that combining these dyes improves performance.

This work highlights how ultrafast spectroscopy helps understand dye interactions in DSSCs. The findings guide the design of better co-sensitized solar cells, advancing affordable and efficient solar energy solutions.

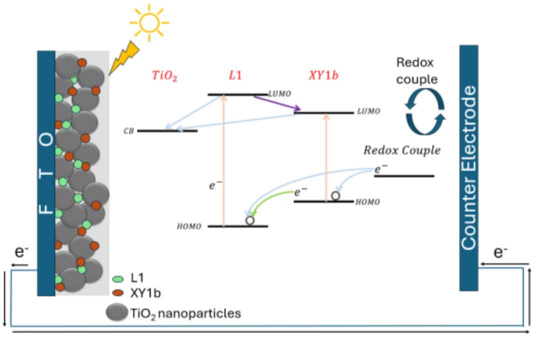

Figure 1. Presence of one dye quenches the other oxidized and excited dye in co-senstized DSSC system.

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Early stages of carbon dots formation: the presence of molecular fluorophores

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Carbon dots (CDs) prepared from inexpensive and widely available precursors by bottom-up methods (e.g. hydrothermal synthesis or solvent-free pyrolysis) are broadly studied as possible cost-effective and environmentally friendly replacement for organic fluorophores and metal-based catalysts. However, their exact composition and structure remain unknown.

In recent years, it has been shown that high temperatures used to induce polymerisation and carbonisation processes may also promote organic reactions leading to the formation of heterocyclic molecular fluorophores (MFs), which strongly contribute to the fluorescence of CDs. MFs are usually formed at the early stages of the CDs formation and may decompose upon further heating. Therefore, we focused on the theoretical and experimental analysis of the thermodynamic and kinetic aspects of early phases of the reaction of citric acid and ethylenediamine. These two common precursors for the synthesis of CDs may form both MFs (e.g., well-known IPCA) as well as oligomeric condensates. By synergizing quantum chemistry and reactive molecular dynamics computational approaches with analytical techniques, we identified several reaction intermediates, including a new five-membered heterocycle. Its formation is more favourable at lower temperatures (180-200 °C) compared to the formation of IPCA due to kinetic reasons. Nevertheless, the latter process becomes dominant at elevated temperatures (>210 °C) owing to the higher thermodynamic stability of IPCA. Although the computed activation barriers for this reaction pathway are rather high, they are comparable to those for the condensation of citric acid and ethylenediamine. Consequently, the formation of MFs and oligomerization become competitive at higher temperatures. [1]

Another widely used system for the preparation of CDs is a mixture of citric acid and urea. We have demonstrated that solvent-free pyrolysis of such a mixture does not yield citrazinic acid, contrary to expectations based on the analysis of hydrothermally treated mixture. [2] Instead, the molecular fluorescence contribution in these CDs results from the presence of two hitherto unknown blue-emitting MFs, whose structures were resolved by NMR and MS methods. The identification of molecular species present in as-prepared CDs and elucidation of mechanisms of their formation is a key prerequiste for explaining the photochemical properties of CDs and clarifying the chemical processes underlying the formation of larger nanostructures.

Acknowledgments

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Fluorescence Quenching of Luminarosine Nucleoside and Its Derivatives by G-Quadruplexes

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G-quadruplexes (G4) are guanine-rich DNA and RNA structures that are readily self-assembled and capable of folding into four-stranded nucleic acid structures under physiological conditions. G4 can form in gene promoters (c-MYC, KRAS, Bcl-2, VEGF) and their presence can inhibit or enhance transcription. In addition, they form naturally at telomeres, where they stabilize their structure. Research is currently underway into G4-stabilising compounds that can: 1) inhibit the expression of oncogenes, 2) prevent telomerase activity.

The aim of this study was to investigate the interactions of the fluorescent derivatives of nucleoside 2',3',5'-tri-O-acetyl-luminarosine (LMR), its aglycone luminarine (LM), and its methylated analogs (9-MeLMR and 9-MeLM) with G4 structures. According to our previous studies concerning the interactions of 9-MeLM ligand with the G-quadruplexes with different topologies, the strongest binding was observed for c-MYC sequence, which adopts a parallel structure.[1] Moreover, we demonstrated that this ligand can serve as a selective fluorescence turn-off probe for parallel G4 DNA.[2] The quenching of the fluorescence of the ligand can be attributed to π-π interaction between the ligand and the exposed guanine tetrad of the parallel G4 structure. The quenching mechanism involves electron transfer from guanosine to the excited fluorophore.[3] In the present study we examined the influence of both the ribofuranosyl group and the methyl substituent in the aglycone ring on fluorescence quenching induced by the c-MYC quadruplex (**Figure 1**).

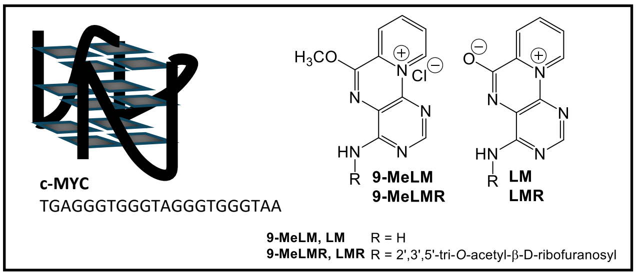

Figure 1. Structure of 9-methoxyluminarine chloride (9-MeLM), 2',3',5'-tri-O-acetyl-9-methoxyluminarosine chloride (9-MeLMR), luminarine (LM), 2',3',5'-tri-O-acetyl-luminarosine (LMR), and c-MYC G-quadruplex.

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Development of Zirconium Oxide-Enhanced Polymer Composites Using Vat Photopolymerization in Additive Technologies

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This study focuses on the development of zirconium oxide-enhanced polymer composites utilizing vat photopolymerization within additive manufacturing processes. The integration of zirconium oxide as an inorganic filler aims to improve the mechanical, thermal, and biological properties of polymer matrices, making them suitable for biomedical applications such as bone tissue engineering. The research involved synthesizing composite formulations with varying zirconium oxide concentrations and analyzing their rheological behavior, viscosity, and curing characteristics. Photopolymerization kinetics were studied using calorimetric techniques and FT-IR spectroscopy to evaluate the influence of filler content on the polymerization process and shrinkage phenomena. The composites were then processed through digital light processing (DLP) technology to produce complex three-dimensional structures, including scaffold-like geometries mimicking natural bone tissue porosity. Mechanical testing, microstructural analysis, and biocompatibility assessments demonstrated that zirconium oxide significantly enhances the composites' strength and bioactivity while maintaining high print resolution and surface quality. These findings highlight the potential of zirconium oxide-reinforced photopolymer composites for advanced bone regenerative implants, contributing to the development of multifunctional, durable, and biocompatible materials suitable for clinical translation in regenerative medicine and personalized therapies.

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New Advanced Iodonium Salts as One-Component Cationic Polymerization Photoinitiators for Cationic Vat 3D Printing

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Vat 3D printing is an excellent alternative to traditionally preparing polymer 3D objects. However, the application of cationic vat 3D printing is still limited by a number of inconveniences such as the lack of suitable photoinitiators absorbing in the emission range of light sources used in printers (about 405 nm).[1] Most of commonly used iodonium salts are diaryl derivatives absorb poorly above 300 nm and need photosensitizers to initiate polymerization efficiently.[2]

Our new innovative chromophore designs allow iodonium salts to be obtained in a selective manner which was previously impossible for the more sophisticated chromophores.[3] Moreover, a double bond was used in these chromophores and, we obtained the first symmetric iodonium salts containing such moiety.[4] Such advances in the structure have produced compounds with excellent absorption properties reaching into the visible light. These new iodonium salts can photolyse efficiently at 365 and 405 nm and can photoinitiate cationic polymerization process of such monomers as epoxides and vinyl ethers. This design leads to a great improvement in photoinitiating properties so that our salts can be used in cationic vat 3D printing.

Figure 1. 3D printing of nanocomposite materials obtained using prepared iodonium salts.

Acknowledgments

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Positional and Electronic Effects of Substituents on Photophysical Properties of BF_2-Based Dyes

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Substituent position near the BF_2 core, affecting its electron-withdrawing character, significantly influences the photophysical properties of fluorophores, including absorption, emission, fluorescence quantum yield (FQY) and two-photon absorption (2PA) parameters such as two-photon action cross section (TPACS)[1]. Incorporation of a π-conjugated system induces a bathochromic shift in absorption and emission spectra, though it may also reduce FQY[2].

This study explores a series of fluorescent dyes bearing a BF_2 core (**Figure 1**), synthesized and evaluated for their photophysical properties, including 2PA. Structural modifications involve introduction of a CF_3 group as an electron-withdrawing substituent at position 3, 4 and 5 of the pyridine ring or an OMe group as an electron donor. Some CF_3-substituted dyes additionally incorporate an extended π-conjugated system.

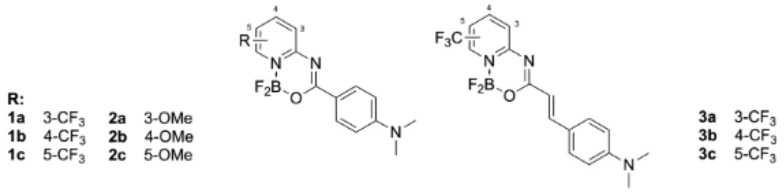

Figure 1 – Chemical structures of synthesized and studied dyes.

Photophysical measurements revealed a strong influence of the substituent's electronic character on dye properties. OMe-substituted compounds exhibited consistently high FQY (>0.8), while CF_3 derivatives showed a broader range (0.2-1.0), with the lowest values for substitution at the 4th position. Extension of the π-conjugated system induced a bathochromic shift in absorption and emission spectra and increased FQY for dyes substituted at the 4th and 5th positions. 2PA measurements showed that the dye **3a** exhibits the highest 2PA cross section, while dye **3c** displays the highest TPACS.

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Optimization of 3D Printing Settings for Enhanced Print Quality in Dental Applications

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3D printing methods based on photopolymerization process have become an essential technology in modern dentistry due to its ability to fabricate precise and highly detailed models tailored to individual patient needs. This type of 3D printing uses liquid resins that are crosslinked into a solid polymer through light irridation of each specific layer [1]. The most popular technolgies in this type of 3D printing are Digital Light Processing (DLP, with a projector as its light source) and Liquid Crystal Display (LCD, with LCD panel as its light source) [2]. Factors that determine the final print quality include the type of 3D printing technology employed, as well as process parameters such as exposure time, layer height, and light intensity [3].

Given the increasing reliance on additive manufacturing and 3D prinitng in the denatl industry, there is a growing need to better understand how those parameters influence the final printour. Variations in printing parameters can lead to dimensional inaccuracies, poor surface finishes, or even print failure [4]. This research seeks to address this by evaluating the key parameters in the printing process.

In this study, the influence of these variables on the quality of the objects produced form a dental resin was studied. Kinetic and rheological analysis were employed to determine the behavior of the resin under printing conditions similair to those in the studied 3D printers. Polymerization shrinkage was meassured and qualitative analysis of the printouts qaulity was used. The findings demonstrated that both the choice of printer and the printing parameters significantly affect the dimensional stability and surface quality of the final prints. Therefore, proper adjustment of them is essential for achieving high-quality dental components with reduced shrinkage and deformation. The results provide valuable guidelines for improving print consistency and enhancing the overall reliability of 3D printing in dental applications.

Acknowledgments

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Competition between Photoswitching and Fluorescence in Hemiindigos and Hemithioindigos

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This study experimentally and theoretically investigates the influence of structural factors on the delicate balance between photoswitching and fluorescence [1]. We demonstrate that *ortho*-OH-substituted hemiindigos exhibit remarkable fluorescence quantum yields while maintaining efficient photoswitchability (total quantum yield of 0.94). Furthermore, we show that these properties are sensitive to the environment, displaying optimal performance in moderately polar solvents, and diminished efficiency in highly polar environments. In contrast, hemithioindigos function as efficient photoswitches, exhibiting weak fluorescence in all studied conditions.

Theoretical calculations performed on representative molecules in the excited state (CC2) suggest that *Z*→*E* photoswitching is a two-step process: $^1\pi\pi^* \rightarrow {}^1n\pi^* \rightarrow S_0$. This mechanism involves two distinct excited-state minima: the fluorescent $^1\pi\pi^*$ state and the photoswitching $^1n\pi^*$ state. The depopulation of the $^1\pi\pi^*$ state is driven by stretch of the C-O bond.The stabilization of the $^1\pi\pi^*$ state in hemiindigos (a phenomenon not seen in hemithioindigos), further enhanced by EDG substituents, promotes efficient fluorescent properties. The synthetic methods of the studied compounds are described in ref. [2].

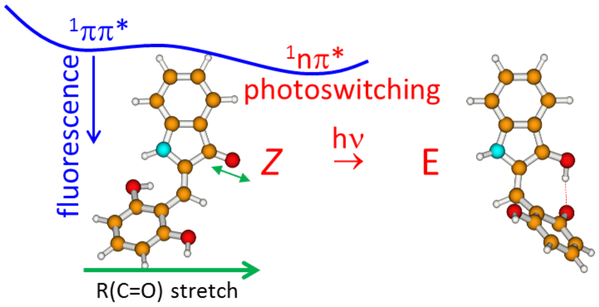

Figure 1 *Z*→*E* photoswitching in hemiindigos and in hemithioindigos is a two-step process involving two singlet excited-state minima: $^1\pi\pi^*$ and $^1n\pi^*$.

Acknowledgments

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BisBF$_2$ pyridoins: a new strong electron accepting platform for use in multi-photon applications - substitution and extension of conjugation influencing the photophysical properties

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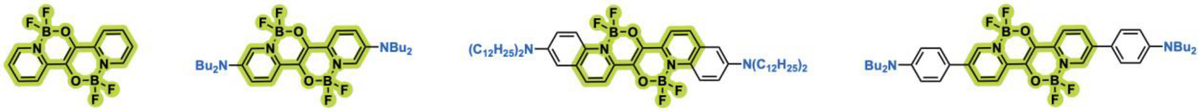
Organic fluorophores with strong two-photon absorption are essential for advanced fluorescence imaging, especially in biological systems where deep tissue penetration and reduced photodamage are crucial. Designing such dyes requires careful molecular engineering to balance position of maximum of absorption and emission, fluorescence efficiency, two-photon absorption cross section. In this study, we present a series of newly developed quadrupolar dyes incorporating two BF$_2$ units, tailored for efficient two-photon excitation within the near-infrared (NIR) window and strong emission. The dyes are based on a symmetric, chrysene-like acceptor core, functionalized with strong electron-donating groups and π-extended linkers. Structural modifications were introduced to investigate the effects of donor–acceptor separation and spacer conjugation on photophysical behavior, focusing on fluorescence quantum yield and two-photon cross-section. The results highlight the role of molecular architecture in optimizing two-photon performance and provide valuable insights for the design of high-efficiency fluorophores for biomedical and optoelectronic applications.



Scheme 1. The structure of studied dyes

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Magnetic nanoparticles coated with hemoglobin - influence on the binding capacity of photosensitive drug and photodynamic effect

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One of the key aims of Photodynamic Therapy (PDT) is the targeted treatment of cancer. This approach involves the activation of a photosensitising agent by light of a specific wavelength, in the presence of oxygen. The resulting photochemical reaction produces reactive oxygen species (ROS), which are capable of selectively destroying cancer cells. Despite its potential, PDT faces several challenges that limit its clinical effectiveness, such as photosensitiser aggregation, poor biodistribution, and tumour hypoxia. As a result, various strategies are currently being investigated to address these limitations and enhance the therapeutic outcomes of PDT [1].

A promising strategy involves the development of suitable carriers for photosensitising agents. Magnetic nanoparticles (MNP@) show considerable potential in this context, owing to their iron content—which is preferentially absorbed by cancer cells—and their readily modifiable surfaces. These properties make MNP@ attractive candidates for enhancing the delivery and therapeutic efficacy of photosensitisers in PDT.

In the present study, MNP@ were synthesised, with cores coated in chitosan modified to include either one or three long-distance amino groups. The impact of these modifications on the nanoparticles' ability to bind bovine hemoglobin (BHb) was investigated. BHb, which shares approximately 90% similarity with human hemoglobin, serves as a model protein and may enhance photosensitiser performance. It contributes by increasing oxygen concentration in the tumour microenvironment—through oxygen binding—and by boosting iron absorption, both of which are beneficial for PDT applications [2–4].

The synthesised materials were characterised in terms of chemical structure (ATR-FTIR, XRD) and morphology (SEM, STEM, DLS, Zeta Potential, and porosity). The capacity to bind the photosensitiser chlorin e6 (Ce6) was also assessed through both physical adsorption and chemical binding. Furthermore, the generation of singlet oxygen by MNP@ was evaluated via ADPA decomposition. Among the materials tested, the formulation incorporating chitosan with three long-distance amino groups, bound to both BHb and Ce6, demonstrated the most promise for PDT use. Its efficacy was validated by assessing the photosensitising effect on HeLa cells.

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Donor–acceptor photosensitizers based on a perylene core: synthesis and photochemical characterization

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Photosensitizers with a donor-acceptor structure have been of interest to researchers since the 1970s.[1] By transferring energy between the donor and acceptor units, it is possible to improve the properties of the resulting systems, e.g., the generation of long-lived excited states and high efficiency generation of Reactive Oxygen Species. In addition, by modifying the donor and acceptor groups, the energy levels of HOMO and LUMO, or the absorption range (from UV to NIR) and other photochemical properties can be adjusted.[2] This structural flexibility allows the design of photosensitisers for a variety of applications, including photodynamic therapy, antimicrobial phototherapy, or new organic photovoltaic (OPV) materials.

In the present work, new photosensitizers with a perylene core were synthesized. Obtaining donor-acceptor structures by modifying PDIs at the *imide* and *bay* positions was performed. Phenothiazines were used as the donor part of the models obtained, due to their ability to donate electrons and charge transfer properties.[3] The optical, photochemical, and electrochemical properties of the systems obtained were characterized. The results obtained show that the position of the donor unit and the chain length significantly affect the properties of the systems. These studies make a major contribution to the study of the photosensitizing properties of perylene diimides in D-A systems.

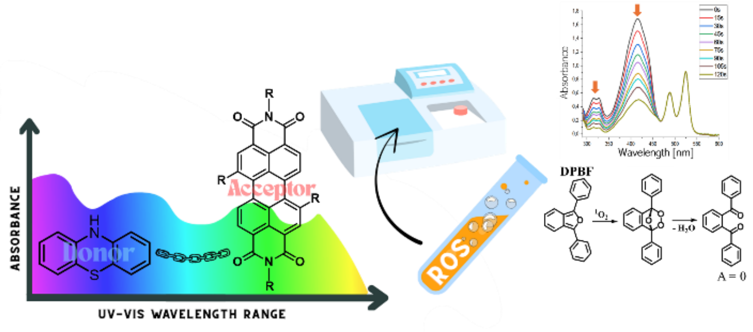

Figure 1. Donor-acceptor systems containing perylene diimide and phenothiazine

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Research on the synthesis of new pyridylcoumarins derivatives as photosensitizers for initiating photopolymerisation processes in 3D printing technology

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3D printing is becoming increasingly popular which has led to an increased need for more effective photoinitiating systems. Photosensitizers are essential in the polymerisation process by absorbing light of the appropriate wavelength, causing a transition to an excited state. Then the energy of the excited state of the photosensitiser is transferred to the initiator, which starts the photopolymerisation process.[1] Current photoinitiating systems often encounter limitations, such as low efficiency in the visible light range or restriction to specific polymerisation mechanisms.

Reaserch focused on two-component photoinitiating systems, which were analysed using UV-Vis spectroscopy, while the polymerisation process was monitored by Real-Time FT-IR and with use of cheaper and more environmentally friendly light sources, such as LEDs. In the experimental part, selected pirydylcoumarins derivatives were synthesised using the Suzuki and Buchwald-Hartwig coupling reactions.[2] The compounds obtained were purified and their structures were confirmed using mass spectrometry techniques (LC-MS).

Further research can enable better optimisation of photopolymerisation, which opens up prospects for the wider use of the developed systems in both industrial and scientific applications.

Acknowledgments

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Photoluminescence of Pt-containing NCN-pincer compounds in solutions and single crystals

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Transition metal pincer complexes are extensively studied due to their important role as catalysts and functional organo-metallic compounds. Pt-containing NCN-pincer compounds feature high photoluminescence (PL) quantum yields and long emission decay lifetimes in µs-range [1] – properties that are highly desirable in optoelectronic applications.

In this work we studied absorption and PL spectra as well as time-resolved emission kinetics of **Pt-15** and **Pt-16** compounds (Fig.1) in solutions and single crystals to get insight of photoinduced processes dynamics. Steady-state and time-resolved emission measurements with ns-resolution were carried out using an inverted microscope Olympus IX73 coupled to a spectrograph with a gated/ intensified CCD-camera (PI-MAX4, Teledyne).

Due to fast intersystem crossing process a ligand-centered triplet state $^3(\pi\pi^*)$ is responsible for emission of **Pt-15** and **Pt-16** in diluted solutions at ambient conditions with decay lifetime ~5.5 µs for **Pt-15** in deaerated $CHCl_3$ or in PMMA films. More complex behavior of photoinduced excitonic processes was observed for single crystals due to close packing of the molecules in slip-stacked arrangements and strong interactions among them.

Absorption spectra of single crystals show linear dichroism (Fig.1) and can be described as a combination of two spectral components. This results in dependence of PL emission on excitation, in polarized emission, and multiexponential decay kinetics with lifetimes from ns- to µs- range. Relation between between crystal structure and photophysical properties of Pt-containing NCN-pincer compounds is discussed.

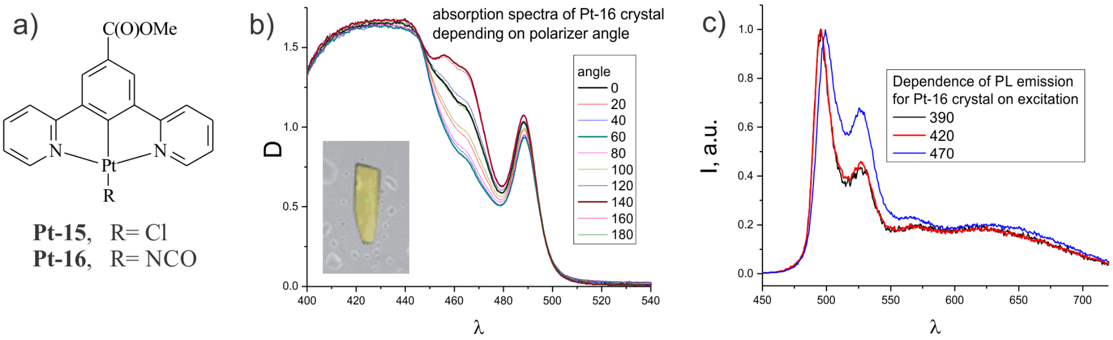

Figure 1. Structures of **Pt-15** and **Pt-16** molecules (a), dependence of absorption spectra for **Pt-16** crystal on polarizer angle (b), dependence of PL emission spectra on excitation for **Pt-16** crystal (c).

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Light-driven strategies for vitamin B_{12} analogues: photooxygenolysis, transmetalation and rhodamine conjugation

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Vitamin B_{12} (cobalamin) is a macrocyclic coordination compound containing Co(III) ion in the centre of a corrin ring. Because of its crucial role in proliferation processes, cobalamin exhibits enhanced accumulation in tumor cells, making it an attractive delivery vector for diagnostic and therapeutic agents.[1] Although it plays a key role in biological processes, native cobalamin is essentially non-fluorescent, limiting its direct use in optical bioimaging. Light-driven strategies for cobalamin analogues employ the unique reactivity and spectroscopic signatures of B_{12}-derivatives to enable both mechanistic insight and biomedical applications.

In the first approach, we exploit photooxygenolysis of native vitamin B_{12}, performed by photosensitized singlet oxygen generation with methylene blue. This process was followed by one-pot demetalation to form metal-free corrin templates.[2] Then other metal insertion was performed to obtain metbalamins bearing i.a. Zn(II) or Cd(II) ion coordinated with corrin ring. These species exhibiting fluorescence were characterized by steady-state and time-resolved spectroscopy, revealing the photophysical properties of demetalated and re-metalated corrin rings. Quantum yields, lifetimes, and emission maxima were systematically compared across metal-free, Zn-, and Cd-corrins, identifying photophysical properties that may serve as a preliminary step toward designing next-generation photochemical B_{12} analogues.

In the second strategy, the cobalamin–rhodamine 6G (B_{12}-R6G) conjugate was prepared by first assembling a R6G–linker (*trans*-1,4-diaminocyclohexane) intermediate via $Al(CH_3)_3$-mediated coupling. The ribose 5′-OH group of vitamin B_{12} was then selectively activated with carbonyldiimidazole (CDI) to form an electrophilic intermediate, which underwent amide bond formation with the R6G-spacer to furnish a fluorescent cobalamin derivative.[3] The product was spectroscopically characterized and its photophysical properties investigated, including UV–vis absorption and fluorescence emission spectra, quantum yield determinations and fluorescence lifetime measurements. The obtained results serve as a foundation for the future use of B_{12}-R6G and other derivatives in diagnostic applications, including fluorescence lifetime imaging (FLIM). Moreover, its potential theranostic utility could be realized by conjugating B_{12}-R6G with cytostatic complexes, enabling simultaneous imaging and targeted chemotherapy.

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Chiroptical Responses of Gold and Silver Nanoclusters

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Metal nanoclusters are atomically precise, ultrasmall materials exhibiting unique size-dependent optical and electronic properties. Their chiral characteristics, arising from intrinsic metal core asymmetry or ligand-induced symmetry breaking, enable photophysical phenomena such as circularly polarized luminescence (CPL) and fluorescence-detected circular dichroism (FDCD). This work investigates the one- and two-photon excited chiral responses of gold and silver nanoclusters, focusing on 6-aza-2-thiothymine (ATT) -stabilized systems (AuATT) and DNA-templated silver nanoclusters (Ag_N-DNAs).

For gold nanoclusters functionalized with ATT and arginine ligands, enantiomeric structures exhibited pronounced chiroptical activity. Two-photon excitation regimes revealed substantially enhanced circular dichroism signals compared to single-photon processes, underscoring the nonlinear amplification of chirality. Similarly, DNA-stabilized silver nanoclusters demonstrated strong two-photon CD responses alongside CPL emission, highlighting their dual capacity for chirality-sensitive light-matter interactions. The DNA scaffold not only stabilizes the Ag clusters but also imposes precise chiral configurations, enabling tailored photophysical behavior.

These findings emphasize the potential of noble metal nanoclusters as versatile platforms for chiral photonics and bioapplications. Their high luminescence efficiency, strong nonlinear optical properties, and tunable chirality make them promising candidates for bioimaging, enantioselective sensing, and optoelectronic devices. By bridging molecular precision with nanoscale functionality, such systems open pathways for designing light-driven materials with controlled symmetry and enhanced photoresponsiveness.

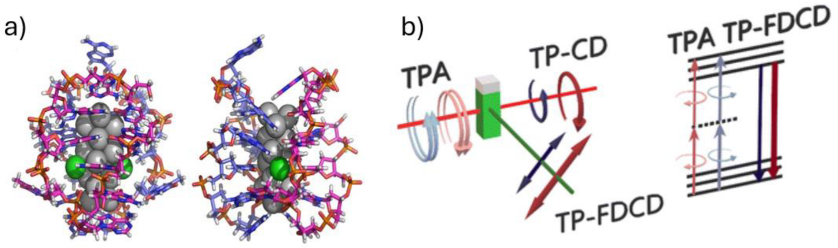

Figure 1 a) Structure of the studied nanocluster $(DNA)_2$\[$Ag_{16}Cl_2$]$^{8+}$ \[5]; b) Schematic representation of two-photon (TP) circular dichroism (CD) and fluorescence-detected circular dichroism (FDCD).

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Photophysical Properties and Photoreactivity of Novel Iridium(III) Complexes for Light-Activated Applications

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Photodynamic therapy (PDT) is a clinically approved, minimally invasive treatment modality that utilises light-activated photosensitizers to generate reactive oxygen species (ROS), thereby enabling the selective destruction of pathological cells. However, the efficacy of current photosensitizers is often limited by poor photostability, insufficient ROS generation, or suboptimal photophysical properties. Therefore, the development of novel, well-defined photosensitising compounds with tunable photochemical behaviour remains a crucial research direction [1].

In this study, a series of newly synthesised cyclometalated Ir(III) complexes were comprehensively investigated for their photophysical and photochemical properties. The compounds differ in ligand structure, which critically influences their optical performance.

The absorption and normalised excitation-emission spectra revealed distinct electronic characteristics and wavelength selectivity among the complexes. Notably, complex T23 displayed a broad red-shifted emission profile, accompanied by excited-state lifetimes. These results suggest T23 possesses a markedly stabilised excited state, making it a promising candidate for photosensitization processes.

Photostability studies under continuous blue-light irradiation (405 nm, 30 min) demonstrated varied degrees of photodegradation. Complex T23 exhibited the lowest photostability, whereas T27 showed complete resistance to photobleaching, consistent with its extended lifetime and potential for singlet oxygen generation. The photoreactivity was further confirmed using the ABDA assay, where ROS production under light exposure corroborated structure-activity relationships derived from spectroscopic and stability data.

Collectively, the findings highlight the critical role of ligand design in tuning photophysical behaviour and ROS-generating capacity, paving the way for further development of Ir(III)-based photosensitizers for applications in photodynamic therapy.

Acknowledgments

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The application of photodynamic inactivation to microorganisms

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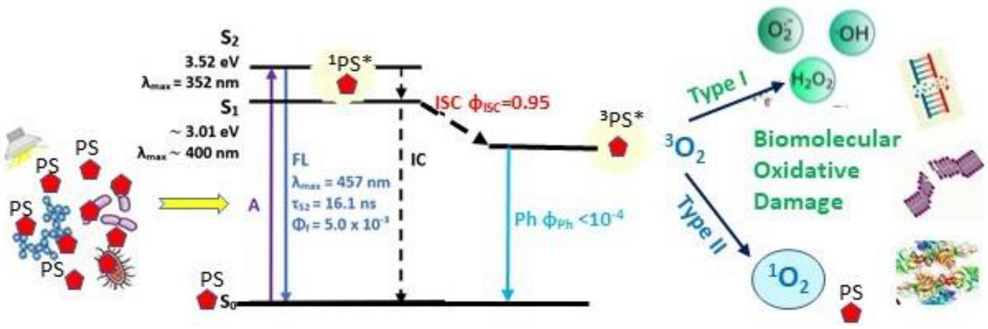
The growing resistance of microorganisms to conventional antimicrobial agents, such as antibiotics, caused by their excessive or inappropriate use, combined with the rapid spread of pathogenic microorganisms in the environment, makes the discovery of new effective therapies to combat these infections extremely urgent[1]. Antibacterial photodynamic therapy (aPDI) appears to be very promising and can be used not only in medicine but also in other fields such as veterinary medicine, agriculture, and food processing.

It is based on the combination of a photosensitizer (PS), light, and oxygen to remove microorganism cells with high metabolic activity, such as fungi, viruses, or bacteria. The main component of aPDI is a photosensitizer excited in a triplet state, whose action can lead to the formation of singlet oxygen and superoxide anions radical, hydroxyl radical and hydrogen peroxide. These highly reactive oxygen species are extremely cytotoxic and interact strongly with various important biomolecules, mainly lipids, proteins, and nucleic acids, leading to irreversible and rapid inactivation of microorganisms.



Scheme 1. Mechanism of photodynamic inactivation action (aPDI) represented by Jablonski diagram.

We investigated a group of compounds that could potentially be used as sensitizers (PS) in aPDI. They are characterized by high quantum yield of triplet excited state formation T_1 $\phi_{ISC}>0.9$. Efficient formation of a long-lived T_1 triplet state ($\tau_T \sim 2.0$ μs) allowed efficient generation of singlet oxygen ($^1O_2$*) and other reactive oxygen species[2] (Scheme 1).

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Influence of the solvent polarity on the slow kinetics of Pyrene time-resolved fluorescence

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Pyrene-based scale, applied to steady-state fluorescence spectra, is widely used for estimating micropolarity. However, published research did not consider the time changes of the spectrum emitted by a molecule after it is excited, which depend on the solvent polarity and other environmental factors. Analysis of these kinetic processes allows for deeper insight into vibronic interactions of the S_1 and S_2 singlet states, leading to breaking symmetry of the fluorescent state, in connection with their dielectric molecular environment. Extraction of this information helps to understand better the temporal behavior of processes that occur in solution, and to answer the question: "How are vibronic interactions of the first and the second singlet states affected by the dielectric molecular environment?"

To solve the above problems, the authors study Pyrene's time-resolved fluorescence vibronic spectra in polar acetonitrile and nonpolar hexane. The critical challenge is estimating the ps-scale temporal behavior, observed at the beginning of the fluorescent decay, whose total duration is long enough in the breaking symmetry process. To improve the low signal-to-noise ratios of the spectra, the processing involved PARAFAC-based compression combined with the Fourier smoothing of 20 time-resolved spectral matrices containing instant fluorescence spectra measured by the streak camera with picosecond resolution.

We found that the intensity ratios of the first to third (I_{13}) vibronic bands, tracked over time, decreased from 8.7 to 0.62 in hexane and from 4.2 to 1.49 in acetonitrile during approximately 2.3 ns. Then the ratios become stable, matching steady-state fluorescence values. This kinetic behavior reflects the formation of the vibronic spectral response to environmental polarity (the time-dependent Ham effect).

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Hydrophilic BODIPY complexes based on organoboron scaffolds as photosensitizers for antimicrobial photodynamic therapy

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The growing antimicrobial resistance is a major challenge for modern medicine and represents one of the leading causes of death worldwide.[1] Therefore, the development of novel and effective strategies for the treatment of microbial infections is crucial. Photodynamic therapy (PDT) is a promising alternative approach for microroganisms' inactivation. The treatment relies on three key elements: photosensitizer, light source, and oxygen. After the administration of the photosensitizer, it localizes in microbial cells. Upon light irradiation, the photosensitizer undergoes transition to the triplet excited state *via* intersystem crossing (ISC), and subsequently interacts with triplet oxygen present in cells. It leads to the formation of reactive oxygen species (ROS), which causes the oxidation of important biomolecules, such as lipids, proteins, and nucleic acids, inducing cell death.[2] The efficacy of the treatment depends on the photosensitizer and its ability to form triplet excited states.

As potential photosensitizers, the BODIPY dyes are intensively studied due to their strong absorption of light within the visible range, relatively simple synthesis, and high structural tunability.[3] Nevertheless, to increase the ISC yields, the structure of the dye has to be designed appropriately. Previous efforts to enhance the ability of BODIPY complexes to generate triplet states have focused on ligand functionalization without considering modification to the boron atom. The most common and highly effective approach is the incorporation of heavy atoms. However, these dyes are often characterized by significant dark cytotoxicity and poor water solubility, which hampers their application in PDT. Thus, the heavy-atom free photosensitizers are desired.

Herein, we present a series of novel, highly photoactive BODIPY dyes without heavy atoms conjugated with biomolecules, such as nucleosides, to increase both cellular uptake and selectivity of the obtained photosensitizers. We demonstrate that partial engagement of the organoboron scaffold in the triplet excited state generation enabled the further structural modification of BODIPY without compromising the photocatalytic properties. Simultaneously, the studies revealed that the presence of the hydrophilic substituents is necessary for the phototoxicity in living organisms.

Acknowledgments
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The origin of the excitation wavelength dependence of fluorescence anisotropy in ESIPT-active compounds

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Excited state intramolecular proton transfer (ESIPT) occuring in some compounds significantly affects their photophysical and photochemical properties. This process leads to the presence of two molecular forms (normal and tautomeric) in excited state. Because of this, fluorescence of ESIPT-active compounds can contain two spectral bands corresponding to emission of each species (Figure 1a). ESIPT is ultrafast process which occurrs in the timescale from femto- to tens of picoseconds. Therefore, lifetime of the normal excited state form is relatively short, as it is limited by ESIPT. This explains the high fluorescence anisotropy of the normal form [1]. Additionally, the emission anisotropy of the normal form clearly demonstrates the dependence on the excitation energy (Figure 1b). For example, it was experimentally found that fluorescence anisotropy of ESIPT-active molecule of 3-hydroxyflavone (in methanol) changes abruptly from about 0.18 to 0.10 with a decrease in excitation wavelength [2]. Two hypothesis have been formulated to explain the observed spectroscopic behaviour: breaking of intermolecular solute–solvent hydrogen bonds upon photoexcitation and excitation of ESIPT-active fluorophore to the higher excited states [2].

In the first hypothesis, a decrease in the molecular system volume caused by breaking of solute-solvent complexes results in a decrease in the rotational correlation time, and thus, in a decrease in the fluorescence anisotropy. In the second hypothesis, the excitation wavelength dependent fluorescence anisotropy is explained by the excitation of ESIPT-active compound to the different singlet states. At long excitation wavelengths, molecules are excited to the first singlet state S_1, while at short excitation wavelengths, molecules are excited to the higher states S_n ($n \geq 2$). Therefore, in the first case, taking into account that the excited state lifetime of the normal form is determined by the ultrafast ESIPT process, the emission anisotropy will be relatively high. In the second case, when molecule is excited to the higher state, the fluorescence anisotropy of the normal form will be lower, because the excited state lifetime will be longer due to the additional time required for internal conversion to the S_1 state before emission, according to the Kasha's rule.

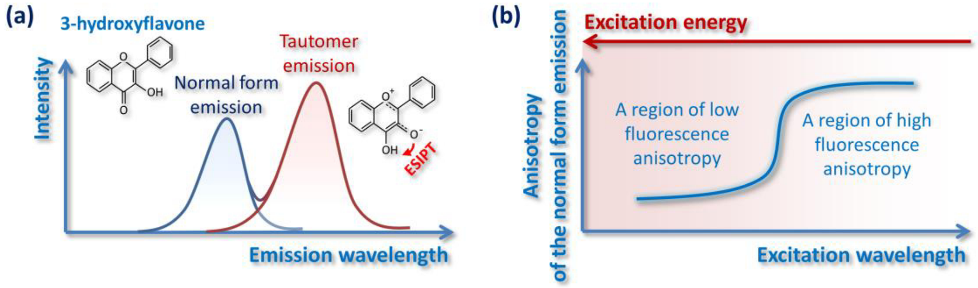

Figure 1. (a) Emission spectrum of the ESIPT-active compounds. (b) Schematic illustration of the excitation energy dependence of fluorescence anisotropy of the normal form of the ESIPT-active compounds.

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Photoresponsive Self-Assembled Pd (II) Double-Walled Triangle: Metal Ion Mediated Instant *cis* → *trans* Isomerization in the Absence of Light

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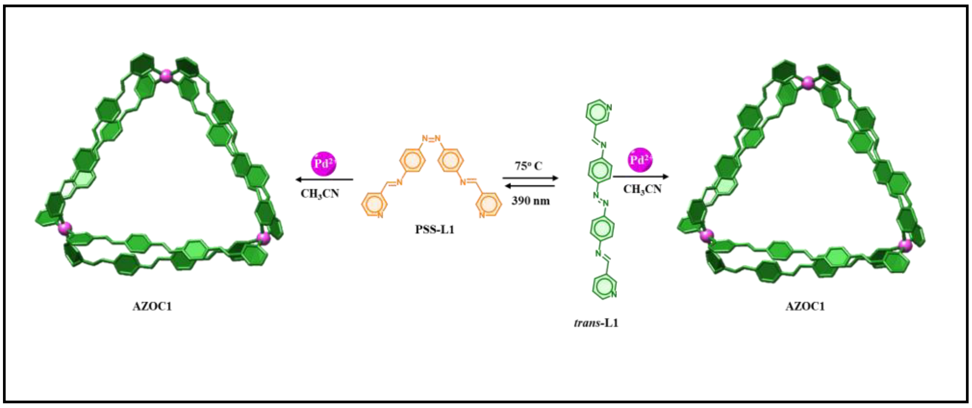
Metal organic architectures are unique because of their distinct, well-defined architectures, adjustable cavities, and wide range of uses, which include molecular recongination, sensing and catalysis etc.,[1]. The integration of photochromic units, such as azo group within their frameworks provide a robust strategy to create systems whose host-guest chemistry, recognition, or catalytic activity can be precisely modulated by light stimulus[2]. Herein we report the synthesis and characterization of a novel palladium (II) double walled triangle utilizing azo unit as a core structural component. Assembled *via* coordination-driven self-assembly of Pd(II) center with azo-based ligand, it possesses a discrete, well-defined architecture. The ligand itself show *trans* to *cis* photoisomerization with high photo stationery state of 72%. Interestingly, regardless of whether the ligand is initially in its *trans* or *cis* configuration, only a single well-defined discrete architecture is observed upon assembly. This observation leads us to hypothesize that the Pd(II) center mediates the *cis*-to-*trans* transformation of the azo ligand during the self-assembly process, negating the need for external stimuli in the initial structural formation. The assembly was characterized by UV-Vis, NMR and MS spectroscopic techniques. This work introduces a new paradigm in metal-mediated *cis*-to-*trans* isomerization of azo unit functionalized materials.



Scheme 1. Schematic diagram of self-assembly of ligand L1 from *cis* and *trans* to Pd^{2+} double walled AZOC1.

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Coumarin-BODIPY Dyad Selectively Localizing in the Endoplasmic Reticulum for Application in Photodynamic Therapy

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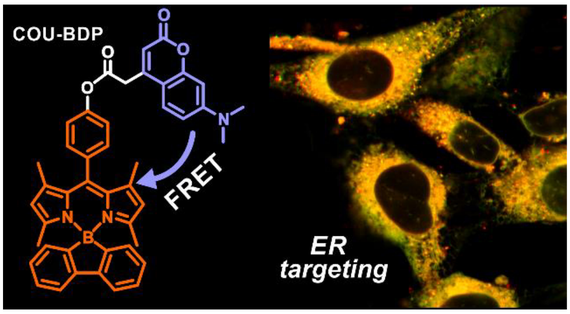
Photodynamic therapy (PDT) is a modern method of cancer treatment that serves as an alternative to chemotherapy and radiotherapy. It involves administering a non-toxic photosensitizer (PS) in the vicinity of the tumor, which, after localizing in cancer cells, is activated by light of a specific wavelength depending on the photosensitizer. Upon excitation, PS generates an excited triplet state, which can transfer energy to molecular oxygen, generating reactive oxygen species (ROS), such as singlet oxygen ($^1O_2$). ROS induce non-selective oxidation of biomolecules inside the cells, leading to their apoptosis.[1]

The search for photosensitizers capable of efficient ROS generation is the subject of intensive research. In particular, BODIPY complexes have drawn attention due to their photosensitizing properties upon appropriate modifications. One strategy for designing effective BODIPY-based PSs involves spatial separation and perpendicular arrangement of electron donor and acceptor groups within the molecule, enabling efficient generation of the triplet state *via* spin-orbit charge transfer intersystem crossing (SOCT-ISC). [2, 3]

We present a novel BODIPY-coumarin (COU-BDP) dye exhibiting good biocompatibility and high singlet oxygen generation efficiency for PDT applications. The coumarin moiety acts as an energy antenna, enabling efficient (> 97 %) Förster resonance energy transfer (FRET) to the BODIPY unit, which enables bioimaging applications by increasing the Stokes shift. Additionally, it serves as a targeting group that directs the photosensitizer selectively to the endoplasmic reticulum (ER), where, upon light activation, the PS induces oxidative stress, leading to cancer cell apoptosis. The physicochemical properties of COU-BDP were thoroughly characterized using diffraction and spectroscopic methods, and its ROS generation efficiency was evaluated.



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Perylene Derivatives as Efficient Photochemical Sensitizers for Light-Induced Polymerization and 3D Printing Applications

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Photopolymerization is a process in which light initiates the polymerization reaction of monomers, leading to the formation of a cross-linked polymer structure. Photopolymerization triggered by visible light (400–700 nm) is currently attracting increasing interest because it offers numerous advantages over traditional UV curing. The most important of these are deeper light penetration, lower risk of damage to sensitive materials, and improved work safety. The key elements of this technology are initiating systems capable of absorbing visible light, including both simple photoinitiators and more complex photoredox systems. Current research focuses on the design of initiators characterized by high quantum efficiency, oxidation resistance, and biocompatibility.

One of the most promising applications of photopolymerization is the production of hydrogels – soft, highly hydrated network materials that can retain large amounts of water while maintaining mechanical integrity. Hydrogels are utilised in various applications, including biomedical engineering, controlled drug delivery systems, diagnostics, and as substrates for cell culture. The advantage of photopolymerization is its ability to precisely shape the architecture of hydrogels and chemically modify them, enabling the design of advanced biomimetic materials.

This paper presents the results of research on various photoinitiating systems capable of absorbing longer wavelength visible light radiation. Their spectroscopic properties were analyzed, and real-time FT-IR was used to study the kinetics of photopolymerization reactions and evaluate the effectiveness of perylene-based initiating systems in hydrogel synthesis. Practical tests were also conducted, which confirmed the suitability of the developed compositions for use in 3D printing technology.

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