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Book of Abstracts

'Photochemistry for a Sustainable Energy Future'

Australian Research Council Centre of Excellence in
exciton science

Contents

PLENARY PRESENTATIONS

PL001

Quantum Engineering of Exciton Transport and Annihilation

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Charge, energy, and information carriers, when considered as quantum-mechanical particles, are attributed to a phase which manifests through coherence and interference, and which is not present for classical particles. Despite the continuing success of quantum mechanics as a predictive theory, we remain surprisingly limited in harnessing this quantum phase for the bottom-up engineering of molecular materials. Here we experimentally demonstrate an exceptional sensitivity of coherent exciton migration and exciton-exciton annihilation (EEA) to the spatial phase relationships of the involved exciton wavefunctions. We employed time-resolved optical microscopy to independently determine exciton diffusion constants and annihilation rates in two substituted perylene diimide aggregates featuring contrasting excitonic phase envelopes. Low-temperature EEA rates were found to differ by more than two orders of magnitude for the two compounds, despite comparable diffusion constants. Simulated rates based on a microscopic theory, in excellent agreement with experiments, rationalize this EEA behavior based on quantum interference arising from the presence or absence of spatial phase oscillations of delocalized excitons. These results offer an entirely new approach for designing molecular materials using quantum phase engineering where low annihilation can coexist with high exciton concentrations and mobilities.

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PL002

Photocatalysis in a New Light: A Biohybrid Approach for Enhanced Reactivity with Low-Energy Excitation

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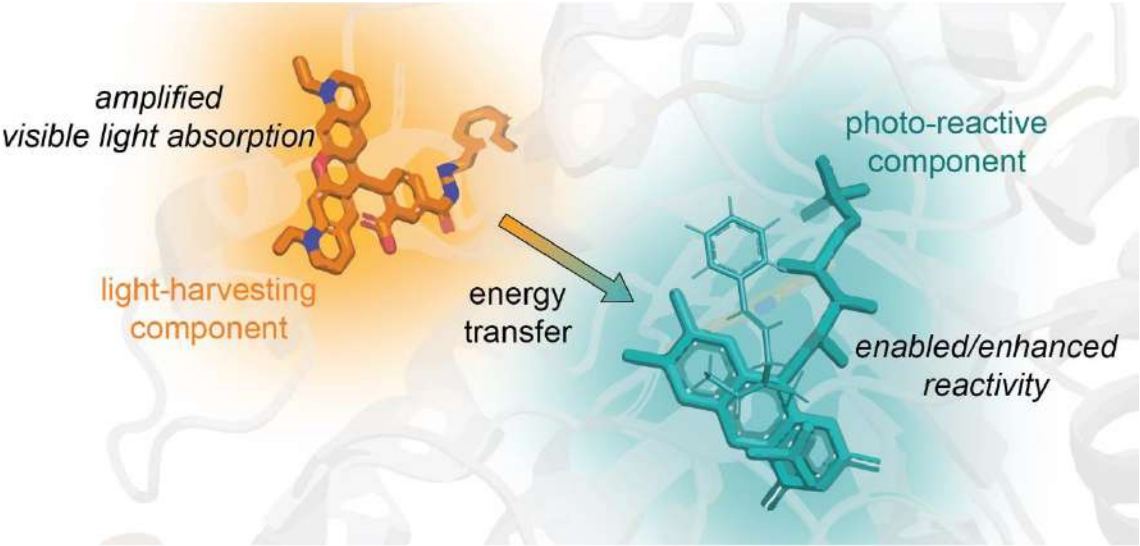
Photocatalysts convert light into chemical reactivity yet are light-limited and often require blue-to-UV excitation. In photosynthesis, light capture and reactivity have been optimized by separation into distinct sites. Inspired by this modular architecture, we synthesized biohybrid photocatalysts by covalent attachment of a light-harvesting component to a reactive component.[1,2] Spectroscopic investigation using pump-probe spectroscopy and fluorescence lifetime measurements found that absorbed energy was efficiently transferred to the reactive component, and the utility of the biohybrids was demonstrated via an increase in product yields using test reactions. This generalizable biohybrid strategy has been demonstrated with photosynthetic proteins or dyes as the light-harvesting component and transition metal photocatalysts or photoenzymes as the reactive component, and it can be readily implemented in future applications.



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PL003

Astrochemistry investigated with *para*-hydrogen matrix spectroscopy

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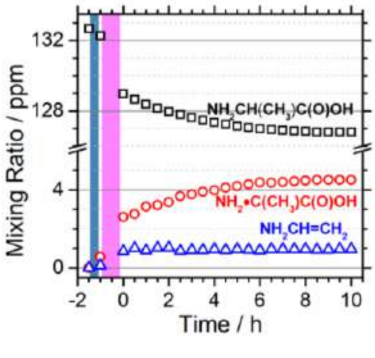
Solid *para*-hydrogen (*p*-H_2) has facilitated applications unachievable with noble-gas matrix-isolation.[1,2] We took advantage of the diminished cage effect of *p*-H_2 to prepare C_6H_6Br from photolysis of $Br_2/C_6H_6/p\text{-}H_2$. The IR spectrum indicates that Br in C_6H_6Br migrates from one carbon atom to another, performing a bevel-gear-type rotation.[3] This motion induces the stereo selectivity in the formation of *trans-ortho-* and *trans-para*-$C_6H_6Br_2$, eliminating the need of the formation of a cyclic (η_2)-C_6H_6Br radical proposed previously to explain the stereo selectivity.

We performed electron bombardment on *p*-H_2 during deposition to produce H_3^+; H_3^+ readily transfers a proton to polycyclic aromatic hydrocarbons (PAH) to form protonated PAH, possible carriers of unidentified IR emission in astronomy. Some protonated species became neutralized to form mono-hydrogenated PAH. Examples include protonated and hydrogenated quinoline and isoquinoline.[4]

We also utilized several novel methods to generate H atoms for reaction; H can efficiently tunnel through solid *p*-H_2 via H−H bond breaking and formation. One method is to add trace Cl_2 and photodissociate it at 365 nm to generate Cl atoms; subsequent IR irradiation generated H atoms via $Cl + H_2 (v = 1) \rightarrow HCl + H$. Another method is to photolyze H_2O_2 at 250 nm to form OH, which reacts with H_2 to form H_2O + H. In addition to the production of various isomers of hydrogenated species via H addition, H abstraction plays important roles in astrochemistry. Examples include stepwise H abstraction from H + methylamine,[5] glycolaldehyde and alanine. Furthermore, we found that *trans*-NMF (N-methyl formamide) can be converted to the higher-energy isomer *cis*-NMF in darkness via coupling of $H + H \rightarrow H_2$.[6] We also found that heavy atoms such as Cl can diffuse through solid *p*-H_2, enabling study of bimolecular reactions in solid *p*-H_2 and leading to a new concept of the quantum diffusion in solid *p*-H_2.



Temporal profiles of a *p*-H_2 matrix containing alanine [$NH_2CH(CH_3)C(O)OH$] and trace Cl_2. The regions shaded with blue and red correspond to periods of UV and IR irradiations, respectively. After time zero, the matrix was maintained in darkness. $[H]_0$/[▯▯alanine] ▯ 2.4 and [▯▯alanine] = 133.7 ppm.

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PL004

Water splitting photocatalysts and their application for solar fuels production

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Sunlight-driven water splitting using particulate photocatalysts has been attracting growing interest as a means of producing renewable solar hydrogen on a large scale.[1] A solar hydrogen production system based on 100-m^2 arrayed photocatalytic water splitting panels and an oxyhydrogen gas-separation module was built, and its performance and system characteristics including safety issues were reported recently.[2] Nevertheless, it is essential to radically improve the solar-to-hydrogen energy conversion efficiency (STH) of particulate photocatalysts and develop suitable reaction systems.[3] In my talk, recent progress in photocatalytic materials and reaction systems for solar fuel production will be presented.

The author's group has studied various particulate semiconductor materials as photocatalysts for water splitting.[4,5] Recently, the apparent quantum yield (AQY) of overall water splitting using $SrTiO_3$ has been improved to more than 90% at 365 nm, equivalent to an internal quantum efficiency of almost unity, by refining the preparation conditions of the photocatalyst and cocatalysts.[6] This observation means that particulate photocatalysts can drive the endergonic overall water splitting reaction with almost no recombination loss as in photon-to-chemical conversion processes in the photosynthesis. For practical solar hydrogen production, however, it is essential to develop photocatalysts that are active under visible light. Ta_3N_5,[7] $Y_2Ti_2O_5S_2$,[8] TaON,[9] and $BaTaO_2N$[10] were shown to be active in photocatalytic overall water splitting via one-step excitation under visible light.

It is possible to combine hydrogen evolution photocatalysts (HEPs) and oxygen evolution photocatalysts (OEPs) to split water into hydrogen and oxygen via two-step excitation. Such a process is recognized as Z-scheme widely. Particulate photocatalyst sheets consisting of La- and Rh-codoped $SrTiO_3$ as the HEP and Mo-doped $BiVO_4$ as the HEP immobilized onto Au and C layers split water into hydrogen and oxygen with STH values exceeding 1.0%.[11,12] Some (oxy)chalcogenides and (oxy)nitrides with long absorption edge wavelengths are also applicable to Z-schematic photocatalyst sheets.

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PL005

Emergent Chiroptical Properties in Assembled Molecules and Materials: From Native Chirality to Global Chirality

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The emergence of chiroptical properties in molecules and materials through their asymmetric organizations has fascinated humankind in general and the scientific community in particular. By adopting molecules, plasmonic systems, and semiconductor quantum dots as examples, the translation of ‘local’ chirality in these building blocks to the ‘global’ chirality when they self-assemble as nanoobjects will be explained. The presentation covers the following aspects.

(i) In assembled molecular systems, induced circular dichroism (ICD) originates through the off-resonance coupling of transition dipoles, resulting in monosignated CD signals. In contrast, exciton-coupled circular dichroism (EC-CD) originates through the on-resonance exciton coupling, displaying bisignated CD signals.[1-3] Bisignation in the CD responses of assembled plasmonic systems results from the resonant plasmon coupling, termed surface plasmon-coupled circular dichroism (SP-CD).[4,5]

(ii) The presentation will draw parallels between the emergence of EC-CD and SP-CD based on the coupling of their transition dipoles.[3] More importantly, our studies have concluded that the sign of the EC-CD/SP-CD depends not only on the handedness of the assembly but also on the sign of the interaction energy between the neighboring dipoles.[6]

(iii) The presentation will also discuss how chiral surface domains of various self-assembled amino acid-based templates transfer chiral information to bound achiral chromophores. The origin of CD and CPL of achiral molecules on these templates are explained based on exciton coupling.[7]

(iv) The presentation will also provide fundamental insight into the interaction of chiral molecules with silicon nanoparticles and the emergence of its CD and CPL.[8]

An open challenge is to develop a universal model which can explain the chiroptical properties of assembled systems based on the transition dipolar coupling and interaction energy: our findings in this direction will be presented.

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The theoretical collaborations with Dr. R. S. Swathi, IISER Thiruvananthapuram (India), Dr. Cristina Sissa and Prof. Anna Painelli, University of Parma (Italy), and Prof. S. Balasubramanian, JNCASR, Bangalore are greatly acknowledged. KGT acknowledges the J. C. Bose National Fellowship and Nanomission project (DST/NM/TUE/EE-01/2019), the Department of Science and Technology, Government of India, for financial support.

PL006

By passing wires – Monolithic Integrated Devices for Solar Driven Hydrogen Production and Solar Batteries

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As we are moving towards a zero-carbon economy, solar will play an integral part in energy generating and storage technologies. Devices that integrate solar energy conversion and fuel production or storage in one unit are potentially attractive for decentralized deployment where energy generation is in the vicinity of the users. They have the added advantages of smaller footprint and shorter deployment time as the need and cost for the supporting infrastructure (e.g., site preparation, “poles and wires”, transformers amongst others for large scale solar farms or wiring, maximum power point trackers, inverters for conventional roof-top systems) are reduced.

In this talk, I will also talk about our work on low cost, high performance monolithic photovoltaic-electrochemical (PV-EC) devices for hydrogen generation using perovskite tandem and single junction solar cells. I will also talk about our work on integrating high-efficiency perovskite/silicon tandem solar cells with novel redox couples for solar flow battery with record performance.

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MASUHARA LECTURESHIP AWARD PRESENTATIONS

AW001

Carrier Dynamics of the Lead Halide Perovskite Nanocrystals

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The lead halide-based hybrid and all-inorganic perovskites continue to receive huge attention worldwide because of their great potential in solar photovoltaic and various light-emitting applications.[1] Considering that an understanding of the fundamental photo-processes, like deactivation pathways and dynamics of the photo-generated charge carriers, is essential for proper utilization of these substances in different applications, we have been looking into the nanocrystalline form of these materials addressing a variety of issues like those mentioned above. This talk will highlight how a combination of femtosecond pump-probe and single-particle fluorescence techniques can provide valuable information on the nature and energy states of the photogenerated species, pathways and dynamics of relaxation of the charge carriers, location and nature of the trap states and their role in fluctuation of photoluminescence of the lead halide perovskite nanocrystals.[2-5]

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AW002

My Journey to the Molecular Excitonic World

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Various synthetic strategies have been developed to devise a variety of artificial molecular arrays in molecular photonics because of their similarities in architecture and subunit structures to the natural photosynthetic light-harvesting complexes. For the molecular arrays to be efficient devices, they should have very regular pigment arrangements which allow a facile light energy or charge flow along the array but do not result in the alteration of individual properties of the constituent pigments leading to the formation of energy or charge sink. In these respects, understanding of photophysical properties of these macromolecular architectures is essential for the rational design of molecular devices for photovoltaic, or optoelectronic applications.

Here, we have revealed that the ultrafast excitation energy migration processes in molecular arrays are strongly influenced by the electronic couplings among the constituent molecules as well as the structural rigidity of overall architectures. Our investigations have been extended to H-type aggregated perylenebisimide (PBI) and polythiophene oligomers (linear vs. cyclic). Not only intermolecular exciton couplings but intramolecular electronic structures have been investigated in a series of expanded porphyrins in conjunction with their molecular structures, the number of π-electrons (Hückel's [4n+2] rule) as well as their conjugation pathways. Our study demonstrates a relationship between the photophysical properties such as absorption/emission properties, excited state dynamics and the aromaticity of expanded porphyrin systems. Based on these spectroscopic observations, we have found the reversal of aromaticity in the excited states of aromatic/antiaromatic expanded porphyrin congeners.[4] Detailed studies of the modulation events are expected to provide additional fruitful insight into the relationship between (anti)aromaticity and electronic structures. To the extent this proves true, it could have far-reaching practical applications that complement the advances in theoretical understanding that our studies are likely to provide.

KEYNOTE PRESENTATIONS

KN001

Tracking ultrafast photochemistry at the water surface by phase-sensitive nonlinear spectroscopy

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The liquid interface provides a unique environment where various important chemical/physical processes take place. However, our understanding of interfacial molecules is insufficient, compared to the plenty of accumulated knowledge about molecules in the bulk. It is because of the difficulty of selectively investigating interfacial molecules by separating them from the vast number of the same molecules present in the bulk liquid phase. Heterodyne-detected vibrational sum-frequency generation (HD-VSFG) spectroscopy that we developed intrinsically has interface-selectivity due to the 2nd order nonlinear process and is advantageous over conventional VSFG spectroscopy because it provides interface-selective vibrational spectra that can directly be compared with infrared and Raman spectra in the bulk.[1]

We have extended HD-VSFG spectroscopy to femtosecond time-resolved measurements.[2-4] In particular, for tracking ultrafast photochemistry at the water surface, we realized UV-excited time-resolved HD-VSFG[5] and succeeded in tracking the photochemical reaction of phenol at the water surface[5]. Our data revealed that the phenol reaction is drastically accelerated by a factor of ~10^5 at the water surface, compared to the reaction in solution[6]. This drastic difference in the reaction dynamics arises from the difference in the hydration environment at the interface, as clarified by the quantum chemical calculation combined with MD simulation.[7]

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KN002

Nontoxic and Robust Hybrid Copper Halides for Solid-State Lighting Technologies

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Energy efficient solid-state lighting (SSL) technologies based on light-emitting diodes (LEDs) and organic light-emitting diodes (OLEDs) are future global lighting solutions. Developing eco-friendly and robust photoluminescent (PL) and electroluminescent (EL) materials that meet the cost and performance standards for use in LEDs/OLEDs represents an important area of today's materials research. In the recent years, we have devoted considerable efforts to the design and optimization of such materials based on hybrid copper halides,[1-12] with an emphasis on the enhancement of their chemical and physical properties by systematically engineering their crystal structure, composition and chemical bonding at the inorganic-organic interface. Our investigations demonstrate strong structure-property correlations in these materials and reveal that their interesting and unique properties are the results of interplay between inorganic and organic constituents. A powerful combination of experimental and theoretical studies has provided explanations and insight on the origin and mechanism of luminescence in these systems. Featured by low synthesis cost, nontoxicity, good solution processability, excellent moisture/thermal/photo-stability, high luminescence efficiency, easy scalability and sustainability, these materials show substantial promise for use as phosphors and/or emissive layers in energy-efficient SSL technologies.

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KN003

Surface-enhanced Raman Scattering Platforms Assisted by Machine Learning for Predictive Biosensing Applications

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In this talk, I will discuss my group's effort in using molecular enhancement strategies and machine learning algorithms to bolster SERS performance for various sensing applications. I will discuss various SERS platform fabrication strategies to bestow desirable chemoselectivity and increase target analyte/biomarker affinity to achieve higher detection sensitivity and selectivity. I will also highlight various emerging research strategies which utilize machine learning algorithms for rapid on-site prediction of disease infection. Specifically, how chemometrics and machine learning algorithms can transform the assimilation and interpretation of complex spectral data in biological samples by discerning more patterns hidden within the data, to achieve high throughput data analysis, sensitivity, and disease prediction. I hope these insights can stimulate the development of innovative and hybrid detection methods across the entire analytical discipline to resolve longstanding challenges in biomarker and analyte sensing and detection.

KN004

Science of Triplet Excitons

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Molecular triplet excitons are ‘dark states’ because of the forbidden nature of the electronic transitions. However, they can be harvested to enhance the efficiency of optoelectronic devices such as organic light-emitting diodes and solar cells. For example, multiexciton generation through singlet fission has the potential of exceeding the Shockley–Queisser limit in photovoltaic devices. However, only very few materials suitable for singlet fission are available at present, and the mechanism of inter- and intra-molecular singlet fission are not fully understood. Detailed knowledge regarding the processes is crucial for developing new materials. In this talk, I will present the molecular design and synthesis strategies to meet the exchange energy and morphology criteria for molecules to undergo singlet fission.

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KN005

Nanophotonic metasurfaces for enhancing photochemistry and energy conversion

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Metasurfaces — nanostructured surfaces of metallic or insulating materials with a pitch well below the wavelength region of interest — provide unprecedented control of harvesting and manipulating of electromagnetic waves. In my talk I will present a number of examples in the context of energy conversion and enhanced monitoring of photochemistry.

A first focus will lie on energy conversion. Here, the tunability of radiative coupling of so-called quasi bound-states-in-the-continuum modes allows critical coupling, and hence optimum coupling, to the incoming radiation field, maximizing absorption. Using nanostructured titanium dioxide, we show that judicious optical design can enable highest energy conversion rates for reduction reactions for low oxygen vacancy defect concentrations, outperforming substrates with much higher extinction. This opens up exciting prospects for energy conversion and photochemistry with low-loss materials.

A second focus will lie on nanostructured electrodes for enhancing mid-infrared surface enhanced infrared absorption spectroscopic monitoring (SEIRA) of chemical conversions in a photo-electro-chemical reactor integrated into a FTIR microscope. We show how hole-based resonances in an otherwise flat film show a generally more stable response than conventional particle-based structures. We evaluate enhanced monitoring performance in the framework of Fano-resonant coupling between vibrational resonances and the antenna modes of the metasurface. Additionally, we will demonstrate how critical coupling considerations influence the strength of the SEIRA signal.

Lastly, I will present our newest results in this general topic.

KN006

Functional Bond-Selective Imaging for Subcellular Bioanalysis

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Innovations in optical spectroscopy and microscopy have revolutionized our understanding in live biological systems at the sub-cellular levels. In this talk, I will present our recent advances in developing and applying functional bond-selective spectro-microscopy for investigating subcellular biological activities with rich chemical information. In the first part of my talk, I will present the novel coupling of the stimulated Raman scattering (SRS) imaging, a nonlinear Raman imaging modality, with the newly developed chemical strategies for Raman-guided intracellular metabolic mapping[1]; quantitative subcellular analysis of cytoplasmic aggregates[2]; photo-activatable and photo-switchable SRS spectral-imaging[3]; intracellular sensing through alkyne-HDX[4]; and toward super-resolution chemical imaging. In the second part of my talk, I will present a new mid-infrared near-infrared two-photon imaging technique for bond-selective fluorescence imaging with single-molecule sensitivity[5].

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KN007

Quantum-Coherence-Enhanced hot electron transfer at Au nanostructure/TiO2 interface under modal strong coupling

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Plasmon-induced hot electron transfer at metal/semiconductor interfaces has attracted much attention as a novel mechanism to promote artificial photosynthesis under visible light irradiation [1-4]. Recently, we reported that Au- NPs/TiO2/Au film (ATA) structures, which exhibit modal strong coupling between the Fabry-Pérot nanocavity mode and localized surface plasmon resonance (LSPR), can be used as photoanodes to enhance water splitting reactions [5]. The light absorption of the ATA structure was promoted across a broad range of wavelengths under the modal strong coupling, followed by a hot electron transfer from Au-NPs to TiO2. We observed an 11-fold increase in the incident photon-to-current conversion efficiency (IPCE) with respect to a photoanode structure with no Au film. Importantly, the internal quantum efficiency (IQE) of photocurrent generation was enhanced 1.5 times under a strong coupling over that under uncoupled conditions.

To clarify the mechanism of the IQE enhancement in the ATA structure, we further investigated the ATA structures using well-size-controlled Au nanodisks (Au-NDs) fabricated on nanocavities using electron beam lithography. Absorption spectra were measured by varying the number of Au-NDs per unit area. The integrated intensities of the absorption spectra were almost constant, independent of the number density of Au-NDs. Near-field spectra obtained from the FDTD simulations also showed the same behavior. On the other hand, the integrated intensities of the absorption spectra of the Au-NDs/TiO2 (AT) structures increased linearly with increasing Au-ND number density. These results suggest that the LSPR of Au-NDs on the nanocavity has a quantum coherent interaction through the nanocavity. Furthermore, measurements of the near-field spatial distribution of Au-NDs on the nanocavity using photoemission electron microscopy strongly support the existence of quantum coherent interactions in the ATA structure. In addition, transient absorption measurements of electrons injected from Au-ND into TiO2 showed that the apparent quantum efficiency (AQE) of electron injection increased with increasing Au-ND number density. On the other hand, for AT, the AQE of injected electrons was independent of the Au-ND number density. From these results, it is inferred that the quantum coherent interaction between LSPR of the Au-NDs through the nanocavity is an important factor that enhances the IQE of photocurrent generation in the ATA structures. In my talk, I will also introduce the results of model calculations and explain how quantum coherent interactions between LSPR of the Au-NDs via nanocavity are involved in the enhancement of AQE [6].

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KN008

UV Spectroscopy and Reaction Kinetics of Criegee Intermediates

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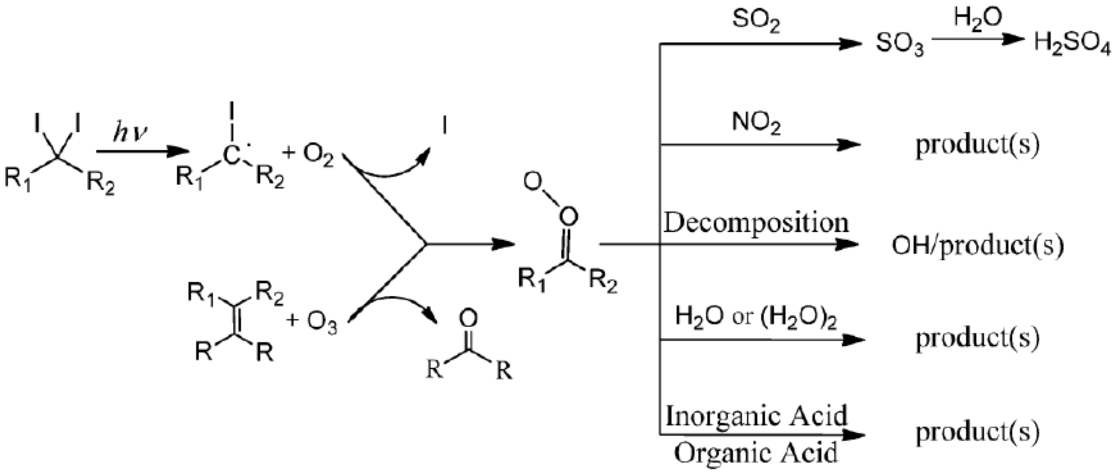
Criegee intermediates (CIs) are very reactive carbonyl oxides which are formed in the ozonolysis of alkenes. CIs are thought to be important in the oxidation of atmospheric molecules including SO_2, NO_2, inorganic and organic acids, and even water. To better assess the roles of CIs of various structures in atmospheric chemistry, it is desired to know the trend of their reactivity. Our group has measured the UV spectra of a few important CIs and determined their absolute absorption cross sections. The intense UV absorption of CIs allows scientists to probe their reaction kinetics. We found that there are strong structure dependences in the thermal decomposition reactions of CIs and in their reactions with water molecules. Furthermore, there is a strong synergy effect in the CI reactions with hydrogen-bonding molecules. Vinyl substituted CIs are more stable due to the extended conjugation of the double bonds, which also affect the reactivity. The fates of various CIs in the atmosphere can be estimated based on the trend of their reactivity.

I will talk about the story of our research on CIs,[1-5] including serendipity.



Schematic showing a few key reactions involving Criegee intermediates.[3]

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INVITED PRESENTATIONS

IN001

Spatiotemporal control of photochromic reaction based on oxygen regulation using supramolecular gel

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Photochemical reactions are widely utilized because light enables remote energy provision with superior spatiotemporal resolution. General photochemical reactions respond quickly to photoirradiation; the initial reaction rate is the highest. In contrast, if there is an induction period between the beginnings of photoirradiation and photoreaction, it leads to unique photofunctions.[1] In this study, we developed photochromic gel materials showing an induction period in the color and fluorescence changes. This behavior is brought by competition between a photoreduction reaction and inhibition of the reaction by molecular oxygen (O_2), which is regulated in the supramolecular gel medium.

When irradiated with UV light, the gel sample was changed from colorless and nonemissive to yellow and emissive due to photoreduction. Interestingly, the photoreduction in the N_2-bubbled gel started just after the beginning of photoirradiation, whereas an induction period (~1 minute) until photoreduction was observed in the air-saturated gel. This induction period was considered as the duration until the dissolved O_2 was consumed by quenching the photoreduction. While the reduced form showed a lifetime of over 1 hour in the gel state, the decoloration was completed instantly upon the gel-to-sol transition by heating. This is because the sol state allows quick O_2 supply from the air in contrast to the gel state.

Moreover, spatiotemporal patterning of the photochromic reaction was conducted (Figure 1). We irradiated UV light to the gel through a photomask. After the photoirradiation, photoreduction had not yet been caused but the information was recorded as the O_2 concentration pattern dependent on the transmittance of the photomask. In the reading process, we irradiated UV light without photomasks. The two-step fluorescence pattern appeared based on photoreduction according to the patterned O_2 concentration. The recorded patterns were erased by the sol-gel transition. These results demonstrated the potential of our system in cryptography and display devices.

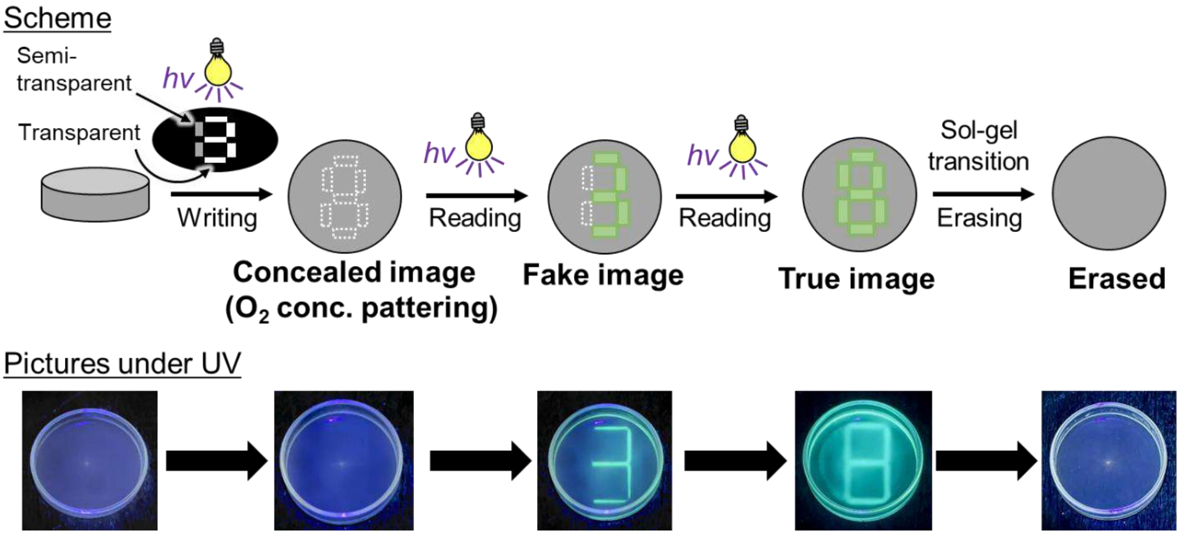

Figure 1. Experimental scheme and sample pictures (under 365-nm light irradiation) in the spatiotemporal photopatterning.

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IN002

Strategies for Enhanced Stability of Black-$CsPbI_3$ Photovoltaic Films

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The unique optoelectronic attributes of $CsPbI_3$ halide perovskites make them suitable for photovoltaic applications. However, stability issues under ambient conditions limit their widespread use. Particularly, the black phase of $CsPbI_3$, which is only stable at high temperatures, transforms into a less desirable yellow phase at room temperature.

Our lab has developed several strategies to address these stability issues, thus paving the way for wider deployment of $CsPbI_3$ in photovoltaics.[1] One technique involves interface engineering by preparing $CsPbI_3$ thin films on substrates with different thermal expansion coefficients. Rapid cooling induces interfacial strain and subsequently extends the stability of the black phase.[2]

Additionally, doping the $CsPbI_3$ films with small quantities of certain elements has shown to increase black phase stability. These dopants introduce local structural modifications that maintain the black phase.[3] We have also explored the role of oxygen atmosphere annealing on $CsPbI_3$ thin film stability. This method facilitates surface oxidation, forming a lead oxide protective layer that inhibits further oxidation and enhances black phase stability.[4]

One particularly effective method involves the use of coarse photolithography to embed a PbI_2-based interfacial microstructure. This microgrid endows the films with moisture resistance and substantially boosts black phase stability for over two and a half years, even in dry environments.[5]

In summary, our work demonstrates the successful application of diverse techniques in enhancing the black phase stability of $CsPbI_3$ films. From interfacial strain induction to doping, interfacial microstructure embedding, and surface oxidation, all these strategies promise to extend the black phase stability. Our findings could significantly advance the use of $CsPbI_3$-based perovskite solar cells, with further exploration expected to yield highly durable and efficient perovskite devices.

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IN003

Surface engineering of plasmonic nanowire toward novel platform of intracellular material sensing and delivery

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Physically addressing site-specific areas of a single live cell with the high spatial resolution is one of the attractive approaches to obtaining a better understanding of cellular behavior. Cell endoscopy offers a promising tools of achieving site-specific access inside a single live cell. In conventional cell endoscopy, various probes, such as glass pipettes, glass fibers, nanowires, and nanotubes, are inserted into a cell, enabling optical studies, material delivery, electrochemistry, and other applications. Optical waveguide probes are increasingly popular due to their ability to easily direct and extract optical information from the cell.

Plasmon-based single live-cell nanowire endoscopy is a promising novel tool for understanding biological processes at a single-cell level.[1] This technique has realized the highly sensitive sensing of Raman signals from site-specific areas in a single live cell with less invasiveness by applying the unique plasmonic properties of a metal nanowire to an endoscopic probe. This technique gives us essential information, such as the interaction between DNA and fluorescence dye inside a nucleus[2], or site-specific intracellular local pH[3]. Furthermore, this technique has great potential to realize intracellular materials delivery systems by engineering the surface of nanowire probes.

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IN004

Graphene-Based Photodetectors: Some Attempts Towards High Performance and Intelligence

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In this talk, we discuss our attempts to improve the performance and intelligence of graphene-based detectors. To begin, we will introduce the strategies for synthesizing wafer-scale single-crystal graphene materials[1] and achieving scalable production. The device fabrication processes compatible with CMOS will also be introduced. Next, we will talk about the construction of graphene-based heterojunction structures, and analyze some interesting phenomena such as polarity-tunable[2] and photovoltage-driven[3] effects. The photoelectric conversion with ultrahigh gain, ultrahigh responsivity, rapid response, and broad spectral sensitivity[4,5] will be discussed. Finally, we will introduce device structures that can exhibit both positive and negative photoresponse, highlighting their self-distinguishable capabilities and their application in optoelectric logic operations.

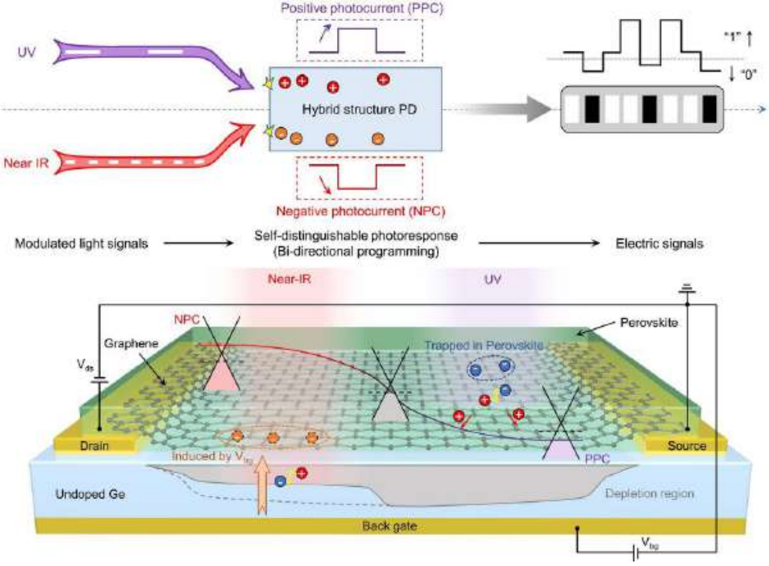

Figure 1 illustrates the self-distinguishable dual-band photodetector which is composed of a perovskite-graphene-Ge heterostructure. A bi-directional photoresponse, namely, positive photocurrent (PPC) and negative photocurrent (NPC) in response to UV and NIR lights, respectively can be generated. This intelligent detector can be used for optoelectric logic operations by collecting modulated optical signals and outputting Boolean electrical signals.

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IN005

Designing an Artificial Light Harvesting System and Monitoring Conformational Dynamics of i-motif DNA Using FRET Approach

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Dipole-dipole interaction among chromophores facilitates the transfer of excited state energy to the other chromophore through Förster Resonance Energy Transfer (FRET).**[1]** This purely non-radiative energy transfer is governed by the distance (2-10 nm) between the FRET pair, and hence, it is referred to as “spectroscopic nanoruler”.**[1]** FRET is extensively employed to a wide variety of systems ranging from designing artificial bioinspired light harvesting system (LHS) to investigate the conformational dynamics of intercalative-motif (i-motif) DNA. Nature has beautifully assembled its light harvesting pigments within the protein scaffolds that ensures a very high energy transfer.**[2]** We generated a highly efficient artificial LHS using a self-assembled nanostructure of a homopolypetide (poly-D-lysine, PDL) making use of their β-sheet structure in aqueous solution.**[3]** Such homogeneous β-sheet structure acts as an assembly hub to align two chromophores in close proximity. The chromophores used are compatible for a highly efficient energy transfer process, are non-fluorescent in aqueous medium but exhibit high fluorescence intensity when bound to the nanostructure of PDL and generates white light emission. On the other hand, the effect of confinement on folding pathway of noncanonical (i-motif) DNA under physiological condition is extensively studied by single-molecule FRET (smFRET).**[4]** Such kind of noncanonical DNA has been considered as a novel drug target in the field of anticancer research.**[5]** Hence, it is pertinent to have a better understanding as to how various drugs interact with the highly dynamic structures of noncanonical DNA. A detailed illustration of the structural dynamics of *c-MYC* promoter-based i-motif conformation has been investigated at physiological condition within a microemulsions having various nanodimensions. It is concluded that the folding of such motifs under cellular-like confined environment is not a direct transition between unstructured random coil to a structured i-motif, rather it occurs through a partially folded intermediate depending, on the confined dimension.**[4]**

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IN006

Quantitative and Selective Bidirectional Photoisomerization with Visible and Near-Infrared Light of 3-Phenylperylenyl-Bridged Imidazole Dimer

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Photochromic molecules can reversibly interconvert between two isomeric forms with different colors and chemical properties by light irradiation at different wavelengths and have been used to switch the properties such as surface polarity, electric conductivity, catalytic activity, and biological functions by light. Visible and near-infrared (NIR) light is arguably more suitable than UV light for most applications, as UV light damages cells and the surrounding environment, and furthermore, is non-selectively absorbed by any chromophores. Therefore, there has been a need to develop photochromic molecules that can be operated in both directions in the visible light range. Selective bidirectional photoisomerization reactions with high conversion ratios between stable and metastable isomers by irradiating photochromic molecules with visible light of different wavelengths have been an important issue for many years.

For negative photochromic molecules known so far[1-3], metastable isomers also absorb UV or visible light in the same region as stable isomers, making it difficult to selectively achieve the reverse reaction by visible light irradiation. We have demonstrated that the absorption bands of the stable and metastable isomers of 3-phenylperylenyl-bridged imidazole dimer (PhPe-ImD) are largely separated more than 140 nm and that the almost quantitative and selective bidirectional photoconversion can be achieved by 660 and 460 nm light.[4] The difference in the magnitude of the absorption coefficients between PP-6MR (ε is 2.21×10^4 M^{-1} cm^{-1}) and PP-5MR (ε is 3.61×10^3 M^{-1} cm^{-1}) at a wavelength of 460 nm confirms the clean conversion (93 %) to PP-5MR upon irradiation with blue LED light (λ = 460 nm, FWHM = 10 nm). Irradiation with red LED light (λ = 660 nm, FWHM = 10 nm) achieves almost complete photoconversion (> 99%) from PP-5MR to PP-6MR. Furthermore, the forward reaction can be achieved completely with near-infrared light of 785 nm.

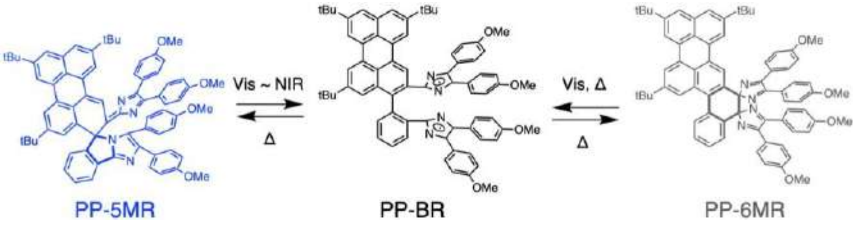

Figure 1. Negative Photochromic Reactions of PhPe-ImD.

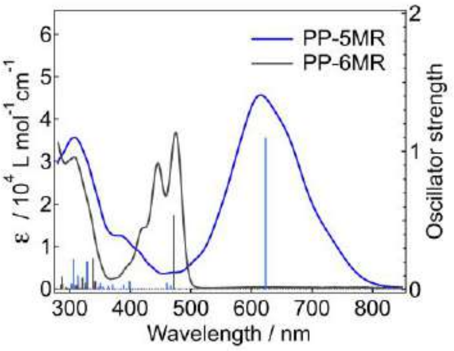

Figure 2. Absorption spectra of PhPe-ImD in benzene. The calculated absorption spectra (TDDFT PBE0/6-311+G(d,p)) are shown by the vertical lines in the same color.

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IN007

Plasmon-enhanced photoluminescence of Au nanostructured transition metal dichalcogenide heterostructures

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Monolayer transition metal dichalcogenides (TMDCs) are direct bandgap semiconductors that exhibit photoluminescence, making them promising for applications in light emitting, chemical sensor, and light-energy conversion devices. In particular, TMDC heterostructures composed of vertically stacked n-type and p-type TMDCs demonstrate a type-II band offset, leading to charge separation. Therefore, they are expected to be applied in photovoltaic and light-emitting devices. However, there are challenges in photovoltaic devices, such as low light absorption resulting in insufficient external quantum efficiency, and in light-emitting devices, where reduced quantum yield occurs due to slower electron-hole recombination caused by charge separation. To overcome these drawbacks, the electromagnetic field enhancement effect through localized surface plasmon resonances (LSPRs) can be utilized. LSPRs can resonate with incident light, thereby increasing the excitation efficiency, enhancing light utilization through light scattering, and accelerating the electron-hole recombination rate via the Purcell effect. In this study, our aim is to investigate the placement of plasmonic nanostructures on TMDC heterostructures to enhance the photoluminescence and elucidate carrier dynamics.

We synthesized n-type semiconductor MoS_2 and p-type semiconductor WSe_2 on Si/SiO_2 substrates using salt-assisted chemical vapor deposition. The synthesized TMDCs were transferred onto glass substrates and stacked using a transfer apparatus with position and angle adjustment capabilities to create TMDC heterostructures. Subsequently, we fabricated Au nanoblocks of arbitrary sizes on the TMDC heterostructures using electron beam lithography/lift-off techniques. Annealing treatment was performed to improve the adhesion between the Au nanoblocks and TMDC heterostructures. Additionally, to minimize the effects of electron and energy transfer, a 1 nm-thick Al_2O_3 layer was inserted between the Au nanoblocks and TMDC heterostructures using an atomic layer deposition system. Photoluminescence and femtosecond pump-probe spectroscopy were employed to investigate the photoluminescence characteristics and carrier dynamics.

Scanning probe microscopy, scanning electron microscopy, and Raman microspectroscopy measurements confirmed the successful fabrication of monolayer MoS_2 and WSe_2 on Si/SiO_2 substrates and the successful transfer to SiO_2 substrates. The photoluminescence spectrum of the TMDC heterostructure revealed the presence of the interlayer exciton band at the longest wavelength around 780 nm when the angle between MoS_2 and WSe_2 was 60°. Carrier dynamics measurements at a pump wavelength of 400 nm and a probe wavelength of 800 nm exhibited a decay curve with a rise component of ~100 fs and a decay component of 24 ps, indicating both charge separation and charge recombination processes, respectively. This revealed a significantly prolonged lifetime compared to the charge recombination of isolated WSe_2. Furthermore, it was revealed that when the wavelength of the Au nanostructures coincided with the interlayer exciton band, a ten-fold increase in photoluminescence intensity occurred due to the Purcell effect.

Acknowledgements
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IN008

Excitons in Halide Perovskite Nanocrystals and Assemblies

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The size-, shape-, and composition-dependent tunable bandgap and emission color of metal chalcogenide quantum dots (QDs) and metal halide perovskite nanocrystals (NCs) are two fascinating inventions in chemistry and materials science in the recent past. These unique properties accompany these tiny crystals to the development of brilliant LEDs, tunable lasers, excellent photodetectors, and high-efficiency solar cells. The optical and electronic properties of these QDs and NCs are further modified by assembly formation. For example, isolated Cs/Ma/$FaPbBr_3$ QDs/NCs showing blue emission and short excitonic lifetimes form random 2D and 3D self-assembled films with intense green emission and long-lived excited states. The blue emission and short lifetime of individual NCs are consistent with a weak dielectric screening of excitons. The green emission and long-living excited states of the self-assemblies suggest a strong dielectric screening that weakens the quantum confinement, allowing excitons to split into free carriers, diffuse, and trap. However, the optical properties of these self-assemblies change by mechanical deformation. Conversely, rationally assembled QDs or NCs form higher-order supercrystals (SCs) with controlled dielectric, electronic, and excitonic properties. For example, bidentate ligand exchanged Cs/MA/PbX_3 (X:Br/I) NCs generate mechanically stable SCs with close-packed lattices, overlapping electronic wave functions, and higher dielectric constants, providing distinct excitonic properties from isolated NCs/QDs or self-assembled films. A perovskite SC shows a smaller spectral shift (<35 meV) than an NC film (>100 meV), a microcrystal (>100 meV), or a bulk crystal (>100 meV). Also, the exciton lifetime of an SC is excitation power-independent in the single exciton regime, comparable to an isolated NC. Therefore, bidentate-ligand-assisted SCs help overcome delayed exciton or carrier recombination in halide perovskite assemblies. Structures and excitonic properties of isolated, self-assembled, and rationally assembled NCs will be discussed.

IN009

Photophysics of Non-fullerene Acceptor Organic Solar Cells

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The recent advent of non-fullerene acceptors (NFAs) has led to the demonstration of organic solar cells with power conversion efficiencies (PCEs) now exceeding 19%.[1] In organic solar cells, the energetic landscape of the heterojunction, specifically the donor-acceptor interface, provides the driving force for efficient exciton quenching and charge separation, prerequisites for such high PCEs.[2] While the mechanism leading to efficient exciton quenching and charge separation in fullerene-based blends has been intensively investigated over the past two decades, there is an ongoing debate about the processes occurring in non-fullerene acceptor solar cells.

In this presentation, I will discuss recent insights into what governs the efficiency of interfacial charge separation and recombination in NFA-based systems, as well as what determines energetic (photovoltage) losses. I will demonstrate that efficient energy transfer from the donor to the acceptor followed by hole (back)transfer at the interface, processes that we investigate by steady-state and advanced transient optical and electro-optical spectroscopies, cause a dependence of the devices' internal quantum efficiencies primarily on the ionization energy (IE) offset.[3,4] In fact, the IE offset limits exciton-to-charge transfer (CT) state conversion in many state-of-the-art low-bandgap NFA-based systems, while the subsequent separation of the CT state into free charges is barrier-less. Finally, I will discuss computational (in-silico) approaches to the design of novel acceptor materials based on the design rules derived from spectroscopic insights into the efficiency-limiting processes in NFA-based blends.[5]

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IN010

Visible-Light Photocatalysis with Surface Engineered Nanomaterials

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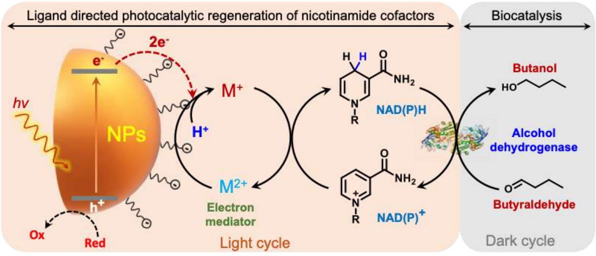
The large absorption cross-section and high photostability of plasmonic nanoparticles (NPs) and quantum dots (QDs) make them ideal candidates for various solar to chemical fuel conversions.[1] However, achieving an efficient separation and utilization of charge carriers from NPs/QDs is still challenging.[2] Our group has developed strategies based on the interplay of forces to improve the charge separation and utilization steps in hybrid nanomaterials.[3] Specifically, a proper choice of surface ligand helped in channelizing and increasing the local concentration of reactant molecules around the surface of the photocatalyst, thereby enhancing the probability of the charger transfer process.[4] By introducing the idea of favourable catalyst–reactant interactions, we were not only able to achieve efficient photocatalysis at low catalyst concentration, but also regulate the catalytic properties between completely 'ON' and 'OFF' states.[4] In this presentation, I will be showcasing the power of surface ligands in photocatalysing the regeneration of nicotinamide cofactors using plasmonic NPs and QDs.[4] In one example, we were successful in achieving a quantitative photocatalytic regeneration of nicotinamide cofactor within 30 min of irradiation. The strong electrostatic interactions emanating from the surface of NP photocatalysts helped in accelerating the charge transfer from the photocatalyst to reactants, thereby enhancing the formation of cofactors. Further, the concept of artificial photosynthesis was demonstrated wherein the nicotinamide cofactors produced in the light cycle participated in an enzymatic reaction in the dark, thereby triggering multiple light-dark cycles. In summary, the use of electrostatics mimic the underlying force involved in various enzyme catalysis, which can serve as a generic approach for other important artificial multielectron photocatalytic reactions as well.



Scheme 1. Surface ligand directed artificial photosynthesis. Nicotinamide cofactor is photogenerated in the light cycle by surface engineered NP photocatalysts, which further participates in an enzyme catalyzed reaction in the dark cycle to produce butanol. During this, the nicotinamide cofactor is regenerated that triggers the next cycle of light reaction.

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IN011

Anisotropic surface quenching of single upconversion nanoparticles

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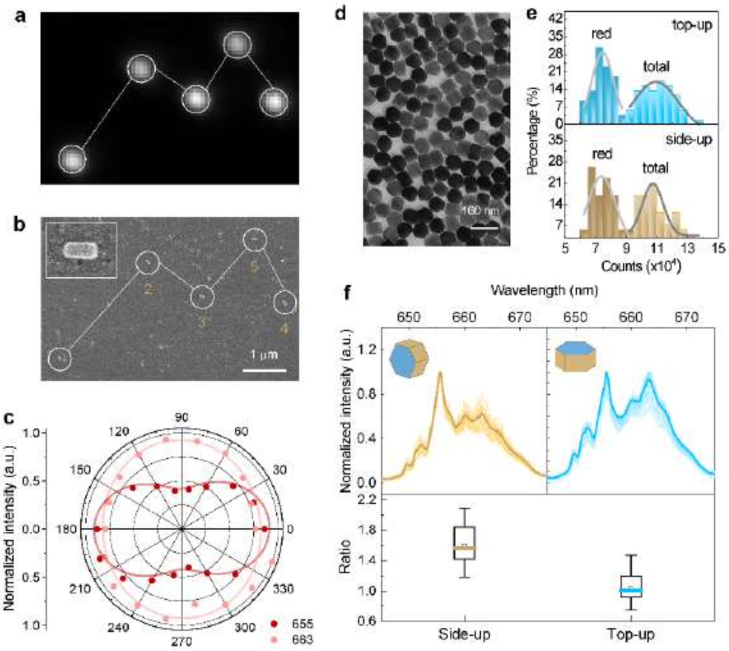
Shape anisotropy at the nanoscale has emerged as a potent way to access new properties and functionalities of luminescent materials. While the controlled synthesis and precise characterization of the anisotropy-dependent properties are important challenges in nanoscience, success has recently been achieved in lanthanides doped nanoparticles. In particular, the lanthanides doped upconversion nanoparticles demonstrate an anisotropy-enabled set of unique and fine-tuned optical properties at the single nanoparticle level. However, it is still unclear how their optical properties relate to the behavior of surface ligands, a factor considered as a significant contribution to energy transfer in nanoparticles, thereby determining emission property. Here, we report a method that employs the splitting spectroscopy of single nanoparticles to reveal the surface ligands participated transition process of lanthanides, leading to a previously unknown exploration of quenching selectivity. We design a nanoplate to correlate its splitting transition intensity ratio with quenching selectivity, in which two polarization orthogonal splitting dipoles will interact with surface ligands selectively on the orthogonal facets. We verify this by implementing single dimensional particle growth to finely tune the quenching selectivity in a series of nanoplates and nanorods with controlled anisotropic aspect ratio. These findings offer insights into the way the surface regulates the ionic electron transition and contribute to the development of selective emissions in anisotropic nanoparticles.



Directional quenching effect revealed by orientation-dependent luminescent properties in single nanoparticles. (a, b) Correlated confocal optical and SEM images of nanorods in the same field of view. (c) I–θ polar diagrams of two splitting peaks of particle 2 in b, verifying their orthogonal polarization patterns under side-up placement. (d) TEM image of nanoparticles with low aspect ratio. (e) Histogram distribution of single particle brightness under two type of placements on a slide. (f) Red upconversion emission spectra and splitting peak ratio of nanoparticles under the side-up and top-up placements. The data are obtained from single-particle measurement under 980 nm laser excitation at 5×10^6 W/cm^2.

IN012

Pump-Probe Spectroscopic Study Toward Exciton Dynamics in Optronic Materials

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Microstructures of conjugated-polymers in condensed-phase have shown to play important roles on governing the performance of polymer-based optoelectronics. We prepared highly-ordered crystalline poly(3-hexylthiophene) particle (P3HT-CP), made with regioregular P3HT (regioregularity>99%) by slow antisolvent diffusion method.[1] Various particle characterization data, including SEM and TEM and x-ray diffraction analysis verified the high degree of crystalline formation, revealing continuous crystalline domains extending over 100s nm scale.[2] Electronic absorption spectroscopy and excited-state dynamics based on fluorescence and ultrafast transient absorption spectroscopy for the P3HT-CP will be discussed.[2] These microscopic and optical spectroscopic results suggest enhanced crystallinity in P3HT-CP, which could be a model system to understand exciton dynamics in polymer crystalline domains and the role of polymer microstructures.

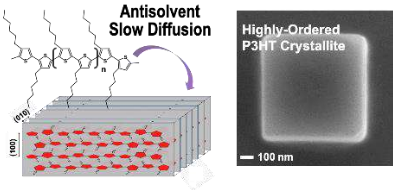

Figure 1. Schematic representation of polymer packing behaviour and representative SEM image of P3HT-CP

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IN013

Control of Reactions and Crystallization under Vibrational Strong Coupling

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Inside an optical cavity, cavity fields can exchange energy with the vibrational transitions of molecules. This repetitive energy exchange leads to the hybridization of molecular and photonic wavefunctions, a phenomenon known as vibrational strong coupling (VSC). Most recently, it was found that the chemical nature of molecules in optical cavities is modulated under VSC. The exploration of VSC chemistry has just started, and the field awaits the development in molecular chemistry.[1]

We demonstrate that VSC of the carbonyl stretch in aldehydes and ketones can influence the rate of Prins cyclization reactions. Specifically, under VSC of the carbonyl stretch, the Prins cyclization was decelerated.[2] Moreover, by applying VSC solely to the ketone group, we achieve site-selective reactions where the aldehyde group reacts preferentially over the ketone group in 4-acetylbenzaldehyde.[3]

Additionally, we investigate the impact of VSC of solvent molecules on the crystallization of metal-organic frameworks (MOFs). Our findings reveal that VSC of the solvent, specifically water, can influence the formation of MOFs.[4] These results demonstrate the versatility of VSC as a powerful tool for modulating chemical reactions, thereby establishing a new cross-disciplinary field bridging quantum photonics and molecular chemistry.

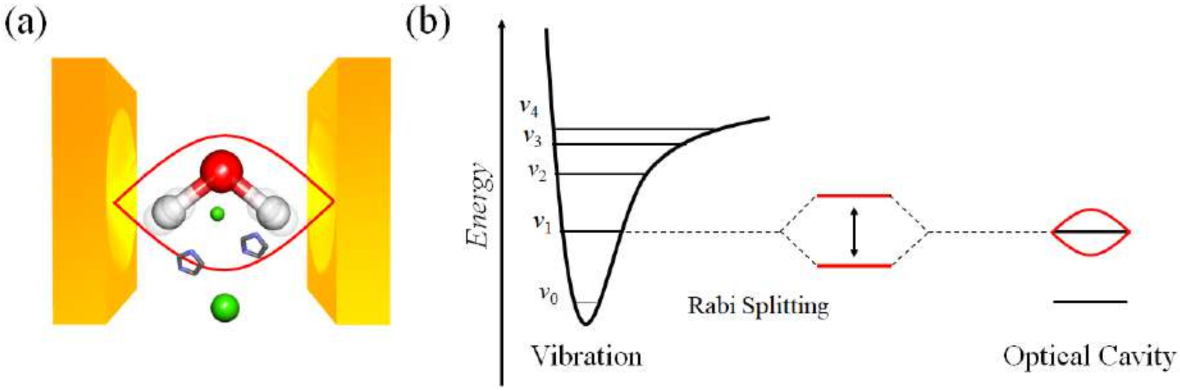

Figure 1. (a) Schematic illustration of molecules placed in the optical cavity consisting of two parallel mirrors. (b) Energy diagram of VSC. The vibrational mode and cavity mode are coupled to form VSC that generates two distinct vibropolarionic states, called Rabi splitting.

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IN014

Cancer therapy using photochemical reactions

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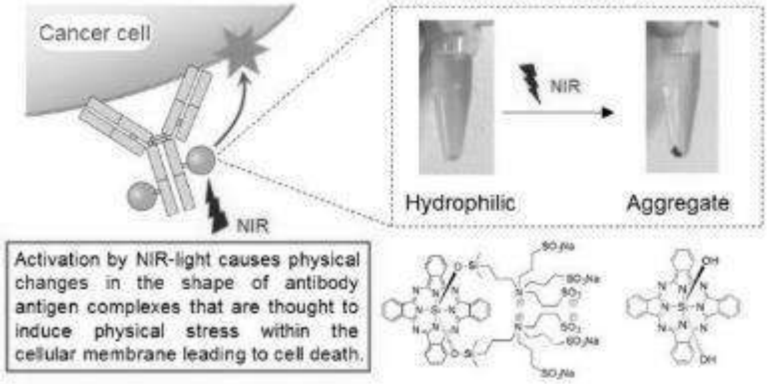
Near-infrared photoimmunotherapy (PIT) is a targeted phototherapy using photochemical reactions[1]. In 2015, a phase I/IIa study was conducted in the U.S. for patients with unresectable locally recurrent squamous cell carcinoma. Then the clinical trials were also started in Japan from 2019. Based on these results, NIR-PIT is approved in Japan in 2020.

For PIT, Si phthalocyanine derivative (IR700) is used as a photo-absorber, and is conjugated to an antibody that binds to the membrane antigen of cancer cells. One of the characteristics of PIT is that the antibody-IR700 complex only needs to bind to the surface of cancer cells, and the drug does not need to be internalized into the cells[2]. In other words, the cell plasma membrane is the starting point for cell injury. We have reported that irradiation of IR700 with near-infrared light cleaves the water-soluble axial ligand via a photochemical reaction[3]. Also, we found that the formation of radical anions as intermediates is important in this reaction[4]. After radical anion formation, axial ligand cleavage proceeds at room temperature, and once the axial ligand is cleaved, stacking of phthalocyanine rings occurs due to π-electron interactions, resulting in insoluble aggregates. These insoluble aggregates are formed even when bound to antibodies, and the cell membrane is damaged by the formation of insoluble aggregates on the cell membrane surface.

Based on the axial ligand cleavage reaction mechanism, the pKa of the axial ligand was considered to be important for cleavage reaction. We have synthesized several compounds with different pKa, and successfully developed more effective compound[5].

Since light induces axial ligand cleavage of phthalocyanine and the release of axial ligands, it can be envisioned to be used like a caged compound. Also, if this axial ligand cleavage can be performed by X-rays, it will be possible to activate the compound deep in the body. We found that radical anion can be formed by X-ray irradiation, and axial ligands was successfully cleaved[6].



Activation by NIR-light causes physical changes in the shape of antibody antigen complexes that are thought to induce physical stress within the cellular membrane leading to cell death.

Mechanism of PIT

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IN015

Single particle dynamics of water-soluble semiconductor nanocrystals

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Cu-containing semiconductor nanocrystals are promising photocatalyst. Fluorescence correlation spectroscopy and femtosecond transient absorption spectroscopy have been used to investigate the photoprocesses in two kinds of such nanocrystals, namely 3-mercaptopropionic acid (3-MPA) capped Cu(I)-doped CdS (Cu:CdS)[1] and Copper Indium Sulphide (CIS)[2] quantum dots (QDs). Photoactivation of the Cu:CdS QDs via dim/dark to bright particle conversion is observed at higher excitation powers. Dispersive blinking[1] kinetics in undoped QDs reflects the involvement of a broad distribution of trap states. A lesser extent of dispersity is observed for doped QDs, in which the hole-capture by the Cu-defect states predominates. Excitation fluence dependence of blinking rate highlights the role of Auger recombination in undoped QDs, which is suppressed significantly upon doping, due to disruption of electron-hole correlation. On the other hand, for the CIS QDs, an unusual excitation wavelength-dependence of photoactivation / photocorrosion is manifested in the increase in the initial correlation amplitude G(0) for λ_{ex}= 532 nm, but decrease for λ_{ex} = 405 nm. This has been rationalized in terms of different contributions from surface-assisted recombination in the two cases. Blinking times obtained from the Autocorrelation Functions (ACF) of the 100-200 ns lifetime component (core Cu-mediated recombination) are almost unaffected by shelling, but those from the ACF for the 10-30 ns lifetime (surface states) increases significantly. Absence of cross-correlation between the two recombinative states of bare CIS QDs and the emergence of an anticorrelation with the introduction of ZnS shell is observed, indicating the diffusive nature of the two states for CIS-ZnS. The diffusion is inhibited in base CIS QDs due to the preponderance of surface states.

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IN016

Opportunities and Challenges for Perovskite Solar Cells

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Organic-inorganic hybrid perovskite solar cell is a promising thin film photovoltaic technology and offers potential of high efficiency and low materials and production cost. The solution based system is attractive for processing of devices using a variety of techniques, such as printing. There have been some very significant progresses made in commercialisation of the technology in recent years. However, there exist some technical challenges, such as difficulties in forming good quality large area thin films and device stability. This presentation will talk about some recent progress in dealing with these challenges and introduce activities in scaling up perovskite solar cell modules.

IN017

Two-Dimensional Nanoassemblies from Plasmonic Matryoshka Nanoframes

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Two-dimensional (2D) plasmonic nanoassemblies are programmable ultrathin materials that one can, in principle, adjust the size and shape of their constituent building blocks to fine-tune collective optical, electrical, and mechanical properties. In this talk, I will introduce a new 2D nanoassembly from structurally complex plasmonic building blocks, namely, matryoshka-like gold (Au) nanoframes. Using a seed-mediated alternating deposition of Au and silver (Ag) elements in conjunction with a selective etching process, we obtain monodisperse matryoshka-like Au nanoframes with a nesting number (Nn) of up to 5. A cubic nanoframe displays dominant intraplasmonic coupling attributed to bonding and antibonding dipolar modes, which shift to blue and red, respectively, with an increased Nn. Combined with polystyrene (PS) ligand exchange and drying-mediated self-assembly, the approach mentioned above can be used to produce 2D plasmonic matryoshka nanoassemblies. Both experimental and simulation results demonstrate the presence of intra- and inter-ridge plasmonic coupling in the nanoassemblies. The 5-nested nanomatryoshka assemblies exhibit a Raman enhancement 14-fold greater than those with 1-nested cubic nanomatryoshka, demonstrating the dominant intraridge hot spot effects. Taking advantage of interparticle distance-dependent optical transparency of 2D matryoshka nanoframe assemblies, we further demonstrate temperature-enabled encryption/decryption using thermos responsive polymers.

IN018

Applications of Lanthanide-Based Nanomaterials in Photochemistry

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In this presentation, I will introduce the use of lanthanide-based nanomaterials in synthetic photochemistry. Firstly, a combined photothermal-catalytic system that contains a single active element, without using different entities for separate roles (catalytic vs. photothermal), is designed for efficient catalytic reactions. Herein, ultrathin (sub-6 nm) rectangular-like $KNdF_4$ nanoplates consisting of 3-4 unit cell layers are prepared where the Nd^{3+} ions act as a Lewis acid catalyst.[1] In addition, the nanoplates undergo light-to-heat conversion when irradiated with NIR light due to cross-relaxation and non-radiative relaxation processes from excited Nd^{3+}. The cyanosilylation of a series of ketones is performed using the nano-hotplate catalysts to give near quantitative yields of the cyanohydrin trimethylsilyl ethers. This is because of the high surface area-to-volume ratio of the thin nanoplates that provides a large number of surface Nd^{3+} catalytic sites for reaction. The reaction kinetics is enhanced by the photothermal effect, leading to the observed > 10-fold increase in product yields.

In the next example, a Nd^{3+}-sensitized upconversion nanocrystal (UCNC) decorated with toluidine blue O (TB) on its surface undegoes upconverted energy transfer from the UCNC to TB when excited by 808 nm light.[2] The photoexcited TB then catalyses the conversion of the dihydrotetrazine (dHTz) moiety in a Van-dHTz conjugate system to tetrazine which undergoes efficient inverse electron demand Diels-Alder reaction with prior attached norbornene molecules on bacterial cell walls. The enhanced affinity of vancomycin (Van) to bacteria by covalent bonding improves the activity of the drug against drug-resistant Enterococci, and the MIC is reduced by 6- to 7-fold as compared to neat Van. We demonstrate that the mode of action is due to increased inhibition of peptidoglycan cell wall biosynthesis. The findings in this study demonstrate that on-demand NIR-light activated bioorthogonal conjugation of Van to microbes is a viable alternative treatment in combating drug-resistant bacteria. Other lanthanide-based nanomaterials will also be discussed.[3,4]

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IN019

Exciton Dynamics in Super-Bright, Highly-Pb-Replaced Perovskite Nanocrystal

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$CsPbI_3$ Perovskite nanocrystal (PNC) absorption spectrum has larger overlap with the solar spectrum than that of any other all inorganic $CsPbX_3$ (X = halide) PNCs. Although $CsPbX_3$ PNCs are bright,[1,2] nonetheless, there is a very strong quest to increase the brightness. Although Brightness = Molar Extinction Coefficient (ε) x PLQY, however, brightness have been increased only through enhancing PLQY,[1,3-6] and no effort has so far been made through increasing ε.

As $CsPbI_3$ PNCs contain toxic Pb, hence, there is a strong quest towards achieving super-brightness in highly Pb replaced and sustainable $CsPbI_3$ PNC. So far, near unity PLQY for $CsPbI_3$ PNC has been achieved only with <10% Pb replacement.[1,4]

In the present effort, super-brightness could be achieved in highly-Pb-replaced (as high as 50%) Zn alloyed $CsPbI_3$ PNC, through two-tongs approach, i.e. through extraordinarily high values of both ε ($\sim 1 \times 10^8\ M^{-1}cm^{-1}$) and PLQY (98%). Therefore, Zn alloyed $CsPbI_3$ PNC is the most-bright nanomaterial among the PNCs[7,8]/QD family.[9-12]

As $CsPbI_3$ PNC absorption spectrum has the maximum overlap with the solar spectrum, hence it is extremely essential investigate whether and how different regions of the solar spectrum control the exciton dynamics. Ultrafast TA experiments revealed that the magnitudes of (a) ultrafast rise time (110 – 750 fs) as well as (b) normalized bleach amplitude are dependent on the excitation energies corresponding to the different regions of the solar spectrum. Fast TCSPC experiments revealed that through Zn-alloying, magnitude of radiative rate constant got enhanced and the magnitude of non-radiative rate constant got reduced very significantly. Ultrasensitive single particle spectroscopic experiments revealed that the magnitude of truncation time in the probability density distribution of ON events duration is dependent on the excitation energies corresponding to the different regions of the solar spectrum.

All these very interesting results will be discussed and correlated with each other.

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IN020

Exploring the Exciton Dynamics at Multiple Temporal Scales in Non-Fullerene Organic Photovoltaic Devices

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Organic photovoltaics (OPVs) have shown significant promise for energy conversion applications. This is due to their high absorption coefficient, ability to tune the band-gap, mechanical flexibility, and variety of color options. In recent years, the power conversion efficiencies (PCEs) of OPVs illuminated with AM1.5G solar spectrum have surpassed 20%, comparable to commercially available ones. This progress brings commercial application of OPVs within reach. To further improve device PCEs, understand operating principles, and enhance photovoltaic stability, it is crucial to uncover the underlying kinetic processes involved in the conversion of light to electricity. While the framework for describing exciton and charge dynamics in OPVs has been established, there are still surprising and controversial observations that require further investigation. Specifically, the dynamic parameters of charge recombination, trap-state response, and kinetic evolution associated with stability need to be explored in non-fullerene-based OPVs. This report aims to discuss and analyze the detailed evolution of excitonic and electronic excitations,[1] electron-phonon coupling,[2] vertical-phase-locking effect,[3] and trap-state-induced recombination effects[4] in OPVs. By understanding these mechanisms,[5-6] we can better identify and address the current and potential issues in OPVs, and develop effective solutions.

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IN021

Excited State Dynamics by Time-Resolved Spectroscopies and Molecular Dynamics Simulations

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Following photoexcitation to an electronically excited state higher than S_1, a molecule undergoes various processes, including internal conversion, intersystem crossing, and chemical reactions. These dynamics are central to molecular spectroscopies and applications including solar energy conversion, organic light-emitting diodes, and photosensors. Time-resolved spectroscopic techniques such as time-resolved fluorescence (TF) and transient absorption (TA) are employed to experimentally investigate these dynamics. While the potential energy surfaces with the Born-Oppenheimer approximation are used to study dynamics in low-lying excited states, dynamics in higher excited states require consideration of the non-adiabatic dynamics, the coupling between electronic and nuclear degrees of freedom, and the quantum effects like conical intersection.

For studying early-time dynamics of highly excited states, time-domain spectroscopies employing ultrashort ~10 fs pulses are essential. Such ultrashort pulses create nuclear wave packets (NWPs) in the initial excited electronic state and the ground state. The NWPs in the excited state are then carried over to product states, while some NWPs orthogonal to the reaction coordinate remain unaffected.[1] The NWPs coupled with the process undergo modifications during the reaction.

To explore the dynamics in the excited states, we recorded TA and TF with high enough time-resolution enabling acquisition of the NWPs. Quantum chemical calculations, quantum mechanics/molecular mechanics (QM/MM) simulations, and nonadiabatic molecular dynamics (NAMD) simulations were performed to comprehend the quantum dynamics in the excited state. We will present a few examples of excited state dynamics, including ultrafast internal conversion and charge transfer.[2] As an example, Figure 1 shows the excited dynamics of rhodamine 800 in methanol following excitation to S_3 state. TA, TF, and NAMD simulations reveal that it undergoes ultrafast internal conversion to S_2 and to S_1 via conical intersections, and results in NWPs in S_1, which can be calculated via NAMD and compared with the experiments.

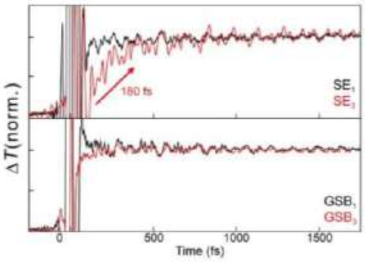

Figure 1. TA signals of rhodamine 800 in methanol following excitation to S_1 or S_3 states. SE and GSB denote stimulated emission and ground state bleach components in TA, respectively, and the subscripts 1 and 3 indicate initial photoexcitation to S_1 and S_3 states, respectively. Because they were created following different paths, NWPs evident in SE_1 and SE_3 are different.

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APA AWARD PRESENTATIONS

PZ001

Extending photoredox catalyst activity through choice of electron donor

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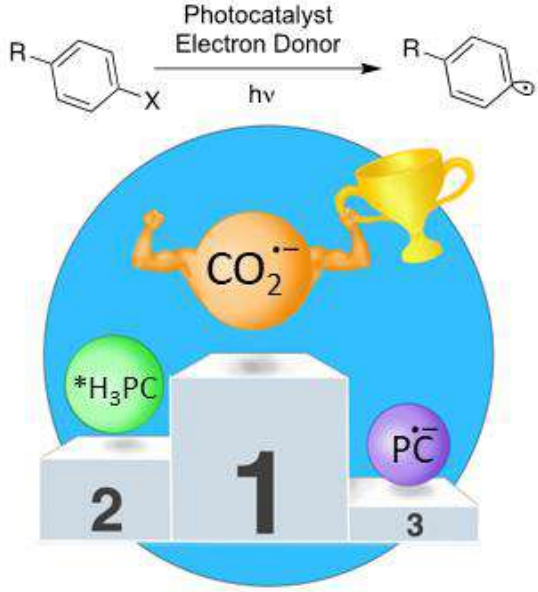
Using visible light to synthesise organic molecules promises a more sustainable future than current methods reliant on high temperature and pressure. The combination of light-driven and redox processes in so-called photoredox chemistry has ignited a decade-long renaissance in synthetic photocatalysis. The predominantly transition metal catalysts that power these reactions undergo photoinduced electron-transfer with a suitable donor or acceptor to form potent single electron reductants and oxidants. A second dark electron transfer event, with a respective acceptor or donor, then returns the catalyst to the ground state. In addition to the organic catalytic substrate (serving as either electron donor or acceptor depending on the reaction), sacrificial additives are routinely employed as a convenient source of electrons.

Many of the most common additives exhibit further chemistry following electron transfer but what occurs after is often overlooked. Tertiary alkylamines such as triethylamine initially form a radical cation, which readily deprotonates to form strongly reducing, neutral α-amino radicals. Similarly, the oxalate radical anion ($C_2O_4^{\bullet-}$) rapidly decomposes to form $CO_2^{\bullet-}$ ($E^0 \approx -2.2$ V *vs* SCE). Here we show that not only are these reactive intermediates formed under photoredox conditions, but how they also impact the desired photochemistry both productively and destructively. Photoredox systems using oxalate as an electron donor are able to engage substrates with greater energy demands, extending reactivity past the energy limits of single and multiphoton transition metal catalysts. Furthermore, oxalate offers better chemoselectivity than the commonly employed triethylamine when reducing substrates with moderate energy requirements.



PZ002

Towards highly efficient circularly polarized luminescence in chiral supramolecular assemblies

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Chiroptical materials with circularly polarized luminescence (CPL) activity have aroused a lot of interests. One essential factor for evaluating the feature of CPL active materials is the dissymmetry factor (g_{lum}), which represents the circular polarization of emitted light. Essentially, for the practical application of CPL, the most important issue is to greatly improve the g_{lum} value. Recently, benefiting from the flexible and efficient design in hybrid donor-acceptor systems, more and more examples involving the g_{lum} value amplification have been reported. In particular, CPL characteristics in various complexes systems including energy transfer (ET), charge transfer (CT), arene-perfluoroarene (AP) interaction, and triplet-triplet annihilation-based photon upconversion (TTA-UC) have been widely demonstrated.[1-5] We proposed the mechanism for the generation and amplification of CPL in these hybrid systems. The corresponding design principle and potential pitfalls in experimental processes will be presented here. We hope that this perspective can shed light on the development of highly efficient CPL active materials.

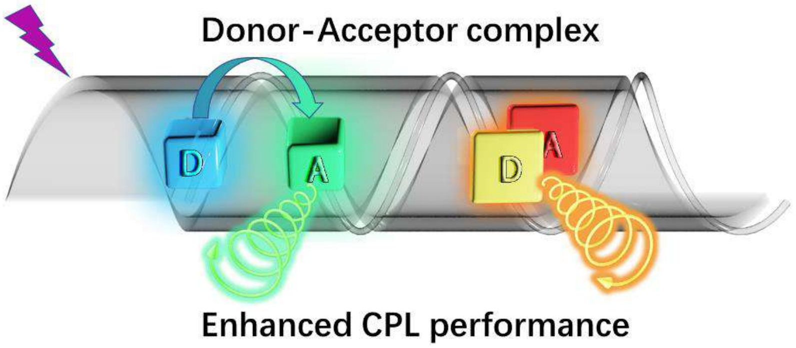

Fig. 1 Enhanced circularly polarized luminescence in hybrid donor-acceptor system.

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PZ003

Study on Emergent Photophysical Properties of Organic Dyes and the Applications

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Aggregates of organic dyes exhibit photophysical properties that differ significantly from those of the monomolecular state. Our research group has discovered that organic dye molecules acquire "photocatalytic activity" or "circularly polarized luminescence properties" by forming aggregates under specific conditions and has successfully demonstrated their potential for energy conversion and phototherapy.

Development of supramolecular photocatalysts based on water-soluble organic dyes for energy and medical applications[1,2,3,4]

Aggregation-causing quenching (ACQ) is a phenomenon induced by aggregation and is a common photophysical property change that occurs in many fluorescent molecules. One of the possible causes of this quenching phenomenon is the promotion of intersystem crossing to the triplet excited state and/or charge separation. Although most of the triplet and charge-separated states generated by these phenomena are deactivated without emission at room temperature, they have relatively long lifetimes and may be used in chemical reactions. Considering ACQ phenomenon from different perspectives, molecular assembly could function as photocatalysts. Based on this hypothesis, our research group has found that various dye molecules acquire catalytic activity through self-assembly and has called them "supramolecular photocatalysts" (Figure 1). These supramolecular photocatalysts could apply to hydrogen generation in water, organic oxidation reactions, and photodynamic therapy. These results demonstrate the potential of non-luminescent organic dye assemblies for energy and biotechnology applications, which has not received much attention so far.

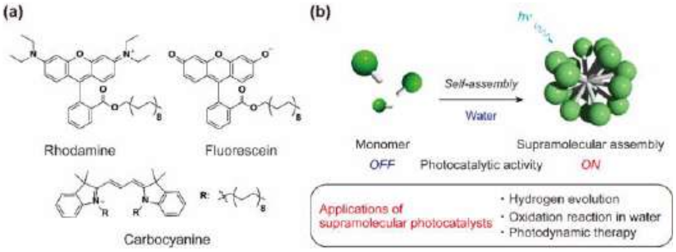

Figure 1. (a) Chemical structures of supramolecular photocatalyst components, (b) schematic representation and applications of supramolecular photocatalysts.

Development of bright circularly polarized emitting molecules based on cyclodextrins[5]

Circularly polarized luminescence (CPL) is expected to be applied to various fields such as three-dimensional displays and biosensing, etc. However, CPL materials derived from small molecules have low luminescence quantum yield and CPL anisotropy. We have succeeded in creating a bright CPL molecule by modifying multiple excimer dyes onto cyclodextrin, a chiral cyclic oligosaccharide, based on an original molecular design strategy.

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PZ004

A General Fluorescence-Based Method for Quantifying and Mapping Biomolecular Polarity

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Spatial discretization of biomolecules in the complex cellular environment is crucial for biomolecular form and function. The ability to better understand the driving force of spatial discretization of biomolecules in the complex cellular matrix remains a challenging task. We report on the robust polarity sensitive solvatochromic probe, **FLAM**, in conjunction with spectral phasor analysis as a general method for studying environmental polarity in biological systems.[1] We find that phase separated proteins of SFPQ have distinct polarity depending on the type of phase separation occurring, suggesting that polarity plays a role in the formation of phase separated condensates. When using **FLAM** in cells, distinct subcellular environmental polarity distribution but similar trend of changes is observed for cells under similar type of stressors. Further application in zebrafish models reveals polarity distribution in different organs and a unique environment of immune cells captured in wounded area. Taken together, our method puts forth an exciting development in the tool set for the study of biomolecular polarity and their involvement in phase separation and stress response in vitro and in vivo.

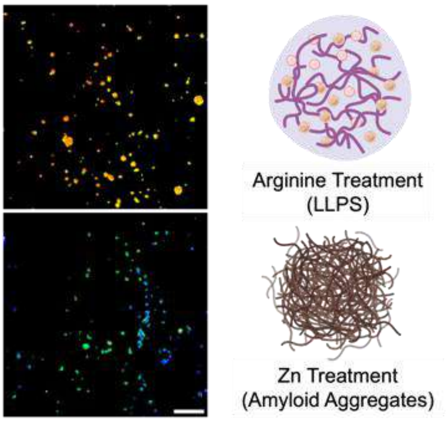

Fig. 1 FLAM reveals distinct polarity within two different types of protein phase separation.

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PZ005

Investigations of Electrified Interfaces under Plasmon Excitations through Electrochemical Spectroscopic Measurements

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Under visible light illumination onto metal nanostructures, a condensed electric field is generated associated with the excitation of localized surface plasmon resonance. Within the field, various unique photochemical responses can be observed via enhanced light-matter interactions. However, the precise controls of plasmonic reactions are still a challenge due to the difficulty of active tuning of the light-matter interaction or the lack of information at plasmonic nanostructure interfaces. From this background, I have attempted to investigate the molecular behavior interacting with the plasmonic field or charge transfer process on plasmon-induced photoelectrochemical reactions through the establishments of highly sensitive microscopic spectroscopy measurements combined with an electrochemical potential control method.

Firstly, the detailed charge transfer process on a plasmonic photoconversion system consisting of wide-bandgap semiconductors and metal nanoparticles was investigated by electrochemical microscopic Raman scattering measurements.[1] As a result, not only the spatial distribution of the reaction active sites but also the absolute electrochemical potential of the generated reactive species within the metal were successfully estimated (Fig. a). This information would be valuable for the design of the photoenergy conversions.

In addition, the active tuning of the strong light-matter interaction, which is recognized as the strong coupling, was achieved by controlling the electrochemical potential of metal nanostructures[2]. I also clarified the information about the spatial distributions of molecules coupling to the plasmonic field (Fig. b). Furthermore, it was demonstrated that such strong interaction could modulate molecular behavior at metal nanostructure interfaces (Fig. c). Through the observations of molecular selective condensation under electrochemical potential control in the bi-analyte solution, I proposed the key factors for the small-sized molecular manipulations at the plasmonic field.[3]

Through investigations, the unique properties of the photo-response under plasmon excitation have been firstly revealed. The above information would provide insights for the design of future photochemical reaction systems.

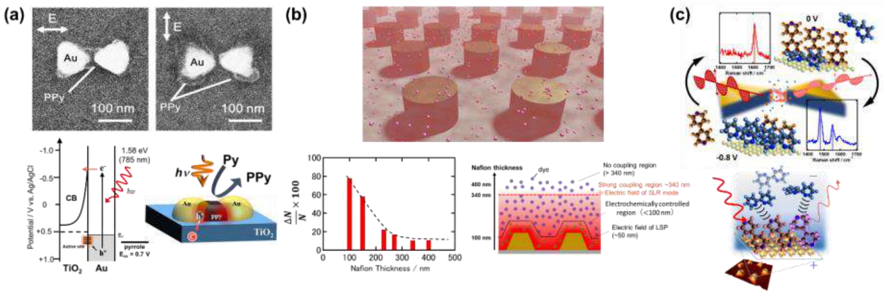

Fig. Schematics of (a) spatial distribution of the reaction active sites and energy diagram for plasmonic photoconversion system, (b) spatial distributions of molecules coupled to lattice plasmon modes, and (c) molecular surface diffusion modulations at plasmonic nanostructure interfaces.

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PZ006

Development of dye-sensitized molecular photocathodes in photoelectrochemical cells for photocatalytic CO_2 reduction with water as a reductant

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We have to develop artificial systems which can convert CO_2 to useful and energy-rich compounds by using renewable energy especially solar energy because of solving the global worming problem and shortage of energy and carbon resources. We have been tackling this target by using transition-metal complexes as main players.[1] In this presentation, I talk about Molecular photocathodes for photocatalytic CO_2 reduction with water as a reductant [1-5]

The molecular photocatalytic systems have a weakness, i.e., weak oxidation power in the excited state. For practical application, water should be used as an electron donor. For overcoming this problem, we have developed a hybrid system consisting of the supramolecular photocatalyst and semiconductor electrodes (Figure). The hybrid photoelectrochemical cell consisting of this hybrid photocathode and n-type semiconductor photoanode induced visible-light-driven CO_2 reduction with water as a reductant to generate CO and O_2.

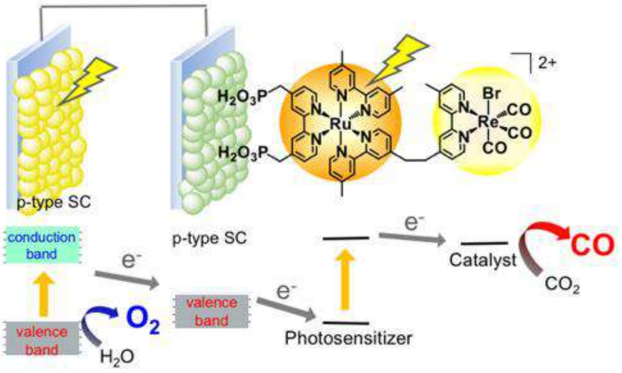

Figure. Photoelectrochemical system for CO_2 reduction coupled to water oxidation.

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PZ007

Control of Photoreactivity and Development of Photoresponsive Functional Materials

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Through a diligent design of molecular systems, the outcome of a photochemical reaction can be manoeuvred in a pre-desired fashion. We have been investigating the phenomenon of photochromism exhibited by the class of diarylbenzopyrans for quite some time.[1-3] I will exemplify enthalpic and entropic control of the photochromism in a rationally designed set of photoreactive systems.

The functional utility of photochemical reactions constitutes the ultimate goal of contemporary chemistry. I will demonstrate how one may imbed photoreactive moieties in molecular systems and develop photoresponsive 2D/3D metal-organic frameworks (MOFs) that exhibit photochromic phenomenon and sensing properties.[4-10]

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CONTRIBUTED PRESENTATIONS

C001

Ultrafast light-driven electron transfer in multiheme cytochrome nanowires

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Multiheme cytochromes are proteins essential for electron capture and shuttling within cellular environments, as well as transmembrane electron transport to extracellular electron acceptors. These proteins and interactions inspire the design of fully engineered systems for advanced electronic device applications. Suggested applications include bioelectricity generation as sustainable energy sources, and cellular scale bioreactors for green fuel production.

While a general understanding of the involvement of multiheme cytochromes in electron transfer processes is already in place, much remains unknown about the rates of electron transfer within cytochromes, and their potential for use in photoactivated systems. Here we examine two important cytochromes known as the small tetraheme cytochrome (STC) and the outer membrane metal reducing protein (MtrC). These are pseudo-linear 4 and 10 heme cytochromes analogous to electron carrying wires (STC shown in Fig. 1). Both were modified by the attachment of a RuII(2,2’-bipyridine)3 complexes, enabling the light-activated injection of an electron at one end. Employing ultrafast transient absorption spectroscopy we elucidate the rate for electron transport between hemes in these biological ‘nanowires’. We find exceptionally high rates of heme-to-heme electron transfer, which are among the highest reported for ground-state electron transfer in biology. Furthermore, we show that modification of a single heme deep within the nanowire creates an electron sink that stabilizes the charge separated state on the 100-μs time scale, which may prove useful for future bioinspired redox chemistry.[1-3]

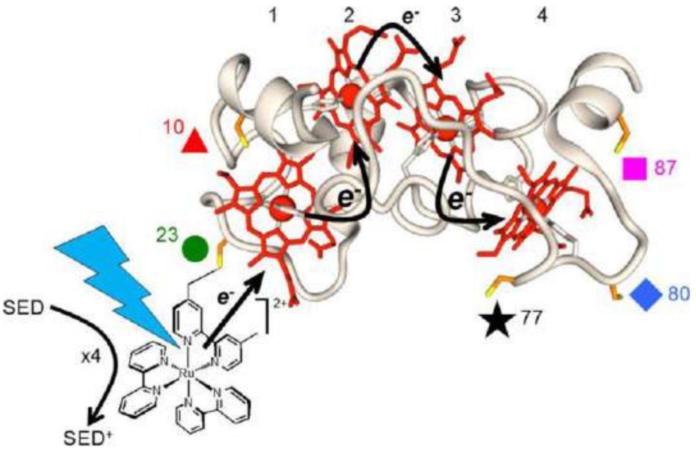

Figure 1. Schematic showing attachment of Ru photosensitizer to STC. The pathway for electron transfer into and along the protein is indicated.[2]

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C002

Shining a Light on Chemical Sensors and Stimuli Responsive Materials

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The development of real-time, highly sensitive chemical sensors for the detection of very low analyte concentrations is of importance for monitoring harmful chemicals in the environment. Strategies to enhance the sensitivity and accuracy of sensors can be achieved through the incorporation of lanthanoid ions enabling the detection of low analyte concentrations, and through using a stimuli-switchable motif. By switching between different states of the chemical sensor, enhanced accuracy of detection in complex matrices can be detected.

Metal-Organic Frameworks (MOFs) are crystalline materials containing inorganic nodes bridged by linkers. The high tunability of MOFs enable the systematic modification of pore chemistry and size. Tailored pore environments can be designed, making these materials well-suited to act as chemical sensors and stimuli responsive materials.[1] Reports of lanthanoid MOFs containing a stimuli responsive motif are still relatively scarce in the literature despite the potential they have for enhanced chemical sensing and the development of switchable materials.

This presentation will detail our latest results in the design of chiral sensors and stimuli responsive materials. The chiral sensing properties of two BINOL-based Zn MOF systems will be highlighted[2], with varying degrees of fluorescence quenching. The mechanism of fluorescence quenching and guest position within the framework as elucidated through time resolved fluorescence and computational calculations will be discussed. The switchable and chemical sensing properties of an isostructural series of lanthanoid MOFs containing a redox-active viologen ligand (Figure 1) will also be presented. The reversible one electron reduction of the viologen from its dication to its radical cation state upon exposure to a light and pressure stimulus are elucidated from photoirradiation and high-pressure experiments on the MX1 beamline at the Australian Synchrotron.

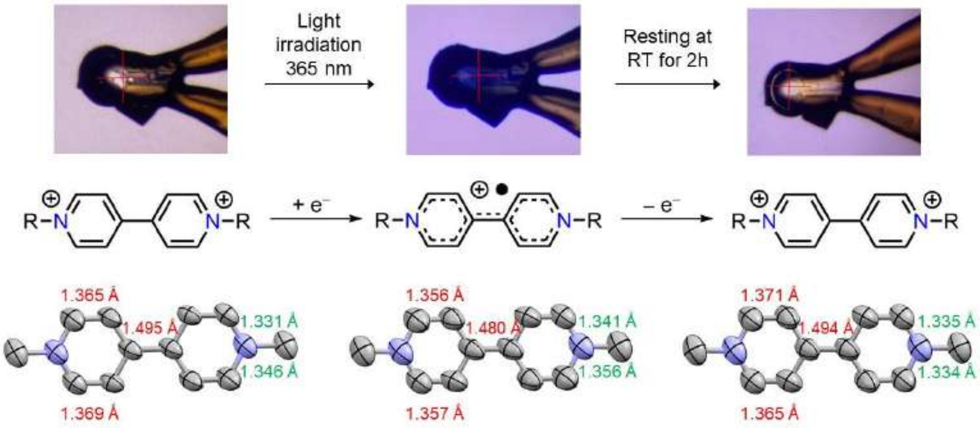

Figure 1. The reversible changes in colour and bond lengths upon irradiation of a single crystal of an Eu(III) viologen containing MOF at 365 nm. A vivid colour change from colorless to blue is observed.

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C003

Unlocking the Colorful World of Spiro-Rhodamines: Rational design and characterization of Switchable Molecules

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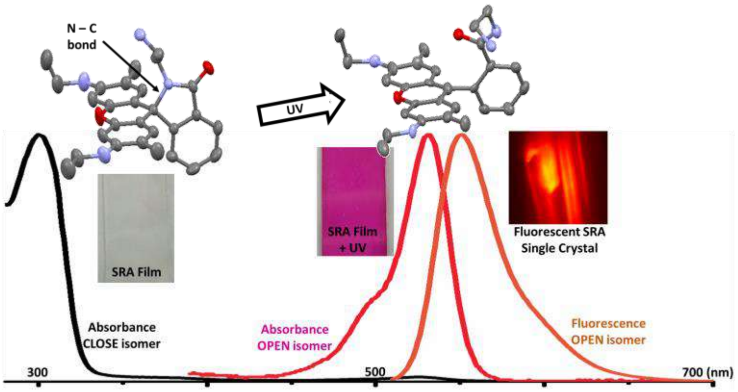
Spiro-rhodamines (SRAs) are photochromic molecules that exhibit a switching equilibrium between an optically inactive isomer (colorless and non-fluorescent) and a highly colored and fluorescent compound[1]. This unique property of SRAs has paved the way for numerous applications beyond the traditional use of Rhodamine derivatives in imaging and cell labeling[2]. The differences between the two isomers provide a rich platform for various applications in diverse fields.

For instance, the reversible switching between spiro and open forms offers opportunities in the development of molecular switches, optoelectronic devices, and stimuli-responsive materials[3]. Moreover SRAs have shown promise in sensing applications, with distinct fluorescence responses used for detecting specific analytes or environmental changes. Tailored spiro-rhodamine derivatives have explored their potential in sensing pH, metal ions, gasses, and biomolecules, expanding chemical and biological sensing avenues[4]. Additionally, SRAs demonstrate potential in data storage and information encoding, acting as molecular switches for encryption and next-generation storage technologies.

In this study, we investigate the structure-function relationship and the novel properties arising from light-induced changes in spiro-rhodamines (SRAs). By carefully designing a family of SRAs with different substituents, we explore their potential for precise modulation of the isomeric transformation in response to external stimuli. We characterize the equilibrium between the isomers (SF and OF) in the solid state using a comprehensive set of techniques, including reflection, absorption, and fluorescence measurements, single-crystal X-ray diffraction, atomic force microscopy coupled with infrared spectroscopy, and computational calculations. Furthermore, we evaluate the changes occurring upon irradiation of the corresponding SF with ultraviolet light and document the observed differences within the synthesized family. These findings highlight promising prospects for the future applications of SRAs in various fields, owing to their distinct properties and controlled isomeric behavior.



Scheme of the switching equilibrium between optically distinguishable isomers.

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C004

Systematic Tuning of Electronic States in Donor-Acceptor Dyes; Steps Towards Designer Compounds for Modern Technologies

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Donor-acceptor dyes are an integral part of modern chemical materials exhibiting unique photophysical properties, such as the electronic charge transfer (CT) transition. This displaces electron density throughout the structure of a compound. A behaviour which can elicit desirable properties that are used in many modern technologies including, solar cells,[1] OLEDs,[2] and molecular sensors.[3] One of the most important aspects for these dyes in each application is the energy at which the electronic CT occurs. Hence, predictable tuning of this feature towards desirable wavelengths would be useful for the design and fabrication of future compounds used in these technologies. Often research will compare the discrepancies between different donor or acceptor moieties in efforts towards CT tuning. However, a much more subtle and controlled approach is to alter the substitutions or linkages within these units.[4] Due to the localisation of the HOMO and LUMO frontier molecular orbitals to the donor and acceptor units respectively, adjustments to these groups can vary the energy of these two orbitals and hence the CT transition. Our investigation has investigated the subtle tuning properties of six donor-pi-acceptor dyes containing the three moieties in Figure 1. These were investigated using DFT calculations and a range of spectroscopy techniques. The dyes portrayed controlled CT tuning, achieved by making these small alterations in addition to other interesting excited state characteristics, lending to potential uses in the afore mentioned technologies.

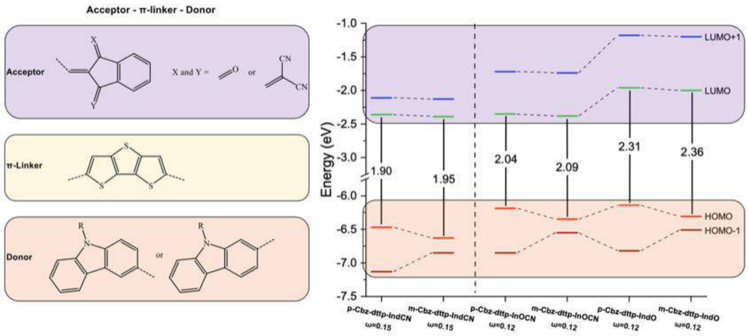

Figure 1: Electronic tuning of HOMO's and LUMO's according to molecular building blocks.

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C005

Photoswitchable Metal-Organic Frameworks for Chiroptical Devices

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Nature has blessed the scientific world with chiral materials and their unique interactions with circularly polarized light resulting in phenomena such as circular dichroism and circularly polarized luminescence. Control over these chiroptical phenomena within materials allows for a plethora of applications in all-optical devices, security, optical displays, biological probing etc.[1] Chiral Metal-Organic Frameworks (MOFs) are hybrid structures that may be the solution to overcoming the limitations of traditional inorganic or organic device materials.[2] Chiral bridging ligands in conjunction with redox-active ligands allow for the control of chiroptical properties through switching the redox state of the ligands within a framework. We aim to develop chiral MOFs that exhibit redox-switchable chiroptical properties with the prospect of elucidating structure-property relationships.

This work describes the synthesis and structure of a series of MOFs composed of chiral camphoric acid and achiral redox-active naphthalene diimide (NDI) derivatives that exhibit light and electrochemically controlled switching phenomena. X-ray diffraction measurements were used to determine the co-facial arrangement of NDI ligands. The redox properties of these MOFs were characterized by a variety of electrochemical and spectroscopic techniques. Measurements of the circular dichroism response of the materials showed spectral changes dependent on the oxidation state of the NDI ligands. These switching properties of our materials allow potential use in a range of photonics applications.

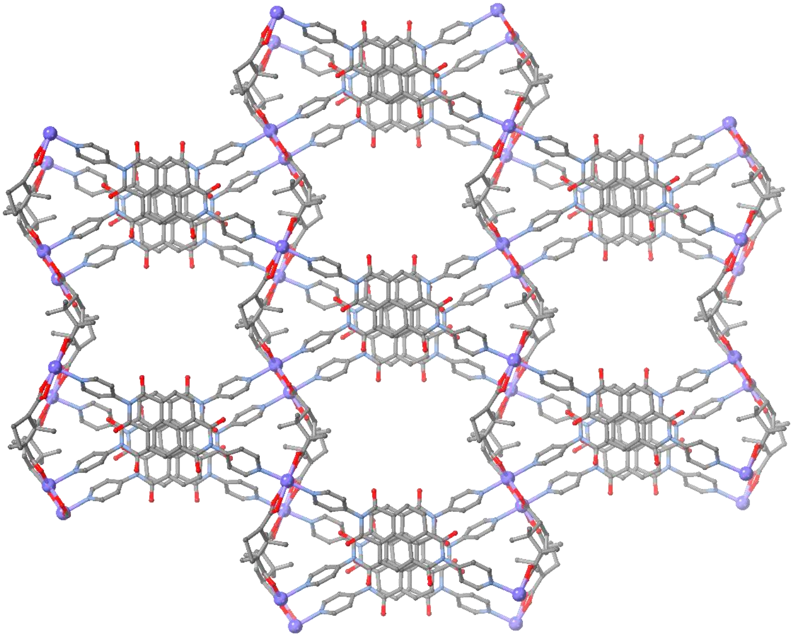

Figure 1. The porous extended structure of a cadmium-based chiral redox-active MOF.

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C006

Excited state engineering in silver nanocluster for bright near-infrared emission via silver complexes modification

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Atomically precise metal nanoclusters (NCs) have emerged as a new class of materials with many practical applications because most NCs could be obtained with a relatively small expense of synthetic effort as nontoxic materials, showing their unique optical, electrochemical, and catalytic properties. Photoluminescence is one of the most intriguing and fascinating characteristics of NCs. However, their low photoluminescence quantum yields (PLQY) are still issues to be solved, and understanding the detailed excited state mechanism in NCs has yet to be accomplished. Some approaches to excited state enable the elucidation of photophysical relaxation processes, leading to the improvement of PL property of NCs.

Here we report an approach to the excited state engineering in $Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ NC (BDT: 1,3-benzenedithiol; TPP: triphenylphosphine) through peripheral modification with silver complexes, which shows bright near-infrared (NIR) emission. The change of excited-state dynamics induced by the modification of silver complexes is discussed based on the results of the single-crystal X-ray diffraction measurement, transient absorption study and temperature-dependent PL study. We reveal that the modification of Ag_{29} NCs with cationic silver complexes is considered to give rise to a triplet excited state responsible for the intense NIR PL. Considering the PL mechanism in Ag_{29} NCs involving the ligand to metal core charge transfer (LMCT) state as a representative excited state, the peripheral cationic silver complexes should be attracted to the more negatively charged core with shifting the relative position in the excited state, leading to the stabilization of LMCT state (Figure 1).[1]

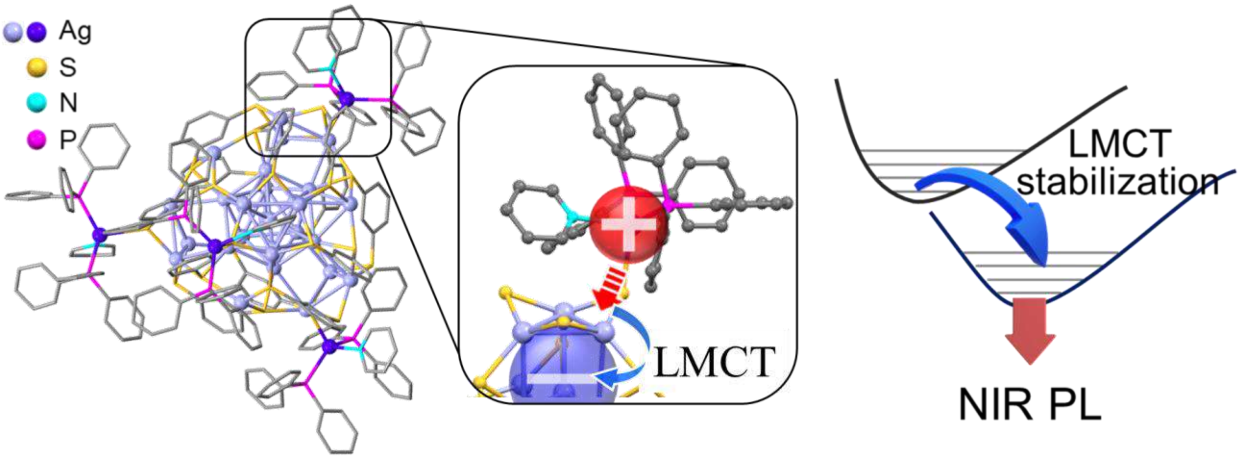

Figure 1. Crystal structure of Ag_{29} NC modified with silver complexes and the plausible mechanism on the NIR PL.

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C007

Improved control of perovskite thin film fabrication via optical In-Situ spectroscopy and reactive spin coating

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Hybrid Perovskites (HP) have attracted a lot of attention in the last decade due to their outstanding optoelectronic properties and high-power conversion efficiency when employed as the absorber layer in a solar cell.

These solar cells require a high-quality HP film, which is typically achieved through a solution-based solvent engineering spin coating approach. In this method, HP crystallization is induced by applying an antisolvent (AS) to the precursor solution film on the spinning substrate after a specific spinning time. The process involves various controllable and uncontrollable parameters that need to be considered.[1,2] As a result, fabrication recipes (such as spin speed and timing of AS dispensing) are usually developed empirically and vary between labs. The human element, including the reaction time of the researcher and the speed of AS dispensing, significantly influences the processing and the resulting perovskite film.[2] Additionally, uncontrollable factors like changes in the atmosphere can introduce substantial variations between and even within batches of devices.

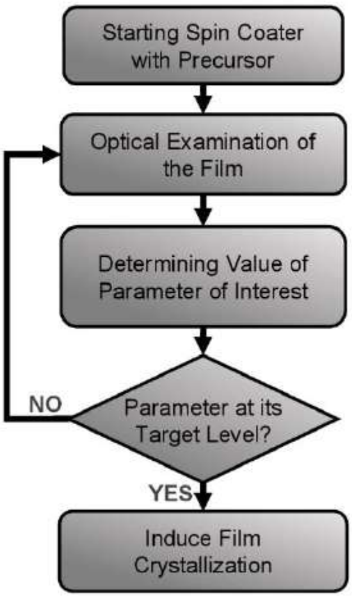

Fig. 1: Flow chart of the automated, reactive spin coating method

In this work we developed a closed-loop feedback system based on our multimodal optical In-Situ spin coater system in combination with a real-time analysis of the optical spectra during spin coating (see fig.1). We optically monitor the solvent layer thickness as the parameter of interest during the spin coating. As soon as the target level is reached, the perovskite crystallization is induced by dispensing the AS via a syringe pump. This method eliminates the human impact on the processing and simultaneously compensates for the effects of uncontrolled parameters, like variation in solvent evaporation rate due to atmospheric changes, thus leading to reproducible film quality.

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C008

Dual-direction Energy Harvesting and Strong Light-Matter Coupling in Twisted Perylene Organic Photovoltaics

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Perylene Diimide (PDI) materials are promising candidates for non-fullerene organic photovoltaic devices however they are plagued by strong intermolecular π-π interactions. Twisted dimers have been proposed to overcome this issue, since breaking the plane of conjugation reduces the extent of crystallization.

Here we report the investigation of perylene monomers (PDI) and twisted dimers (TPDI) as non-fullerene acceptors paired with the polymer donor PTB7-Th in organic photovoltaic blends and devices. TPDI devices are shown to far outperform PDI devices, having PCEs of 4.4% compared to 1.2%.[1] Intensity-dependent optoelectronic characterization reveals that PDI devices suffer from geminate and non-geminate recombination at short circuit. Transient absorption (TA) spectroscopy demonstrates dual-direction energy harvesting, since charge transfer states are formed from excitation of both PTB7-Th and (T)PDI. TA also reveals that charges live significantly longer in TPDI blends, are more successful at reaching the interface, and are less susceptible to bimolecular recombination.

Additionally, we explore the effects of using strong light-matter coupling to alter the energetics and thus the recombination mechanisms within these devices. Strong light-matter coupling causes splitting of the energy levels such that new energy levels, termed polariton branches, are created. We compare bare and cavity-based devices and demonstrate that strong coupling has a significant effect on device recombination mechanisms.

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C009

Metal-free photocatalyst for hydrogen production at extended visible light

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Carbon based metal-free photocatalysts are much sought after because of their ability of visible light absorption, long-lasting stability in the whole pH range (0 - 14), and facile synthesis from earth-abundant inexpensive raw materials, for example, C, N and O.[1,2] Among these metal-free photocatalysts, graphene oxide and polymeric carbon nitride are the most notable. Not to mention, polymeric carbon nitride gained the prime attraction and intensely been studied.[3] However, both graphene oxide and pristine carbon nitride are mostly active under 450 nm of visible light absorption as a hydrogen evolution photocatalyst.[2,4] These photocatalysts in their pristine form are not suitable to design a photocatalyst system to achieve a solar-to-hydrogen conversion efficiency of 5-10% that is required to meet economic viability for mass-scale hydrogen production.[5] High temperature post modification of pristine carbon nitride can extend the visible light absorption but reduce the catalytic efficiency due to poor charge transport kinetics impacted by structural inhomogeneities.[6] Often at high temperature, carbon nitride turned into graphene derivatives that is not suitable for photocatalytic hydrogen production.[7] Beyond polymeric carbon nitride, we therefore intended to design a carbon catalyst that would have extended visible light absorption, while we are not interested to end up with synthesis of graphene or graphene derivatives.

In such pursuit, we report here the facile synthesis of hierarchical microstructure of semiconducting carbon that resembles a sponge-like freestanding monolith. It has brownish-blackish appearance with metallic lustrous glittering. Electron microscopy reveals that the monolith is stemmed from intercalated and overlapped nanosheets ensembles. We have employed various analytical techniques to understand its physicochemical properties. Of particular interest, along with intrinsic absorption centred at 420 nm, it shows an exceptional tail absorption beyond 550 nm that induces an intermediate band in the gap between conduction and valence band of the material. This intermediate band is active in photocatalytic hydrogen production from sacrificial water reduction reaction. This photocatalyst therefore introduces a new member in the genre of metal-free photocatalysts for hydrogen production.

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C010

Perovskite Quantum Dots for Solar Cells and Beyond

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Halide perovskite solar cells have witnessed great successes recently while their instability is a big hurdle for practical application. Herein we discuss our recent progress in addressing the stability of perovskite solar cells, including introduction of capping layers to improve the stability against moisture and heat, and perovskite size engineering to suppress phase segregation. In particular, quantum dots (QDs) have the advantages of quantum confinement effect, defect-tolerant nature, and processability for flexible devices. We discuss a new surface ligand engineering strategy in designing new hybrid perovskite QDs with controllable compositions and sizes The QDs have been used as building blocks in quantum dot solar cells delivering a certified record efficiency of 16.6% with excellent long-term operation stability. By using QDs as light absorbing materials, the QD based photocatalysts also exhibited good stable performance in photocatalytic hydrogen production. The combination of perovskite QDs with Metal-Organic Framework (MOF) materials to form new composites led to ultrastable photoluminescent property for > 10,000 hours. The integration of perovskite solar cells and rechargeable batteries have led to a single module type rechargeable solar batteries with an overall storable solar energy conversion efficiency of >12%.[1-7]

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C011

Ultrafast Excited State Dynamics in Porphyrin Donor Dyads

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Our understanding of the fundamental principles governing photophysical properties of molecular systems and how they can be harnessed and controlled is rapidly expanding due to the state-of-the-art time resolved spectroscopic techniques that are becoming the norm in research laboratories. Unprecedented ability to infer structure-property relationships based on this knowledge is allowing the design of novel photoactive molecular systems with properties precisely tailored to specific applications. In particular, the versatility in photophysical behavior of π-conjugated chromophores due to the ease in their structural tuneability has led to a vast variety of applications in medicine, catalysis, sensors, light-harvesting, and many more fields. Porphyrins are one such class of useful chromophores, where structure can be relatively easily tuned through peripheral/axial substitution, core alterations or metal coordination.[1] Research into their properties has led to the design of increasingly complex tailored photonic materials. Here we report the outcomes of ultrafast transient absorption spectroscopy and DFT/TDDFT calculations of several photoactive porphyrin donor dyads that highlight the structural factors that determine energy and electron transfer in these molecular systems (Figure 1). The implications of the results on the overall photochemistry of these systems will be discussed.

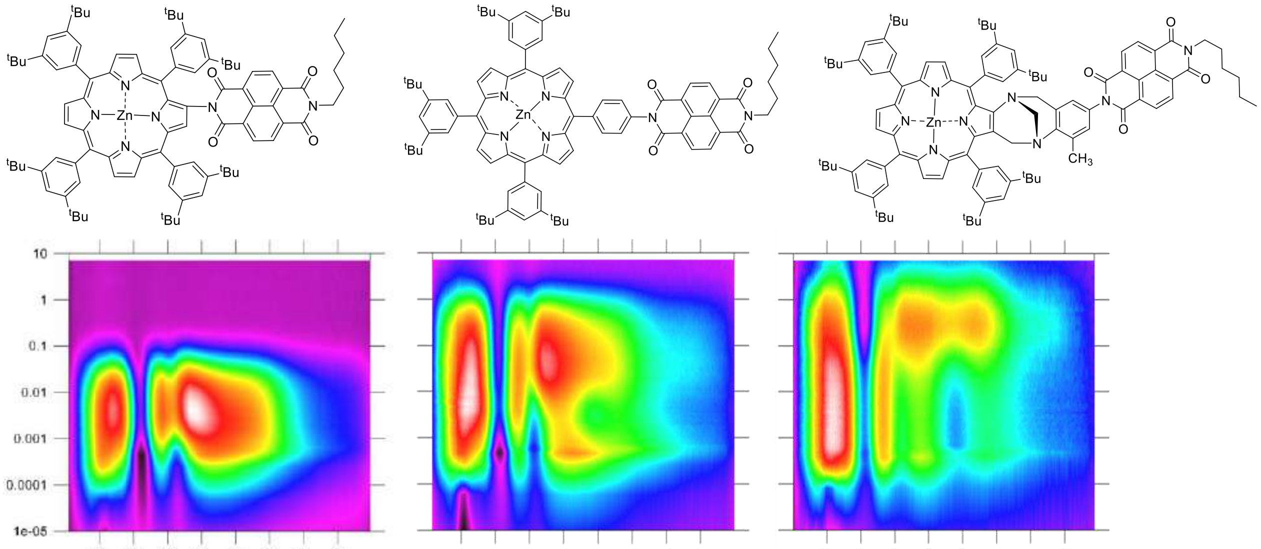

Figure 1 Structure and transient absorption spectra contour plots of porphyrin-naphthalene diimide (NDI) dyads in toluene, excited at 440 nm

Acknowledgement: We thank Dr Imam Ansari for provision of compounds.

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C012

Conspicuous assignment of organic vibrational modes of $CH_3NH_3PbBr_3$: Raman spectroscopy and first-principles calculations

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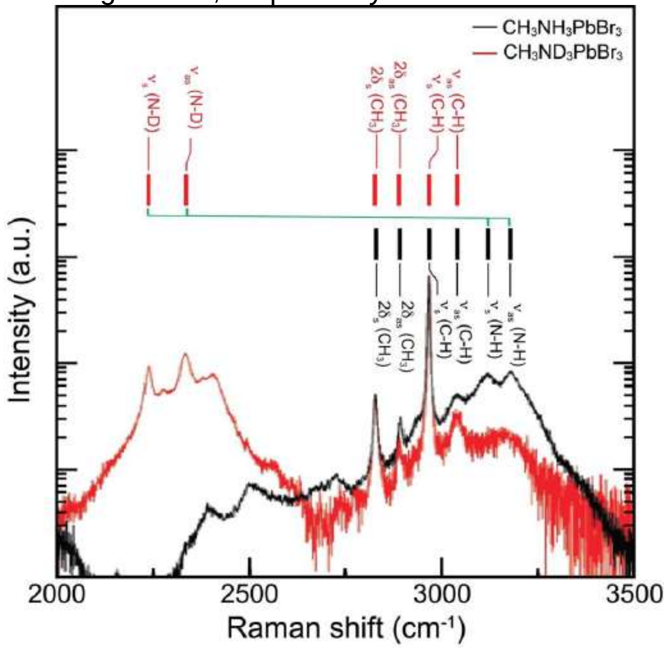
Hybrid organic-inorganic perovskites have attracted great attention because of their optoelectronic applications. For example, methylammonium lead bromide ($MAPbBr_3$) forms a perovskite structure with hydrogen bonding between MA^+ and octahedral $(PbBr_6)^{4-}$ framework. Identifying the vibrational modes of MA^+ is crucial to ravel their roles in probing the interior force and in affecting the properties of mixed halide perovskites. Several experimental and theoretical efforts[1] of these vibrational modes, however, obtained inconsistent results because of low signal-to-background ratio and poor spectral resolution. In this work, the Raman spectra of $CH_3NH_3PbBr_3$ and $CH_3ND_3PbBr_3$ were measured. The comparison of first-principles computation with the experimental results facilitates the mode assignment.

The Raman spectra of $CH_3NH_3PbBr_3$ and $CH_3ND_3PbBr_3$ (see the figure below) show that the peaks at 3041, 2967, 2893, and 2827 cm^{-1} are unchanged and the peaks at 3181 and 3120 cm^{-1} are downshifted upon the deuteration. The DFT calculation of cubic $MAPbBr_3$ lattice showed that the peaks at 3041 (3181) and 2967 (3120) cm^{-1} are associated with the CH_3 (NH_3) asymmetric (ν_{as}) and symmetric (ν_s) stretching modes, respectively. The calculation also assigned the peaks below 2000 cm^{-1}, but it failed to predict the 2893- and 2827-cm^{-1} peaks, suggesting their association with the overtones of the C−H bends. Applying *ab initio* anharmonic algorithm to solvated cluster $CH_3NH(D)_3^+ \cdots (HBr)_3$ to calculate the Fermi resonance between the overtones and the C−H stretches[2] attributed the 2893- and 2827-cm^{-1} peaks to the overtones of CH_3 scissor (δ_{as}) and umbrella (δ_s) bending modes, respectively.



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C013

A link between shape dependent lifetimes of quantum structures and thermal escape

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Quantum dots and rings exhibit significantly different relationships between radiative lifetime and temperature[1,2]. This suggests that the geometry of a quantum structure is important in determining this relationship. We use the finite element method to construct models of each of these structures to determine their spectra of states. These sets of states are then used as inputs into a thermal escape model permitting us to quantify the lifetime-temperature relationship. By examining a range of geometries, we can specifically determine how this relationship is dependent on geometry.

Part of our explanation for how temperature affects radiative lifetime is based upon the type of thermal emission from each structure. We conclude that, on average, the quantum dots thermally emit uncorrelated electron-hole pairs whereas quantum rings emit excitons. Determining how charge carriers are thermally excited out of quantum structures has been widely discussed[3-8]. Our contribution to the debate is that the geometry of the structure may be a key factor in explaining thermal emission properties.

C014

Investigations of a ferrocene-based dual-responsive chiroptical switch

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Chiroptical switches are molecules or materials whose chiroptical signal can be reversibly, and controllably, converted between two (or more) states which have different chiroptical signals.[1] Switching is achieved through application of external stimuli such as temperature, redox potential, pH, light, or host-guest interactions which generate a corresponding change in the intensity, peak position, or handedness of the chiroptical signal. Chiroptical switches exhibiting good reversibility over many switching cycles and high sensitivity to the applied stimulus are highly desirable with potential applications in electronic devices, optical displays, and chiral sensing.

Here we report the synthesis and characterization of a chiral ferrocene derivative (FcAlaAPBT) which functions as a chiroptical switch in response to two distinct stimuli: temperature and redox potential. Circular dichroism (CD) and circularly polarized luminescence (CPL) measurements were performed at varied temperatures, magnetic field, and applied potential to investigate the sensitivity of the CD signal in response to these stimuli. The reversibility of the chiroptical switching was also demonstrated for multiple cycles.

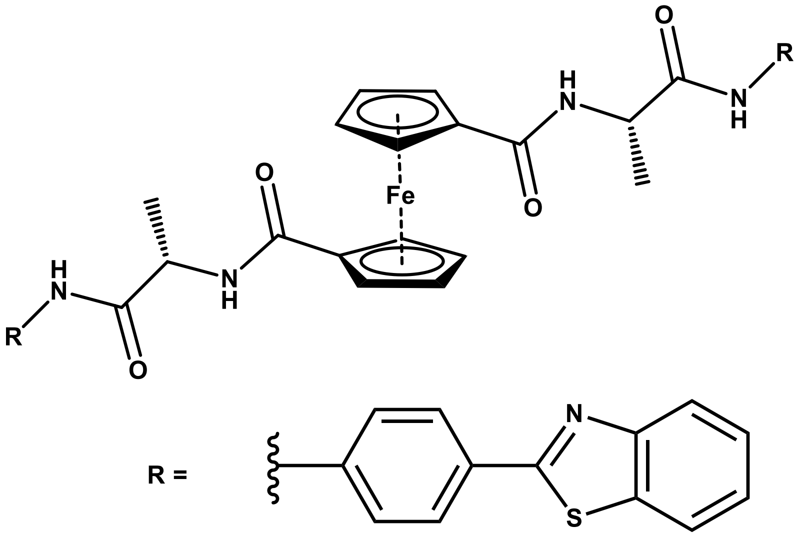

Figure 1. Structure of FcAlaAPBT

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C015

Frequency modulated photoluminescence and electroluminescence for polaritonic light emitting diodes

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Lighting as major consumer of energy, accounts for around 15% of the world's total electricity consumption[1]. Traditional lighting sources (e.g., incandescent/fluorescent bulbs) are inefficient, contribute to climate change, and environmental issues. A more sustainable and efficient alternative is Light Emitting Diode (LED) lighting, which uses up to 75% less energy[2] and has a longer lifespan. Nevertheless, even LEDs can still be much improved in terms of energy efficiency, and wavelength and angular control (beaming) of emission.

Incorporating polaritons into LEDs (PoLEDS) is a promising approach to further improving their color quality and efficiency[3]. Polaritons are quasiparticles that arise from the strong coupling of excitons and photons in the active materials within an optical cavity. As this interaction is between the cavity optical mode and the collective oscillator strength of all the molecules/materials interacting with it, motional narrowing results in sharpened emission bands. Meanwhile, the cavity imposes a specific momentum (angular) dependence to the emission, allowing for further precise control of the emission properties. Finally, polaritons might reduce interactions with non-radiative recombination centers due to their shorter lifetime compared to excitons, resulting in a more efficient photon output.

While most reported polaritonic LEDs relying on optical pumping, while electrical excitation is preferred for everyday use. However, to achieve an efficient electrically pumped polaritonic LED, it is crucial to gain a better understanding of how polaritonic states can be populated from free carriers. This is a complex process involving multiple particles, including electrons, holes, excitons, and photons. We herein established "FreqGlow" test facility (schematic shown in Figure 1), which utilizes multifrequency modulation/demodulation photoluminescence (PL) and/or electroluminescence (EL) for the acquisition of various signals (such as EL/PL, carrier/defects density through the impedance module) simultaneously following photo or electrical excitation. This is crucial for emerging polaritonic devices, as the device under test (e.g., ion migration, phase segregation in perovskite-based devices, or dielectric breakdown in TADF-based LEDs) is known to undergo changes under excitations. The FreqGlow can also discern the contribution of different quasiparticles to a single signal due to their distinct effective masses, resulting in a frequency-dependent response. Specifically, FreqGlow could analyze the spectral response of the polariton, including its angular dispersion, which is essential for optimizing PoLED design.

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C016

Toward photoinduced reversible switching of charge mobility in the solid state

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In the last decade heteroaryl azoswitches (i.e., azobenzene having heterocyclic rings in place of one or both phenyl groups) have attracted a great deal of attention. The presence of heterocyclic rings greatly expands the range of possible functionalities which can be added to the structure enabling a fine tuning of their photophysical properties and adding the unique possibility to access light-affected molecular properties.[1]

The work hereby reported focuses on the investigation of a new class of photoswitches, the azo-oligothiophenes[2], in which the extend of the π-conjugation of the electro-responsive thiophene moiety was increased according to two strategies (Fig. 1a.): (i) introduction of α-linked thiophene oligomers; (ii) introduction of fused oligothiophene subunits. The presence of the thiophene hetorocycle infers a possible photo-induced charge mobility modulation at the single molecule level. Upon disclosure of the photochemical properties of the azo-oligothiophene compounds, a new azo-oligothiophene was synthesized (Fig. 1b.) to be studied in the solid state (i.e., spin-coated thin film and crystals), which possess a dithienothiophene moiety and a three-dimensional bulky group, where the former ensures good electrical conductivity properties and the latter prevents a tightly packed disposition and allow photoisomerization in the solid state.

In light of the outstanding solid-state photoreactivity observed, this work suggests that it could be possible to realize a new light-effected semiconductor material based on azothiophene photoswitches in which the interplay between photoisomerization and electrical conductivity properties occurs at the single molecule level.

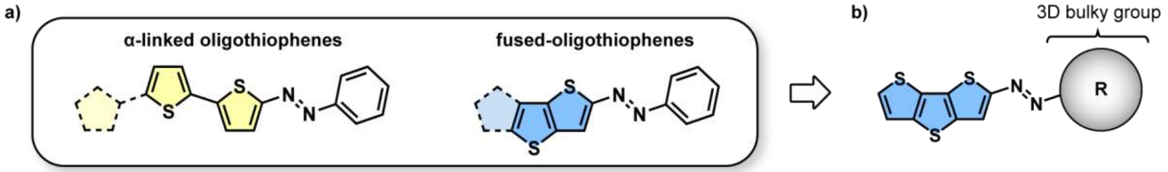

Figure 1. a) Molecular structure of the classes of azo-oligothiophene photoswitches studied. **b)** Molecular structure of the three-dimensional variant of the azo-oligothiophene studied in solid state.

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C017

Pushing to MWIR and Beyond: Colloidal InSb Quantum Dot Photodetectors

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Green, highly-responsive, solution-processed and high working-temperature mid-infrared materials are needed for next generation photodetectors. One material which potentially meets these requirements is colloidal InSb (or InSb quantum dots). We report a new synthesis, which breaks the present size-limitations (radius <10 nm) and enables the growth of large particles up to a radius of 60 nm, which can respond to mid-infrared light for the first time.[1] The colloidal InSb quantum dot photodetectors afford high responsivity and short response time, competitive with current quantum dot materials. InSb quantum dots have been integrated into photodetectors which operate at room temperature and which exhibit response times in the microsecond time regime. This opens up mid-infrared photodetectors to many new application areas in intelligent driving, firefighting, meteorology, industry monitoring, and security.[2, 3]

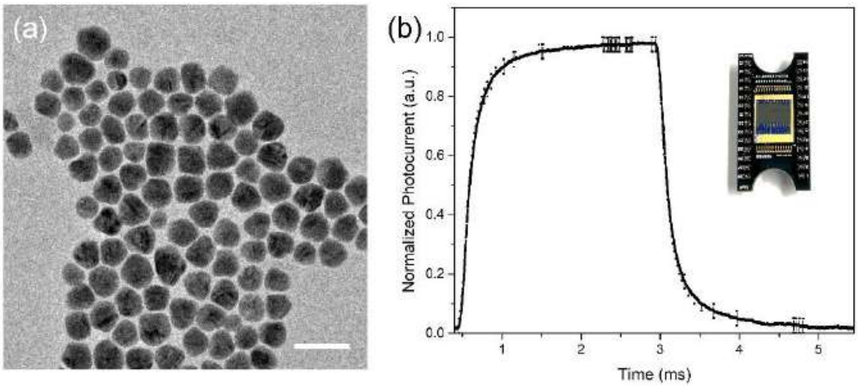

Fig 1 (a) A TEM image of InSb quantum dots. Scale bar: 50 nm. (b) Normalized photoresponse of InSb colloidal photoconductors to pulsed illumination at 4.5 µm. Inset is the InSb photodetector mounted on a dual in-line chip holder.

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C018

Ultrafast coherent dynamics and interactions in 2D semiconductors and their heterostructures

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Interactions between quasiparticles are of fundamental importance and ultimately determine the macroscopic properties of complex systems, from quantum matter, to macro-molecules and biological system. However, resolving, quantifying and understanding these interactions can be difficult. Multi-dimensional coherent spectroscopy (MDCS)[1], including 2D optical spectroscopy, utilizes femtosecond laser pulses to measure the evolution of real and imaginary parts of the optical conductivity and thereby resolve interactions between electronic states and other degrees of freedom, such as vibrations/phonons, magnons or other spin excitation, excitons, and the local dielectric environment.

In this work we explore interactions amongst excitons, free electrons, polarons, biexcitons and phonons in monolayer WS_2 and a WS_2/MoS_2 heterostructure using multi-dimensional coherent spectroscopy (MDCS)[1]. WS_2 and MoS_2 are part of the family of monolayer transition metal dichalcogenides, which possess remarkable properties that make them excellent candidates for revealing fundamental physics, as well as for device applications.

The 2D spectra from monolayer WS_2, such as the one in Fig. 1, allow us to separate and identify the various different interactions. In particular, the peaks around 2.06 eV arise from interactions between Fermi polarons – that is, excitons dressed by a Fermi sea of free electrons. The underlying trion fine structure leads to the splitting observed, and the valley specific optical selection rules allow us to use polarization control to identify the specific interaction pathways, and states involved. At moderate electron doping densities, we find that the dominant interactions are between polaron states dressed by electrons with the same spin[2]. The strongest cross-peak arises from the biexciton, and alternative 2D spectra reveal details of the biexciton binding energy[3]. Additionally, exciton-exciton interactions and exciton-phonon interactions are quantified by analysing the peak shapes as a function of temperature and excitation density. Finally, new results exploring interactions and charge transfer dynamics in heterostructures will be discussed.

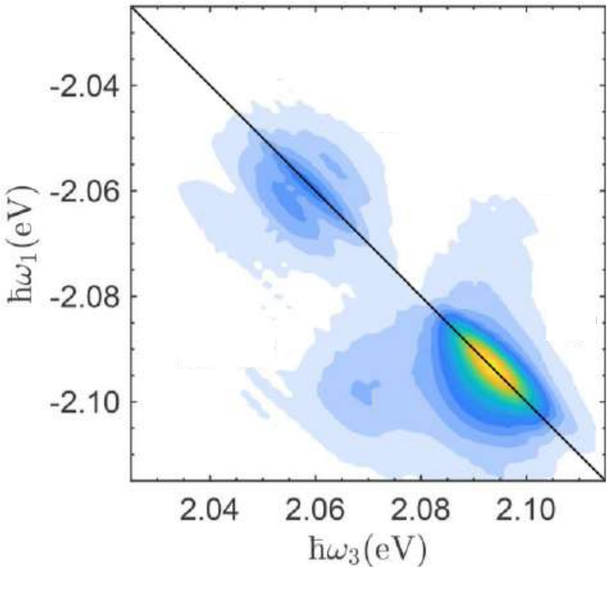

Fig. 1 2D spectrum from monolayer WS_2 with linearly polarized pulses.

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C019

Elucidating Deactivation Mechanisms in NIR Organic Semiconducting Emitters: Insights from Advanced Ultrafast Spectroscopy Techniques

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Organic semiconductors underpin modern photonics with their performance intricately linked to the morphology and deactivation mechanisms of their active layers. Our study dives into these mechanisms, particularly in high-efficiency Near-Infrared (NIR)-emissive organic molecules, using two state-of-the-art ultrafast spectroscopy techniques - Multiple Plate Continuum Generation based Transient Absorption (MPC-TA)[1] and Transient Grating Photoluminescence Spectroscopy (TGPLS).[2]

The MPC-TA method utilises a high brightness, ultrashort supercontinuum source, paving the way for a pump-probe spectroscopy platform based on a singular continuum light source. Boasting a high spectral density broadband probe and high temporal resolution, MPC-TA is invaluable in studying excitation dynamics. Simultaneously, TGPLS, integrated with high-power femtosecond light sources, effectively captures ultrafast emission dynamics that span from UV to NIR regions. Serving as an exceptional tool for studying advanced light-emitting materials, TGPLS provides crucial insights into photochemistry mechanisms within sub-picosecond time scales. Together, the synergistic application of these two powerful spectroscopy techniques presents an ideal approach to investigate optoelectronic materials.

These techniques elucidate the deactivation mechanisms in aggregated Pt(II) complex 4H, an efficient NIR emitter.[3] Our results expose collective out-of-plane motions in excited states with a frequency of 32 cm^{-1} (0.96 THz), also observed in analogous Pt(II) complexes with notable NIR emission efficiency.[4] These low-frequency vibrational coordinates suppress nonradiative decay, enhancing NIR emission. Our study thus underscores the crucial influence of excited-state vibrations in nonradiative processes, paving the way for prospective advancements in device performance.

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C020

Ultrafast Deformation Dynamics of Cycloparaphenylenes in the Excited State Probed by Femtosecond Stimulated Raman Spectroscopy

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Cycloparaphenylene (CPP, Figure 1a) derivatives are one of molecular nanocarbon and show unique physical properties owing to their distorted and strained ring structure. Such properties originate from the structural change in the excited state, as represented by fluorescence with large Stokes shift. In this context, it is important to elucidate the structure-property correlation in the excited state. In the present study, to this end, we have investigated the structural dynamics of several CPP derivatives ([8]CPP, [9]CPP and [12]CPP) with different ring size using transient absorption (TA) and femtosecond stimulated Raman spectroscopies (FSRS).

A positive band due to the S_1 state was observed in 600-700 nm upon photoexcitation in transient absorption spectra of [8]CPP and [9]CPP. This absorption band is shifted toward longer wavelength by 5-10 nm on the timescale of several hundreds of femtoseconds while the absorption band of [12]CPP is relatively broader and show no remarkable spectral shift. On the other hand, FSRS spectra of [8]CPP are characterized by a Raman band at 1190 cm^{-1}, which is assigned to in-plane CH bending. As shown in Figure 1b, this band shows a slight down-shift with a time constant of ca. 1 ps. Although this spectral shift was not detected in [12]CPP, intensities of several Raman bands at 803, 1215 and 1580 cm^{-1} decreased a few picoseconds after the photoexcitation (Figure 1c), which is probably due to change of vibronic interaction during the geometrical relaxation along the S_1 potential energy surface. A series of TA and FSRS results experimentally show that smaller CPP undergoes large structural deformation in the excited state than larger one. In addition, quantum chemical calculation indicates that this structural deformation is driven by change of the electronic structure from aromatic character to quinoidal one.

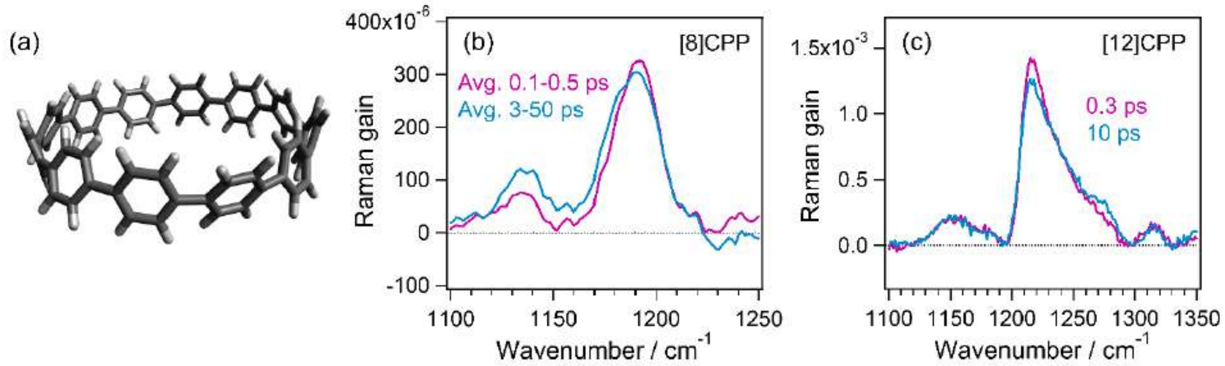

Figure 1. (a) Chemical structure of cycloparaphenylene. (b,c) Femtosecond stimulated Raman spectra of [8]CPP and [12]CPP in tetrahydrofuran.

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C021

Enhancing Upconversion Emission by Dye Hybrid Strategy

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Lanthanide doped upconversion nanoparticles (UCNPs) are capable of converting lower energy near-infrared (NIR) light into visible emissions. Their many distinguished properties, including broadly tunable emission colors and low cytotoxicity, are highly attractive for a range of applications, such as bioimaging, single-molecule tracking, super-resolution microscopy. Typically, sensitizer ion (Yb^{3+}) and activator ions (Er^{3+}, Tm^{3+}, or Ho^{3+}) are codoped in an optically inert host, such as $NaYF_4$. The small absorption cross sections of lanthanide ions largely limit the light conversion efficiency of UCNPs. Hybrid upconversion nanosystems have been reported to improve the low absorption efficiency of UCNPs.

In this presentation, I will discuss the dye strategy to sensitise the upconversion nanoparticles, which enable five to six orders of magnitude of upconversion emission enhancement. I will introduce the advance of organic-inorganic hybrids, the design principle of these hybrid photonic materials, and our recent progress on new discovery in this field. I will discuss our recent achievement in enhancing the quantum yield of NIR dyes and improve their stability by deactivating the photoinduced oxidization. Taking together the synergistic effect, we have achieved a 242-fold upconversion emission enhancement over the benchmark of IR806-sensitized system and an ~800,000-fold increase than the bare UCNPs.

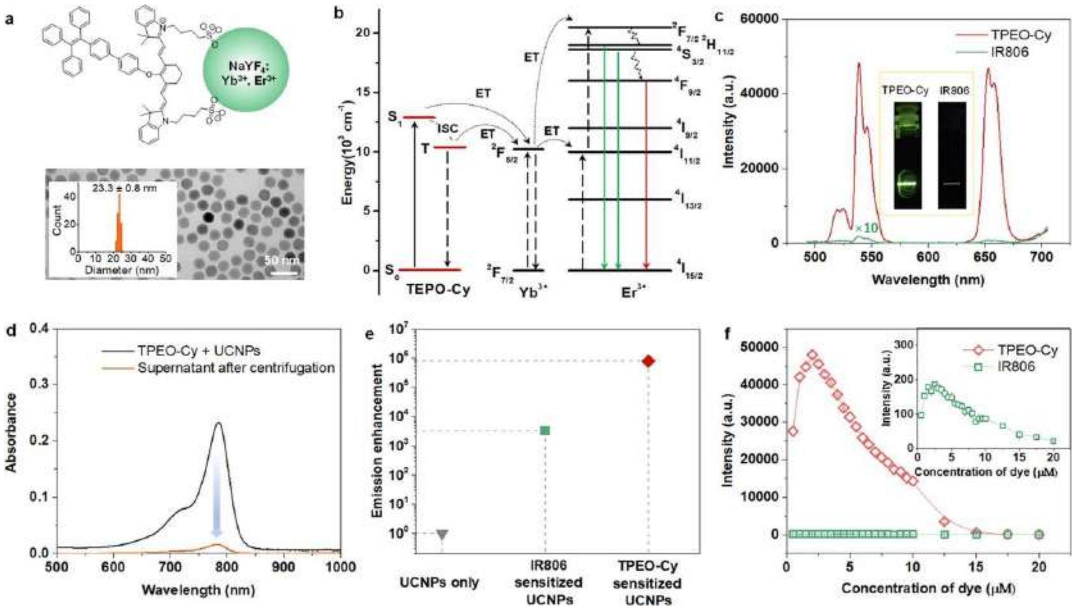

Figure 4. Upconversion enhancement of TPEO-Cy-sensitized UCNPs. (a) Schematic illustration of a upconversion nanoparticle coupled with TPEO-Cy and TEM image UCNPs. (b) The energy transfer and upconversion diagram. (c) The upconversion emission spectra of dye-sensitized UCNPs (1 mg/mL UCNPs). (d) The absorption spectra of TPEOCy-sensitized UCNPs and its supernatant after centrifugation. (e) Emission enhancement from UCNPs only (gray), IR806-sensitized UCNPs (green), and TPEO-Cy-sensitized UCNPs (brown). (f) The upconversion emission intensity as a function of dyes' concentration.

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C022

Synthesis of Novel Mediator-Emitter Conjugates for Applications in Hybrid Nanomaterial-Organic Dye Upconversion Systems

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Efficiently utilising high-energy photons is desirable in many different fields, ranging from applications in optoelectronics such as light emitting diodes (LEDs),[1] photocatalysis[2] and photovoltaics,[3] to biomedical applications such as bioimaging.[4] Accessing increased levels of high-energy light can be achieved by a process known as photon upconversion (UC), which converts low-energy photons into higher-energy photons. UC using organic dyes is commonly achieved via a process called triplet-triplet annihilation (TTA). The efficiency of TTA is quantified by the efficiencies of each contributing process in the mechanism, these processes involve two chromophore species: the sensitiser, which absorbs the incoming photon, and the emitter, which undergoes the TTA process and emits the high-energy photon. Newly emerging TTA systems are achieving efficiencies of up to 20.5%,[5] however none have yet reached the maximum efficiency of 50%. As such, further investigation into TTA systems and optimisation of their components remains crucial. It has been established that nanocrystal/organic sensitiser hybrid models are able to achieve efficient upconversion.[6] However, for efficient transfer of energy within these systems, energy transfer should be facilitated by a mediator bound to the surface of the nanocrystal. The mediator thus becomes another step in the overall process, which has potential for energy loss. As such, this work aims to reduce energy loss and increase triplet lifetimes by investigation of a novel mediator-emitter conjugate in a hybrid nanocrystal/organic dye system.

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C023

Photochromic Dyes for Dye-sensitized Solar Cells

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Dye-sensitized solar cell (DSC) is one of the representative third generation photovoltaic technology. The function of the dye in a DSC is to absorb light and turn to the electricity in the first step. The merit of DSC is that it can be designed with a high degree of freedom such as shape, color, and size for unique applications, although the power conversion efficiency of DSC is still lower than the other two representative third generation photovoltaics such as organic solar cell and perovskite solar cell. A new type of sensitizer called photochromic dye was development for DSC recently. The characteristic property of the photochromic dye is that it can turns the color (absorbing light with different wavelength) by absorbing light with certain wavelength (most probably UV light). In this talk we will present the designed organic and ruthenium based photochromic dyes and their photovoltaic performance when applied in DSC. Furthermore, the important parameters, such as the kinetic and reversibility of the color change as well as the structure related photochromic property, for photochromic dyes existed in a DSC will be studied.

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C024

Photobleaching effect in chemically treated WS2

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Two-dimensional transition metal dichalcogenides (TMDs) semiconductors are promising candidates for nanoelectronics and optoelectronics applications with unique electronic and optical properties[1]. Large-area triangle tungsten disulfide synthesized from a chemical vapor deposition method and their optical properties are studied using hyperspectral imaging. The intrinsic structural defects such as sulfur and tungsten vacancies result in inhomogeneity in the photoluminescence (PL) intensity[2]. In this work, we treated CVD-grown WS_2 few-layers with organic molecules Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), as well as lithium bis(trimethylsilyl)amide (LiHMDS).

The enhancement in the PL intensity is attributed to the rise in trion density by introducing holes with LiTFSI treatment as a p-dopant. However, photobleaching indicates to scavenging of the carriers results in quenching of the PL. Atomic force microscopy analysis provides topography and surface potential information that reveal the WS_2 flake varies in thickness and defects distribution from edge to the centre.

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C025

Multi-photon Photoredox Catalysis and Electrochemiluminescence

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In photoredox catalysis, the energy of light is used to drive single electron transfer reactions via an electronically excited catalyst (Figure 1a).[1] Electrochemiluminescence is essentially the reverse process, in which single electron transfer reactions are used to generate an electronically excited species that returns to the ground state by the emission of light (Figure 1b).[2] Despite their disparate applications in chemical synthesis and analytical chemistry, there is great overlap in the transition metal complexes and electron donors/acceptors found to be most effective.

This presentation describes new approaches to extend the scope of photoredox catalysis and electrochemiluminescence beyond the fundamental photophysical and redox limitations of their conventional reaction pathways.[3-6] These draw from advances in both phenomena, exploiting the interaction of multiple transition metal complexes introduced in combination or formed by *in situ* catalyst transformation, and a judicious selection of electron donors/acceptors. Advances in these areas enable synthesis with more energy demanding substrates, and enhanced chemical measurement through increased sensitivity, internal standardization, and/or multi-color (multiplexed) detection.

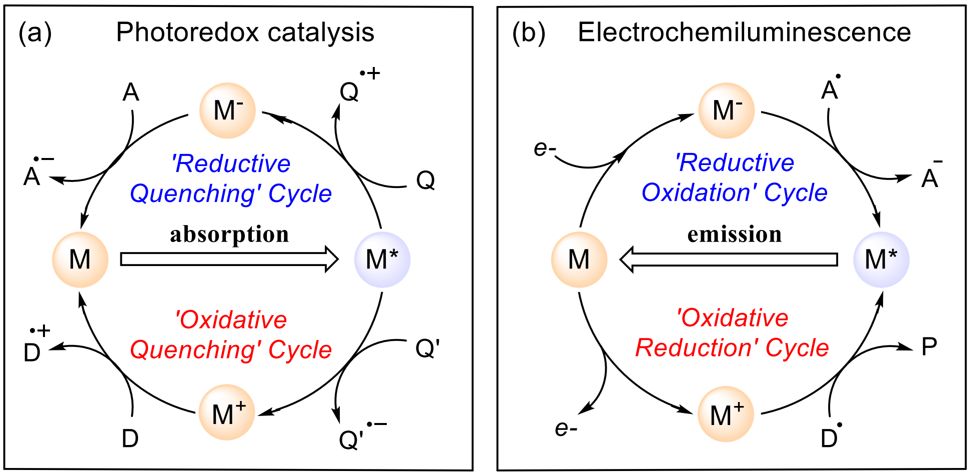

Figure 1. Generalized pathways of (a) electron-transfer quenching of the excited state of a transition metal complex (M) in photoredox catalysis, and (b) electron-transfer formation of the excited state of M in electrochemiluminescence. Key: A = electron acceptor. D = electron donor. Q = reductive quencher. Q' = oxidative quencher. A• = oxidant derived from the reduction of A. D• = reductant derived from the oxidation of D.

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C026

Biocompatible Electrochemiluminescence and Photocatalysis with Water Soluble *N*-Methyl(pyridyl)pyridinium Cyclometalated Iridium(III) Complexes

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Biocompatible synthesis and analysis typically require mild conditions across a sensitive pH and temperature range within buffered aqueous environments.[1] Iridium(III) complexes are attractive candidates for such chemistry, as they are often used in photocatalysis[2] and analytical detection systems – particularly electrochemiluminescence (ECL)[3] – due to their tuneable redox properties, long-lived excited state lifetimes, and high quantum efficiencies. Unfortunately, the use of these complexes in aqueous solvent is hindered by their poor water solubility.[4]

In this work, we focus on the use of water-soluble iridium(III) complexes bearing *N*-methyl(pyridyl)pyridinium cyclometalating ligands (Figure 1) in aqueous photocatalysis and ECL detection. We were particularly interested in these complexes as they exhibit unusually high oxidation and reduction potentials.[5, 6] This is desirable in two ways – the first being that the more ‘positively-shifted’ reduction potentials allows their use in aqueous cathodic ECL using peroxydisulfate as co-reactant; and the second being that these high oxidation potentials extend catalytic activity beyond traditional photocatalysts, and allow for the synthetic modification of more energy demanding substrates. Moreover, the use of water as a solvent offers a promising means of accessing sustainable chemistry.

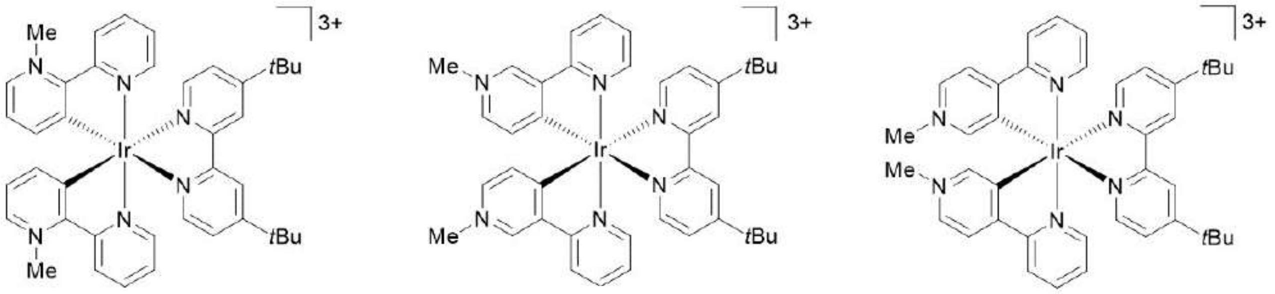

Figure 1: Iridium(III) complexes used in this work.

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C027

Decomposition of Perfluoroalkyl Substances by Irradiation of Incoherent Visible Light to Semiconductor Nanocrystals

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Perfluoroalkyl substances (PFAS) such as Teflon and Nafion are practically used in various industries, while their extremely high stability causes serious environmental persistence. Several decomposition methods have been reported: such as heating over 300-400 degree Celsius, strong oxidizing reagents, and irradiation of deep ultraviolet light. However, these methods are too harsh, and technology for decomposing PFAS has not been established to date. Recently, we reported that the powder of Cu-doped zinc sulfide (ZnS) NCs exhibit photochromic reactions by irradiation of 365-nm LED (Fig 1a).[1] The origin of the coloration is the ultralong-lived charge-separated (CS) state. We came up with the idea of using the ultralong-lived state to generate a higher excited state by stepwise two-photon absorption processes.[2]

In this study, we demonstrate that Cu-doped ZnS and CdS NCs can decompose perfluorooctanesulfonic acid (PFOS) and polytetrafluoroethylene (PTFE) by near UV and visible LED light at room temperature and atmospheric pressure (Fig 1b).

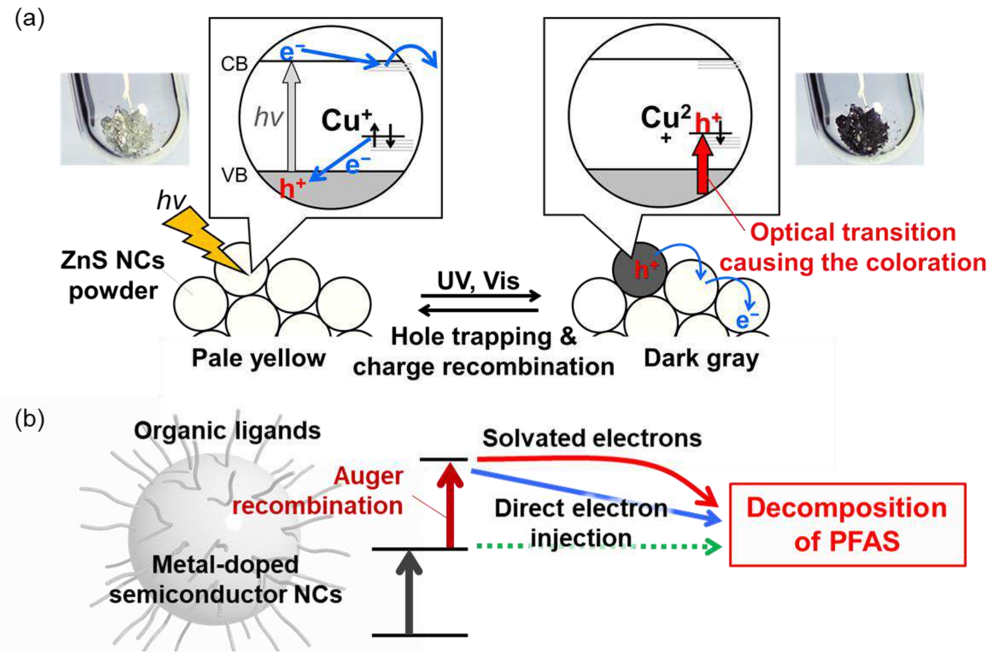

Fig. 1 (a) Photochromic reaction scheme of Cu-doped ZnS NCs and (b) plausible decomposition scheme of PFAS using Cu-doped ZnS NCs by irradiation of near UV and visible light LED light.

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C028

Highly Photosensitive Photochromic Terarylenes, Simultaneously Enhanced Photoreactivity and Extinction Coefficient

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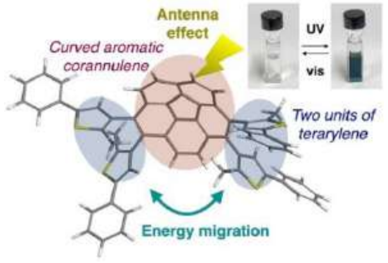
Photochromic substances display reversible isomerization uppon light irradiation and their photosensitivity has been one of central topics of photochromic chemistry and organic photochemistry. Among various photochromic suubstances, photochromic diarylethenes and related substances such as terarylenes have been most widely studied as highly photosensitive photochromic molecules. As one of typical example, we have reported photonquantitative isomerization reaction in photochromic terarylene, in which photoreactive conformation is systematically and retionally stabilized in solution phase via the specific intramolecular hydrogene bonding and specific S/N tethering atomic contacting interation [1]. Another approach was also made for photochromic terarylenes, which is induced by cascade reaction scheme triggered by chemical, electrochemical, photochemical or radiochemical oxidation reaction [2]. We also confirm possible energy storage under UV light irradiation and on-demand release of heat with the cascade ring-opening reaction [3].

In this presentation, we are going to focus on our recent new approach to simultaneously promote significantly enhanced optical absorptivity and photochemical quantum yield in photochromic substances based on corannulene as the central bridging part of terarylene structure [4]. We rationally characterized their photochemical quantum yield higher than 90%, which is significantly higher than the population ratio of reactive conformation for peri-cyclization to form cyclohexadiene unit. We further observed significantly large ectinction coefficient because of expanded conjugated electron system on the corannulene unit.



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C030

Unraveling the structure-activity-selectivity relationships in furfuryl alcohol photoreforming to H_2 and hydrofuroin over $Zn_xIn_2S_{3+x}$ photocatalysts

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$Zn_xIn_2S_{3+x}$ has emerged as a promising candidate for alcohol photoreforming based on C-H activation and C-C coupling. However, the underlying structure-activity-selectivity relationships remain unclear. Here we report on $Zn_xIn_2S_{3+x}$ with varying Zn:In:S ratios for visible-light-driven furfuryl alcohol reforming into H_2 and hydrofuroin, a jet fuel precursor, via C-H activation and C-C coupling (Figure 1)[1]. $S^{-\bullet}$ radicals are directly identified as the catalytically active sites responsible for C-H activation in furfuryl alcohol, promoting selectivity toward H_2 and hydrofuroin. The optimum $Zn_xIn_2S_{3+x}$ activity derives from a trade-off between enhanced carrier dynamics and diminished visible light absorption as the x value in $Zn_xIn_2S_{3+x}$ increases. Further, a higher Zn-S:In-S layer ratio prolongs the $S^{-\bullet}$ lifetime in the Zn-S layer, promoting C-H activation and delivering a higher C-C coupling product selectivity. The findings represent a step toward further establishing sulfide-based photocatalysts for sustainable H_2 production via organic photoreforming.

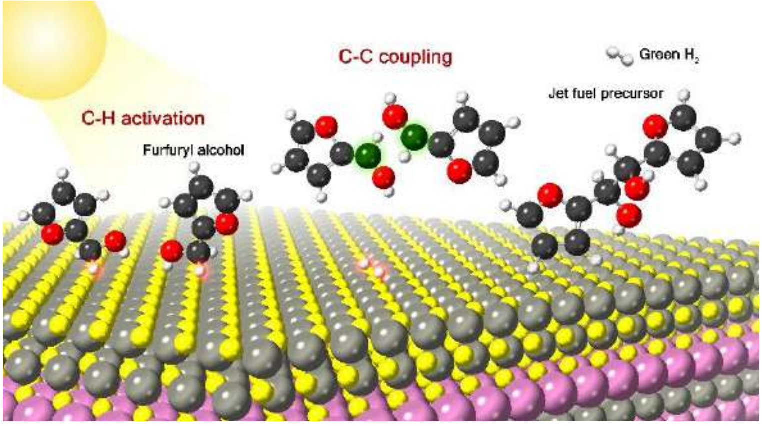

Figure 1. Furfuryl alcohol is photoreformed into H_2 and hydrofuroin (a known jet fuel precursor) over $Zn_xIn_2S_{3+x}$ photocatalysts via C-H activation and C-C coupling pathway.

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C031

Photochemical C-H Oxygenation of Hydrocarbons with Chlorine Dioxide

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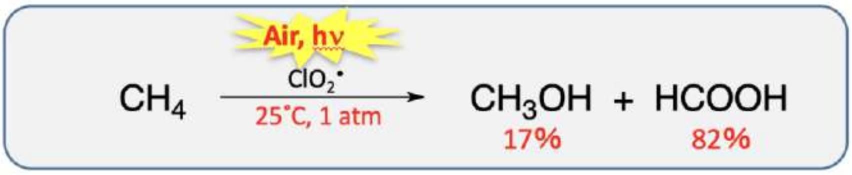
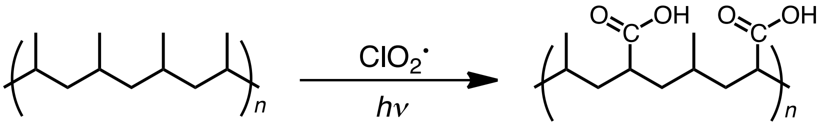
Selective aerobic oxygenation of CH_4 into liquid products without the concomitant formation of CO_2 and CO has served as an elusive target reaction. The one-step transformation of CH_4 into methanol (CH_3OH) is carried out in nature using methane monooxygenases. However, under chemical conditions, the selective oxygenation of CH_4 to CH_3OH with molecular oxygen (O_2) has been unknown because the oxidation of oxygenated products, CH_3OH and formic acid (HCOOH) is much easier than that of CH_4, leading to over-oxidation products such as CO and CO_2.

Here we report that oxygenation of methane photochemically occurred in the presence of $ClO_2^{\bullet}$.[1-3] The yields of methanol and formic acid as products were 17% and 82%, respectively, with a methane conversion of 99% in a two-phase system comprising perfluorohexane and water under ambient conditions.



Surface oxidation of PP was performed under photoirradiation (60 W LED lamp; λ = 365 nm) in the presence of $ClO_2^{\bullet}$ gas. We confirmed increase in hydrophilicity of PP surface after reaction by measuring contact angle of water drops. In addition, the results of IR and XPS measurements revealed that oxygen containing groups were successfully introduced into the PP film surface, such as carboxy group.



The surface hydrophilicity was significantly increased by introduction of polar substituents to make possible stain with water soluble dye having amino group. The carboxylic-acid substituted PP surface makes possible stain with a toluidine blue dye (3-amino-7-(dimethylamino)-2-methylphenothiazin-5-ium chloride) by the amide bonding.

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C032

Understanding the vacancy-mediated energy transfer from perovskite hosts to lanthanide dopants for efficient quantum cutting

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Quantum cutting is a process in which the energy from individual blue or ultraviolet (UV) photons absorbed by the material is re-emitted in the form of pairs of near-infrared (NIR) emitted photons. Efficient quantum cutting is observed in $CsPbCl_3$ perovskite nanocrystals (NCs) doped with Yb^{3+} ions. The lead- vacancy-induced trap state is widely accepted to mediate the energy transfer from host perovskites to Yb^{3+} ions which undergo efficient quantum-cutting emission in the NIR region.[1,2] Different dopants ions (e.g. Mn, Ni, Cd, etc.) have been co-doped to influence this mediating energy transfer process to understand and optimize this efficient NIR quantum-cutting emission. In co-doped NCs, highly efficient emission has been observed in blue, orange, and NIR regions when excited with UV light. Furthermore, anion exchange reactions were conducted to tune the band gap and modulate the relative emission contributions across a broad spectral range (Figure 1). Detailed energy transfer dynamics have been studied with steady-state and transient emission spectroscopies. Structural and morphological characterizations have been conducted through X-ray diffraction, transmission electron microscopy, and X-ray electron spectroscopies.

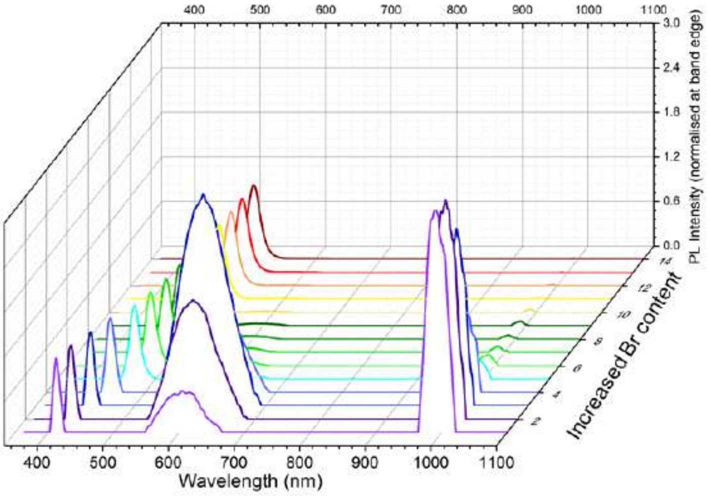

Figure 1. PL emission spectra of Mn- and Yb- co-doped $CsPbCl_3$ nanocrystals undergoing anion exchange with bromide ions. The PL emission intensity is normalized to 1 at excitonic emission.

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C033

Physical Property and Chemical Reaction of Materials under Extreme High Pressure

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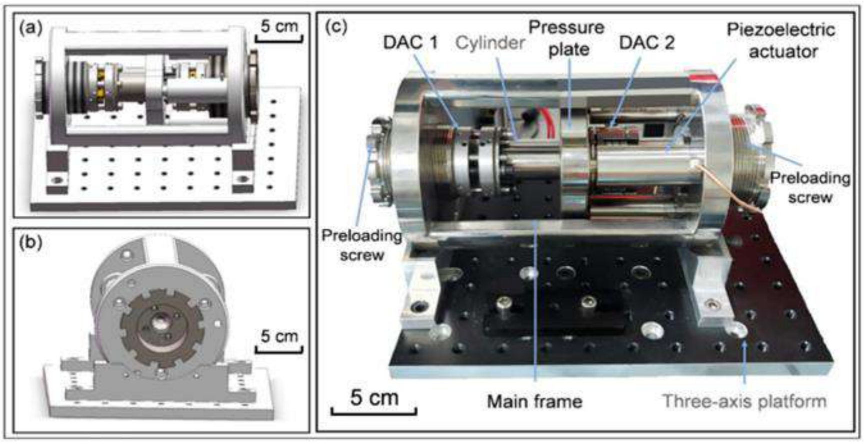
Static high-pressure experiments are a steady pressure loading process in which the system is assumed to be thermally balanced with its surroundings. In contrast, dynamic high-pressure experiments could be considered to be adiabatic because of the rapid pressurization. In fact, there is another mode of pressure loading/unloading that is exemplified by the static and dynamic diamond anvil cell (s-dDAC) in our work, for which the pressurization rate can be controlled consistently and accurately between that of static high-pressure technique and dynamic high-pressure technique therefore the physical process involved is neither isothermal nor adiabatic, but a special intermediate process.

On behalf of the s-dDAC device, time-dependent high pressure non-equilibrium dynamics processes, including phase transition kinetics, metastable phase formation and interception, crystal growth, chemical reaction, strain and stress processes and so on could been investigated powerfully. Recently in our lab, the abnormal mechanoluminescence behavior of ZnS:Mn,[1] the crystalline phase transition kinetics of pyridine[2] and the pressure induced polymerization of methyl methacrylate[3] were systematically studied and illustrated using this device.



The s-dDAC assembled with two DACs for compression and decompression: (a) schematic front view; (b) schematic side view; (c) photograph and details of the components.

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C034

Study on the photodegradation mechanism of chain-linked Pyrene/DMA exciplex system

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Photodegradation is an inevitable consequence of the interaction between light and molecules, and it often has a significant adverse effect on the performance of molecules used in the fields of pharmaceuticals, environment, artificial photosynthesis, fluorescence microscopy, and organic light-emitting diodes (OLEDs). Thus, understanding its mechanism is useful for optimizing the operating conditions for the molecules.

Pyrene (Py), aniline, and their derivatives are common molecular moieties used in the development of OLEDs because Py has high thermal- and photo-stability,[1] and they have a high yield to form an exciplex.[2] With the development of OLEDs using thermally activated delayed fluorescence (TADF) in recent years, researchers have shown interest in the exciplex systems. In this research, we focus on elucidating the photodegradation mechanism of a representative Py-aniline-based exciplex system with liquid chromatography-UV-mass spectrometry (LC-UV-MS), tandem mass spectrometry, FT-IR spectroscopy and NMR spectroscopy. The chain-linked pyrene-$(CH_2)_{12}$-O-$(CH_2)_2$-*N,N*-dimethylaniline (Py-12-O-2-DMA) was prepared in acetonitrile solution. The alkyl chain ensures a 1:1 ratio of Py to DMA and a high yield of an exciplex formation, allowing for experiments in solution with a few micromolar concentrations (~5 μM). We identified Py-12-O-2-MMA (monomethylaniline), Py-12-O-2-MFA (methylformanilide), Py-12-O-2-aniline, Py-12-O-2-FA (formanilide), and products containing hydroxylated pyrene as photodegradation products. A photodegradation mechanism for Py-12-O-2-DMA was proposed that includes oxidative formylation, demethylation, deamination and hydroxylation based on the identified products. The mechanism suggests that the excited state singlet oxygen ($^1O_2$) plays a key role to initiate the process, which was supported by the control experiment under deoxgygenated condition. This work is expected to provide a guideline for the design of the photodegradation-resistant Py-aniline-based exciplex systems.

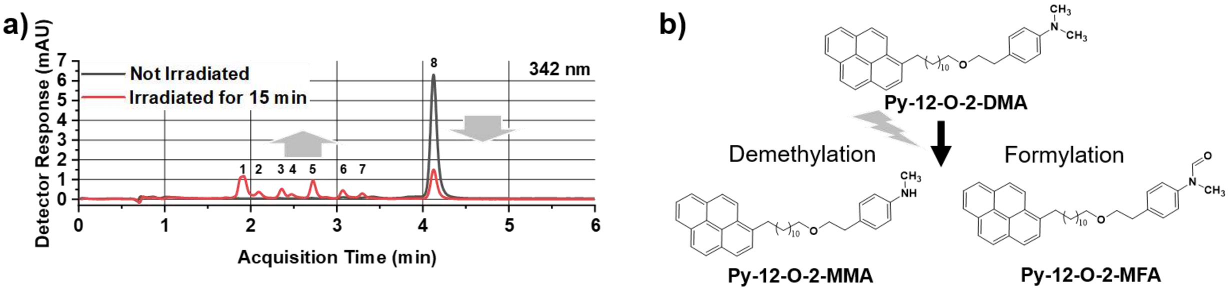

Figure 2. (a) UV chromatogram of Py-12-O-2-DMA before and after irradiation. (b) A simplified schematic of the photodegradation process.

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C035

Improving Photochemical Upconversion via Steering Energy Gradient

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Photochemical upconversion, also known as triplet-triplet annihilation upconversion (TTA upconversion), has great potentials in solar energy conversion, anti-counterfeiting, and display. Understanding and regulating the photophysical processes in photochemical upconversion systems is critical in developing efficient solid-state upconversion systems. In the present study, we incorporate endothermic triplet energy transfer and single energy harvesting gradients in photochemical upconversion systems, to expand the anti-Stokes shift of upconversion emission, suppresses the energy back transfer from the upconverted excited-state to the photosensitizer, and then improve the efficiency of upconversion.

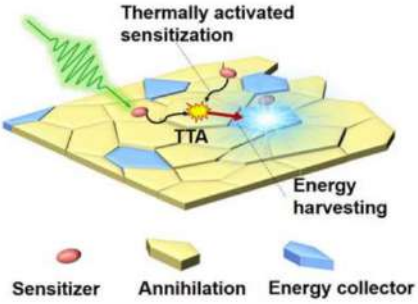

Fig. 1 Schematic diagram of energy flow in TTA upconversion

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Acknowledgement
Financial support from the National Natural Science Foundation of China (22273117 and 22090012) is gratefully acknowledged.

C036

Highly Flexible and Acid-Alkali Resistant TiN Nanomesh Transparent Electrodes for Next-Generation Optoelectronic Devices

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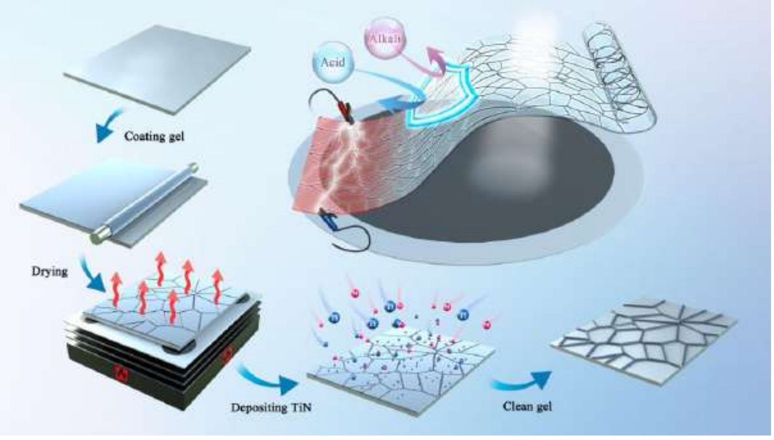
Transparent, flexible electrodes are pivotal for diverse optoelectronic applications, including wearable tech, flexible displays, and crucially, solar energy devices such as solar cells and batteries. Traditional materials like indium tin oxide (ITO) and emerging alternatives often present limitations in terms of flexibility, stability, and cost. Our research introduces a versatile alternative: a low-cost, flexible, and acid-alkali-resistant titanium nitride (TiN) nanomesh electrode.

We developed this unique electrode by sputtering a TiN coating onto a naturally cracked gel film substrate. The resulting TiN nanomesh electrode maintains stable electrical performance through numerous bending cycles and displays robust chemical and thermal stability, resisting strong acid and alkali corrosion.

Distinctly, the TiN nanomesh offers superior light transmission (88% at 550 nm), low sheet resistance (~200 Ω/sq), and a high work function (~4.8 eV), positioning it as a suitable anode for organic electronic devices and importantly, solar cells and batteries. The nanomesh's resilience in harsh environments addresses existing stability problems with electrodes when in contact with acidic/alkaline materials and solvents during optoelectronic device fabrication.

We've successfully demonstrated the use of the TiN nanomesh electrode in electric heaters and electrically controlled thermochromic devices, underlining its broad potential. With the advent of our TiN nanomesh electrode, we foresee significant advancements in solar energy materials and devices, paving the way for resilient, next-generation optoelectronic devices operating in harsh environments.



C037

Enhancing Photochemical Conversion with Triplet-Triplet Annihilation Upconversion

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Photochemical conversion of solar energy holds the promise of clean energy. Developing photochemical conversion technology that captures as much of the sun's energy as possible is highly desirable. Triplet-triplet annihilation (TTA) upconversion, has great potentials in solar energy conversion. Upconversion of low-energy photons into high-energy photons provides a feasible way to enhance the light harvesting capability of photochemical conversion systems. In this contribution, we report the incorporation of TTA upconversion microcrystals with conventional photocatalysts to construct solar energy conversion systems. The TTA upconversion benefits the photoproduction of hydrogen by converting the red photons into blue and green ones that can be utilized by the photocatalyst.

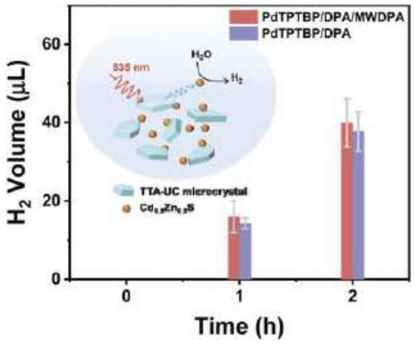

Figure 1. Upconversion photoproduction by $Cd_{0.5}Zn_{0.5}S$ combining TTA upconversion microcrystals.

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Acknowledgement
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C038

Singlet fission in TIPS-anthracene thin films

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Singlet fission (SF), the conversion of a high-energy singlet state (S_1) into two lower-energy triplet states (T_1) via a correlated spin intermediate ^{1}(TT), has gained interest for its potential to surpass the detailed balance limit of a single-junction photovoltaic cell (Figure 1).[1] Tri-isopropyl silane (TIPS) ethyne substituted acenes, such as TIPS-tetracene and TIPS-pentacene, have served as soluble materials for the investigation of the mechanism and kinetics of SF.[2] However, these materials have T_1 energies below the 1.2 eV bandgap of silicon – inhibiting triplet energy transfer at the interface. Computational studies of TIPS-anthracene (T_1 = 1.37 eV)[3] show that in the solid-state SF is efficient, with a triplet yield of ~170%.[4] Experimental evidence, however, is lacking.

In this presentation time resolved measurements of thin films of TIPS-anthracene are discussed. The results from the magnetic field effect (MFE), which confirm SF, will also be presented. Finally, a kinetic model is applied to the MFE data to gain insight into the loss mechanisms for SF in TIPS-anthracene.

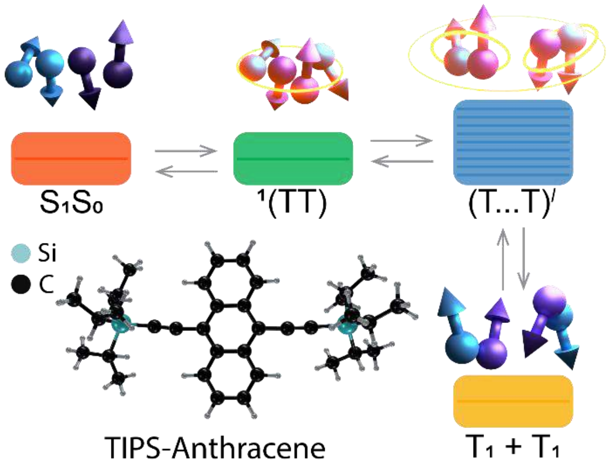

Figure 3: The mechanism of SF and structure of TIPS-anthracene. SF proceeds through the coupling of a molecule in the ground state (S_0) with neighboring molecule in its excited state (S_1). These molecules then form a strongly coupled triplet pair state ^{1}(TT) before losing electronic coherence to form the weakly coupled state (T…T)$^{l.}$ The final step sees the formation of two triplet excitons (T_1).

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C039

Density functional theory for difficult excited states

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Time-dependent Density functional theory (TD-DFT) is well known as a low-cost approach for prediction of excited states. Unfortunately, it struggles to describe difficult excitations relevant to photochemistry and other important processes. It is less well known that time-*in*dependent DFT can yield difficult excited state properties inaccessible to TD-DFT, by working from ensembles of pure states. Facilitating excited states requires exact functionals to be carefully generalized to avoid spurious interactions from misapplied ansatze. This talk will discuss recent advances on rigorous definitions for the kinetic, Hartree and exchange[1-2] and correlation[3-4] ensemble energy functionals, which together *yield a complete generalisation of pure state DFT to excited states*. These works reveal unusual (yet tractable) properties of density functionals – notably the need for multi-configurational Kohn-Sham states, and a strong absence of weight-dependence in the low density limit. Ensemble generalized Kohn-Sham theory based on these functionals, and its successful applications (Figure 1) to excited state chemical problems[5-7], will finally be discussed.

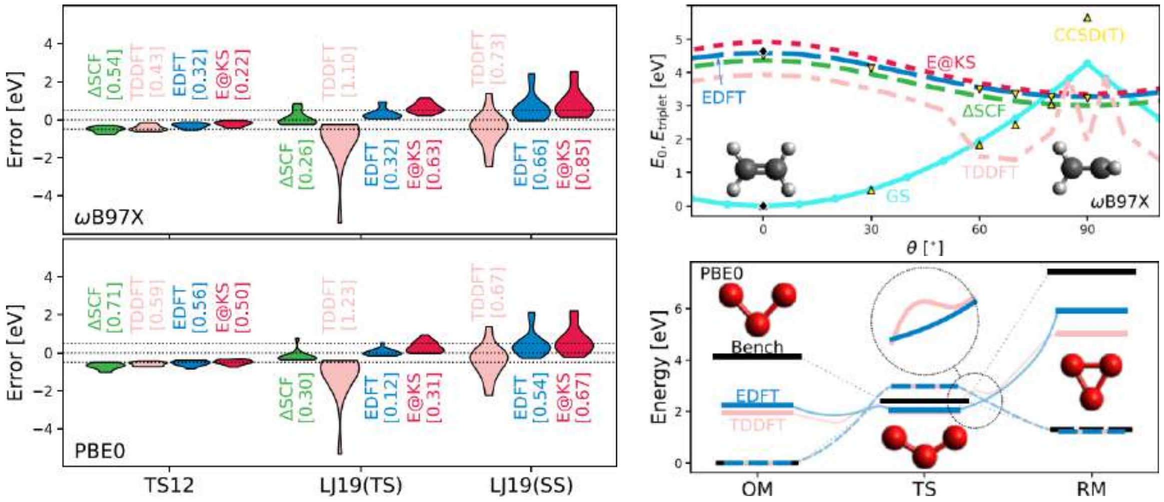

Figure 1: Ensemble approaches to excited state density functional theory out-perform TD-DFT on difficult low-lying excited states and avoid fundamental issues. Figures from [X].

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C040

Metal doping of perovskite metal oxides to enhance photocatalysis

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Perovskite metal oxides, ABO_3 , are the current benchmark water-splitting photocatalysts with recent reports showing ~100% quantum efficiency ($SrTiO_3$ with 365 nm irradiation).[1-2] A major strategy to enhance photocatalytic performance is aliovalent doping.[3]

This presentation will investigate doping strategies of $SrTiO_3$ and $NaTaO_3$ to enhance photocatalytic efficiency. Photocatalysts were prepared via high temperature solid state synthesis. The prepared photocatalysts were characterised with UV-Vis diffuse reflectance spectroscopy, XRD, SEM, Raman spectroscopy, and high-angle annular dark field (HAADF) STEM with energy-dispersive X-ray spectroscopy (EDS) and electron energy loss (EELS) mapping.

Photocatalytic performance was screened by monitoring the breakdown of an anionic organic test molecule (4-[(4-dimethylamino)phenylazo]benzenesulfonate) under irradiation from an LED array. Low levels of doping of Al into $SrTiO_3$ or La in $NaTaO_3$ was able to significantly enhance the photocatalytic rate. The most active photocatalysts were then used for the degradation of perfluoroalkyl substances (PFAS). A correlation between doping and PFAS conversion was observed.

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C041

Observation of the local charge carrier dynamics for Pt / TiO_2 film by using the time-resolved pattern-illumination phase microscopy

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Photocatalyst is attracting much attention because it can be used for decomposition of pollutants in air and water and water splitting. Photocatalytic reactions starts when charge carriers are generated upon the photoirradiation, and it is essential that photo-excited charge carriers are separated well and used for the redox reactions without losing them by recombination. Charge carrier dynamics have been studied by using time-resolved techniques, but photoexcited carriers have a wide range of lifetime due to complex recombination processes because of its inhomogeneous nature. Recently, we have developed a new time-resolved microscopic technique called the time-resolved pattern-illumination microscopy (PI-PM) method.[1] Furthermore, we could succeed to classify the types of charge carriers based on the pixel-by-pixel responses shapes obtained by the PI-PM method.[2] In the previous research, by applying these methods in an inert solvent with/without scavenger, we could successfully distinguish multiple charge carriers for TiO_2 particulate films. In this study, Pt used as cocatalysts on TiO_2. It is known that Pt not only accumulate electrons, but also work as effective reduction site. We studied charge carrier dynamics in Pt/TiO_2 by the PI-PM method.

Figure 1(a) shows the time-sequence of the PI-PM image sequences for Pt/TiO_2 in ACN. The black regions at the bottom indicate the irradiation area with UV-light. Figure (b) and (c) shows the average response (normalized) obtained from the PI-PM image sequences((c): particulate TiO_2 and Pt/TiO_2 in ACN, (d): Pt/TiO_2 in ACN, EtOH and NB/EtOH, where EtOH and NB/EtOH were used as hole and electron/hole scavengers.). From the responses, the response peak time region of Pt/TiO_2 was slower than particulate TiO_2, and the responses for EtOH and NB/EtOH were slower than that for ACN. From these results, it was suggested Pt accumulate electrons, prevent charge carrier recombination and extend the lifetime of electrons and holes.

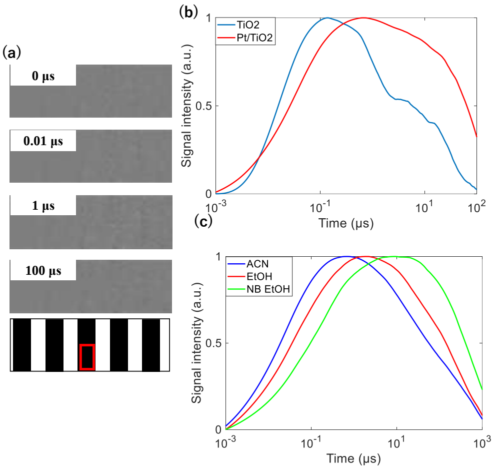

Figure1 (a) PI-PM image sequence of Pt/TiO2

(b) Time response obtained by PI-PM method for TiO2 and Pt/TiO2

(c) Time response of Pt/TiO2 in different solvent

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C042

Implications of Back-Electron Transfer in Photoredox Catalysis

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Transition metal photoredox catalysis is an increasingly popular method for challenging organic syntheses, including carbon-carbon bond formation and synthesis of enantiopure compounds. Despite its popularity, further growth in the field is inhibited by a limited understanding of what makes a good photocatalytic system. While usually selected based on electrochemical and photophysical properties; molecular photocatalysts with similar properties often demonstrate marked differences in reactivity.[1] Furthermore, sacrificial reagents are commonly used to donate or accept electrons within the catalytic cycle but are often chosen with disregard for their mechanism and efficacy of action.[2] These limitations need to be addressed by investigating the relationships between catalyst structure, activity of sacrificial reagents and photocatalytic power.

The critical reaction step in the conventional photoredox mechanism is often considered to be photo-initiated electron transfer (PET). In a reductive quenching cycle, the elementary PET step is defined by the bi-molecular interaction between a photocatalyst excited state (PC*) and a suitable electron donor (D) to form the charge-separated encounter complex $[PC^{-}:D^{+}]$, surrounded by a solvent ‘cage’. A successful photoredox reaction requires the subsequent dissociation of this encounter complex (cage escape), however back-electron transfer is a competitive process regenerating D and the catalyst ground state. effectively wasting the absorbed photon required to generate PC*. Poor cage escape efficiency drastically decreases the photochemical quantum yield, yet the processes governing this step are poorly understood.

In this work, we use *in situ* spectroscopic techniques to study the kinetics of back-electron transfer under typical photoredox reaction conditions. We demonstrate how the electron donor plays a critical role in controlling back electron transfer, and how minimizing this parameter significantly improves reaction rate, overall yield, and atom economy. We expect these results will direct the design of improved photocatalytic systems exhibiting increased catalytic efficiencies and requiring lower energy inputs.

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C043

Tuning the Photoluminescence Anisotropy of Semiconductor Nanocrystals

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Semiconductor nanocrystals are promising optoelectronic materials. Understanding their anisotropic photoluminescence is fundamental for developing quantum dot-based devices such as light-emitting diodes (LEDs), solar cells, and polarized single-photon sources. In this study, we experimentally and theoretically investigate the photoluminescence anisotropy of CdSe semiconductor nanocrystals with various shapes, including plates, rods, and spheres, with either wurtzite or zincblende structures.

We use defocused widefield microscopy to visualize the emission dipole orientation and find that spheres, rods, and plates exhibit the optical properties of 2D, 1D, and 2D emission dipoles, respectively, as illustrated in Fig. 1(a). Both quantum dots (spheres) and disk nanoplatelets (plates) exhibit donut-like defocused emission patterns in 1-2, 7-8 in Fig. 1c, implying the existence of multi-dimensional transition dipoles. The rods have bi-lobed defocused emission patterns (3-4), which are the characteristic patterns for a 1D dipole. The long nanoplatelets have donut-like defocused emission patterns but also with some features of a 1D dipole.

We rationalize the seemingly counterintuitive observation that despite having similar aspect ratios (width/length), rods and long nanoplatelets exhibit different defocused emission patterns by considering valence band structures calculated using multiband effective mass theory and the dielectric effect. The principles are extended to provide general relationships that can be used to tune emission dipole orientation for different materials, crystalline structures, and shapes.

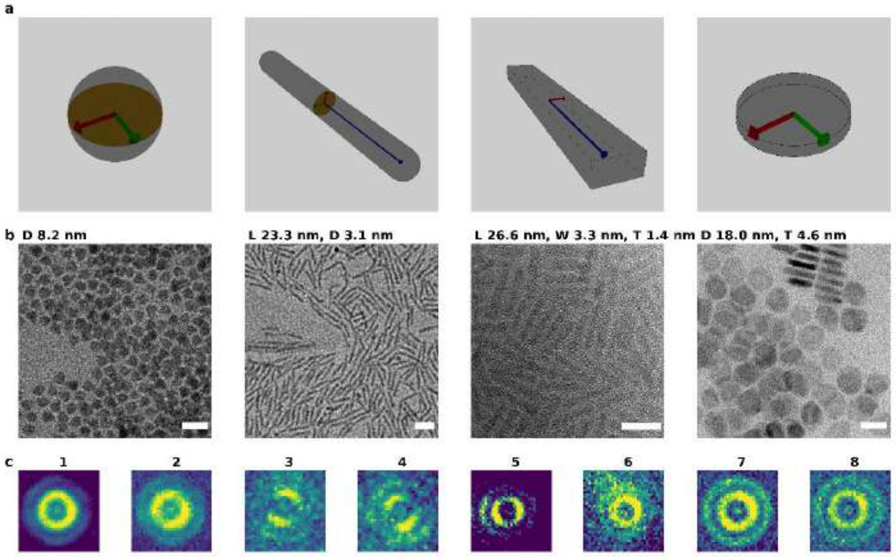

Fig.1 Defocused patterns of CdSe nanocrystals with four shapes: from left to right, spheres (CdSe/CdZnS quantum dots, diameter 8.2 nm), rods (CdSe, length 23.3 nm, diameter 3.1 nm), long nanoplatelets (CdSe, length 26.6 nm, width 3.3 nm, thickness 1.4 nm), disk nanoplatelets (CdSe/CdZnS, diameter 18.0 nm, thickness 4.6 nm). **(a),** Shapes and dipoles of the four kinds of nanocrystals. **(b),** TEM images, the average size (diameter or length) is indicated on the top left. Scale bar: 20 nm. **(c),** Eight defocused emission patterns are displayed, representing quantum dots (1,2), rods (3,4), long nanoplatelets (5,6), and disk nanoplatelets (7,8).

C044

Binaphthalimide Scaffolds with Thermally Activated Delayed Fluorescence Based on Davydov Splitting

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In OLEDs, it is desired to use triplet excitons for efficient light emission. Organic based thermally activated delayed fluorescence (TADF) and phosphorescence materials using noble metal complexes have been extensively studied [1]. Recently, Dr. Aizawa, et al, reported a negative excited singlet-triplet energy gap molecule with the double-excitation effect for the stabilizing excited singlet state (**S_1**) [2]. We here consider Davydov splitting (DS) as a new approach to selectively stabilize **S_1** state which could even lead to an inversion of **S_1** / **T_1**, (excited triplet state). DS is observed among two (or more) chromophores whose electric transition dipole moments are weakly coupled to each other. In the classic model, splitting of the chromophore energy level, J is as follows, $J = \mu_1\mu_2\frac{cos\varphi}{r^2}$ with μ_1 and μ_2 the electronic transition dipole moments of the two chromophores involved, r and φ referring to the distance and angle between molecules respectively. As phosphorescence is electronically spin forbidden transitions, the DS is expected to be much smaller in the **T_1** [3] [4].

In this study, electron donor-acceptor (D-A) monomers are connected to form D-A-A-D dimers, and their DS is studied. The D-A-A-D dimers **1**, **2** and D-A monomers **3**, **4** are shown in **Figure 2**. We introduced carbazole as donor and naphthalimide as the acceptor. For the solubility and tuning of D-A interactions, two types of molecules were compared with cyclohexane and pentafluoro-benzene. Both dimers include a chiral axis which gave us additional insight in the DS via the Cotton effect in the CD spectra. As results of photo physical measurements, both dimers exhibit TADF and we could efficiently decrease ΔE_{ST}, (the energy difference between **S_1** and **T_1**), with dimerization. The splitting width difference between **S_1** and **T_1**, with J_{S1} **>>** J_{T1}, is considered to significantly reduced ΔE_{ST}.

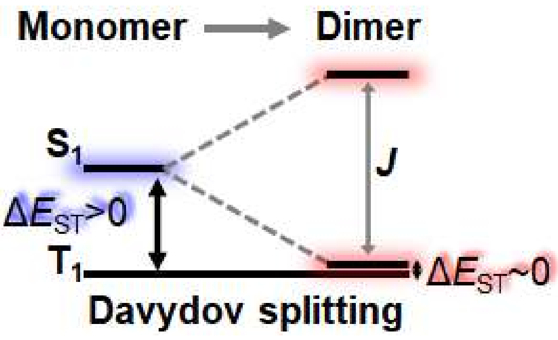

Figure 1. Conceptual diagram of this study.

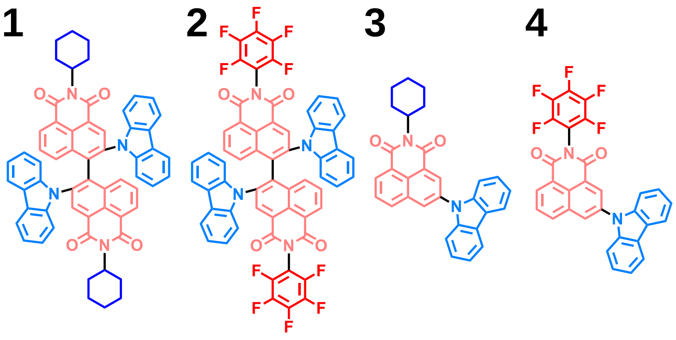

Figure 2. Chemical structures of the **1**, **2**, **3**, and **4**.

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C045

Characterising the photophysics of BODIPY: a widely used lipid droplet dye

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The organic fluorophore BODIPY 493/505 is routinely used to visualize cellular organelles called lipid droplets (LDs) for sub-cellular microscopy[1]. It was previously thought that LDs were simple lipid storage within the cell and principally involved in metabolism. More recent studies have used BODIPY to uncover novel roles of LDs in immunity[2] and cancer progression[3]. Although BODIPY is widely used to study LDs, the molecular mechanisms by which it brightly and specifically labels LDs remain unclear. The importance of visualising LDs to understand disease and health warrants the need to understand the photophysics of BODIPY-LD fluorescence.

Here we report ongoing work to characterise the photophysical properties of BODIPY for fluorescence microscopy of LDs. Conventional spectroscopic measurements revealed significant fluorescence enhancement of BODIPY in increasingly non-polar solvents with more than a tenfold brightness increase when comparing water to oil. We also measured unexpected results of BODIPY enhancement dependent on the lipid composition of the oil solvent, and on the aqueous/oil interface. Fluorescence microscopy of live COS-7 cells stained with BODIPY showed increasing LD emission with increasing BODIPY concentration. Conversely, LD emission decreased upon washing the cells in buffer. This suggest BODIPY is only partially sequestered into LDs and maintains an equilibrium between the lipophilic and aqueous environments.

While the molecular mechanisms are not yet fully elucidated, our ongoing work suggests BODIPY is specifically sequestered into LDs and behaves as a polarity-sensitive fluorophore, becoming brighter in non-polar environments. Further work is required to understand its dynamic properties within the biochemically complex cellular interior. Additionally, under appropriate imaging conditions, the observed fluorescence properties of BODIPY may be used for single molecule localization super-resolution microscopy of LDs. The improved sub-microscopic resolution would reveal the biomolecular composition of LDs and its interactions with cellular proteins.

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C046

The Up’s and Down’s of Internal Conversion from first principles

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Internal conversion (IC) is an important photophysical mechanism corresponding to non-radiative decay where electron spin is conserved (same-spin). IC is notorious for being insanely complex: to model the coupling between two same-spin states, one need to accurately model the nuclear coupling, electronic coupling, and vibrational coupling, all the while accounting for occupational quanta within normal mode framework. In fact, this ends up being analogous to the 0-1 knapsack problem, a famous NP-complete problem, and therefore for large systems is intractable.

Despite the inherent complexity, IC remains an incredibly important mechanism in exciton dynamics models, competing with mechanisms of interest such as fluorescence, multi-exciton mechanisms like singlet fission and triplet-triplet annihilation, and energy transfer mechanism like FRET. Therefore, a model which can accurately model it is vital for a complete and concise exciton model.

This talk will focus on IC and how it can be modelled from first principles. Our research group has chosen to focus on this difficult problem, and I will share with you all of the successes and failures we have experienced on the subject matter. I will begin with how one can overcome the numerical complexity of the problem[1], and then show the basic method for calculating actual rate constants within a DFT framework[2]. I will then discuss how this theory can be used to calculate the full exciton dynamics of a chromophoric system[3,4], before highlighting where further work is required[5], as well as where the model currently fails[3,5].

In short, the model is currently robust, and provides valuable insight into the nature of a chromophoric-system, but still requires some improvement. This talk will highlight all of this; the up’s and down’s.

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C047

The Extreme Confinement Regime: A Critical Juncture for the Mechanical and Optical Properties of Semiconductor Quantum Dots

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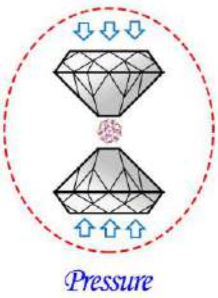
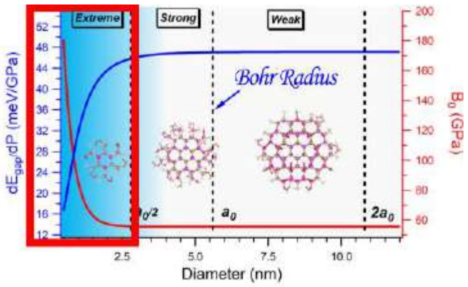
The Bohr Radius has long been considered a defining characteristic of conventional quantum dot systems. However, our research demonstrates that as quantum dot size approaches the extreme confinement (EC) regime, the wavefunction becomes more delocalized, leading to the breakdown of the Bohr radius. Through a combination of comprehensive experiments (high hydrostatic pressure absorption and fluorescence spectra) and simulation techniques (density functional theory and molecular dynamics), we show that the EC regime is a critical juncture at which both the mechanical and optical properties of quantum dots differ significantly from conventional expectations. Specifically, the mechanical properties of CdSe quantum dots deviate from bulk values only within the EC regime, where the Brus equation's effective mass approximation is no longer valid. Furthermore, the absorption spectra of CdS clusters become increasingly sensitive to surface chemistry and solvent environments, with varying behaviors observed for the wurtzite and zincblende structures. Our findings provide new insights into how to manipulate wet chemistry synthesis conditions to adjust optical properties while maintaining stability, emphasizing the significance of the EC regime as a fundamental regime for investigating quantum dot/cluster systems.





$$\frac{dE_{\rm gap}}{dP} = \underbrace{\left\{\alpha_0 + \frac{V_0(\{R\})\pi}{9B_0}\left[\frac{h^2}{R^5}\left(\frac{1}{m_e}+\frac{1}{m_h}\right)\right] - \frac{V_0}{9B_0\epsilon}\frac{1.8e^2}{R^4}\right\}}_{\mathcal{D}} + \underbrace{\left[\frac{h^2}{8R^2}\frac{\partial}{\partial P}\left(\frac{1}{m_e}+\frac{1}{m_h}\right) - \frac{1.8e^2}{4\pi R}\frac{\partial}{\partial P}\frac{1}{\epsilon}\right]}_{\mathcal{U}} + \mathcal{O}(P).$$

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C048

Simulations of photophysical properties of TADF and anti-Hund molecules

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Organic photoactive molecules are used in a host of technological and biomedical applications. In particular, emitters exhibiting thermally activated delayed fluorescence (TADF) have been used, e.g., in organic light-emitting diodes, photocatalysis, bioimaging, and photodynamic therapy. The efficiency of such materials depends on a number of photophysical properties, most notably on the rates of electronic transitions and the optical spectra involving both singlet and triplet excitations. It is also well-recognized that such properties depend strongly on molecular environments like solvents or solid-state matrices.

In this contribution, we will present a computational framework[1] for simulations of photophysical properties like absorption and emission spectra and rate constants of radiative and intersystem crossing transitions. The methodology is based on the nuclear ensemble method, which relies on sampling the distributions of molecular geometries due to the vibrational motion at finite temperatures. The solvent effects are accounted for through the perturbation-theory-based state-specific non-equilibrium polarizable continuum model, which allows us to simultaneously calculate solvent corrections to all excite state energies in multiple solvents. We apply the framework to classical TADF emitters and a novel class of anti-Hund molecules[2], characterized by an inverted singlet-triplet structure. The latter is possible thanks to a significant contribution of double excitations in the low-lying excited states. Due to this unusual correlation effect, standard TD-DFT approaches fail to predict the inversion, so higher-level methods need to be used.

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C049

Overlayers in photocatalytic applications

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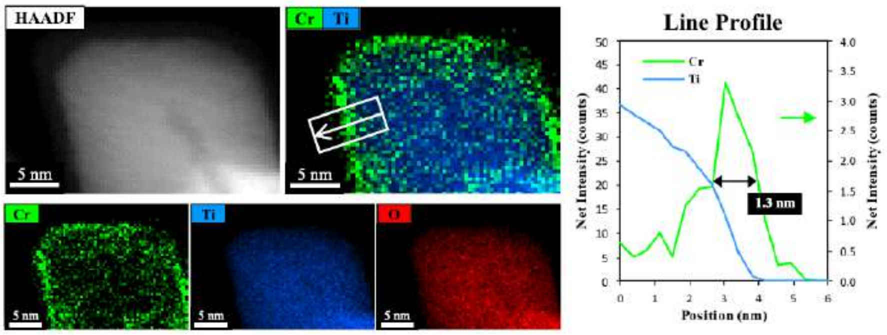
Significant advances in single system photocatalysts (i.e. not photo-electrochemical systems) have recently been achieved that have finally crashed through their past limitations and realized (demonstrated) their long-held potential to be the lowest cost form of hydrogen production. Particulate photocatalysts of Al:SrTiO3 have recently been reported that operate at near unity efficiency, albeit at low overall solar-to-hydrogen (STH) efficiency, and been scaled up to 100 m2.[1] Nanowires of InGaN have demonstrated up to 9% STH at increased temperature under concentrated solar irradiation.[2] To achieve such outstanding performance requires several architectural features of the photocatalyst material to operate synchronously and in perfect harmony; (i) strong absorption of photons, (ii) efficient separation of charge carriers and transport to specific crystallographic planes of the particle surface, (iii) addition of suitable co-catalysts that productively participate in the reduction and oxidation steps to produce hydrogen and oxygen, respectively, and (iv) a coating to prevent the back reaction from occurring. This latter function is often overlooked but is essential to ensure that maximum efficiency is achieved.

For the two photocatalyst examples listed above, the coating used is an ultra-thin 2 nm overlayer of Cr_2O_3 that allows transport of H^+ and H_2 between the surface and co-catalyst but not OH^- and O_2, which stops recombination back to H_2O. We have investigated Cr_2O_3 overlayers on a range of substrates using a suite of sensitive surface spectroscopic and imagining techniques. It is found that the chemical and physical properties depend significantly on the type of substrate. Even similar substrates can have vastly different interactions with the overlayer. For example, the Cr_2O_3 was found to diffuse into the anatase phase but remain at the surface of the rutile phase of P25.[1,2] The overlayer exists as $Cr(OH)_3$ on $BaLa_4Ti_4O_{15}$ but converts to Cr_2O_3 and diffuses slightly below the surface upon annealing. However, for Al:$SrTiO_3$, the Cr_2O_3 remains stable and on the surface. In addition, some of the overlayer reduced to metallic Cr after annealing. Even differences in surface roughness of TiO_2 films can lead to differences.[3] These effects and the ramifications for photocatalysts will be presented and discussed.



STEM-EDX elemental mapping with line analysis of a P25-Cr_2O_3 particle before annealing

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C050

Synthesis of Organic Conjugated Molecules as Catalysts for Carbon-dioxide Photoreduction

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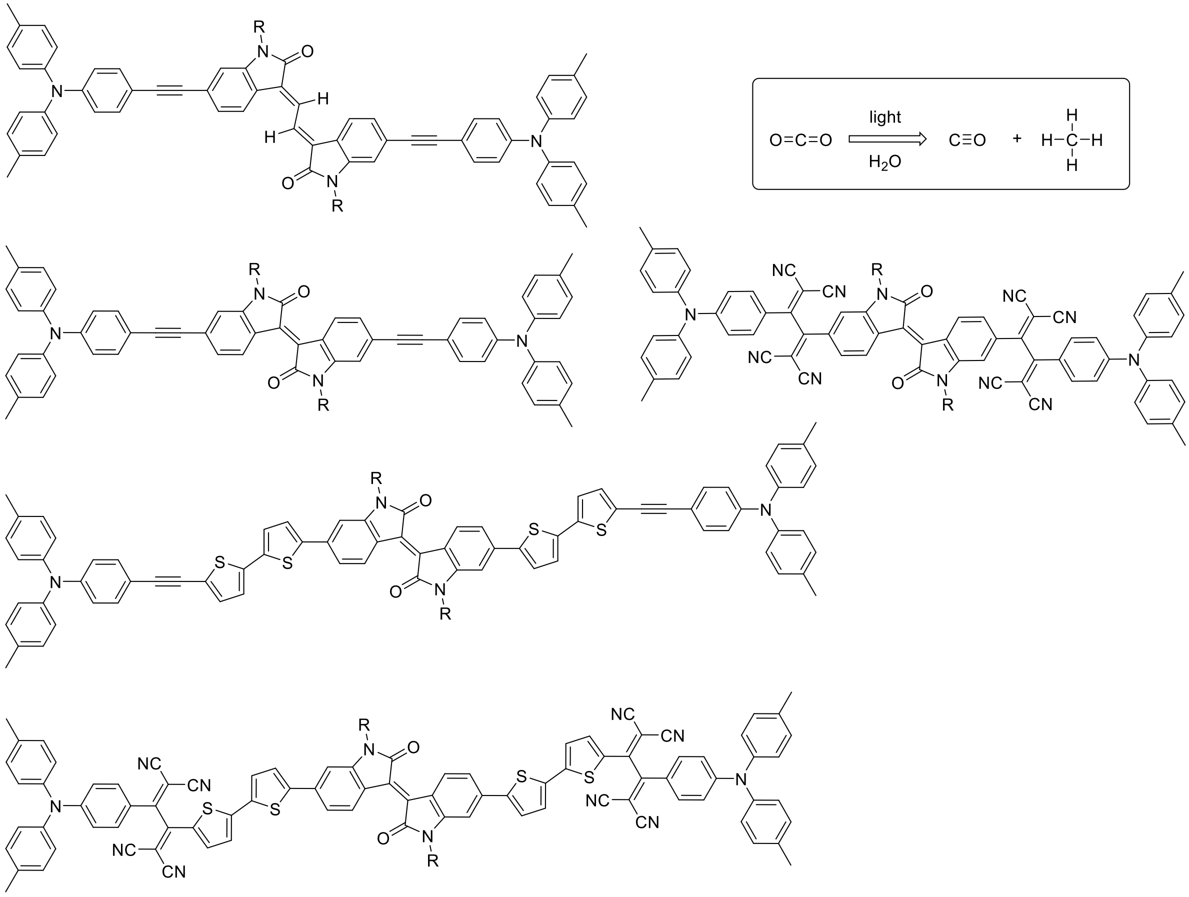
CO_2, upon illumination, can be reduced to chemical fuels, such as CO and CH_4, with the assistance of a photocatalyst. An active catalyst in CO_2 photoreduction requires light-harvesting and charge-transfer abilities. Various metal-based catalysts have been developed and demonstrated to be active in CO_2 photoreduction. Organic conjugated molecules have tunable light-harvesting and charge-transfer abilities. For instance, organic donors with the electron-pushing features and acceptors with the electron-pulling characteristics construct organic donor–acceptor molecules. The variation in the chemical functionality yields copious donor and acceptor building blocks. The change in the linking mode furnishes distinct molecular architectures. Side-chain engineering regulates intermolecular interactions. These synthetic approaches are able to regulate the light-harvesting and charge-transfer abilities of the corresponding conjugated molecules, rendering them suitable for photocatalysis. To this end, numerous organic photosensitizers have been synthesized and examined in CO_2 photoreduction in our group (Scheme 1).[1] CO_2 reduction to CO and CH_4 is realized, demonstrating that organic conjugated molecules are potential catalysts for CO_2 photoreduction.

Scheme 1. Chemical structures of organic photosensitizers



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C051

Bimetallic Shells on Semiconductor Nanoparticles

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Hybrid nanoparticles combining metal and semiconductor materials have garnered significant attention due to their potential applications in catalysis, energy conversion, and storage.[1,2] These nanoparticles offer the advantage of different chemical reactivities at the nanoscale, allowing for the generation of diverse architectures. While there has been extensive research focused on the deposition of metal nanoparticles onto semiconductor nanoparticles, little exploration has been conducted on the synthesis and investigation of semiconductor-coated metal shells. The metal shells can be tuned to optimise plasmon resonance, leading to enhanced light absorption by the semiconductor core and generating more electron-hole pairs for efficient photocatalysis. Moreover, the presence of a metal shell provides protection against environmental degradation and supports the stability of the semiconductor nanoparticles.

However, achieving the formation of complete metal shells on semiconductor nanostructures poses a significant challenge. In this study, we propose a novel approach utilising slow injection to precisely control nucleation and successfully synthesise bimetallic-semiconductor hybrid nanoparticles. These nanoparticles feature PbS semiconductor nanostructures encapsulated within gold and silver shells. Gold and silver, distinguished noble metals renowned for their well-established plasmonic properties, are combined in bimetallic or dual metal shells, offering advanced control over material structures and improved properties suitable for a wide range of photocatalytic applications. The resulting metal shells exhibit remarkable stability when subjected to electron beam imaging. This work provides valuable insights into the synthesis and characterisation of semiconductor-coated metal shells, thereby contributing to the advancement of research in this field. These findings hold promise for future investigations and potential applications across various disciplines.

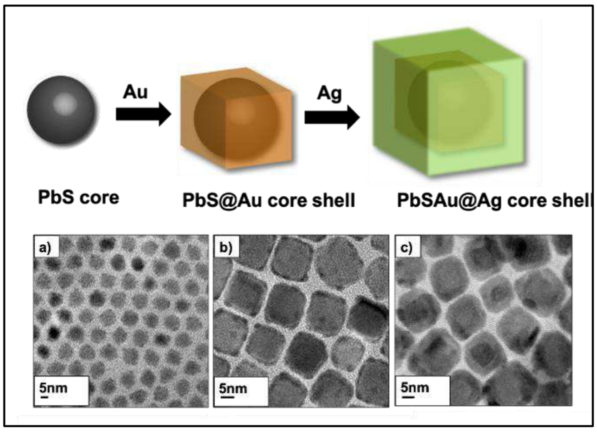

Figure 4 Schematic and TEM images of a)PbS nanoparticles b) Au shelled PbS nanoparticles c) Ag shelled Au-PbS nanoparticles

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C052

Molecular Cages for Nanocrystal Synthesis: Towards Microporous Photosensitizers

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Porosity is a property rarely observed in molecular materials, especially in organic systems. By extension, traditional nanocrystal-2D ligand systems do not exhibit porosity, which is paramount for photocatalytic efficiency. Furthermore, energy transfer from nanocrystal to ligand is often hindered due to optically and electrically insulating ligands or recombination due to lack of active sites.

In this presentation I will discuss an emerging class of 3D molecules known as porous organic cages which can nucleate and grow noble metal nanocrystals and even semiconductor quantum dots. Resonant tuning of the porous cage excitons with nanocrystal resonances allow efficient transfer of energy between the systems while maintaining porosity.

C053

Unique Photochemical Behavior of Dyes on the Inorganic Flat Surface

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In photo-functional organic/inorganic composites, it is possible to develop its functionalities such as absorption and emission capabilities by combining the advantages of them. For instance, dye-sensitized solar cells and artificial photosynthesis systems, which convert solar energy to electric and chemical one, are typical examples for organic/inorganic composites. Among the inorganic host materials, nanosheet materials (NS) such as synthetic clay nanosheet (CNS) and titania nanosheet (TNS), are known as unique host materials, due to their atomically flat surfaces with negative charges. Research groups, including us, have reported a variety of dye/NS composites from a view point of surface- and photo-chemistry. For example, cationic porphyrins were adsorbed on SSA and TNS without aggregation even at high density adsorption conditions. This phenomenon was named "size-matching effect"[1,2]. Because an aggregation tends to decrease the excited lifetime of sensitizer, this high-density adsorption structure without aggregation is suitable for a construction of photochemical reaction systems. In addition, it was turned out that the photo-physical property of dyes on the NS surface shows unique phenomena such as emission enhancement[3-5]. In some cases, non-fluorescent or weakly fluorescent molecules become highly fluorescent upon interacting with the clay surface. Based on its mechanism, we name this effect of NS on emission enhancement as “Surface-Fixation Induced Emission (S-FIE)”[3-5]. In some cases, the emission enhancement ratio of molecules by the fixation on the NS surface reached to more than 100. The increase in the radiative decay rate constant (k_f) and the decrease in the non-radiative decay rate constant (k_nr) for the excited state of the molecule are typical factors contributing to the observed emission enhancement. The unique effects of the atomically flat surface are also observed for other chemical behaviors such as dehydration reaction of aromatic diol[6] and enzymatic behavior of HRP[7].

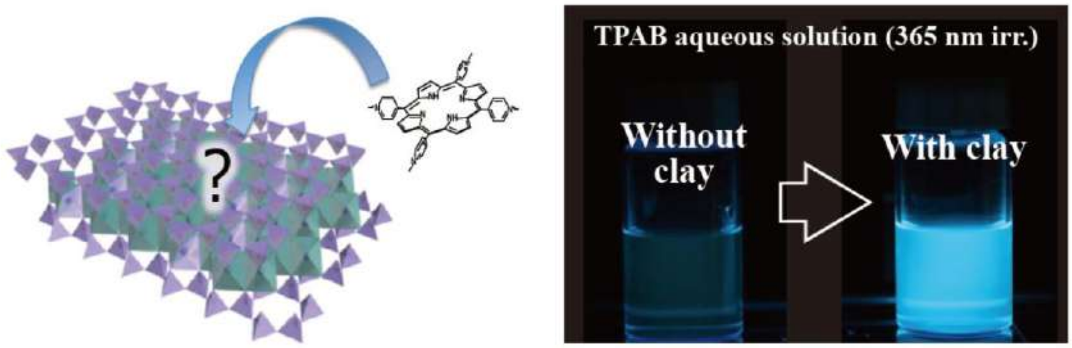

Fig. 1. The fluorescence enhancement of dyes on the clay surface.

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C054

Study of the Decomposition of Hydrofluoroolefins

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Hydrofluoroolefins (HFOs) are the most important 4th generation refrigerants and are hydrofluorocarbons (HFCs i.e. the banned 3rd generation) that incorporate a carbon-carbon double bond, making them reactive in the troposphere. They have short atmospheric lifetimes, zero ozone depletion potential and are currently classified to have global warming potentials (GWPs) of approximately 1 (determined by their contribution to surface heating over a century relative, by mass, to CO_2)

However, their atmospheric decomposition is often not fully characterised and mostly inferred from the known chemistry of analogous compounds, end-product analysis, as well as computational chemistry predictions. These studies suggest benign atmospheric decomposition products, however, we've recently shown that the primary decomposition product (CF_3CHO) of one the most important HFOs (1,3,3,3-tetrafluoropropene) photolyses, in part, to fluoroform (GWP 12 400), which is the most environmentally hazardous HFC and would change the ultimate GWP of the parent HFO. This would have a profound impact on international regulatory commitments if these GWPs were revised above a certain GWP (*e.g.* 150 in the European Union) and withdrawals, reformulation and remediation would need to begin. Indeed, this HFO is incorporated in HFO/HFC blends targeting existing regulations and tuned to a GWP ~150.

The aim of this project is to develop a new flow reactor instrument (Figure 1) that will allow us to characterise the entire lifecycle of an emitted HFO. This will yield the identities of reaction products and intermediates, as well as the kinetics of their formation – leading to a general understanding of the atmospheric chemistry of fluorinated organic molecules allowing the atmospheric fate of current and future refrigerant gases to be determined prior to largescale emission.

This talk will review the state-of-the-art of this research area, detail the design and development of the instrument and present some preliminary results.

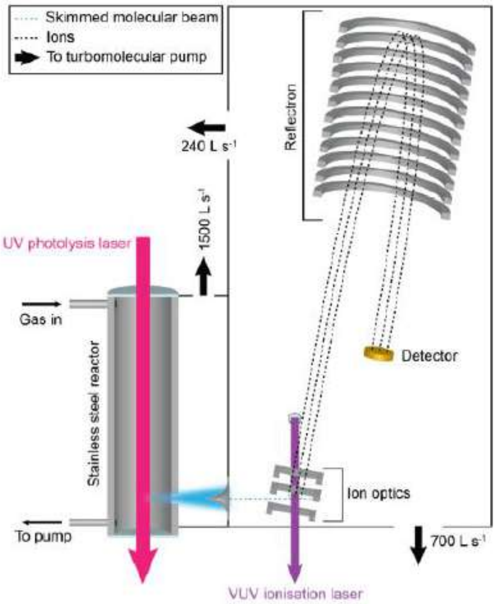

Figure 1. Schematic of the instrument.

C055

The role of oxygen in the photophysics and photodegradation of polyacenes

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Polyacenes, such as tetracene and pentacene, are common materials used for the study of photophysical phenomena such as singlet fission and triplet fusion -- processes which may lead to increased photovoltaic efficiencies. Whilst they exhibit desirable photophysical properties, these materials are not photostable, and will convert to unwanted materials such as epoxides in the presence of oxygen and light, preventing their use in real-world applications. Not only does oxygen degrade polyacenes, but it can also affect their photophysics, leading to both the sensitisation and quenching of different excited states. In this study we characterise the effect of oxygen on TIPS-tetracene and TIPS-pentacene using transient absorption spectroscopy, and show that oxygen can significantly influence the population of excited states, in particular enhancing the triplet population. We additionally combine time-resolved excited-state dynamics with photodegradation studies to examine the predominant mechanism of photooxidation, which until now has been somewhat unclear. This work has implications both for the design of new materials that can avoid photooxidation, as well as informing the study of their photophysics in real-world environments.

C056

Singlet Fission, Intersystem Crossing and Triplet Dynamics of TIPS-Pentancene

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Photovoltaics that use a single junction to harness solar energy have a fundamental limit of approximately 30% in their power conversion efficiency. Singlet fission (SF) has the potential to overcome this efficiency limit in solar energy harvesting. In SF, a singlet exciton (S_1) is converted to two triplet excitons (T_1) through a spin-allowed process involving two adjacent molecules that are electronically coupled. TIPS-pentacene is a model system for SF, exhibiting a SF yield of approximately 2. In recent years, our group has developed methods for controlling intermolecular distance,[1] morphology (crystalline[2] or amorphous[3]) and size of TIPS-pentacene nano-aggregates. The effects of morphology will be discussed in this talk. In amorphous aggregates, we showed that as the size of the aggregate decreases, SF becomes slower and triplet exciton decay becomes faster.[2] The results indicate an increased morphological disorder as the aggregate size decreases, weakening the intermolecular couplings that is required for SF. In crystalline TIPS-pentacene aggregates, we found that triplet excitons diffuse in a highly anisotropic manner, with the diffusion coefficient in the crystalline *a* axis an order of magnitude higher than those in other directions.[3] This efficient 1-dimensional diffusion results in an exciton diffusion length of approximately 500 nm. Finally, the talk will address an ongoing issue in SF. Despite over a decade of research, the assignment of time-resolved spectroscopic signals to SF and intersystem crossing remains unclear. An accurate assignment of SF and intersystem crossing is critical to avoid under- and over-estimation of the triplet yield. By analyzing the time-resolved spectroscopic data of TIPS-pentacene and -tetracene solutions of various concentrations, we showed that SF in solution reported in several studies had been mischaracterized as intersystem crossing.[4] This work highlights the critical role of accurate assignment in determining the rate constants and yields of SF.

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C057

Deciphering Signatures of Coherence Transfer in Bacterial Reaction Centers Through Two-Dimensional Electronic Spectroscopy

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Coupled vibrational-electronic (vibronic) motions lie at the helm of wide-ranging ultrafast phenomena spanning chemistry, biology, and physics. Examples include photoisomerization in mammalian vision, energy and charge transfer in photosynthesis[1] and photo-induced phase transitions in strongly correlated materials. Synthetic design to engineer functional vibronic couplings and steer reaction outcomes has increasingly relied on spectroscopic input gained from monitoring the fate of impulsively excited wavepackets. However, such wavepackets may or may not be coupled to the reaction coordinate, and just like impulsive photoexcitation, ultrafast reactions can themselves generate coherences. Thus, identifying vibrations which promote non-adiabatic mixing between electronic states, against a backdrop of vibrations which are spectators in or byproduct of ultrafast internal conversion becomes a central challenge for spectroscopists.

In this regard, the unique ability of two-dimensional electronic spectroscopy (2DES) for spectral decongestion along with typical sub-10 fs time-resolution has been exemplary. However, ambiguous spectroscopic signatures can still arise and influence interpretations regarding mechanistic significance of quantum coherences. For example, recent 2DES experiments on multichromophoric photosynthetic reaction centers[2,3] (RCs) and monomer molecules have reported apparently similar and reportedly perplexing spectroscopic signatures from these disparate systems. Thus, before 2DES can become a powerful tool for gleaning out intricate quantum dynamical details and guiding synthetic design, it comes imperative to resolve such conflicts and establish precise connections between rich 2DES signatures and the underlying quantum dynamics. I will talk about our recent progress[4,5] in this direction and show that these apparently similar observations arise from spectator vibrations alone which *do not* participate in ultrafast electronic relaxation. By resolving conflicting spectroscopic observations, I will illustrate new mechanistic insights gained by connecting microscopic interference between wavemixing signal pathways to macroscopic observables such as 2D lineshapes.

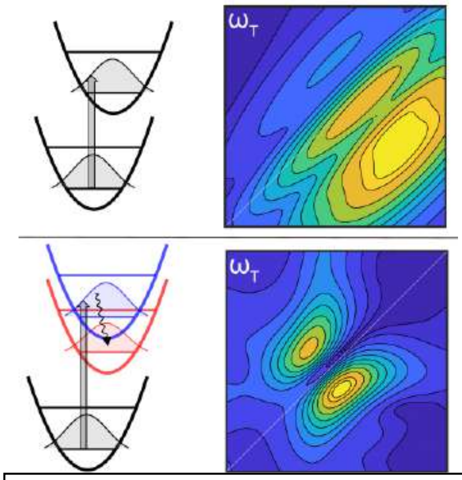

Figure 1. (Top) Node-like lineshapes in 2DES coherence maps arise from destructive interference of ground and excited state vibrational coherences. (Bottom) Nodal lineshapes in RCs[2,3], with apparent similarities[2] to those bacteriochlorophyll monomers, arise from coherence transfer of vibrational coherences during donor-acceptor energy transfer[4,5].

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Tuning vibrational light-matter coupling with plasmonic cavities

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Mid-infrared optical resonators have various applications in optics, life science, and catalysis. Here we present a detailed investigation of the optical properties of vertically and laterally coupled plasmonic arrays comprising metal disk arrays and quasi-Babinet complementary hole arrays in the mid-infrared spectrum. Our results reveal that the plasmon resonance effect leads to extraordinary light transmission through the arrays. We also show that the size of the disks primarily governs the plasmon excitation energy, while the hole size has little influence on it. Furthermore, we found strong enhancements in the electric near-field within close proximity of the plasmonic slabs. These findings highlight the immense potential for facilitating a robust method for weak vibrational light-matter interactions, which forms the basis of surface-enhanced infrared spectroscopy. Further, we show how vibrational strong light-matter coupling can be achieved with plasmonic arrays and PET-based, freestanding etalons and how the Etalon's optical resonances can be fine-tuned to match vibrational modes.

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C059

Fluorescence fluctuation spectroscopy of protein transport as a function of oligomeric state

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Nuclear proteins can modulate their DNA binding activity and the exploration volume available during DNA target search by self-associating into higher order homo-oligomers and formation of hetero-complexes, which exhibit different stoichiometry. Directly tracking this process in the nucleoplasm of a living cell is, however, a complex task. Thus, in recent work we developed a series of fluorescence microscopy methods based on brightness correlation spectroscopy to track the movement of fluorescently tagged nuclear proteins as a function of stoichiometry (1-2). By simply performing a rapid single or dual frame scan acquisition, brightness image correlation spectroscopy has the capacity to detect within each pixel, protein homo- or hetero-oligomer formation, and extract the size dependent obstruction nucleus architecture imparts on complex mobility across sub-micron distances. From application of this technology to inert versus biologically active oligomeric transcription factors that form heterocomplexes, we demonstrate protein stoichiometry to differentially regulate chromatin accessibility and interaction with the DNA template.

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C060

Collectivity and energy transfer in optical cavities

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This talk will outline recent work in our laboratories on the induction of coordinated behaviour in ensembles of molecules separated by macroscopic distances, via their interaction with light fields confined by photonic nanostructures, and driven to interact in the strong light-matter coupling regime. This long-distance cooperativity has implications for light harvesting and chemically reactivity, and may also have evolved in biological contexts.

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C061

Light Induced Lattice Modulation of 2D Mixed Halide Perovskites

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Two-dimensional metal halide perovskites (2DHPs) are a class of crystalline materials that consist of metal halide octahedral layers that are separated by bulky organic cations to stabilise the structure and control the interlayer spacing. Similar to three-dimensional (3D) perovskites, the ability to tune the bandgaps by controlling the halide composition can also be applied in 2DHPs, which further broad their potentials in real applications. The spatially separated octahedral layers in 2DMHPs confine the exciton-lattice interactions along the in-plane octahedral direction, which further confine the halide migration pathway within in-plane. In this work, we quantitively identify the crystallisation of mixed halide 2DHPs following a unique strategy with bromine preferentially taking the equatorial position while iodine taking the axial position. We report halide positions within the octahedral can be actively tuned between axial and equatorial positions with light through the strong exciton-lattice interactions in 2DHPs, and we investigate the lattice modulation depth by in situ monitoring the change of emission bandwidth and halide positions within the structure. Our work creates a new pathway for the application of 2DHPs in lithography-free photonics, optical switching, LED and memory applications.

C062

Optical trapping and swarming of gold nanoparticles: Optical and material control of its morphology

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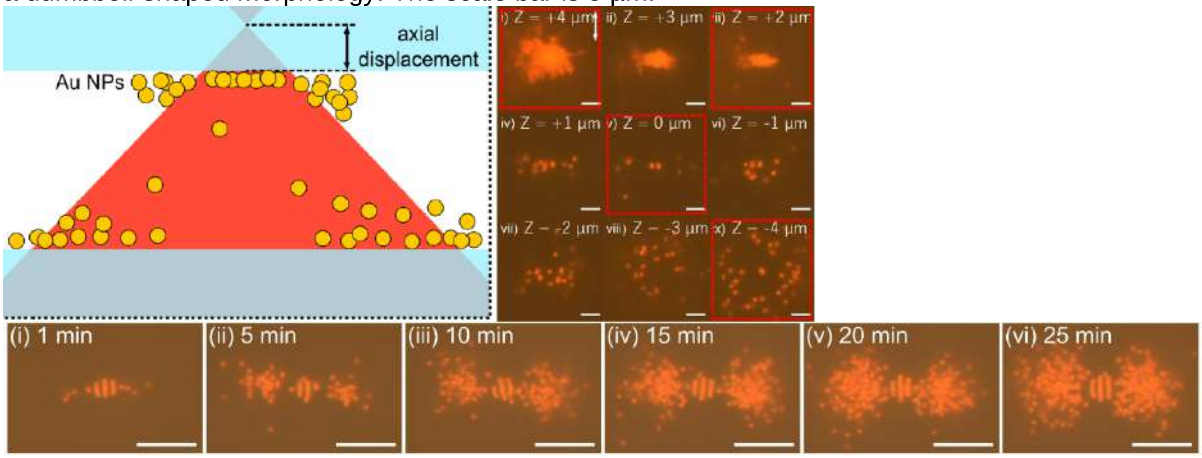
We have been systematically studying optical trapping phenomena of microparticles (MPs), nanoparticles (NPs), and proteins at solution interfaces. Completely different from the trapping in solution, their assembly expands along the interface, giving a disk-like morphology with a size of a few ten µm to submillimeter, which we name “optically evolved assembling at interface”.1) In the case of Au NPs at glass/solution interface, initially trapped NPs scatter the trapping laser and expands the optical potential, where the following au NPs join. The expansion depends on the trapping laser polarization, and the Au NPs dynamically fluctuates like bees in air or fishes in sea, on which we call this behavior “optical trapping and swarming”.2) In the present report we describe various approaches to control the swarming morphology and elucidate their mechanisms. The heavy Au NPs in water are distributed on the bottom (Figure 1A). Upon switching on the trapping laser of linear polarization, the NPs in the cone are pumped up to the upper glass and periodically aligned due to optical binding.3) This scatters the trapping laser efficiently along the perpendicular direction of trapping laser, leading to the formation of the dumbbell-shaped swarms (Figure 1C). Utilizing a dual objective lens microscope, we observe the behavior at the interface and demonstrate how assembling and swarming morphology is changed by the focal position (Figure 1B).4) The results are interpreted in terms of momentum transfer from the laser to the Au NPs. Also, the trapping and swarming morphology depends on size and shape of Au NPs,5) while a unique behavior is observed for silica-coated NPs, depending on solvent. The swarming morphology on nanolithographically patterned Au discs and in 3D-printer fabricated microchannels is exciting, showing a high potential in plasmonic science but also in micromachine application. Integrating these results, the dynamics and mechanisms will be considered.

Figure 1. A (Left upper) Illustration of sample solution containing Au NPs. The red cone indicates a focused trapping laser. B (Upper right) Au NP assembly observed at the interface while the trapping focus is vertically shifted. C (Lower) Temporal evolution of Au NP swarming by a linearly polarized laser, giving a dumbbell-shaped morphology. The scale bar is 5 µm.



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C063

Cavity controlled photophysics in organic semiconductors

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Strong light-matter coupling in organic media holds the promise of efficient room temperature optoelectronic devices as it opens new avenues to reshape and tune excitonic potential energy surfaces. This can be achieved by incorporating excitonic materials inside optical cavities where they can be strongly coupled with light to form exciton-polaritons.[1] Here I will present two linked examples from our ongoing work in manipulating molecular photophysics under strong light-matter coupling regime.

In the first instance, we show that due to the large extent of exciton-polariton wavefunctions (orders-of-magnitude reduction in their effective mass relative to excitons) makes condensation feasible demonstrated by polariton lasing at room temperature using perylene dyes.[2-3]

Exciton-polaritons also inherit the angle(momentum)-dependent energy levels of the hybridized cavity photon, thereby resulting in the formation of new polariton states. We show that strong light matter coupling can indeed tune the charge transfer energy levels in donor-acceptor PTB7/PCBM bulk heterojunction photoactive layers subsequently allowing access to charge carriers of longer lifetimes in organic photovoltaic devices.

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C064

Ultra-resolution in the T cell nucleus with single molecule expansion microscopy

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Over the past two decades, multiple super-resolution (SR) microscopy methods have been developed which circumvent the diffraction limit of light. These are now delivering insights and discoveries, particularly when applied inside cells. However, even with the best resolution gains – up to an order of magnitude with single molecule (SM) methods – much detail of the sub-cellular environment remains obscured. Expansion microscopy (ExM) is a new imaging modality that provides sub-diffraction information by expanding samples so that previously unresolvable detail can be visualised directly without specialised optics or photophysical manipulation.[1] Because ExM is achieved purely through the sample, combination with other SR techniques is readily achievable with essentially cumulative resolution gains. When combined with SM-SR methods, ultra-resolution – imaging at sub 10 nm – becomes possible.[2]

This contribution will discuss our recent work on developing ultra-resolution methods to visualise key cellular structures focussing on application of super-resolution and ExM inside the cell nucleus.[3] In this endeavour, we have applied the SR technique of *d*STORM to visualise epigenetic histone modifications in T cells and have established the nuclear lamin as a suitable reference structure for quantification of these (Figure 1). We have demonstrated that expansion of T cell nuclei preserves the distributional features observed in unexpanded nuclei opening the way to investigate the nucleus at near single biomolecule resolution.

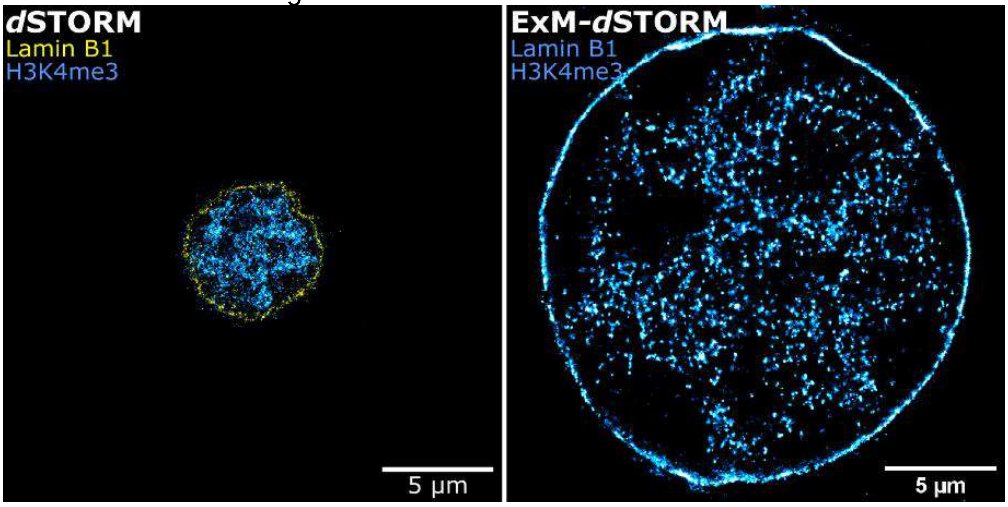

Figure 1. Single molecule super-resolution (left) and ultra-resolution (right) imaging of Lamin B1 and the histone modification H3K4me3 in T cell nuclei

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C065

Nanoparticle-enhanced infrared neuromodulation for retinal prostheses

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Retinal degeneration, where progressive photoreceptor death leads to partial or total vision loss, is the leading cause of blindness in industrialised countries. Visual prostheses aim to restore vision in blind patients by exogenous stimulation of surviving retinal ganglion cells (RGCs) or bipolar cells. However, conventional electrical stimulation techniques tend to produce diffuse patches of response due to current spread. In contrast, some recent works have demonstrated substantial vision rescue in awake rodents by optical stimulation of subretinally-injected organic semiconductor nanoparticles,[1] or plasmonic gold nanorods bound to genetically modified photoreceptors.[2] In contrast, we have shown that nanoparticle-enhanced infrared neural modulation (NINM), a plasmonically-mediated photothermal neuromodulation technique, can be applied directly to RGCs without the need for genetic modification.[3] Gold nanorods provide tunable absorption in the near infrared, which reduces interference with any residual vision. Laser pulses of wavelength 780 nm were applied with 100 µs, 500 µs and 200 ms duration to RGCs in explanted rat retinae exposed to gold nanorods. Single-cell responses recorded via patch-clamping showed that the shorter laser pulses evoke robust RGC stimulation by capacitive current generation, whilst the long laser pulses are capable of inhibiting spontaneous action potentials by thermal block. We show that the essential features of these responses can be reproduced in an extended Hodgkin-Huxley type model. Importantly, an implicit bias towards OFF-type inhibition was observed. Given that the capacity for both stimulation and inhibition is essential for the differential modulation of ON- and OFF-type RGCs at a single cell level, these results suggest that NINM may be uniquely well-suited to future high-acuity retinal prostheses.

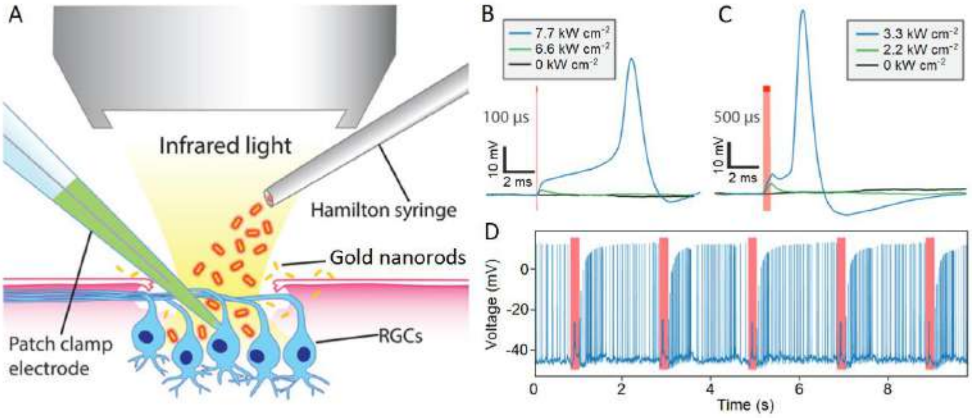

Figure. (A) Nanorod delivery and illumination procedure. Examples of subthreshold and suprathreshold stimulation of RGCs by (B) 100 µs and (C) 500 µs laser pulses (marked by red bars). (D) A typical inhibitory response for 200 ms pulses.

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C066

Voltage imaging with fluorescent nanoparticles

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Voltage-sensitive fluorescent probes have provided a relatively simple and non-invasive approach to studying the electrical activity of biological systems compared to traditional electrode-based techniques.[1] The compatibility of these probes with standard fluorescence microscopy instrumentation, the lower technical skill requirements and the capacity for measurements over multiple cells have made their use relatively commonplace. However, all commercially available voltage-sensitive probes suffer from limitations intrinsic to organic fluorophores, including a low photostability that limits their application for long-term measurements.

Quantum dots and quantum rods, which display a voltage-sensitive emission, have been proposed as photostable alternatives to voltage-sensitive dyes.[2] However, their application for voltage imaging in biological environments has been extremely limited to this date, mainly due to challenges related to targeting, orientation, and stability of the nanoparticles in the cell membrane. In our work, we have studied the voltage imaging capabilities of red- and near-infrared-emitting quantum dots and found an unexpected challenge: developing a robust calibration platform for inorganic voltage-sensitive probes. Here, we will discuss the key considerations – and the pitfalls to avoid – when studying the voltage sensitivity of fluorescent nanoparticles and discuss our results with CdSe/ZnS quantum dots as voltage sensors.

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C067

Nanoscale spectroscopy of halide perovskite films, nanocrystals and related systems

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All-inorganic, as well as organic-inorganic hybrid halide perovskites are one of the most promising class of semiconductors for new generation of energy conversion and optoelectronic applications. While there has been tremendous technological progress in device development, especially in the field of perovskite solar cells, the advancement of fundamental photophysical properties of perovskite materials, which is equally important, been lacking behind. Here, we report study of nanoscale structural and optical properties of mixed cation halide perovskite films and of inorganic perovskite nanocrystals using single-molecule fluorescence microscopy and spectroscopy. We study nanoscale properties in a series of mixed cation (MA/FA) halide perovskite films[1,2] to reveal the film large compositional heterogeneity. The heterogeneity is most prominent for FA 50% films which contain purely MA domains, purely FA domains, as well as domains composed of mixed MA/FA cations of varying ratios. The films also show photoluminescence (PL) intensity fluctuations (blinking) which reflects dynamic non-radiative quenching. The PL blinking is correlated between locations that are several micrometers apart, indicating that the grain boundaries do not represent barriers for charge transport and do not work as traps, enabling efficient charge migration over micrometer distances. Further, we study complexes of all-inorganic perovskite nanocrystals with metal-organic frameworks (MOFs) in which the MOFs can shelter the perovskites from the degrading effect of the environment. Using a series of $CsPbX_3$-MOF composites based on twinned Pb-X-based MOFs (X = Cl, Br) we explore the effect of local ionic environment on individual nanocrystal formation and growth kinetics. The composition of the MOFs plays a dominant role in the perovskite compositional heterogeneity. We next report PL blinking in individual perovskite nanocrystals which is affected, among other factors, by the nanocrystal environment and externally applied electric field,[3] or by the exciation mode (PL vs electroluminescence).[4] We examined the effect of surface ligands on the PL blinking characteristics by comparing properties of $CsPbBr_3$ nanocrystals before and after ligand exchange with a quaternary amine. On ensemble level, the ligand exchange causes an increase of the PLQY which, on the single particle level, is reflected by significant suppression of the PL blinking.[5]

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C068

Photoinduced Energy Transfer from InP Quantum Dots to mCherry

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Semiconductor quantum dots (QDs) offer numerous possibilities as energy transfer conjugates and have found numerous applications across biology.[1,2] The design and biological applications of various FRET pairs comprising of QDs and fluorescent proteins have been previously reported; however, the toxicity of heavy-metal QDs has been a cause of concern.[3,4] Indium phosphide (InP) QDs has recently garnered considerable interest in the design of bioprobes due to their non-toxic nature and excellent optical properties. We have recently developed a FRET pair comprising glutathione-capped InP QDs (InP(G)) and the red fluorescent protein, mCherry.[5] Biocompatible glutathione capped InP QDs (InP(G)) is obtained from InP/GaP/ZnS QDs synthesized via high temperature colloidal synthesis by adopting a ligand exchange strategy. We have further expressed and purified mCherry consisting of a hexahistidine tag, which efficiently binds to the surface of the QDs. We have monitored the steady state and time-resolved spectra of InP(G) in the presence of mCherry and observed an efficient non-radiative energy transfer from the QDs to the fluorescent protein. Selective excitation of InP(G) in the presence of mCherry shows a decay of the emission of the QDs and a concomitant growth of the acceptor emission. Time-resolved investigations reveal a reduction in the radiative lifetime of the QDs in the presence of mCherry and the formation of the excited state of the protein, which categorically confirms the occurrence of FRET. Further, the scope of two-photon-induced energy transfer between InP(G) and mCherry is investigated by exciting the samples at 800 nm (optical transparency range) which facilitates the effective penetration of light into the tissues and reduces the photodamage to the sample. These aspects will be presented in the poster.

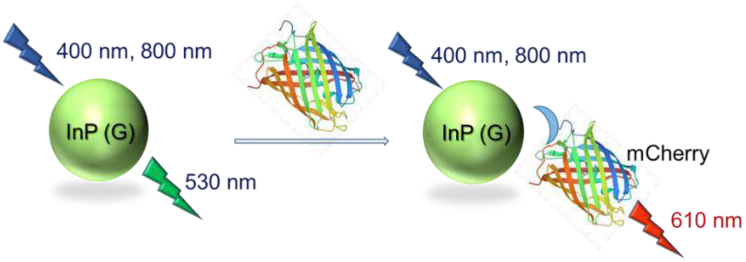

Fig. Schematic representation of single- and two-photon induced FRET between InP(G) and mCherry.

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C069

Light Harvesting Studies with Indium Phosphide Quantum Dots

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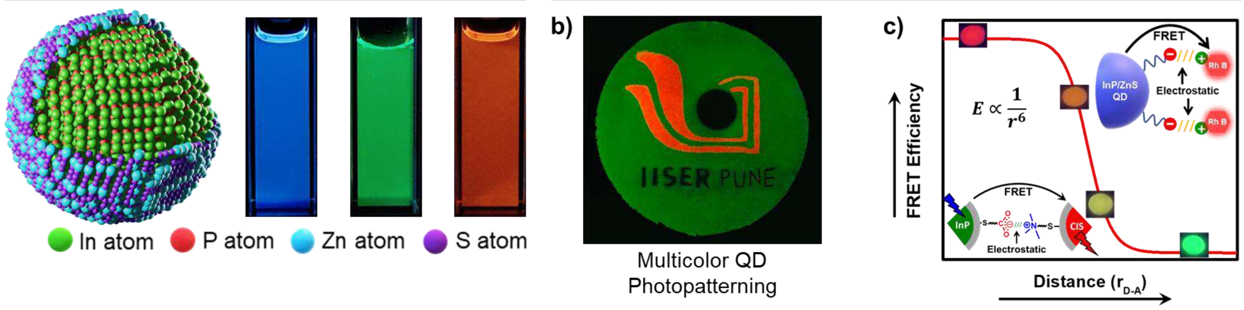
Indium phosphide quantum dots (InP QDs) have emerged as a practical alternative to traditional Cd and other toxic metal based QDs because of their environmentally benign nature.[1-2] Our group is interested in replicating the fantastic light harvesting properties of traditional QDs in InP QDs, as well as demonstrating advanced properties. With this in mind, we have developed water-stable and highly luminescent InP QDs emitting from the pure-blue to red region of the spectrum, by fine-tuning the kinetics of the core as well the shell growth (Fig. 1a). In one study, the superior photostability of InP QDs over organic dyes was used for the photoregulation of electron and energy transfer processes, this led to the creation of high-contrast multicolor luminescent patterns from a single QD nanohybrid film (Fig. 1b).[3] In another set of studies, the surface of the InP QDs was appropriately functionalized to achieve Förster resonance energy transfer (FRET) process. In one example, ~60% efficient FRET process was demonstrated in all-QD based donor–acceptor system comprising of electrostatically bounded [-] InP/ZnS QD:::[+] CuInS2/ZnS donor:::acceptor complex (Fig. 1c).[4] In another example, we have expanded the range of solar spectrum in FRET studies by developing highly luminescent pure-blue emitting InP/ZnS QD, with an absolute quantum yield of ~50 % and a colour purity of ~80 % (CIE 0.16,0.15) in water.[5] Installing a favourable electrostatic interaction turned out to be crucial in achieving an efficient FRET process (~75%) from blue-emitting InP/ZnS QDs to rhodamine B dye (Rh B). Thus, the demonstration of interaction driven FRET in environmentally friendly InP QDs is fundamentally intriguing, and can have far reaching applications in the areas of biophysics as well as light harvesting devices.



Multicolor QD Photopatterning

Fig. 1. (a) Optical tuneability, (b) high-contrast multicolor luminescent patterning, and (c) electrostatically driven FRET in InP QDs based hybrid systems.

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C070

Fluoroform production from trifluoroacetaldehyde photolysis and implications for the atmospheric decomposition of hydrofluoroolefins

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Hydrofluoroolefins (HFOs) are the leading synthetic replacements for compounds successively banned by the Montreal Protocol and amendments. HFOs readily decompose in the atmosphere to form fluorinated carbonyls, including trifluoroacetaldehyde (CF_3CHO) in yields up to 100%, which is then photolysed. A longstanding issue, critical for the transition to safe industrial gases, is whether atmospheric decomposition of CF_3CHO yields any quantity of CHF_3 (HFC-23), which is one of the most environmentally hazardous greenhouse gases. This comprehensive experimental investigation confirms this reaction occurs under atmospheric conditions and provides pressure-dependent quantum and molar yields.

C071

Double Resonance Raman for Defect Analysis in 2D Materials and Devices

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Raman spectroscopy enjoys frequent use in literature as a fundamental vibrational characterization technique for a range of molecular and material systems. However, the potential for energy-selective resonance Raman to strategically probe complex light-matter interactions is seldom considered, or remains limited to specialized scattering studies in ideal systems. Recent studies of 2D materials using tunable excitation resonance Raman have demonstrated the ability to reveal intricate electronic and structural details via the investigation of higher-order electron-phonon scattering pathways in crystalline semiconductors.[1,2] Such information can be used to identify and characterize defects, probe intervalley and intravalley scattering processes, and quantify momentum-resolved shifts in electronic structures due to dopants, boundaries, heterostructure alignment, and phase segregation.

In this work, we explore the higher-order scattering pathways of a range of semiconductor systems, with a focus on understanding the roles of defects and their consequences on the performance of 2D materials and solar cell devices. We employ a home-built tunable laser and Raman microscope, which can be used to probe excitonic processes and charge carrier transport in a range of semiconducting materials by finely tuning excitation energy across band gaps and electronic energies of interest. These results provide validation for extending the Double Resonance Raman framework to the structural and electronic characterization of semiconductor materials beyond graphene and transition metal dichalcogenides.

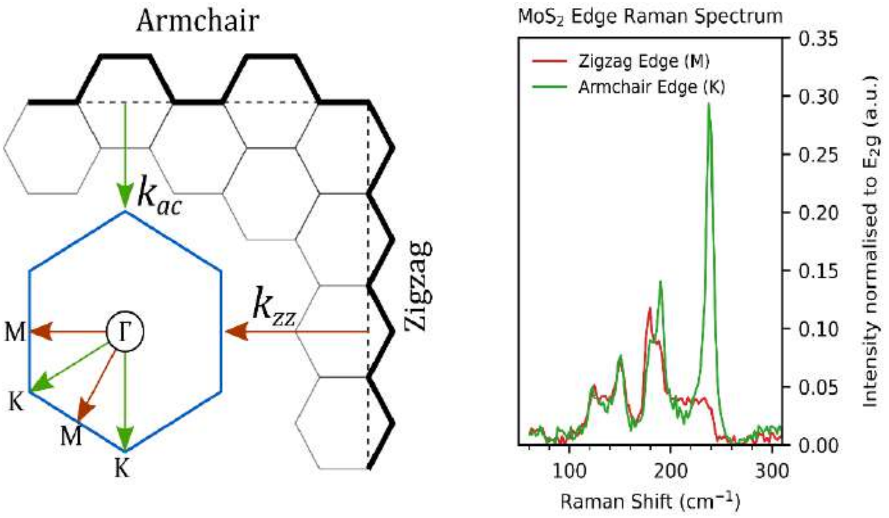

Figure 1 – Left: Wavevector conservation in real space (black outlined edges) and reciprocal space (blue hexagon) limit phonon interactions in defect-mediated (Double Resonance) scattering processes.

Right: This results in different features in the Raman spectra at each edge type, allowing differentiation between zigzag and armchair edge structures.

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C072

Photoelectrochemical properties of plasmonic photocathode using nickel oxide

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Hot electron and hole pairs generated via nonradiative decay of localized surface plasmon resonances (LSPRs) attract considerable attention for triggering chemical reactions. Recently, we have reported that the light absorption and water oxidation ability were dramatically enhanced by modal strong coupling between LSPR and a Fabry–Pérot (FP) nanocavity [1-3]. The photocathode composed of a plasmonic metal and a positive-type (p-type) semiconductor effectively induces reduction because hot electrons reduce the substances, which involves hot-hole injection from the metal to the p-type semiconductor. We found that the strong coupling between the LSPR and a FP nanocavity also enhances the absorption and reaction efficiencies on the photocathode [4]. We employed Au-NPs as a plasmonic metal, nickel oxide (NiO_X) as a p-type semiconductor, and a Pt film as a reflection layer. In this study, we evaluated the impact of the fabrication condition of the NiO_x layer on the photoelectrochemical properties of the Au-NPs/NiO/Pt photocathodes.

The NiO_x layers were prepared on the SiO_2 substrate coated with Pt or SnO_2 (Pt/SiO_2 or SnO_2/SiO_2 substrates) by sol-gel and subsequent annealing methods. The NiO layer was also deposited by plasma oxidation process. Au-NPs were loaded on the NiO_x layer by annealing a Au thin film deposited by vacuum evaporation. The transmission and reflection spectra were measured using a spectroscopic reflectometer. The photoelectrochemical properties of the photocathodes were evaluated using a standard three-electrode system with a platinum wire counter-electrode and a Ag/AgCl reference-electrode.

The optical spectra of the NiO_x layer on Pt/SiO_2 showed resonance peaks derived from the formation of FP nanocavity. After the loading of Au-NPs, the absorption was dramatically increased. This suggests the formation of coupling between LSPR of Au-NPs and FP nanocavity. The photoelectrochemical performances of the photocathode strongly depend on the preparation condition of the NiO_x layer, such as the annealing temperature and concentration of the precursor. Additionally, the combination of sol-gel and plasma oxidation processes enhances the photoelectrochemical reaction efficiencies. We discussed the effect of the crystallinity, grain boundary, and density of the NiO_x layer on the photoelectrochemical performances of the photocathode.

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C073

Suppressing Excimer Emission of Multiple-resonant TADF in optical cavities

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Thermally activated delayed fluorescence (TADF) has gained great attention in organic light emitting diodes and organic lasing due to its potential of reaching 100% efficiency by recycling dark triplet excitons back into bright singlet excitons by thermal energy. However, reducing molecular aggregation is a significant challenge in multi-resonant thermally activated delayed fluorescence (MR-TADF) emitter systems. Aggregate formation can lead to formation of excimers that show a large Stokes shift and broader emission. Here, we show that excimer emission can be appreciably suppressed by placing a thin film of MR-TADF emitters embedded in a host PMMA matrix within an optical cavity. Strong light matter coupling in these microcavities result in Rabi splitting larger than 200 meV, placing lowest singlet excited state, i.e., lower polariton state close to the triplet state. Under the strong coupling regime, excimer emission is significantly reduced due to strong emission from the lower polariton states. Rate constants of reverse intersystem crossing to the lower polariton states is increased up to 33% in optical cavities, resulting from a lower activation energy barrier. This work highlights that the strong light-matter interaction can mitigate excimer emission towards efficient light emitting devices.

C074

Tantalum-Based Metal Oxides for the Photocatalytic Degradation of PFAS

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There is an imminent need to develop degradation pathways for Per- or Polyfluoroalkyl Substances (PFAS) to relieve current global contamination. PFAS are toxic, ubiquitous and consist of the C-F bond which is recalcitrant to current degradation processes. This study considers tantalum based perovskite metal oxides for the photocatalytic degradation of PFAS molecules. $ATaO_3$ (A = Li, Na, K) photocatalysts are among the most efficient photocatalysts reported to date.[1] However, their wide band gap (>3.5 eV) requires UV light which renders their use cost-prohibitive in most applications.[1] Since there is no alternative for PFAS remediation, photocatalytic degradation with UV light is a viable option.[2] Furthermore, the wide band gap gives the photocatalyst a large redox potential to drive the reduction/oxidation of the C-F bond.

$ATaO_3$ (A = Li, Na, K) were first synthesised via a solid-state high temperature synthesis with varying La mol% doping, following previous studies.[1] The band gap of the photocatalysts were determined from UV-Vis DRS, the crystal structure was determined by powder XRD, and the morphology and particle size were analyzed by SEM. Degradation reactions with PFAS were conducted in a continuous flow reactor system under UV-LED irradiation. PFAS conversion was monitored by Liquid Chromatography-High Resolution Mass Spectrometry (LC-HRMS) and fluoride was quantified using an ion selective electrode. Our results highlight the effect of La doping mol% and the A site element on photocatalytic PFAS conversion efficiency, and selectivity toward producing fluoride.

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C075

Identification of the contributing factors to the photoelectric conversion efficiency for hematite photoanodes by using machine learning

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Hematite has much attention in the field of photocatalysis as the one of the most promising materials for photoanode of photoelectrochemical (PEC) water splitting. However, the process to improve the performance of this material suffers from serious bottleneck such as quite low reproducibility. Actually, a hundred or greater samples which have the same fabrication conditions were observed a significant difference in performance (Figure 1). Moreover, the physical properties that constitute the dominant factors of PEC performance and the origin of that variation have not yet been elucidated. To clarify these, we used machine learning calculation for combination of several analytical data of hematite photoanode. In our previous work[1,2], we succeeded to identify the dominant factors of variation of PEC performance by the regression calculation for predicting photocurrent density. However, the existence of samples with quite low PEC performance were revealed. Therefore, we labeled those samples as "inactive", and attempted to clarify the dominant factor of those by constructing the prediction model for sample activity. As a result, we accomplished the construction of highly accurate prediction model (Figure 2) and several dominant factors were identified.

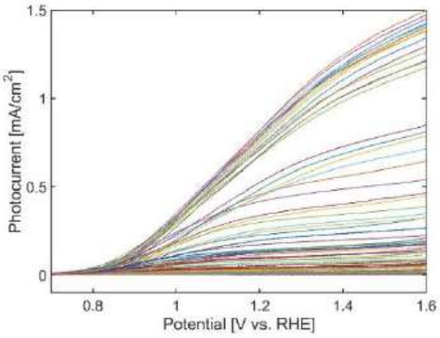

Figure 1 The PEC curves for 101 hematite photoanodes.

In addition to that, one of these approaches, focusing on the resistance at the interface between hematite and FTO, has significantly improved not only that property, but also the physical properties of hematite bulk and surface. In this work, we provide a method for identifying factors that contribute to PEC performance using analytical data and the impact of the performance improvement process focused on these factors.

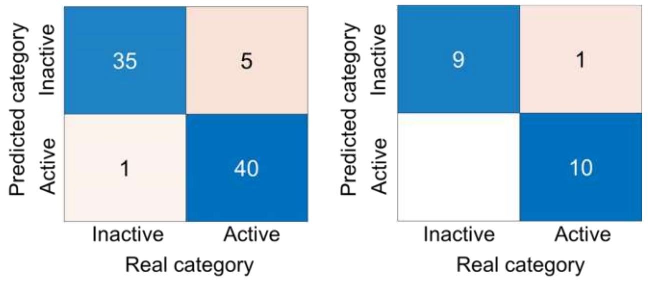

Figure 2 Confusion matrix that evaluates the performance of the prediction model and indicates the accuracy of the classification.

(Left) Training set for constructing the prediction model, (Right) Test set for evaluation of the model.

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C076

Perovskite oxides for photocatalytic water-splitting from visible sunlight

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To prevent global temperatures rising by 1.5 °C by 2050, it is critical to develop cost-competitive alternatives to fossil fuels. Green hydrogen is a key renewable fuel – able to decarbonize the 25% of world CO_2 emissions which can't be electrified.[1] However, renewable H_2 is currently cost-prohibitive.

Photocatalysts are nanoparticulate semiconductors which absorb sunlight, splitting water into H_2 and O_2. Photocatalysts are simpler and cheaper than other methods for renewable H_2.[2] However, state-of-the-art photocatalysts fall short of the 5 – 10% conversion of sunlight to hydrogen (STH) needed for commercial viability. Fabricating photocatalysts which are active to the visible, and most abundant, region of sunlight is the most significant way to reach these STH targets.[3]

This work adopts the technique of doping Rh into the crystal structure of an ABO_3 perovskite, $SrTiO_3$, developed by Kudo et al.[4] Combined with a codoping strategy developed by Domen et al.[3] Briefly, the first strategy works by introducing Rh^{3+} states which modify the electronic structure of $SrTiO_3$ narrowing its bandgap and enabling visible light activity.[4] However, this technique also introduces Rh^{4+} defect states which facilitate charge-recombination, mitigating the improvements attained from doping. By codoping La with Rh, La^{3+} states are introduced which suppress the formation of Rh^{4+} states.[3]

A suite of 6 ABO_3 perovskites were synthesized and codoped with La and Rh to combine and expand these techniques. Characterization demonstrated the light absorption range for all 6 materials was extended without compromising the perovskite structure of the base material. Photocatalytic water-splitting tests also found that most of the doped perovskites could now produce H_2 from visible light (Figure 1). These results expand the viability of the combined techniques to perovskites other than $SrTiO_3$ and provide a pathway to rationally search for a commercially viable, visible light photocatalyst.

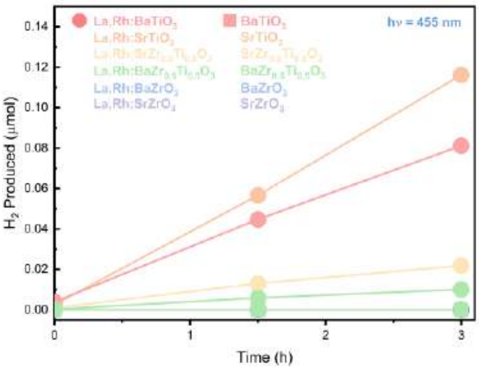

Figure 5: Photocatalytic H_2 production of doped perovskites (circles) and undoped perovskites (squares) in CH_3OH & H_2O

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C077

Triplet fusion upconversion from nanoporous solid-state sensitization

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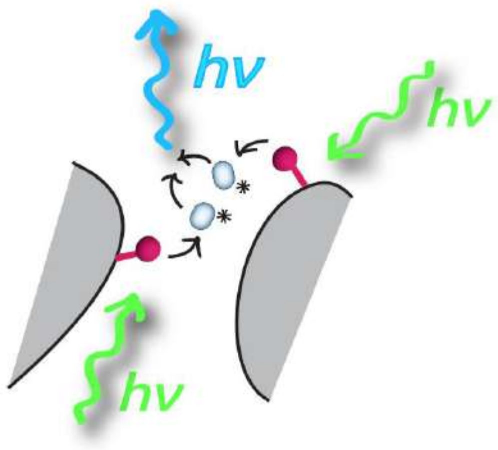
Photochemical upconversion of low energy green light to higher energy blue light is demonstrated in nanoporous alumina thin films stained with a metalloporphyrin sensitizer. The porphyrin sensitizer (nano-tetra(4-carboxyphenyl) porphine Pt(II), PtTCPP) anchors to the surface of the alumina nanostructure through carboxylic groups. The pores of the nanoporous alumina structure are filled with concentrated diphenylanthracene (DPA) emitter solution. Efficient upconversion with a photon generation quantum yield of 9.4% is achieved, demonstrating that high efficiency upconversion is possible with solid-state sensitization of a nanostructured thin film.[1]



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C078

Understanding the stabilization of perovskite solar cells with Ionic salts

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Notwithstanding many recent advances in perovskite solar cells (PSCs), the inherent instability of the active perovskite material still presents a major obstacle in attaining long-term durability and commercialization of the technology. One of the most formidable challenges in enhancing the long-term stability of PSCs is ion migration within the perovskite structure, which is triggered by exposure to heat and light. Herein, we demonstrate that ion migration can be mitigated by incorporating small amounts of various ionic liquids/salts into the perovskite films, and aim to provide a fundamental understanding of the origins of this favourable effect. Introduction of these liquids/salts were found to drastically improve both the efficiency and stability of the PSCs. We explain this promoting effect by the combination of the following factors: (i) improved homogeneity of the perovskite film with less PbI2 admixture formed, (ii) formation of a very thin layer of the salts at the interface between perovskite and hole-transporting material, which favourably adjusts the electronic structure of the former, and (iii) suppression of the thermally induced ion migration and degradation of the perovskite. We also demonstrate that our ionic liquids/salts can assist in the formation of more stable perovskite films than those with the widely used imidazolium salts, and propose selection criteria for the salt additives. The findings of this work might guide future research and development of practical, stable PSCs.

C079

Molecular energy transfer in optical microcavities: towards a quantum battery

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Quantum batteries are a new class of energy storage device which utilise quantum mechanical effects and lead to advantages over classical electrochemical devices.[1,2] One such effect is superabsorption *via* strong light-matter coupling in an optical microcavity. The modification of energy levels in optical microcavities allows for control of molecular energy transfer pathways *via* the newly-formed hybrid light-matter states.[3,4] However, such a device also exhibits superradiance, limiting the time over which energy can be stored. In this presentation, I will describe our approach to a quantum battery design, where a modified donor-acceptor molecular energy transfer pathway in an optical microcavity facilitates storage of optical energy in molecular triplet states with long storage times.

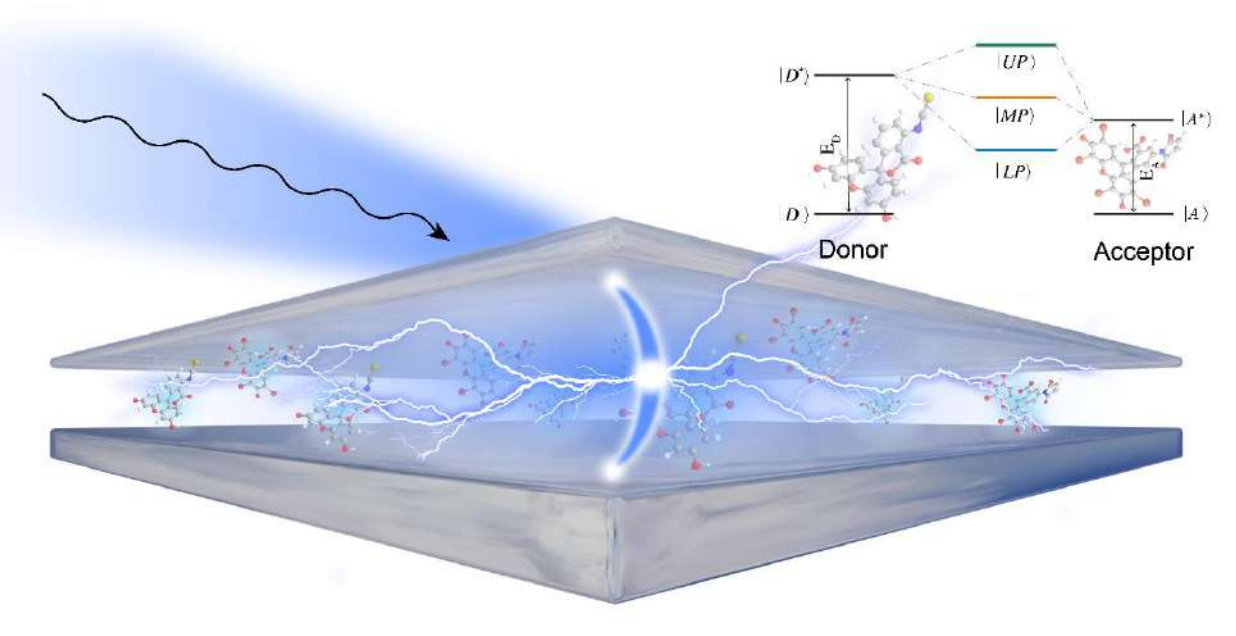

Figure 1. Strong coupling in an optical microcavity-based quantum battery with long storage times in molecular triplet states. Adapted with permission from Tibben *et al.*[3]

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C080

Combinatorial Plasmonics: A Quest for Nanoparticle Assemblies with Maximum Surface-Enhanced Raman Scattering

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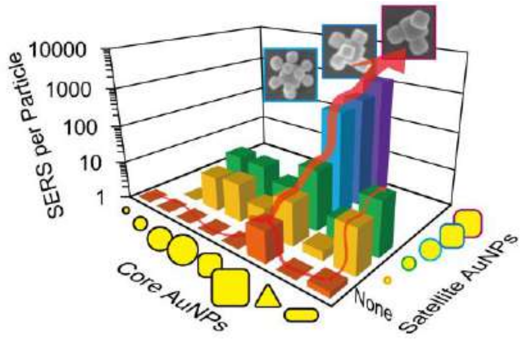
Plasmonic nanoparticles exhibit unique properties that distinguish them from other nanomaterials, including vibrant visible colors, generation of electric fields, production of hot charge carriers, and localized heat emission. These properties are particularly enhanced in the narrow nanogaps formed between nanostructures. Therefore, creating nanogaps in a controlled fashion is the key to achieve a fundamental understanding of plasmonic phenomena originating from the nanogaps and develop advanced nanomaterials with enhanced performance for diverse applications. One of the most effective approaches to create nanogaps is to assemble individual nanoparticles into a clustered structure.[1,2] In this study, we present a fast, facile, and highly efficient method for preparing core@satellite (CS) nanoassembly structures using gold nanoparticles of various shapes and sizes, including nanospheres, nanocubes (AuNCs), nanorods, and nanotriangular prisms.[3] The sequential assembly of these building blocks on glass substrates allows us to obtain CS nanostructures with a 100% yield within 4 h. Using nine different building blocks, we successfully produce sixteen distinct CS nanoassemblies and systematically investigate the combinations to search for the highest Raman enhancement. As a result, we discover that the surface-enhanced Raman scattering (SERS) intensity of AuNC@AuNC CS nanoassemblies is two orders of magnitude larger than that of other CS nanoassemblies. Theoretical analyses reveal that the number of molecules in the interfacial region, as well as the intensity and distribution of the electric field induced in the nanogaps by plasmon excitation, collectively contribute to the unprecedentedly large SERS enhancement observed for AuNC@AuNC. This study not only presents a novel assembly method that can be extended to produce many other nanoassemblies, but also identifies a highly promising SERS material for sensing and diagnostics through a systematic search process.



A new assembly method enables us to prepare various combinations of core@satellite nanoassemblies in a fast and effective manner, through which we search for the nanostructure exhibiting the highest SERS signal intensity.

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C081

Size Separation of Quantum Dots with Plasmonic Thin-layer Chromatography

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Semiconductor quantum dots (QDs) have tunable properties propertied depending on their size. Recently, they have been intensively investigated for the application to photovoltaics, photocatalysts, bio-markers, and light-emitting devices.[1] We prepared novel multinary QDs composed of less toxic elements, such as $Ag(In,Ga)S_2$ and $ZnS\text{-}AgInS_2$ solid solution (ZAIS), and clarified their photochemical properties depending on particle size, shape, and composition.[2,3] Here, we report a novel method for the size separation of QDs by combining plasmonic optical trapping and thin-layer chromatography (TLC), which we named “plasmonic TLC”.[4] The photoexcitation of localized surface plasmon resonance (LSPR) of Au nanoparticles (NPs) immobilized on a TLC plate enabled to size-selectively trap QDs.

Au NPs (diameter: 12 nm) were immobilized on a silica gel particle layer of a TLC plate to form a band-like Au NP immobilized area (AuNP-band), which were located in the range of Rf = 0.20–0.375 after the development. The Rf value was defined as the ratio of the distance traveled by the QDs to the distance of the eluent front line from the origin on the TLC plate. ZAIS QDs with various sizes were prepared by previous methods[5] and spotted on the Au-TLC at the origin. Thus-obtained TLC plates were developed in chloroform-oleylamine mixture solution as eluent without or with light irradiation at 820 nm (the intensity of 0.71 W/cm^2). Under the light irradiation, QDs of 8 nm or larger in size were optically trapped in the AuNP-band, although the smaller QDs (the size: 6 nm or less) migrated across the AuNP-band. Any types of ZAIS QDs went through the AuNP-band without irradiation and reached the position at Rf = 0.60–0.80. Furthermore, we found that the difference in the particle shape and energy gap of QDs also affected their plasmonic trapping efficiency in the AuNP-band. In the near future, plasmonic TLC will become a useful strategy for separating nano-objects, such as metal nanocrystals, QDs, and biomolecules, by their size, shape, and optical properties.

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C082

The Life Cycle of Polarons in Photocatalytic Organic Donor:Acceptor Nanoparticles

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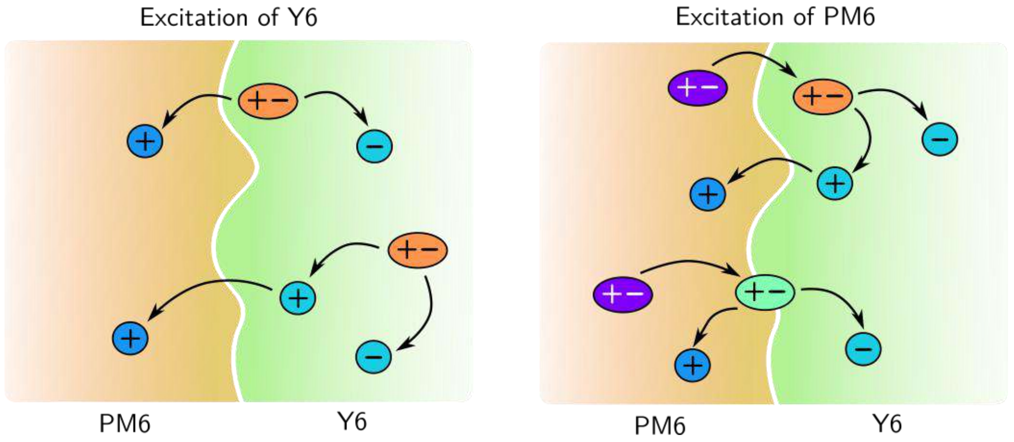
Green hydrogen is a promising replacement for traditional fossil fuels. Semiconducting photocatalytic nanoparticles are an emerging material with the potential to produce inexpensive and renewable hydrogen. These particles absorb light, generate charges, and split water in a simple particulate system. Inorganic photocatalysts are most commonly used, however they are typically only active under UV light, which limits their efficiency under solar conditions. Organic semiconductor nanoparticles are an alternative material with strong visible light absorption. Recently, we and others studied the hydrogen production of nanoparticles of the high-performing blend of polymeric electron donor PM6 and non-fullerene acceptor Y6.[1,2] We found that these nanoparticles produce hydrogen at high rates under visible and near-infrared light, through excitation of either component. Despite the high performance of PM6:Y6 blends, there is confusion in the literature regarding the mechanisms of charge generation.

Here, we present a detailed spectroscopic analysis of the photophysics of PM6:Y6 nanoparticles. We find that under excitation of Y6, most polarons are first generated within Y6 domains, with PM6 holes formed via migration of Y6 holes to PM6 domains. Under excitation of PM6, two charge generation mechanisms exist: the conventional electron-transfer mechanism as well as one involving FRET to Y6 domains. We also examine the system under photocatalytic conditions with the addition of the Pt co-catalyst and sacrificial electron donor ascorbic acid. We find that the interaction with the co-catalyst and sacrificial reagent can occur on both fast (ps-ns) and slow (us) timescales, involving all polaron species generated.



Mechanisms of charge generation in PM6:Y6 blends

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C083

Yolk-Shell Nanostructure a Unique Architecture as a Promising Photocatalyst Towards Photocatalytic Hydrogen Generation

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In recent years, hydrogen comes as a potential and green alternative to limited fossil fuels. Photocatalysis (PC) water splitting is one of the promising ways for hydrogen generation using solar energy and photocatalyst. Till now, a number of semiconductors have been proposed as the photocatalyst for PC hydrogen generation such as doped/alloyed nanocrystals, particle-decorated nanostructures, core-shell and yolk-shell nanostructures etc. Among all yolk-shell nanostructures comes with highlighted particular architecture with moveable core, permeable shell and confined space. The movable core and permeable shell create a new pathway for enhanced active sites which including confined space which can facilitate the diffusion of reacting species, and large surface area which can provide abundant active sites. In the present work, we design Au@AgCuS yolk-shell nanostructures as a photocatalyst for PC hydrogen generations. The yolk-shell samples were prepared by a sequential ion-exchange reaction on template Au@Cu_2O core−shell to Au@Cu_7S_4 yolk-shell via anion exchange, and further to Au@AgCuS via cation exchange with Ag. A pure counterpart AgCuS are also synthesized without using gold. Further photocatalytic PC hydrogen generation experiment results showing that yolk-shell nanostructures Au@AgCuS showing higher performance towards hydrogen generation as compared to pure counterpart AgCuS. Moreover, the influence of change in void size on PC hydrogen generation performance of different Au@AgCuS photocatalyst has been systematically investigated and found that Au@AgCuS with largest void size is showing highest hydrogen generation rate i.e., 0.89 μ mol h^{-1}. The present study showing that unique architecture of yolk-shell nanostructure like movable core and void space is critical parameter for a photocatalyst in Photocatalysis.

C084

Enhanced Photocatalytic Hydrogen Evolution by Pseudo-Homojunction Organic Semiconducting Nanoparticles

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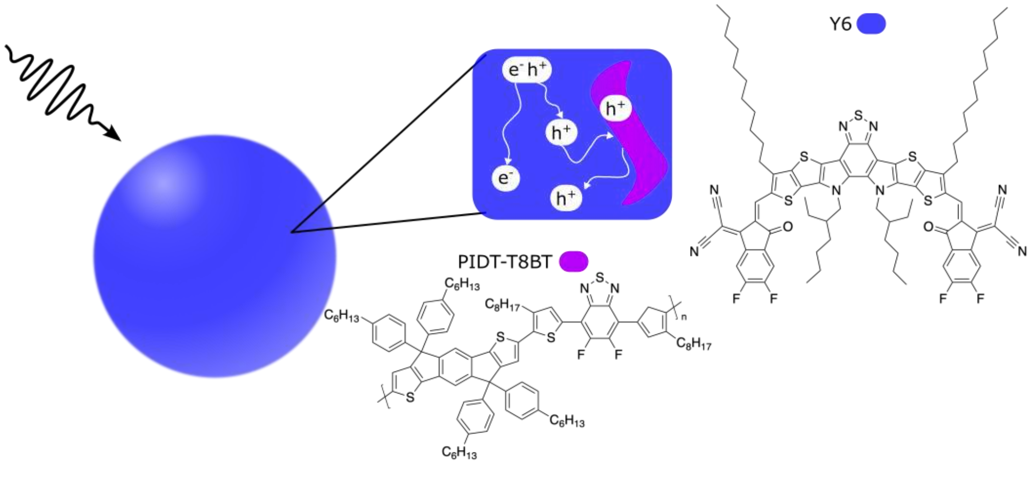
Organic semiconducting nanoparticles (NPs) are increasing in popularity as viable hydrogen evolution reaction (HER) photocatalysts largely due to their strong visible-light absorption. All the highest performing organic photocatalysts have used materials which have shown prior success as organic photovoltaics (OPVs). Development in both OPVs and organic photocatalysts has focused on utilising the bulk heterojunction between electron donor and acceptor materials, opposed to a homojunction with a single semiconducting polymer or small molecule. Bulk heterojunctions advantageously promote charge separation and carrier lifetime but reduce the phase purity leading to lower charge diffusion lengths.

Here we report high photocatalytic activity from electron donor-acceptor (D-A) NPs using non-fullerene acceptor Y6, and indacenodithienothiophene derived polymer donor, PIDT-T8BT.[1] In contrast to conventional donor-acceptor systems, the charge generation in PIDT-T8BT:Y6 NPs is mainly driven by Y6, allowing high photocatalytic performance at a D:A mass ratio of 1:50. Such low ratios have generally been thought to yield lower efficiency than the more conventional 1:1 (NPs), or 1:1.2 (OPVs). However, our results show that a 1:50 ratio exhibits a rate that is enhanced by 50% compared with that of neat Y6. We hypothesise that this improvement arises from the polymer acting as a hole reservoir, temporally separating the electron and hole to decrease the rate of charge recombination. Interestingly, for the PIDT-T8BT:Y6 system, as the polymer concentration in the NP is increased, we observe a reduced photocatalytic performance, with the 1:1 blends performing at 45% the rate of neat Y6. This work presents a novel method of improving photocatalytic performance in organic photocatalysts by utilising the benefits of a heterojunction while retaining much of the bulk phase purity for fast charge diffusion.



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C085

Formamidinium Caesium Lead Perovskite Solar Cells from Lead Acetate

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Lead halide perovskite solar cells have great potential to replace or enhance silicon photovoltaics. Her we will present some of our recent work which proposes a novel lead-acetate based synthesis route for the formation of mixed-A-cation perovskites[1].The use of lead acetate allows to produce ultrasmooth perovskite thin films, without the need for antisolvent quenching or the presence of strongly complexing solvents such as DMSO. We propose the use of ammonium iodide as alternative halide source to produce phase-pure formamidinium caesium mixed-A-cation perovskite films from lead acetate. Solar cells fabricated from these films exhibited energy conversion efficiencies of up to 21%. The robustness of the film formation process in the lead acetate route makes it highly amenable to large-scale industrial production. We demonstrate the scalability of our new synthesis route by producing 10 cm2 active area solar cell sub-modules via a blade-coating process in air, producing solar cells with efficiencies of up to 18.8% and no evidence of efficiency loss after 3300 hours storage at 65□C.

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C086

Investigating New Emitter Molecules For Triplet-Triplet Annihilation (TTA) Upconversion

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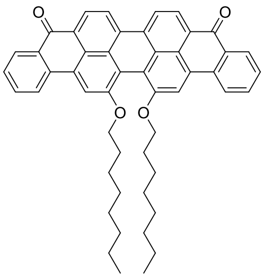
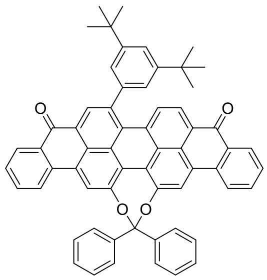
Photochemical upconversion (PUC) in organic molecules, specifically triplet-triplet annihilation (TTA) upconversion, offers a promising approach with spectral flexibility and high efficiency under low light levels. However, challenges arise due to the sensitivity of molecular triplet states to oxygen, resulting in energy loss and potential damage.[1] To address these issues, the utilization of triplet states with energies below the oxygen triplet energy has been proposed. Violanthrone (V79), a molecule capable of performing TTA in the presence of oxygen molecule, exhibits a triplet state below 0.98 eV, enabling the utilization of light from sub-bandgap regions for upconversion.[2]

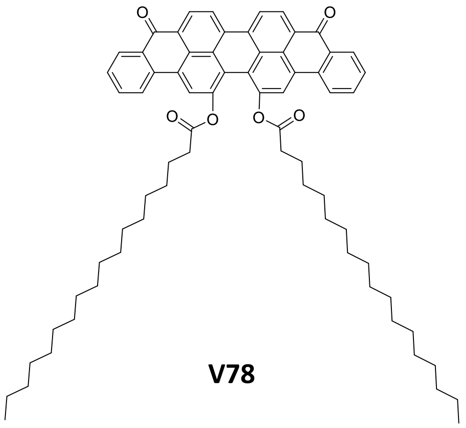
The focus of recent research has been on improving the overall upconversion efficiency. Although V79 has shown promise as an emitter for PUC, its low quantum yield hinders the overall quantum efficiency of upconversion. In this study, we compare the two commercially available derivatives of violanthrone, V79 and V78, with our newly synthesized violanthrone derivative called V(OCO). We investigate their quantum yield efficiencies, TTA capability, and oxygen sensitivity.



V79



V(OCO)



V78

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C087

Reconstructing the Na distribution and revealing its influence on grain growth of CZTSSe in 2-methoxyethanol-based precursor solution

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Sodium doping is one of the mature technologies that has been used both in chalcopyrite and kesterite solar cells. A suitable Na doping can be used to improve the crystalline quality, electrical properties, and effective defect passivation of the absorbers. Compared to a high-temperature absorber deposition process that facilitates a bottom-up crystal growth together with Na diffusion in CIGS, the state-of-art absorbers in CZTSSe are always achieved with a multi-layer structure, containing a lot of horizon grain boundaries, makes it difficult to regulate the Na distribution from bottom substrate to top grain growth regions. Herein, a method of uniform Na doping through precursor solution has been proposed. Instead of obtaining the Na from the substrate of soda-lime-glass (SLG) during the high-temperature selenization process, Na with accurate amount of substance can be added into the 2-methoxyethanol based CZTS precursor solution directly and affects the grain growth at the very early stage of the formation of CZTSSe phase at the top surface of the absorbers. Surprisingly, a better crystallinity has been achieved and corresponding Cu_{Zn} defects has also been passivated. Nonradiative recombination in CZTSSe was effectively suppressed by uniform Na doping, and a favorable more uniform lifetime mapping with sub-micrometer resolution was shown, demonstrating the improved the PV performance to over 12% PCE.

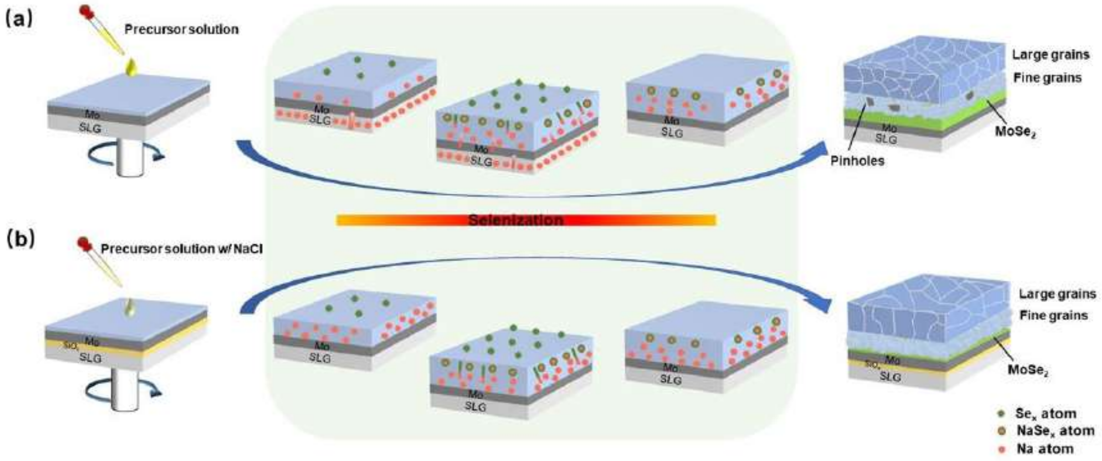

Figure. Schematic illustration of Na diffusion and distribution mechanisms for a）SLG-Na and b) Uniform-Na samples.

C088

A Self-assembly Strategy Towards Closing the Lab-to-fab Gap of Organic Photovoltaic

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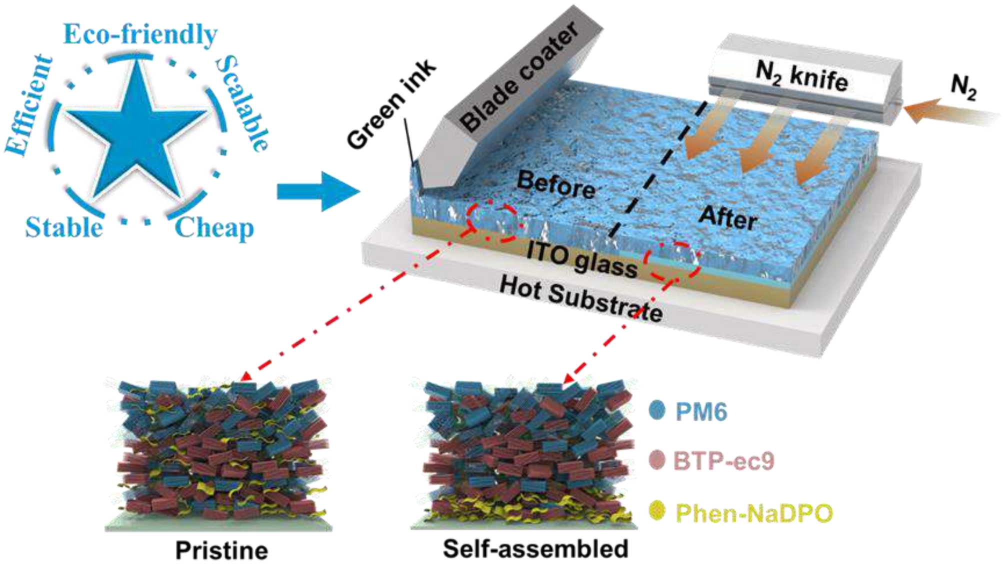
The emergence of nonfullerene acceptors (NFAs) has triggered a rapid advance in the performance of organic solar cells (OSCs), endowing OSCs to arise as a promising contender for 3rd generation photovoltaic technologies.[1, 2] The ultimate objective of OSCs is to provide affordable, stable, efficient, scalable, and sustainable solar-to-power solutions in support of global carbon neutrality. However, achieving a balance between these five critical factors for OSC commercialization is highly challenging. In this presentation, I will show our self-assembly strategy, designed to bridge the gap between high power conversion efficiency (PCE), long-term stability, sustainability, scalability, and cost-effectiveness of OSCs. We will demonstrate our sustainable and open-air-printable OSCs, which feature a simplified device architecture, enhanced PCE, and improved stability under shelf, thermal, and light illumination conditions. Further, I will demonstrate a comparison of self-assembled and traditional devices, providing detailed insights into the enhanced photovoltaic performance and stability through in-situ and ex-situ multimodal characterizations. Finally, I will present our results on scale-up fabrication and perspective to apply our self-assembly strategy to close the lab-to-fab gap of OSCs toward commercialized cheap, stable, efficient, scalable, and eco-friendly OSCs.[3]



Schematic drawing of the self-assembly strategy

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C089

Spin Effects in Triplet–Triplet Annihilation: Rethinking Atkins and Evans' Theory

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In triplet–triplet annihilation (TTA) the molecular energy of two photons is pooled and emitted as fluorescence of a single photon of higher energy. TTA is a promising means of accessing solar irradiance below the silicon bandgap and surpassing the Shockley–Queisser limit. In addition, TTA allows the output light wavelength to be tailored to a specific application via choice of molecule and functionalisation.

As TTA is a spin-selective process it exhibits a magnetic field response, which has traditionally been described and modelled in the context of Atkins & Evans' Theory.[1] Here, we revisit the theory, motivating the origin of key equations and evaluating the assumptions behind them. We rederive the theory, which captures the typical situation for TTA in solution. We compute the relative contributions of all spin channels, not only the singlet channel as in the original. These new conditions change the evolution of decoherence in the system, and thus the final magnetic field response equations. The ramifications of these updates are discussed in light of recent experimental results.[2,3]

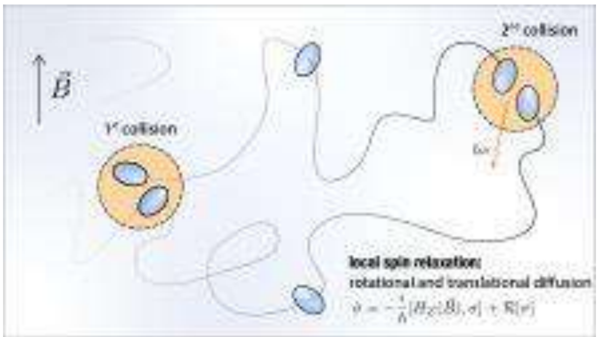

Figure 6: Relaxed triplets hosted on two molecules undergo a first encounter, resulting in energy exchange. The two spins evolve under the effect of the Zeeman Hamiltonian and the stochastic rotational/translational diffusion of the host molecule. This induces a local spin relaxation. The triplets undergo a second collision. The probability of upconversion (emission of a photon) depends on the strength of the magnetic field and the roto-translational parameters.

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C090

Quantifying Relaxation Dynamics of High-Lying Excited States in Perylene

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Information processing with molecular excitons presents opportunities for developing sub-nanometre, ultrafast and biocompatible computational devices.[1,2] One potential method of developing excitonic circuitry is to use high-lying molecular excited states to gate logical processes,[3] but relatively few molecules have higher electronic excited states with sufficiently long lifetimes to facilitate this. However, recent reports have suggested that the polycyclic aromatic hydrocarbon perylene exhibits non-negligible excited-state lifetimes upon excitation to high-lying excited states,[4] and may also undergo singlet exciton fission from one or more of these states.[5] Despite these promising early results, the exact nature of these high-lying excited states in perylene is currently unclear, and further work is necessary to identify these states and quantify their relaxation dynamics.

In this work, we use femtosecond pump-probe and pump-push-probe spectroscopies to study the relaxation dynamics of higher electronic excited states in perylene (Fig.1). Three electronic excited states are identified: the optically active $1B_{3u}$ and $2B_{2u}$ states and the dark $2A_g$ state, accessible only via an excited-state absorption from $1B_{3u}$. Excitation to either the $2B_{2u}$ or $2A_g$ states in dilute solution results in sub-picosecond internal conversion to the $1B_{3u}$ state, followed by vibrational cooling over tens of picoseconds. We demonstrate that the perylene $2B_{2u}$ state has a lifetime of only ~500 fs (significantly shorter than previously estimated) and the lower-energy $2A_g$ state relaxes over an even shorter lifetime of 340 fs, consistent with the energy-gap law. These results therefore suggest that while the higher excited states of perylene do persist for non-negligible lifetimes, harnessing these states to perform logical operations will require the introduction of ultrafast competing relaxation pathways.

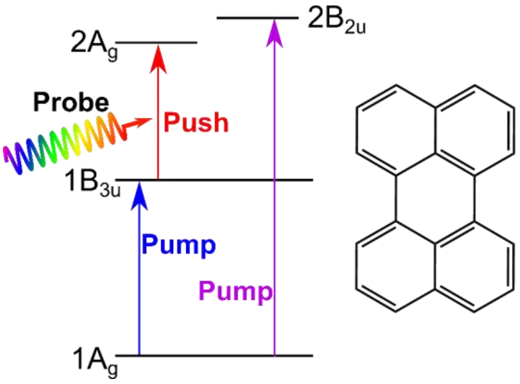

Figure 1: Femtosecond pump-probe and pump-push-probe spectroscopies are used to study the relaxation dynamics of high-lying electronic excited states in perylene.

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C091

Solid State Photon Upconversion

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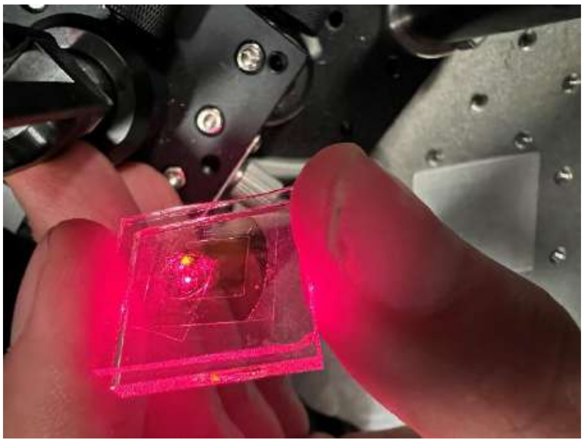
The upconversion of light has numerous potential applications ranging from photocatalysis, photovoltaics, imaging, and advanced manufacturing.[1,2] The strategies being investigated to achieve this include energy transfer upconversion in lanthanide nanoparticles, and sensitized triplet fusion, also known as photochemical upconversion or triplet–triplet annihilation upconversion. The latter involves the generation of triplet excited states by a sensitizer and their subsequent transfer to an emitter. Emitter triplets annihilate (fuse) to generate an emissive singlet state from which a photon is emitted. This strategy is spectrally adaptable, and high efficiencies are routinely achieved in solution, approaching the quantum yield ceiling of 50 %.

Recently, there has been progress in translating triplet fusion upconversion into the solid state, which is desirable from a device engineering standpoint. There are many possible solid-state device architectures. Broadly these can be categorized into materials wherein the sensitizer is distributed, and heterogeneous devices where triplet generation is spatially separated from triplet fusion. The latter strategy is attractive, as the upconverted singlet state is protected to an extent from Förster resonance energy transfer back to the sensitizer.

Here we demonstrate a strategy using organic dye sensitizers supported on a mesoporous metal oxide substrate. In an architecture reminiscent of dye-sensitized solar cells, we adsorb a metalloporphyrin to a nanostructured alumina film. Unlike DSSCs, where the photogenerated exciton injects an electron, on this high band gap semiconductor the triplet state survives, and is available for harvesting by emitter molecules. Using time-resolved spectroscopies, we show that the sensitizer triplets are long-lived, do not suffer an untimely demise and can be efficiently transferred to the emitter chromophores.



Solid-state-sensitized red-to-yellow upconvertor.

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C092

Charge Transfer Behaviors Induceds by a Change of Excited-state Aromaticity

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Molecular excited-state aromaticity and its application have attracted much attention based on the critical role of ground-state aromaticity in organic chemistry. Since structural changes and stabilizations in photosynthesis are dominated by the excited state aromaticity, controlling the excited state aromaticity became essential for designing a new synthetic pathway of photoactive materials.

In regarding to this issue, Baird's rule suggests a description of the excited-state aromaticity, in which [4n]π (or [4n+2]π) systems are Baird aromatic (or antiaromatic) in the excited triplet states in contrast to Hückel rule for the ground state.[1] This concept for excited-state aromaticity, termed as 'aromaticity reversal', has a large significance that the completely reversed aromaticity in the excited state provides crucial insight into understanding of excited-state processes and involved photo-physics and chemistry, which has brought intensive theoretical and experimental efforts for the demonstration of aromaticity reversal in the excited states.[2]

Here, we discovered an intramolecular CT process provokes the aromatization of TMTQ in the excited state.[3] The analysis of C≡N stretching modes by the time-resolved IR spectroscopy revealed that the intramolecular CT process accompanies the shift of electron density towards the dicyano groups. The qualitative analyses of C=C stretching modes and geometry optimization results showed that the CT process leads to a local [8]π formally dicationic M10A core, which becomes aromatic in the excited state by Baird's rule. This observation obviously demonstrates the concept of excited state aromaticity in the annulene system. Furthermore, the CT induced aromatization provides a direct insight into the role of aromaticity in the modulation of excited state properties and designing photoactive materials.

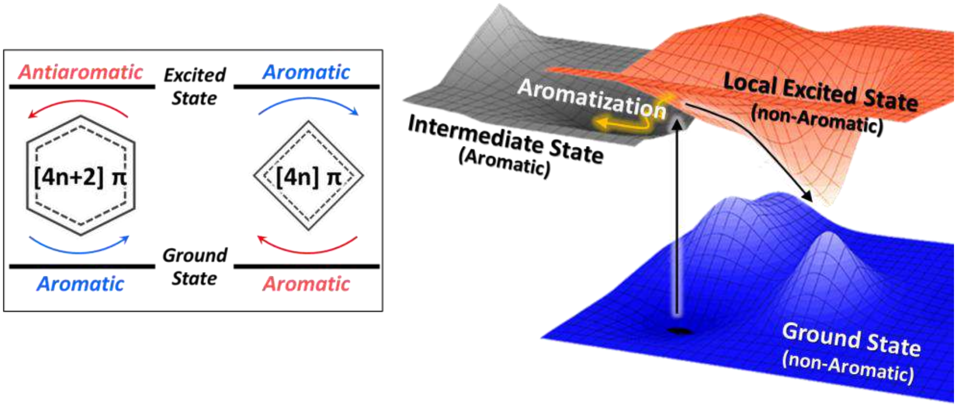

Figure 1. Schemes for Baird's rule for excited-state aromaticity and effect of excited-state aromaticity.

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C093

Quasi-reversible photoinduced displacement of perylenebisimide derivatives from semiconductor nanocrystals

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Organic ligands on the surface of colloidal inorganic nanocrystals (NCs) play a crucial role in the stability and properties of nanomaterials. Therefore, it is important to understand the basic properties of organic ligands to control and optimize the properties of nanomaterials. These days, organic-inorganic nanohybrids using semiconductor NCs coordinated with aromatic organic molecules have been widely studied in the fields of optoelectronic materials, such as solar cells, photocatalysis, and photon upconversion. Many of these studies assume that coordinated organic molecules remain anchored to the surface of nanomaterials during photophysical and photochemical reactions. However, this assumption is not always valid. If organic ligands can be displaced by light on demand, this process can be applied to develop advanced photofunctional materials such as photocatalysts that can expose the active facets of NCs for catalytic reactions on demand, and photoconductive circuit patterning of nanocrystalline solid-state films. Therefore, exploring the ligand properties of organic−inorganic nanohybrid systems is important for various fields of materials science. In this study, we demonstrate that the coordination bonds between ligand molecules and NCs by carboxyl groups are displaced quasi-reversibly by light irradiation using zinc sulfide (ZnS) NCs coordinated with perylenebisimide (PBI, Figure 1a inset) as a model system (Figure 1a).[1]

Subpicosecond-to-nanosecond transient absorption measurements show that the hole transfer occurs from the highest occupied molecular orbital (HOMO) of PBI to ZnS NCs in PBI-ZnS. The molar ratio of PBI and ZnS NC (PBI/ZnS NC) was 7.0. The ultrafast hole transfer from PBI to ZnS NCs was further revealed by time-resolved impulsive Raman measurements and the quantum chemical calculation of a model cluster of PBI-ZnS. Moreover, the comparison of the transient absorption spectra of PBI-ZnS in chloroform and the polymer film (poly(methyl methacrylate)) indicates that PBI was displaced by light irradiation.

Interestingly, the PBI radical anion generated by light irradiation survives over some seconds (Figure 1b). If PBI remains bound to the surface of ZnS NC, the radical anion would not survive such a long time. Therefore, the long-lived PBI radical anion suggests that PBI is displaced with the surface of NC by light irradiation. We also conducted the same experiments in CdS or CdS/ZnS core-shell NCs coordinated with PBI, and found that the amount of PBI radical anions generated by light irradiation is greatly enhanced in the core-shell NCs. Details will be explained in the presentation.

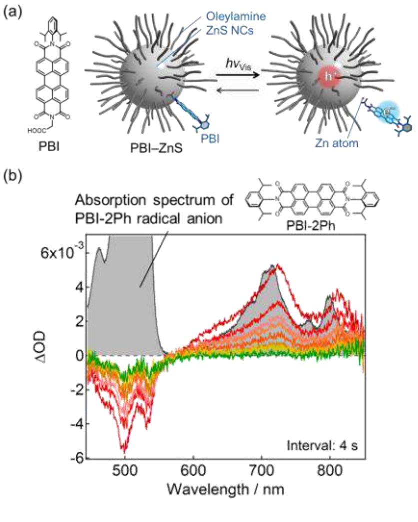

Figure 1. (a) The molecular structure of PBI and schematic of the quasi-reversible photoinduced displacement of PBI-ZnS. (c) The absorption spectrum of a PBI radical anion (PBI-2Ph) and the transient absorption spectra of PBI-ZnS (PBI/ZnS NC = 6.8) in chloroform.

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C094

Hot Carrier Cooling Dynamics in Lead Halide Perovskites via Ultrafast Multi-Pulse Spectroscopy

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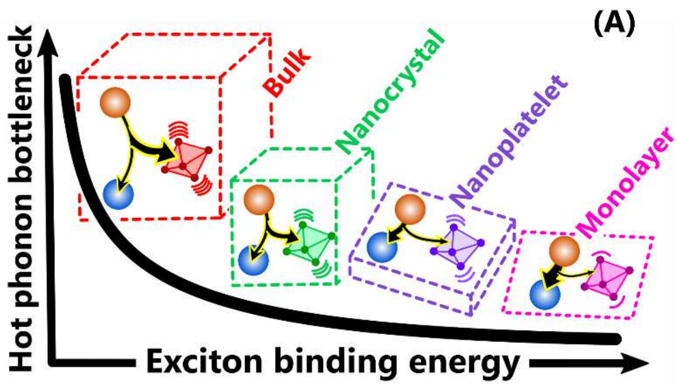
The rapid (<1 ps) intraband relaxation of above-gap photocarriers places a fundamental limit on the efficiency of single-junction solar cells. This 'hot carrier cooling' is governed by carrier-phonon and carrier-carrier coupling, and so the systematic study of their dynamics also reveals the underlying photophysics operating in optoelectronic materials. Hot carrier cooling in lead halide perovskites (LHPs) has typically been investigated using broadband transient absorption, revealing the existence of the hot phonon bottleneck which slows carrier cooling at high excitation density. However, signatures of hot carriers can be obfuscated by other temporally and spectrally overlapping processes.

Here, ultrafast pump-push-probe (PPP) spectroscopy is presented as a means of isolating hot carrier dynamics in a range of LHP systems. We employ a near-infrared probe to study LHP nanomaterials spanning a range of confinement regimes, revealing the suppression of the hot phonon bottleneck in systems with higher exciton binding energy due to greater carrier-carrier scattering (Fig. A);[1] while the use of a few-THz probe on single-crystal $CsPbBr_3$ points to the existence of a hot local lattice which suppresses carrier mobility after carriers have undergone intraband relaxation (Fig. B).[2] These findings not only have implications for the rational design of LHP-based devices, but also directly for the interpretation of results from multi-pulse experimental methods that are becoming more widely used.



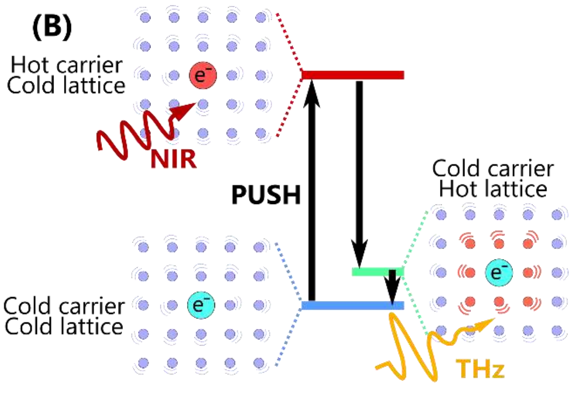


Fig. A: The hot phonon bottleneck becomes more suppressed with increased confinement due to stronger carrier-carrier coupling.

Fig. B: THz-PPP spectroscopy reveals the influence of the hot local lattice on carrier mobility.

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C095

Structural changes of chromophores with excited-state intramolecular charge transfer

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Photoinduced intramolecular charge transfer (ICT) often shows structural changes of chromophores in the □-backbones, which connect the electron donor and acceptor moieties. We have investigated ultrafast structural changes of several push-pull chromophores with the backbones of stilbene, biphenyl, styrylpyran, styrylpyridinium, etc., by femtosecond stimulated Raman spectroscopy.[1] The $□_{8a}$ and $□_{C=C}$ modes in the frequency range of 1500-1650 cm^{-1} appear sensitive to the structural changes of chromophores, especially in the □-backbones.

In this work, femtosecond stimulated Raman spectroscopy (FSRS) with both high temporal (<50 fs) and spectral resolutions (<10 cm^{-1}) is used to probe the structural changes of chromophores in the excited state. The multimodal vibrational signature of chromophores obtained from FSRS measurements may provide evident structural changes of push-pull emitters upon the charge transfer. The ICT dynamics of push-pull chromophores, including the *para*- and *ortho*-isomers of 4-*N*,*N*-diethylamino-*N*□-methylstilbazolium tosylate[2] (Fig. 1a) and well-known fluorescence probe thioflavin T (Fig. 1b) will be presented.

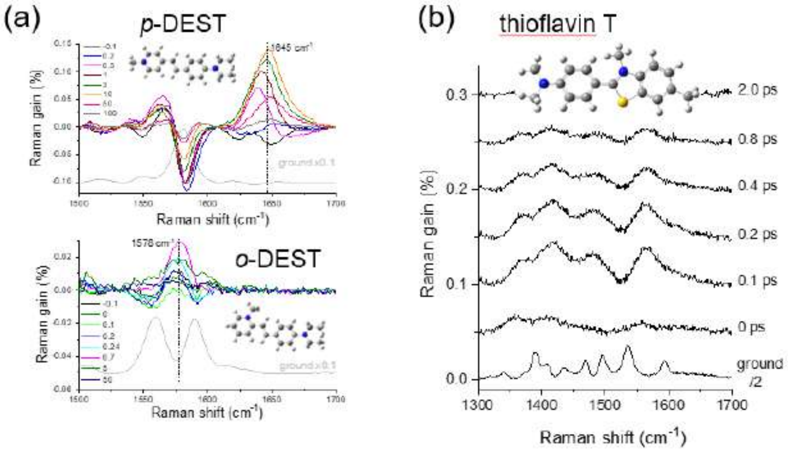

Fig. 1 Femtosecond stimulated Raman spectra of (a) *ortho*- and *para*-isomers of 4-*N*,*N*-diethylamino-*N*□-methylstilbazolium tosylate and (b) thioflavin T.

Besides, the recent progress in the development of impulsive stimulated Raman spectroscopy (ISRS) and preliminary results on the early ICT dynamics of thioflavin T will be introduced. Although the vibrational relaxations in the ICT state only were observed in the FSRS measurements, the structural changes in the low-frequency vibrational modes, including the in-plane and out-of-plane deformations occurring on the early ICT dynamics of thioflavin T, have been obtained from the ISRS measurements. By combining the FSRS and ISRS results, the multimodal ICT dynamics of thioflavin T with the backbone of phenylbenzothiazole will be discussed.[3]

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C096

Preparation and Ultrafast Spectroscopy of WS_2–Au Nanohybrid Systems for Photocatalysis Under Visible Light

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Nanosheet semiconductor materials, with their unique optical, electronic, and chemical properties, have gained significant attention in recent years for various applications such as photodetectors, light emitters, photocatalysts, and biosensors. In this study, we focused on tungsten disulfide (WS_2) nanostructures fabricated through pulsed laser ablation in liquid.[1,2] We compared the effects of nanosecond and femtosecond lasers and found that the latter was more suitable for nanosheet fabrication. To enhance the visible light response, we attached gold nanoparticles (AuNPs) onto WS_2 nanosheets. By employing femtosecond diffuse reflectance spectroscopy, we characterized the charge transfer dynamics in the WS_2-Au nanohybrid system. We observed that the nanosheet structure reduced the bulk carrier property, and the modification with AuNPs induced charge transfer from WS_2 nanosheets to AuNPs. These findings have significant implications for the future design of metal-nanosheet semiconductor hybrid systems.

Furthermore, we successfully developed a new photocatalytic material responsive to visible light by combining WS_2, AuNPs, and titanium dioxide (TiO_2) as a highly active photocatalyst.[3] The synthesis of the ternary nanohybrid materials was achieved through ultrasonic milling and hydrothermal synthesis methods, resulting in improved visible light photocatalytic performance. To understand the mechanism behind this enhanced performance, we conducted detailed characterization of the structural properties, spectroscopic properties, photocatalytic reaction properties, and electron transfer reaction dynamics using femtosecond transient absorption spectroscopy.

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C097

Gold Nanodrum Resonators

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Electromechanical nanodrum resonators using only nanometre thick gold films as drumheads are fabricated. The method introduced is favourable for large-area array manufacture of arbitrary shapes. The vibration behaviours of the drumheads are monitored by a laser Doppler vibrometer (Polytec LDV 400)[1]. The gold drumhead is highly reflective. From the Doppler shift between the incident and reflected laser induced by the displacements of the drumheads, we can identify the vibration frequencies and modes.

The drum resonators exhibit natural vibration frequencies of the fundamental modes in MHz regime at room temperature. Drum arrays of various thicknesses and sizes are fabricated. For circular ones, as the thickness-radius ratio varies from 10^3 to 10^5, we can see a clear transition from membrane regime to plate regime in the resonance behaviour of the drums[2]. The drum can be driven electrostatically at arbitrary frequencies as well, regardless of the resonance regime. In the MHz range, no distortion between driving signals and response signals is detected. The Q-factor ranges from 10~300 among the devices we fabricated, and we can see a clear dependence between the Q-factors and the dimension of the resonators. The stable and robust resonators possess great potential for acting as biosensors such as monitors of the mass and motion of a DNA molecule.

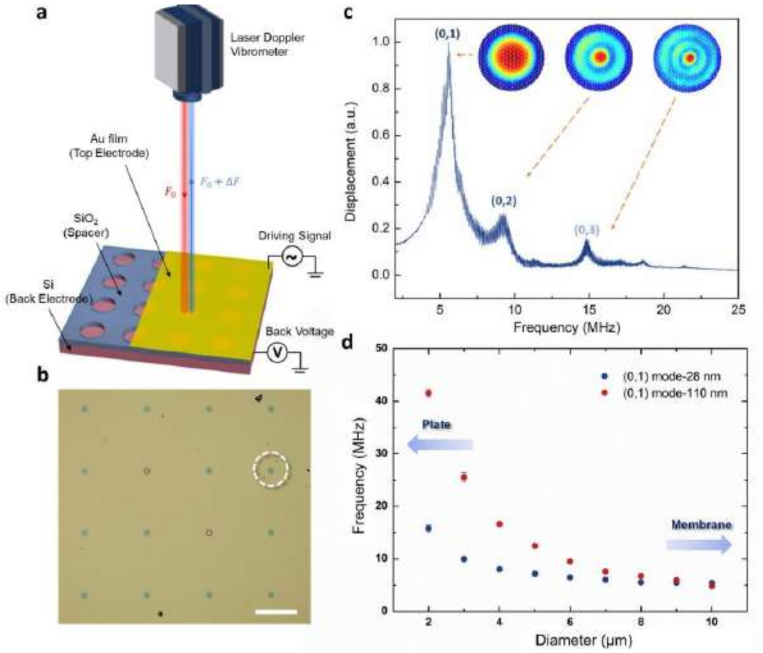

Figure 1. (a) Schematic of the gold nanodrum resonator arrays and the vibration behaviour characterisation system. (b) Optical microscope image of a circular drum array. The diameters of all the drums are 10 microns. The thickness of the gold film is 28 nm. Scalebar: 60 µm. (c) Resonance spectrum taken in the centre of the circled drum in (b). Inset: mode displacement shapes constructed from a mapping measurement. (d) The frequency of the fundamental mode dependence on the diameters of the circular drums of two different thicknesses.

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C098

State-specific reaction dynamics of the nonvalence bound state of the anion

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Non-valence bound state (NBS) of the anion is ubiquitous in nature and plays the essential role of the doorway into anion physics and chemistry. Here, we have investigated the state-specific chemical dynamics of the metastable NBSs using the picosecond time-resolved pump-probe spectroscopy on the cryogenically cooled anions using the velocity-map electron imaging technique. The nature of the mode-dependent dynamic behavior of the NBS in terms of the autodetachment and/or concomitant fragmentation reactions has been unraveled.[1-5] Deprotonated anions such as (halogen-substituted) phenoxides, for instance, have been generated by a home-made electrospray apparatus before they were mass-selected and collimated into the cryogenically cooled ion-trap. The autodetachment rate of the NBS has been precisely measured in a state-specific way for various chemical systems of the phenoxide, 4-cyanophenoxide, or *o*- (*m*- or *p*-) halogen substituted phenoxides. Fermi's golden rule is found to be extremely helpful for the rational explanation of the experiment whereas the more sophisticated theoretical model is definitely required for the more quantitative analysis.[1] For (*ortho*-, *meta*-, or *para*-) iodophenoxides, the C-I bond rupture (giving the I^- fragment at the asymptotic limit) has been found to be mediated by Feshbach resonances of the NBS, providing the foremost evidence for the dynamic doorway role of the NBS in the anion chemistry and physics. Autodetachment and the NBS-VBS (valence bound state) transition processes are kinetically competitive, promising the quantum mechanical control of the anionic reaction. The role of the correlation effect in the formation and relaxation of the NBS becomes more evident in several model cases, challenging sophisticated theoretical explanations.

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C099

Investigating the Role of Solvent in Cavity Catalysis under Cooperative Vibrational Strong Coupling

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In the field of photochemistry, understanding the interaction of light and matter remained intriguing for researchers. Light-matter strong coupling made this quest even more vivid since no external photon is required to excite the system. In vibrational strong coupling (VSC), an IR transition and resonant cavity photon are coupled, leading to the formation of hybrid vibro-polaritonic states having unique properties.[1] Cooperative VSC is a smart way to achieve cavity catalysis in which a solvent bath is coupled collectively to the reactant via a cavity photon (Figure 1).[2-4] Here, low reactant concentration can be used with a solvent which has matching vibrational bands. In the current work, three reactants, para-nitrophenyl acetate (PNPA), 3-methyl-para-nitrophenylbenzoate (PNPB), and Bis-(2,4-dinitrophenyl) oxalate (DNPO) and two solvents namely ethyl acetate (EtOAc) and cyclopentanone (CyPen) are chosen to study the effect of VSC on the solvolysis reaction rates.[5] Under strong coupling, both solvents showed enhancement in the rate but at slightly different temperatures, whereas DNPO did not show any modification due to the absence of Cooperative VSC. Thermodynamic parameters were calculated and compared to reconfirm the results. Detuning at elevated temperature was also conducted. In conclusion, the observations indicate that solvation dynamics play a crucial role in cooperative VSC, and further studies are required to fully understand the phenomena.

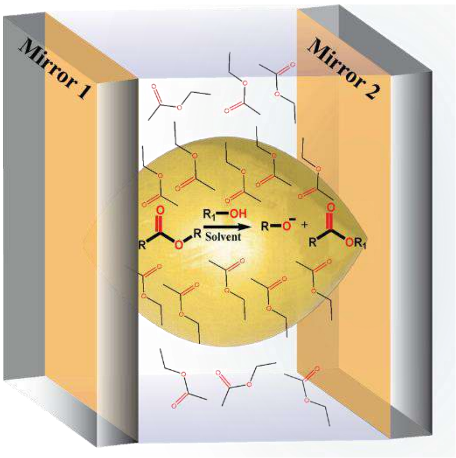

Figure 7. Schematic depicting cavity catalysis using a simple Fabry-Perot cavity.

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C100

Suppression of Phosphine-Protected Au_9 Clusters Agglomeration on $SrTiO_3$ Particles Using a Chromium Hydroxide Layer

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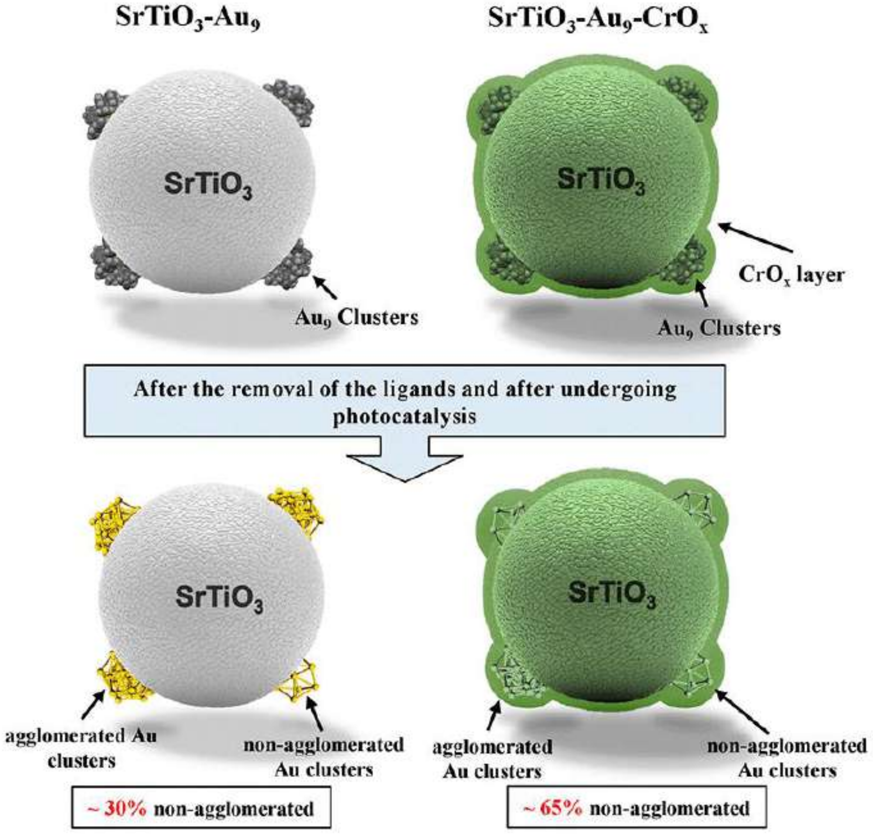
Gold clusters have been shown to have great potential for use as co-catalysts in photocatalytic water splitting. Agglomeration of Au clusters deposited onto semiconductor surfaces into larger particles is a major challenge. Metal oxide overlayers can be used to improve the stability of Au clusters on surfaces and avoid their agglomeration. The aim of this work is to investigate the inhibition of phosphine-protected Au_9 clusters beneath a $Cr(OH)_3$ overlayer to agglomerate under conditions of photocatalytic water splitting (i.e. UV irradiation)[1]. Au_9 was deposited on the surface of $SrTiO_3$ using a solution impregnation method followed by photodeposition of a $Cr(OH)_3$ layer. After UV light irradiation for 7 hours for photocatalytic water splitting, uncovered Au clusters on $SrTiO_3$ agglomerated into larger particles. However, agglomeration was inhibited when a thin $Cr(OH)_3$ layer was deposited onto the $SrTiO_3$-Au_9 system. From careful XPS measurements, the chemical state of the overlayer is initially determined to be $Cr(OH)_3$ but upon heating at 200 °C for 10 min it converts to Cr_2O_3. Through photocatalysis experiments it was found that the $Cr(OH)_3$ overlayer blocks the sites for O evolution reaction on the $SrTiO_3$-Au_9.



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C101

Machine learning for optimizing cobalt phosphate deposition parameters on thin film α-Fe_2O_3

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Photoelectrochemical (PEC) water splitting has emerged as a promising method for utilizing solar energy in the form of hydrogen, leading to the discovery and development of numerous photocatalytic materials. Among these materials, α-Fe_2O_3, also known as hematite, has shown significant potential, while its PEC efficiency is limited by several drawbacks. Moreover, the reproducibility of the performance is not satisfactory. To address this type of issues, our group has employed an interdisciplinary strategy that incorporates machine learning (ML) methods with analytical data of the photoanodes.[1,2] As shown in Figure 1, the features extracted from the analytical data of the photoanodes are applied to determine the dominant descriptors from the ML functions, which are then tested by the nonlinear model (GPR) to evaluate prediction performance. Along with parameter optimization, the indirect relationship between the parameters and the target could be eventually established. In this study, cobalt phosphate (Co-Pi), an excellent cocatalyst for oxygen evolution, was introduced to enhance the oxidation reaction of hematite. The cocatalyst was deposited through a photo-assisted electrodeposition process. To investigate the effects of Co-Pi deposition on hematite surface, we applied ML to the analytical data of hematite and Co-Pi/hematite. The prediction accuracies are markedly high with a data size of 94 (Figure 2). Correlated with the dominant descriptors selected, the experimental parameters of Co-Pi deposition, applied potential bias and deposition time, will be optimized for developing highly reproducible and efficient Co-Pi/hematite photoanodes.

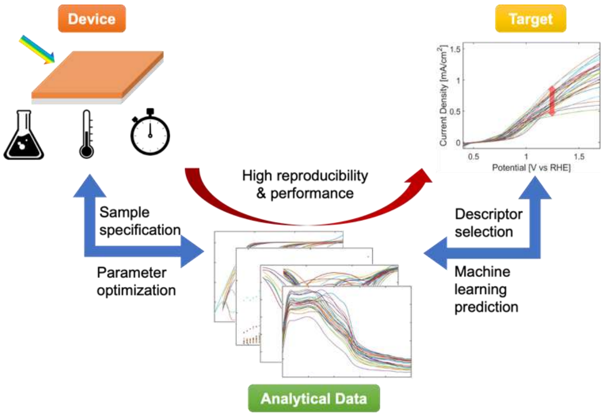

Figure 1. Scheme of applying machine learning method to optimizing the device with analytical data.

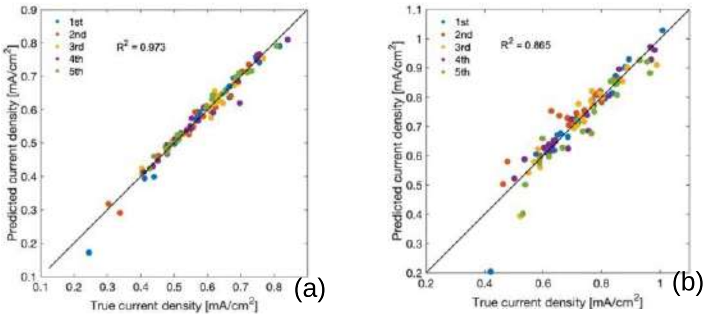

Figure 2. GPR prediction for the test dataset of (a) hematite and (b) Co-Pi/hematite photoanodes.

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C102

Dual-functional photocatalysts for simultaneous H_2 production and biomass conversion

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Semiconductor-assisted photocatalysis is one of the sustainable and eco-friendly technologies for hydrogen (H_2) production, where H_2 is a promising substitute for non-renewable fossil fuels.[1] $CdIn_2S_4$ (CIS), is an exciting photocatalytic material because of its high visible light harvesting capacity and tunable band gap (2.0-2.4 eV).[2] However, the main drawback of CIS photocatalysts is rapid electron-hole recombination. The incorporation of metal atoms/ions can enhance the photocatalytic performance of CIS.[3] Herein, we focused on the fabrication of ultrathin CIS nanosheets *via* a facile hydrothermal method with in-*situ* deposition of Ru atoms to enhance the optical properties and photocatalytic performance of CIS toward the photocatalytic H_2 production in the presence of a biomass intermediate, Furfuryl alcohol (F-OH), as a hole scavenger, **Figure 1a**. The results showed the successful synthesis of CIS nanosheets (**Figure 1b**) with the typical cubic crystalline structure (**Figure 1c**). Besides, the results showed the positive effect of the dispersion of Ru on the CIS to shift the absorption edge of CIS and further enhance its absorbance in the visible region (**Figure 1d**). Additionally, about 6:43-fold enhancement was achieved in the x%Ru-CIS samples where the 1%Ru-CIS sample achieved a H_2 production rate of 2781 μmol g^{-1} h^{-1} compared to the bare CIS nanosheets that achieved 65 μmol g^{-1} h^{-1} (**Figure 1e**). Finally, the selective oxidation of Furfuryl alcohol (F-OH) to Furfural (F-CHO was achieved with high conversion % (~60%) and ~ 100 selectivity% where the F-CHO production rate of ~409 μmol g^{-1} h^{-1}. Hence, these outstanding results showed the synergetic effect of Ru atoms to enhance the optical absorbance and photocatalytic performance of CIS nanosheets *via* improving the optical absorbance, enhancing the charge separation, and consequently, augmenting the H_2 production rates.

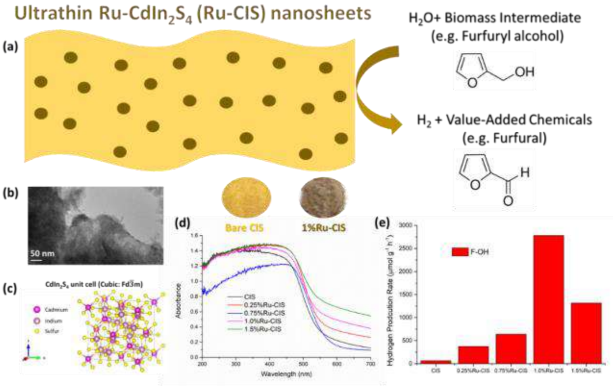

Figure 1. (a) Schematic representation of dispersion of Ru atoms on the ultrathin CIS nanosheets for simultaneous H_2 production and biomass conversion, (b) TEM image of CIS nanosheets, (c) the unit cell of CIS, (d) the DRS spectra (insets: photographic images of bare CIS and 1%Ru-CIS), (e) the photoproduced H_2 production rates of bare CIS and x%Ru-CIS nanosheets in the presence of F-OH.

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C103

Perovskite Photocatalysts for Environmental Remediation

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Per- and polyfluoroalkyl substances (PFAS) are a ubiquitous class of stable, synthetic organic compounds that pose a significant threat to the health of humans and the environment. The fluorinated alkyl chain within PFAS molecules makes them impervious to environmental degradation and metabolic breakdown, exacerbating toxicity. There is a need to develop effective means of degradation.

Complex metal oxides with a perovskite (ABO_3) structure, such as $SrTiO_3$, are being investigated for photocatalytic water-splitting due to their unique photophysical properties. Aliovalent doping of Al^{3+} into the B site within these structures replaces the Ti^{4+}, thus preventing the self-reduction to Ti^{3+} mid-gap states and reducing recombination rates. This method has been shown to enhance photocatalytic efficiency by >100-fold relative to un-doped samples[1]. Aliovalent doping as a form of defect engineering may prove pertinent to improving photocatalysis activity across a range of applications.

This presentation will investigate the viability of transferring this technique to organic pollutant degradation, particularly PFAS. The effect of Al doping density on rates of photocatalysis using methyl orange as a model pollutant will be discussed, and results reported for a solid-state reaction of $SrCO_3$ and $TiO_2$to yield $SrTiO_3$, which then underwent a $SrCl_2$ flux-mediated reaction with AlO_3 to dope controlled amounts of Al into the perovskite structure. Conformation of these structures was obtained through X-ray diffraction (XRD), UV-Vis diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). Photocatalytic remediation of the model pollutant methyl orange showed a strong dependence on Al concentration.

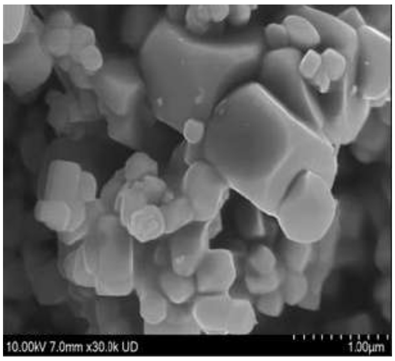

Figure 1. SEM imaging of $SrTiO_3$ doped with 5 mol% Al.

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C104

Light Harvesting with Organic Fluorophores

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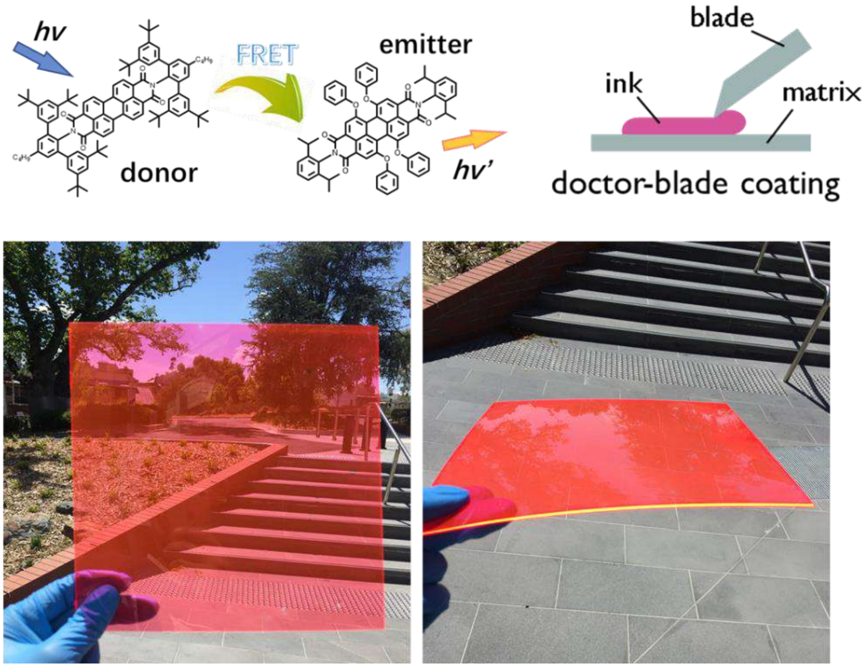
Light harvesting is an integral part of energy conversion of sunlight into chemicals and electricity. Luminescent solar concentrators (LSCs) are light harvesting devices that are ideally suited to light collection in the urban environment where direct sunlight is often not available. LSCs consist of highly luminescent compounds embedded or coated on a solid substrate that absorb solar radiation over a large area. The resulting luminescence is waveguided to the thin edges of the substrate where the concentrated light can be used by photovoltaic devices. There are many energy loss pathways in an LSC device, some of which can be addressed through designing new chromophores.

Our work on LSCs examines the use of emissive dye aggregates and energy migration strategies to enhance light harvesting from the perspective of the chromophore.[1] We have successful demonstrated the incorporation of dyes with aggregation-induced emission behaviour as well as molecularly insulated fluorophores in LSC devices. We have also demonstrated selective alignment of fluorophores to improve light trapping efficiency as well as fabrication of large-area LSCs by doctor-blade coating. This presentation summarizes our work and discusses future directions.



Chemical structures of a perylene diimide donor-acceptor FRET pair used in a light harvesting coating.

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C105

Effect of Organic Spacer Cation on Dark Excitons in 2D Perovskites via Magneto-Optical Spectroscopy

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Two-dimensional (2D) perovskites have attracted significant attention in recent years due to their unique optoelectronic properties.[1,2] They have shown promise for optoelectronic applications, including solar cells with enhanced stability[1] and light-emitting diodes.[2] However, a comprehensive understanding of their electronic and optical properties is currently lacking, despite being crucial for further advancements in these technologies. Here, we use temperature-dependent magneto-optical spectroscopy to gain insight into the influence of the organic spacer on dark excitons in Ruddlesden–Popper (RP) perovskites.[3] Using this method, the spin-forbidden dark-exciton state can be identified and its emission properties significantly modulated, up to temperatures of 15 K. At low temperatures, an increase in collected photoluminescence efficiency of >30% is demonstrated, and we describe this mechanism arising from a transfer of oscillator strength from bright to dark exciton states. The exciton fine structure and the degree of magnetic-field-induced mixing are significantly impacted by the choice of organic spacer cation, with 4-methoxyphenylethylammonium (MeO-PEA) showing the largest effect due to larger bright–dark exciton splitting. We have also found significant evidence that a lower energy state interacts with the dark exciton state in $(PEA)_2PbI_4$ and $(MeO–PEA)_2PbI_4$ and mimics its magnetic-field-induced photoluminescence brightening. Overall, these findings provide valuable insights into the underlying mechanisms behind the exciton fine structure in 2D perovskites and highlight the importance of the organic spacer cation in controlling their optoelectronic properties. Our results are important for the design and development of next generation, efficient photovoltaic devices and other optoelectronic technologies based on 2D perovskites.

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C106

Coupling Singlet Fission Molecules to Mixed Dimensional Perovskites

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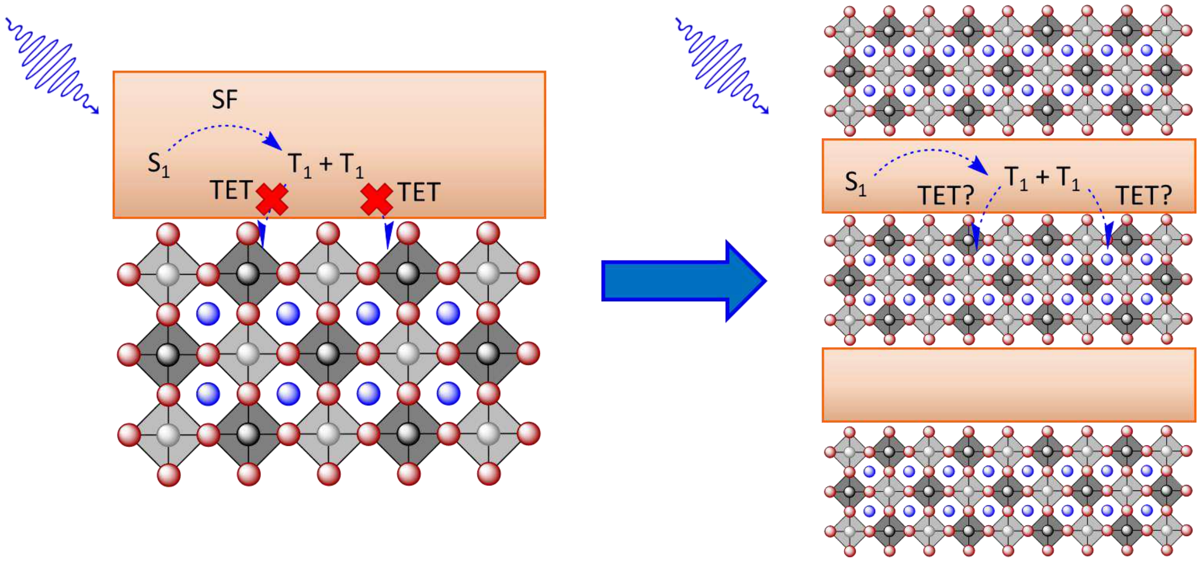
The coupling of singlet fission capable molecules to bulk semiconductors is a potential route to overcoming the Shockley-Queisser limit of single-junction photovoltaic cells.[1] The major obstacle that is commonly encountered in attempts to do this is the lack of the necessary triplet energy transfer from the organic overlayer where singlet fission occurs to the bulk semiconductor.[2-4] This has been partially attributed to the lack of a sufficient interface forming between the two materials.

We have investigated the potential of incorporating singlet fission capable molecules into mixed-dimensional Ruddlesden-Popper and Dion-Jacobson phase lead and tin halide perovskite thin-films. Preliminary work has resulted in several novel perovskites that display promising signatures of energy transfer between the incorporated singlet fission capable molecules and perovskite phase, suggesting that these materials may hold promise in uniting singlet fission with bulk semiconductors.



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C107

Active characterizations of biological macromolecules at the single-molecule level by optical tweezers-coupled Raman spectroscopy

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Intrinsically disordered proteins (IDP) lack stable secondary structures as monomers in aqueous environments, but sometimes self-assemble into oligomers with various structures and further grow into amyloid fibrils, which are associated with the incurable neurodegenerative diseases. However, the detailed molecule mechanisms remain unclear due to the challenge of detecting the transient, low-populated, and heterogeneous oligomers among predominating monomers.

Here, we develop an in situ optical tweezers-coupled Raman spectroscopy to visualize and control the hotspot between two Ag nanoparticle-coated silica beads, generating tunable and reproducible surface-enhanced Raman spectroscopy (SERS) enhancements with single-molecule level sensitivity. This dynamic SERS detection window is placed in a microfluidic flow chamber to detect the passing-by proteins, which precisely characterizes the structures of three globular proteins without perturbation to their native states. It resolves the structural variations of alpha-synuclein arisen from its transient species in the low population at physiological concentration, which are buried under the averaging signals in the conventional bulk measurements but crucial for the initiation of its amyloid aggregation associated with Parkinson’s disease[1]. Furthermore, we have constructed a simple plasmonic junction between two silver nanoparticle-coated silica microbeads to exert optical plasmonic trapping upon on/off laser excitation to control the formation of dynamic nanocavity with high turnover efficiency, reaching single-molecule level sensitivity to unveil rare pH-dependent amylin (hIAPP) species[2]. In addition, our platform offers extra control to trigger the photo-sensitive proteins and characterize their cellular functions simultaneously, holding the promise to regulate and resolve the structural details of individual biomolecules in complex systems[3].

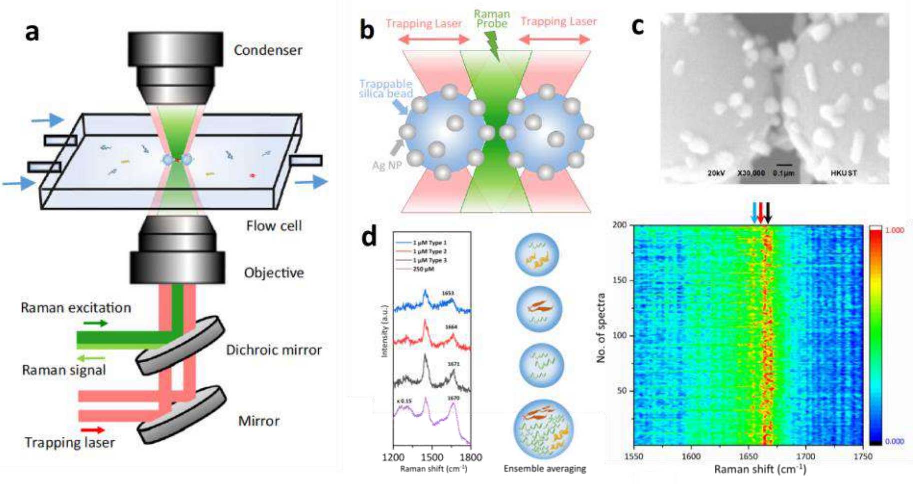

Fig.1 a. Optical tweezers-coupled Raman spectroscopic platform. b. Illustration of controllable hotspot. c. SEM image of Ag nanoparticle-coated silica beads. d. Spectra of alpha-synuclein.

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C108

Observation of lasing dynamics in a $CH_3NH_3PbBr_3$ crystal by femtosecond transient absorption microscopy

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Organic-inorganic lead halide perovskite materials have various attractive properties for solar cells and LED and nanoscale lasers because of their wavelength tunability and low lasing threshold. Such an efficient lasing is indispensable for their applications, and the essential needs are miniaturization and low threshold. However, the low-threshold lasing mechanism of lead halide perovskites has not been established due to various theories on the interaction state between light and carriers generated in the cavity at the initial stage and the carrier-carrier interaction state, which has greatly hindered progress in improving performance.

In the present study, we have measured transient absorption spectra and transient absorbance images of a single $CH_3NH_3PbBr_3$ microcrystal using a femtosecond transient absorption microscopy to reveal the initial carrier process that induces nonlinear luminescence[1].

Fig. 1(a) shows the transient absorption spectra of lead halide perovskite excited at the intensities below the lasing threshold. The spectral signals that were not observed before the time origin (-1 ps) were significantly observed with modulated spectral shape after the time origin (≥0 fs). The spectral bleaching around 540 nm indicates carrier generation by the excitation light, and the relaxation of the bleaching indicates the recombination of electrons and holes. Fig. 1(b) shows the transient absorption spectra of lead halide perovskite excited at the intensities over the lasing threshold. A bleaching signal appeared at around 557 nm, that was not represented in the transient absorption spectrum excited at the intensity below the lasing threshold. This signal is suggested to be due to amplified stimulated emission[2].

We will discuss the mechanism of modulation and low threshold lasing at the conference site.

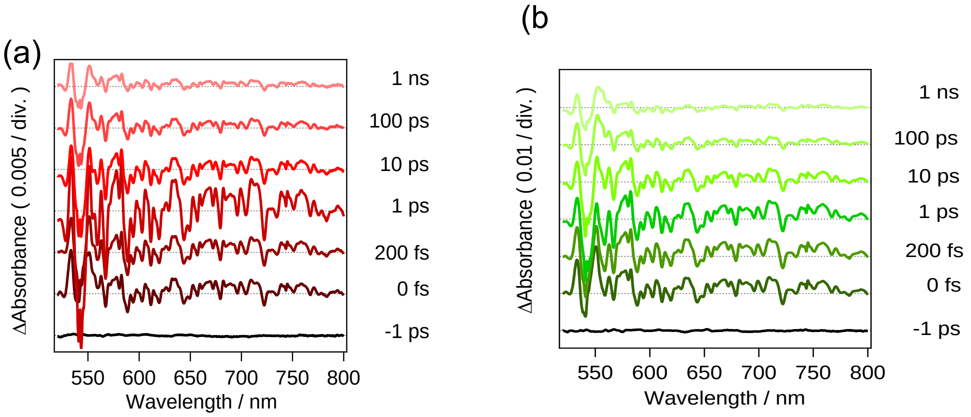

Fig. 1. Emission image of lead halide perovskite excited with a femtosecond laser pulse at 400 nm. Excitation light intensities were (a) 4.2 mJcm^{-2} and (b) 11.4 mJcm^{-2}.

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C109

Intermittency Analysis: Probability Density Distribution (PDD) to Fluorescence Lifetime Correlation Spectroscopy (FLCS)

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Charge trapping in semiconductor quantum dots (QDs) causes interruptions in the fluorescence intensity, when investigated on a single particle level, called photoluminescence (PL) intermittency or PL blinking.[1] Intensity fluctuations can be utilized for exploring trap state distributions and charge carrier dynamics in individual QDs, which are otherwise masked in ensemble-level measurements. In a single QD, a broad distribution of blinking rates is observed, resulting in high PL ON-state and low PL OFF-state ranging from microseconds to hundreds of milliseconds. We recently studied the PL fluctuations in CdSe QDs using time-resolved PL spectroscopy, at the single-particle level, by systematically varying its core size and maintaining a constant shell thickness. We calculated the trapping and de-trapping dynamics of charge carriers using probability density distribution (PDD) analysis.[2] In this case, blinking analysis requires a user-defined bin time and threshold to separate ON- and OFF- events. Later, we analyzed the blinking of the CdSe/CdS dot in a rod using fluorescence lifetime correlation spectroscopy (FLCS). The photons in the intensity time trace are assigned to emission originating due recombination of excitons from band edge or from trap state based on their lifetime, and after that, autocorrelation functions (ACF) are constructed. The ACFs for each process are fitted using the stretched exponential equation, and the characteristic blinking time constant is calculated. FLCS of immobilized QDs were successfully used to interpret and derive the photophysical properties which cause the PL intermittency.[3] The method presented in the poster can pave the way for the unbiased, threshold-free analysis of PL intermittency of QDs in the microsecond to millisecond time window.

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C110

Machine Learning for Investigating the Factors Contributing to the Performance of $WO_3/BiVO_4$ Photoanode Electrodes

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Photo electrodes combining WO_3 and $BiVO_4$, called as a heterojunction, have been reported as a promising material due to their band position matching and efficient charge separation. However, heterojunction electrodes exhibit more complex factors influencing photocurrent compared to single-layer electrodes. Previous studies have attempted to enhance photocurrent values by adjusting fabrication conditions based on research and experience. However, the impact of these changes remains unclear due to limited understanding of the structural and physical factors affecting electrode performance. To address this, we developed a machine learning-based method that correlates analytical data with photocurrent values for bare hematite and $BiVO_4$ electrodes, uncovering unknown factors for the performance [1] [2]. In this study, I applied this method to $WO_3/BiVO_4$ electrodes and identified key factors influencing photocurrent density.

Sixty electrodes were analyzed using photocurrent density measurement, X-ray diffraction (XRD), photo-electrochemical impedance spectroscopy, and UV/Vis diffuse reflectance spectroscopy. Through 5-fold cross-validation, three descriptors were selected for predicting photocurrent density. The prediction model achieved a coefficient of determination (R^2) of 0.81 for training data and 0.79 for test data, indicating its ability to capture photocurrent density trends. The identified factors included XRD peak intensities associated with $BiVO_4$ (strong correlation with photocurrent), the absorption edge for $BiVO_4$, and the [004] facet peak intensity in XRD for WO_3. The descriptors related to $BiVO_4$ were particularly significant, indicating that the optimization should involve $BiVO_4$ crystallinity and its absorption edge. Future plans involve heterojunction

optimization based on these identified descriptors.

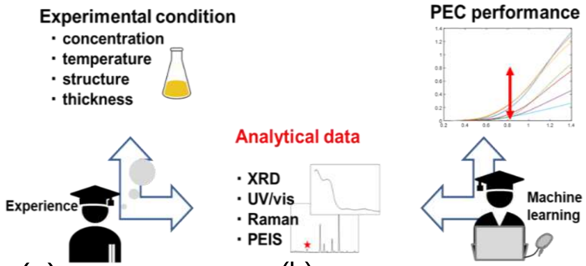

Figure 1. Scheme of applying machine learning method to optimize the photo device with analytical data

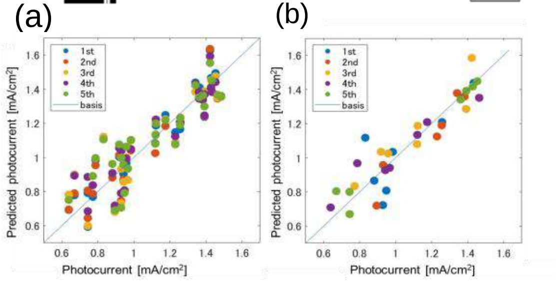

Figure 2. Scatter plots of predicted photocurrent versus real measured photocurrent

(a) Training dataset, R2 = 0.81,

(b) Test dataset, R2 = 0.79

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C111

Efficient Binding Au_9 Clusters to $SMTiO_2$: Study of Photocatalytic Degradation of Azo Dyes by RSM

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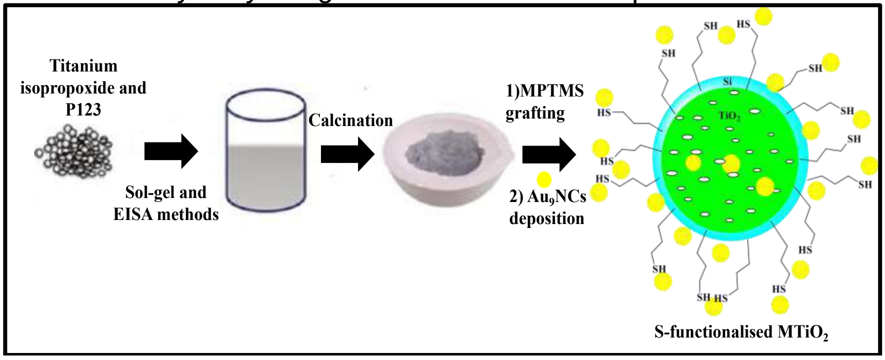
Since the concept of a green planet came into existence, energy demand, fossil fuel depletion, and the impacts of pollution on the environment have risen to become substantial global challenges for humanity. So, in this study, we are working on clean drinking water scarcity, which is among the concerns of a grown potential ecological disaster that is seriously threatening human well-being. Chemical and food industries make hazardous run-offs, the leading causes of water pollution today [1]. An effective strategy to solve these environmental crises is to employ semiconductor-mediated photocatalysis at competitive costs, ecological friendliness, recyclability, great accessibility, and excellent degradation effectiveness. A range of procedures have been applied to increase the photocatalytic activity of semiconductors. It can be achieved by two kinds of modifications: i) morphological modifications and ii) chemical modifications. The3 first can be achieved by using porous networks and the second by incorporating additional components onto the surface to inhibit the recombination of the photogenerated electron-hole pairs or/and increase the active sites enhancing the photocatalytic activity [2].

Gold nanoclusters smaller in size than Au nanoparticles are used to modify surface properties. The number of atoms forming an Au NC strongly influences the catalytic properties of cluster-modified surfaces. Agglomeration of NCs, however, leads to an increase in NC size and a loss of the size dependent properties of the NC, and should be avoided [3].

Mesoporous TiO_2 semiconductors with a high density of surface defects, high surface area, and extensive 3D pore network are used in the present work to prevent agglomeration of Au clusters [4]. Surface functionalizing methods are used to achieve strong bonds between Au_9NCs and the $MTiO_2$ surfaces. Photocatalytic dye degradation results will be presented.



Au_9NCs/$SMTiO_2$ nanocomposites preparation procedure

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C112

Evolving Hydrogen Gas Using Triplet Excitons Of An Organic Photocatalyst

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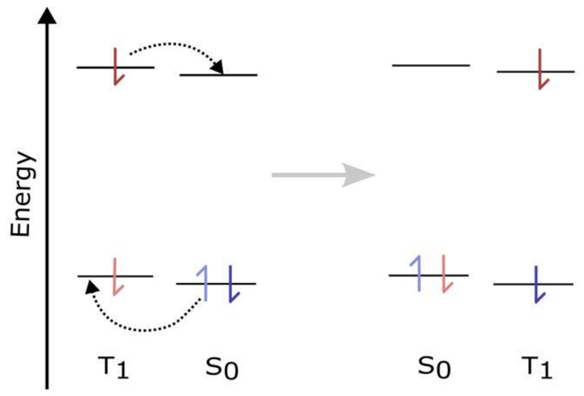
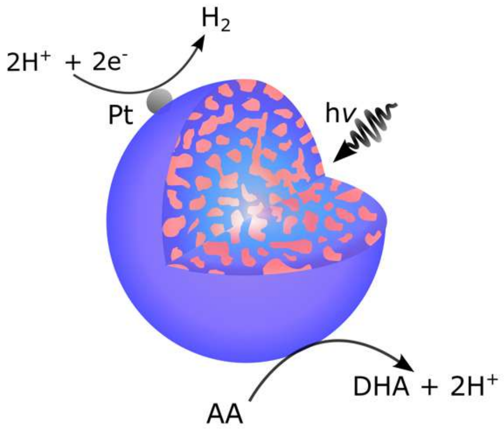
Hydrogen gas (H_2) is an important resource that has been gaining significant attention due to its use as a carbon-free fuel. However, the main methods of H_2 production currently use carbon-based fossil fuels, resulting in the release of carbon dioxide. A possible cost-effective, green alternative is photocatalytic H_2 evolution using nanoparticles of organic semiconductors. Typically, this process uses light to generate a singlet excited state (exciton), which then undergoes charge separation at interfaces between an electron donor and acceptor material. In this work, however, we present a novel approach of using the triplet exciton to potentially increase the efficiency of H_2 evolution. Triplet excitons are long-lived species due to their spin-forbidden relaxation to the ground state. As a result, exciton losses in the organic semiconductor may be reduced due to the long excited-state lifetime, allowing excitons a long time to separate into charge. The use of triplets could pave the way for singlet fission, a process that converts a singlet into two triplets, to be explored for maximising the efficiency of H_2 evolution in organic semiconductors.



Triplet Energy Transfer



Evolving Hydrogen Gas Using Triplet Excitons

SPONSOR PRESENTATION

SP001

ByteScience: A Large Language Model Platform to Extract Complex Structured Materials Information at Scale

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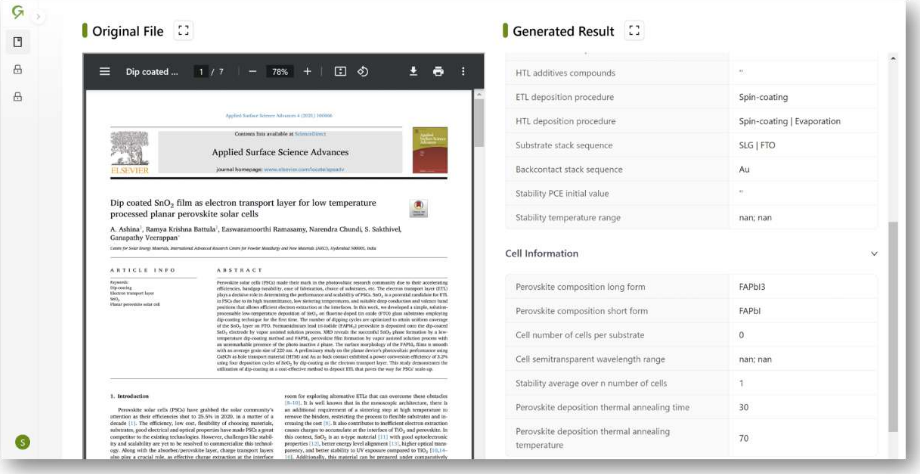
The emerging field of Materials Informatics, blending materials science with machine learning, promises significant advancements in the understanding, selection, development, and discovery of novel materials. However, a major challenge lies in the scarcity of structured empirical data, as most information resides in unstructured text formats within scientific literature. This work introduces ByteScience, a novel cloud-based Large Language Model (LLM) platform, specifically designed to address this issue by extracting structured materials data from extensive scientific corpora.

ByteScience leverages Natural Language Processing (NLP) and structured information inference (SII) to efficiently transform unstructured text into structured, machine-readable data. It utilizes an open-source, nature-science-dedicated LLM named DARWIN for this task. Our platform allows researchers and engineers to fine-tune this LLM with minimal annotations, creating a customized material structure data extraction tool. This enables the rapid extraction of high-quality material data from millions of documents, significantly enhancing the capabilities in materials engineering.

The platform's architecture, developed on AWS cloud service, supports a zero-code, fully automated pipeline for custom model creation and data extraction. It demonstrates exceptional accuracy and recall in information extraction, requiring only 20 to 50 well-annotated papers for effective fine-tuning. The ByteScience platform, thus, stands as a transformative tool in the field of Materials Informatics, offering an unprecedented ability to unlock the vast reservoir of empirical material data embedded in scientific literature.



Applied Surface Science Advances

Dip coated SnO_2 film as electron transport layer for low temperature processed planar perovskite solar cells

A. Ashina[1], Ramya Krishna Battula[1], Easwaramoorthi Ramasamy, Narendra Chundi, S. Sakthivel, Ganapathy Veerappan*

ARTICLE INFO

ABSTRACT

HTL additives compounds	''
ETL deposition procedure	Spin-coating
HTL deposition procedure	Spin-coating | Evaporation
Substrate stack sequence	SLG | FTO
Backcontact stack sequence	Au
Stability PCE initial value	''
Stability temperature range	nan; nan

Cell Information

Perovskite composition long form	FAPbI3
Perovskite composition short form	FAPbI
Cell number of cells per substrate	0
Cell semitransparent wavelength range	nan; nan
Stability average over n number of cells	1
Perovskite deposition thermal annealing time	30
Perovskite deposition thermal annealing temperature	70

Figure 1. Screenshot of ByteScience user interface showing an example article's data extraction outcome.

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POSTER PRESENTATIONS

PP001

Solvent Dielectric Delimited Nitro-Nitrito Photorearrangement in a Perylenediimide Derivative

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The discovery of vibrant excited-state dynamics and distinctive photochemistry has established nitrated polycyclic aromatic hydrocarbons as an exhilarating class of organic compounds.[1] We report the atypical photorearrangement of nitro-perylenediimide (NO_2-PDI) to nitrito-perylenediimide (ONO-PDI), triggered by visible-light excitation, giving rise to linkage isomers in the polar aprotic solvent acetonitrile (ACN, Figure 1).[2] ONO-PDI has been isolated and unambiguously characterized using standard spectroscopic, spectrometric, and elemental composition techniques. Although nitritoaromatic compounds are conventionally considered to be crucial intermediates in the photodissociation of nitroaromatics, experimental evidence for this has not been observed heretofore.[1] Ultrafast transient absorption spectroscopy combined with computational investigations revealed the prominence of a conformationally relaxed singlet excited-state (S_1^{CR}) of NO_2-PDI in the photoisomerization pathway.[3,4] Theoretical transition state (TS) analysis indicated the presence of a six-membered cyclic TS, pivotal in connecting the S_1^{CR} state to the photoproduct state. This work addresses the prevailing knowledge gaps in the field of organic linkage isomers and provides a comprehensive understanding of the unprecedented photoisomerization mechanism operating in NO_2-PDI.

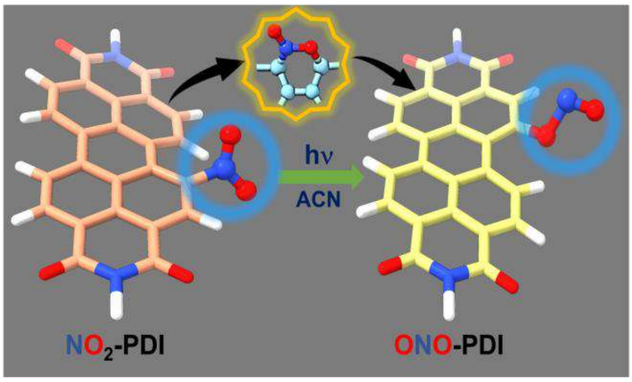

Figure 1. Pictorial representation of the photorearrangement of NO_2-PDI to ONO-PDI in acetonitrile solvent triggered via visible light excitation.

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PP002

Excitation Wavelength Dependent Fluorescence in Crystalline Tetrabromodibenzo[a,e][8]annulene

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Wide-range tunable emission colors in the crystalline state of single fluorophores are a formidable task.[1] We report a tetra-bromo dibenzo derivative of cyclooctatetraene (**DBCOT-Br$_4$**) exhibiting excitation wavelength-dependent fluorescence in a kinetically stable polymorphic form via strong electronic coupling among the individual molecules (Figure1).[2] Depending on the solvent evaporation rate, **DBCOT-Br$_4$** crystallized in unique kinetically and thermodynamically stable polymorphic forms evidencing distinct excitonic interactions. One of the polymorphs showcasing excitation wavelength-dependent fluorescence properties has shrunk in the cyclooctatetraene core with a higher torsional angle than the other polymorph. The two polymorphs revealed diversity modulated by non-covalent weak interactions in three-dimensional packing and room-temperature phosphorescence properties. A significant contribution towards nonadiabatic coupling and weak spin-orbit coupling highlights the relevance of vibrational pathways in the crystalline tetra-brominated dibenzo derivative of cyclooctatetraene.

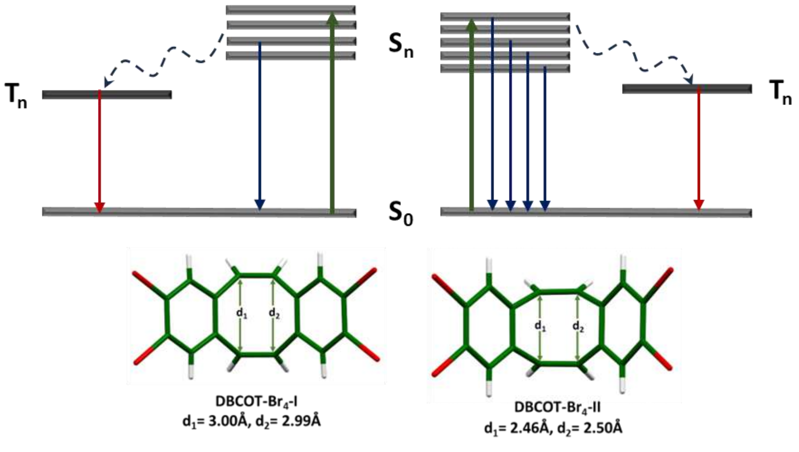

Figure 1: The excitation wavelength-dependent fluorescence in one of the polymorphs of cyclooctatetraene derivative via strong electronic coupling.

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PP003

Induced Photocatalytic Activity by Self-Assembly of NIR Dyes and the Hybridization System with an Enzyme

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Near-infrared (NIR) light, with wavelengths above 700 nm, accounts for 52% of solar energy and holds significant potential for solar energy conversion. NIR light exhibits better biopermeability than visible light and suppresses cell damage due to its lack of interaction with endogenous chromophores. This excellent property has led to the development of photomedicine applications, such as photodynamic therapy (PDT) and photopharmacology, targeting deep tissues. Therefore, NIR light has great potential for both solar energy utilization and medical applications. To date, numerous photocatalysts based on inorganic or polymer compounds have been developed[1]. However, these photocatalysts primarily function under high-energy visible light. NIR photocatalysts are still rare, and there is currently no established design for them.

In this study, we have discovered that a supramolecular assembly of an amphiphilic rhodamine derivative functions as a NIR photocatalyst (Figure 1). We have previously demonstrated that xanthene dyes acquire photocatalytic activities through self-assembly in aqueous solutions[2,3]. In the supramolecular assemblies, charge separation states are formed upon photoirradiation, and the generated holes and electrons undergo various redox reactions. Here, we reveal that a supramolecular assembly of NIR dyes also exhibits photocatalytic activity. In this presentation, we will discuss the molecular design and the mechanism behind this emergent photocatalytic activity. Furthermore, we have successfully created a hybrid system by combining the NIR supramolecular photocatalyst with an enzyme for artificial photosynthesis. The supramolecular photocatalyst and the enzyme function orthogonally in the mixture, and their reactions proceed cooperatively to generate energy carrier chemicals using NIR light.

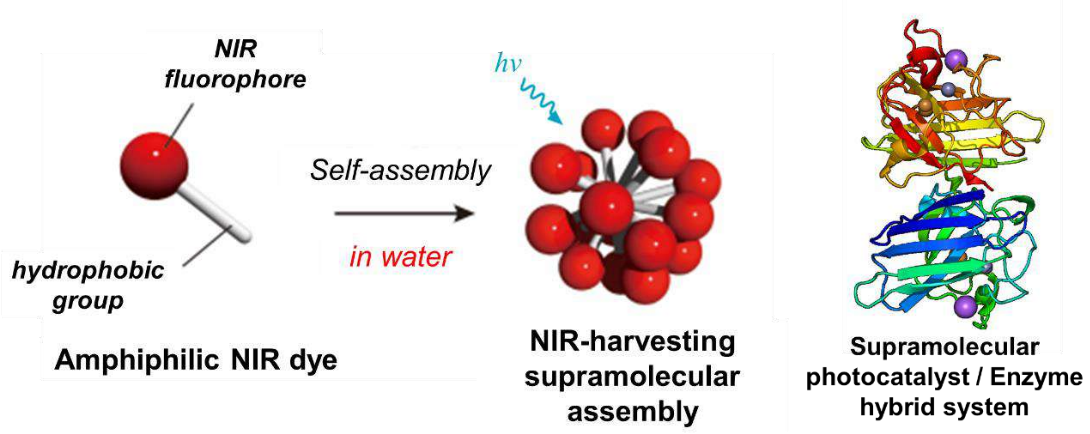

Figure 1. Schematic representation of a supramolecular photocatalyst based on an amphiphilic near-infrared (NIR) organic dye, along with its hybridization with an enzyme for artificial photosynthesis.

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PP004

A Multimodal Ultrafast Transient Absorption Microscope for Next Generation Photovoltaics

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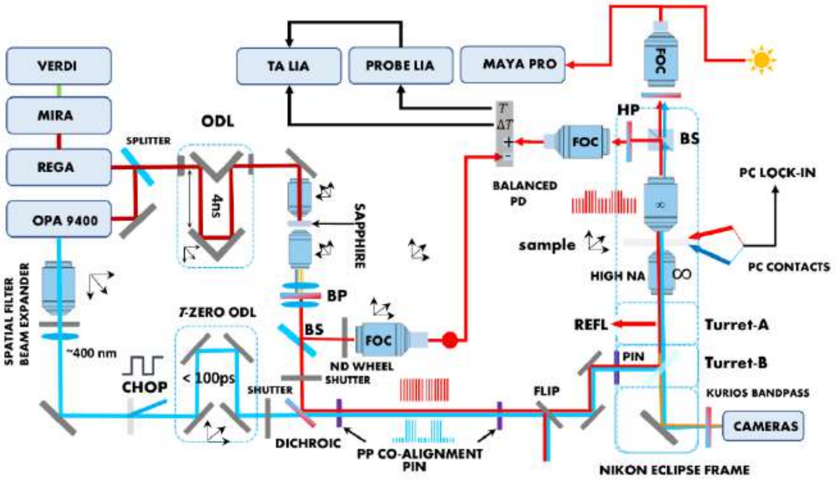
Advanced optical techniques like Ultrafast Transient Absorption Microscopy (TAM) have proven extremely useful in elucidating charge carrier dynamics in absorber films and polymer blends for next generation photovoltaics[1–5]. Nowadays however, the photophysics of carrier generation and relaxation requires further, spatially correlated information to provide impactful results. To this end, multimodal TA microscopy is fast becoming a norm in the field. In this presentation we describe and illustrate by way of example the multimodal ultrafast TAM developed at the University of Melbourne. Numerous modes include Transient Absorption (TA), Intensity Modulated Photocurrent Microspectroscopy (IMPS imaging)[6], TCSPC and hyperspectral absorption microscopy are included. The system is briefly reviewed with an emphasis on obtaining a Signal-to-Noise ratio high enough to afford rapid scanning of fragile materials such as perovskite and OPV materials. Several of the correlative modes are explored for the case of perovskites and Y6:PM6.



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PP005

Multiple aggregation pathways of the non-fullerene acceptor Y6 and its impact on exciton dissociation

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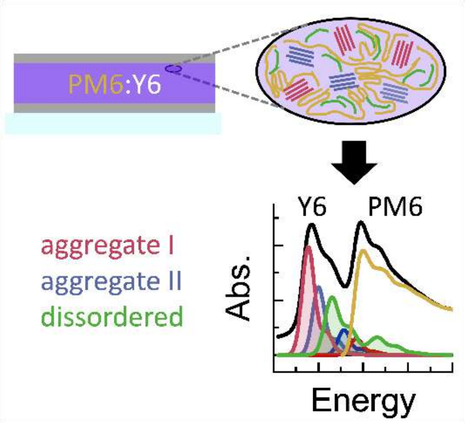
The efficiencies of single-junction organic solar cells (OSCs) based on non-fullerene acceptors (NFAs) have recently considerably improved, achieving power conversion efficiencies (PCEs) of over 19%. This advancement was induced by the introduction of the Y-type NFAs, with the most prominent representative Y6. Due to this enormous improvement, a lot of groups put effort into understanding the correlation between film properties and the outstanding optoelectronic properties, in particular blended with the donor material PM6. Here, in NFA acceptors the opto-electronic properties of the device not only depend on the chemical structure of the compound, but also strongly on the morphology, and therefore, intermolecular interactions or order.

We want to contribute to the understanding of the blend film morphology by performing a detailed investigation and analysis of the aggregation behaviour of Y6 and PM6.[1,2,3] To first gain an insight of the signatures of aggregates and the aggregation behaviour, we use temperature-dependent steady-state UV-Vis absorption and photoluminescence (PL) spectroscopy combined with Franck-Condon analysis of the neat materials. Then we transfer the gained knowledge to blend films with PM6. We find that Y6 forms two types of aggregates,[1] the ratio of which can be controlled by using solvent additives. We investigate the film formation and aggregation process of those different systems by in-situ absorption and PL measurements during spin-coating and find significant differences in the film formation, which we can attribute to the different solvent additives. Additionally, we study the impact different aggregation of Y6 has on the exciton dissociation by performing transient absorption measurements.



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PP006

Evaluation of Oxygen Evolution Activities of Micro-structured Electrode via Video Observation

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Water electrolysis is an important method for the industrial hydrogen production. The oxygen evolution reaction (OER) is a anodic counterpart in the cathodic hydrogen evolution reaction. The multiple processes in the OER can be a problematic for the efficient energy catalysis. In addition, water electrolysis under neutral condition is more challenging in acidic or basic condition. This is because water molecules possess the low electrochemical reactivity. To date, various OER catalysts have been investigated.[1] The reaction efficiency can be further improved by controlling the interfacial hydration structure at electrode-electrolyte interface.[2]

Recently, it has been reported that vibrational strong coupling of molecular vibrations and cavity mode can be an alternative strategy for the modification of molecular properties. We showed that the vibrational coupling of OH stretching mode with cavity mode increases proton conductivity via dynamic hydration modification.[3] Here, we utilized micro structured electrode for the coupling with the water molecules via vibrational strong coupling toward efficient OER process.

We fabricated micro-structured electrode. Micro-structured glass substrate was fabricated by photo-lithography and dry etching methods. Ni was vapor-deposited to use for micro-structured electrode. The OER catalytic activity of structured electrode was evaluated simultaneously by generated O_2 bubbles from micro-structures. As a results, modulation of OER activity depending on micro-structured electrodes was confirmed. It provides a new guideline for controlling the catalytic activity of OER by the surface structure of the electrodes.

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PP007

Observation of carrier diffusion dynamics between monolayer and few-layer WSe$_2$ by femtosecond transient absorption microscopy

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Introduction

Recently it has been reported that transition metal dichalcogenides, which are layered materials, exhibit novel electrical conductivity and luminescence properties when exposed to a single layer and adsorbed on a substrate, attracting much attention. Although transition metal dichalcogenide materials are n-type semiconductors with relatively high mobility of electrons, WSe$_2$ is an essential material for fabricating electronic devices such as diodes and transistors because it exhibits p-type semiconductor properties. Since WSe$_2$ bilayers exhibit different physical properties depending on the stacking state, the measurement and analysis of these bilayers are more complicated than those of monolayers[1]. Therefore, we observed the carrier dynamics in a monolayer and bilayer WSe$_2$ using transient absorption microscopy.

Experimental

WSe$_2$ samples deposited on SiO$_2$ substrate by CVD method were used[2]. The detail of the wide field transient absorption microscopy set-up was previously reported[3].

Results and Discussion

Fig. 1a shows the transmittance image of the WSe$_2$ sample, and Fig. 1b shows the transient absorption image with monitoring at 760 nm (Ex. 400 nm, 15.1 μJ/cm^2) delayed at 1 ps after excitation. Transient absorbance is consistent with the transmitted image shading, especially the fact that the transient absorbance of the central triangle is twice as strong a signal as the surrounding monolayer, indicating that the center area is a bilayer. The modulation of transient absorbance was observed near the boundary between the WSe$_2$ monolayer and the bilayer. This result suggests the existence of charge-transfer absorption between the monolayer and bilayer. We will discuss the carrier diffusion dynamics between monolayer and bilayer WSe$_2$ at the conference site.

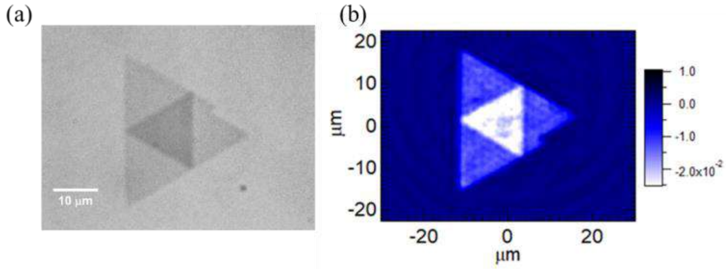

Fig.1 (a) A transmittance image of a WSe$_2$. (b) A transient absorbance image of a WSe$_2$ with monitoring at 760 nm.

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PP008

Photochromism of Binaphthyl-Bridged Asymmetric Imidazole Dimers

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Photochromic compounds have attracted much interest in recent years because of their potential applications as molecular switches for fluorescence, conductivity, magnetism, and the macroscopic shape of materials owing to their remote controllability with high temporal and spatial resolutions. Red or near-infrared (NIR) light responsive molecules have received much attention for biological and material applications because potentially harmful UV light for materials and cells is not required for the photochemical reactions. Although some molecular designs for photochromic molecules to increase the photosensitivity to red or NIR light have been reported, the strategies are limited to the extension of π-conjugation length and the utilization of charge transfer transition or energy and electron transfers.

Recently, we have achieved a successful synthesis of a binaphthyl-bridged imidazole dimer (BN-ImD).[1] This negative photochromic compound exhibits a distinctive behavior of isomerization when exposed to visible light, transforming from a stable colored isomer to a metastable colorless isomer through a biradical intermediate. The colored and colorless isomers of BN-ImD have five- and six-membered ring structures, respectively. Therefore, the colored isomers are denoted as 5MR and the colorless isomers are denoted as 6MR. The absorption band in the visible-light region of 5MR can be attributed to the π−π* transition on the diazafulvene chromophore. 5MR photochemically generates BR by the homolytic bond cleavage of the C−N bond upon visible-light irradiation. On the other hand, when 6MR is exposed to UV light, the C−C bond connecting the two imidazole rings of 6MR is homolytically cleaved to form BR. Photogenerated BR can then isomerize to either 5MR or 6MR in a kinetically controlled reaction. The energy levels of 6MR and BR are relatively close to each other, and 6MR is in equilibrium with BR. This means that 6MR can be converted to BR and back to 6MR through thermal excitation. Furthermore, we have also developed of BN-ImD derivatives, exhibiting near-infrared responsivity[2,3] or two-photon reactivity[4].

In this study, we have achieved the synthesis of asymmetric imidazole dimers bridged by a binaphthyl group. We will provide a comprehensive description of the synthetic methodology and the details of the photochromic properties.

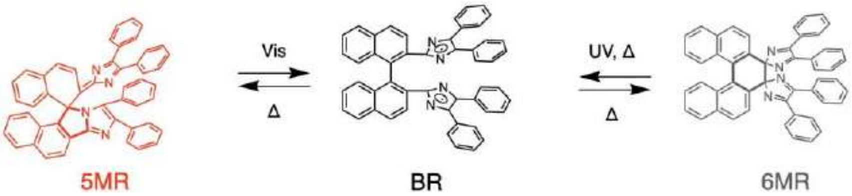

Figure 1. Negative Photochromic Reactions of BN-ImD.

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PP009

High-throughput Evaluation of Aggregation Induced Emission in Cyclometalated Iridium(III) Complexes

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Most luminophores are susceptible to aggregation caused quenching, whereby emission is significantly reduced in an aggregated state. Such quenching limits the utility of a given luminophore in applications where aggregates often form. In contrast, aggregation induced emission (AIE) sees increases in luminescence when molecules form higher order aggregates. This is beneficial for applications such as OLEDs,[1] bio-imaging,[2] bio-sensing,[3] and latent fingerprint detection[4] that depend on high-intensity luminescence.

Cyclometalated iridium(III) complexes are versatile luminophores owing to tunable emission energy, good photostability and high quantum yields. While select iridium(III) complexes are known to exhibit AIE, previous studies are *ad hoc* by design and the structural factors that elicit this phenomena remain poorly understood.[5,6] In this work we use a combination of high-throughput combinatorial synthesis and *in situ* analysis to evaluate the AIE properties of a large library (>1000) of discrete heteroleptic iridium(III) complexes of the type $[Ir(C^\wedge N)_2(N^\wedge N)]^+$, where C^N is a cyclometalated ligand bound through a carbon and a nitrogen and N^N is an ancillary ligand bound via two nitrogen's.

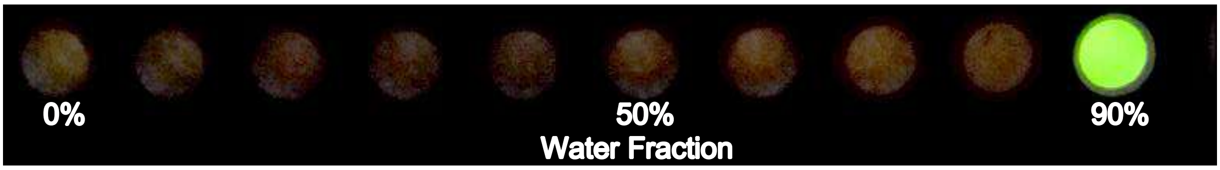

Figure: AIE of $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ in THF/water with increasing water fractions

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PP010

Systematic Investigation of the Exciplex Between Polycyclic Aromatic Hydrocarbons and *N,N*-dimethylaniline

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Exciplex is an emissive charge-transfer complex, formed by photo-induced electron transfer (PET) from a ground state donor (D) to photon-excited acceptor (A*). Due to its radiative properties, exciplex has been widely studied for PET mechanism and the development of organic light-emitting diode (OLED).

The aim of this work was to systematically investigate how the optical properties of exciplex depend on A/D pairs. A series of polycyclic aromatic hydrocarbons (PAHs), anthracene, pyrene, perylene, and tetracene were chosen as A and *N,N*-dimethylaniline (DMA) as D because they are well-known A/D pairs to form the exciplex.

Steady-state and time-resolved spectroscopy were measured, and a simple kinetic model was constructed to obtain the efficiency of exciplex formation and radiative decay. The results suggest that the large driving force (about 0.5 eV) of PET, coupled with the long lifetime of excited A, causes the high efficiency of exciplex formation. A strong correlation between the computationally calculated oscillator strength of exciplex and the efficiency of radiative decay of exciplex was found.

This study will provide insights into the understanding of exciplex systematically and offer the details on the radiative decay properties of exciplex formed between various PAHs and DMA.

PP011

Understanding Charge Transport in Disordered Carbon Nitride

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Carbon nitride, arguably, is the most popular metal-free polymeric semiconductor for various energy related conversion and storage applications, particularly for photocatalytic hydrogen production from water.[1] The photocatalytic performance of disordered carbon nitride (d-CN) is low which is mainly attributed to its poor transport of charge carriers.[2] This is largely due to the non-aromatic connection between the polymer strands of CN that causes photogenerated singlet excitons to be typically confined to the tri-*s*-triazine unit of CN.[3] The excitons in CN therefore experience larger binding energy (>> k_BT, here k_B is Boltzmann Constant, T is temperature in Kelvin. At room temperature, k_BT is ~0.26 mV) to be split into free electrons and holes due to electron–lattice and electron–electron Coulomb interactions.[3,4] To achieve a charge separated state, the exciton should be dissociated within its lifetime, which is in picosecond time scale.[5] Additionally, the carriers must survive recombination before reaching to the catalytic sites.

The charge transport becomes further exacerbated by the residual chemical defects (e.g., dangling bonds, interstitials, vacancies, etc.) in the crystal structure due to the incomplete polycondensation of precursor monomers or doping/adsorption of heteroatoms in C–N networks.[6] Pendant amine groups are the root cause of surface dangling bonds that create shallow trap states in CN and act as potential sites for charge carrier trapping.[7] Being in this regime, charge trapping detrimentally reduces the charge carrier mobility and makes the interfacial charge transfer difficult. It causes a kinetic competition between charge separation and non-radiative recombination at the semiconductor–water interfaces and therefore presents a significant photophysical challenge.[8]

To optimize the charge transport dynamics, it is often required to incorporate Pt as a co-catalyst. Reduced graphene oxide (rGO) instead of Pt can be employed as a metal-free cocatalyst to enhance the photocatalytic production of hydrogen. However, from a photo-physical point of view, the role of rGO as a co-catalyst is not well understood. With the help of ultrafast transient absorption spectroscopy, femtosecond time-resolved photoluminescence spectroscopy and transient photocurrent measurements, we explore and decipher the ultrafast dynamics of the photogenerated charge carrier separation and transport in d-CN facilitated by rGO. It is found that rGO substantially suppresses bimolecular and trap-assisted recombination and provides a faster separation of charge carriers. As a result, it increases the lifetime of the charge carriers to be transported to the surface catalytic sites

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PP012

Single-particle Investigations of Plexcitons in Bimetallic Nanorods

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Coupling between plasmons and excitons results in the emergence of novel spectroscopic features directed by the interaction energy. For example, strong coupling results in the formation of new bands,[1] whereas weak coupling leads to the enhancement of spectroscopic signals.[2] The plasmon-exciton interaction energies are often determined at the ensemble level, in solution, by tuning and detuning the plasmonic resonance frequency. Herein, we present an efficient method for determining the dispersion curves and the Rabi splitting energy of chromophore-bound bimetallic core-shell Au-Ag nanorods by recording their single-particle scattering spectra using dark-field scattering spectroscopy/microscopy in two ways: by placing them on a glass slide and a micron-reference transmission electron microscope grid.[3] The resonance frequency of the plasmonic system is varied by changing the thickness of the silver shell and investigating the coupling with the J-aggregates of 1,1′-diethyl-2,2′-cyanine iodide. The single-particle scattering spectra of bare Au@Ag NRs are conveniently recorded by removing the bound chromophore using methanol. The ensemble-level investigations provided similar dispersion curves and interaction energy, further confirming the reliability of the present method. Moreover, the DFM-TEM method presented herein provides a good correlation between the experimental scattering and the theoretical scattering spectra obtained using the finite-difference time-domain simulations.

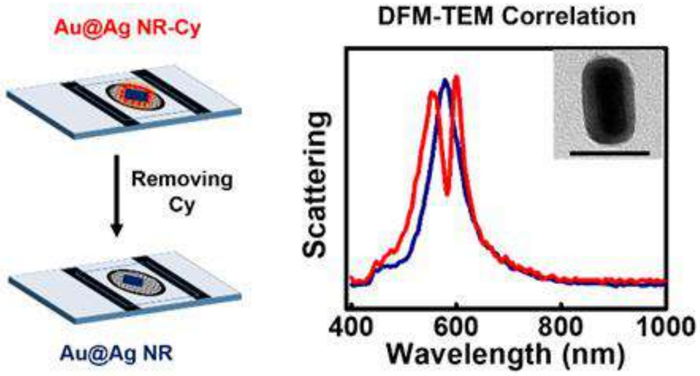

Figure 1: The single-particle investigation of plasmon-exciton coupling in bimetallic nanorods

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PP013

Landscape of Charge Carrier Dynamics in CdSe-CdS Heteronanostructures

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Band alignment in the heteronanostructures (HNS) is an indispensable parameter that dictates their carrier delocalization and photophysical properties.[1,2] Herein, we probe the dependence of the degree of delocalization of the electronic wave function in CdSe-CdS HNS with tadpole morphology by systematically varying the core size of CdSe and shell length of CdS.[3] This is achieved by investigating the exciton recombination and photoinduced electron transfer rates by employing time-resolved photoluminescence (PL) investigations at ensemble and single-particle levels. Neutral exciton lifetime extracted from PL blinking trace showed a linear dependence with the shell length of CdS and inverse relation with the core size of CdSe. Moreover, time-resolved single particle electron transfer to the acceptor molecule such as viologen resulted in a reduction in neutral exciton lifetime. This effect is prominent in the case of HNS with a smaller CdSe core size due to their prominent quasi type-II character. Our findings on the role of core size and shell length on the carrier delocalization in CdSe-CdS HNS is pivotal in designing HNS for various photophysical applications.

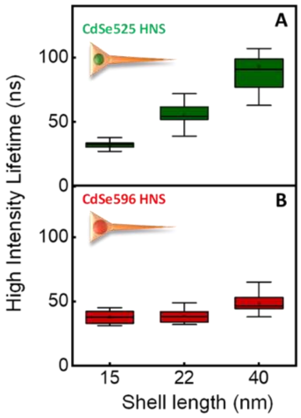

Figure. Box plots of high-intensity lifetime of (A) CdSe525CdS HNS and (B) CdSe596CdS HNS as a function of CdS shell length.

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PP014

Plasmon Modulation in $Cu_{3-X}P$ Nanocrystals

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Degenerate doping of semiconductors generates excess free carriers. Oscillation of these carriers upon interaction with an external electric field result in a plasmon resonance in IR or THZ region.[1] Most of these semiconductors are either metal oxides or chalcogenides. Many studies have been conducted to understand the origin, modulation and application of plasmon resonance in these materials.[2]

One of the relatively less explored semiconductors in this regard is non-stoichiometric copper phosphide ($Cu_{3-x}P$). Due to Cu vacancies, plasmon resonance is generated in the IR window.[3] Non-stoichiometric $Cu_{3-x}P$ nanocrystals has found application in electrocatalysis, photothermal therapy and synthesizing phosphide-based semiconductors.[4] It is important to note that all of these are related to the inherent Cu vacancies which in turn can be gauged by the intensity and frequency of the plasmon peak.

Here we demonstrate the modulation of plasmon peak in $Cu_{3-x}P$ nanocrystals[5] by varying the carrier concentration using redox chemistry. Oxidation results in the blueshift and enhancement of plasmon resonance whereas reduction induces redshift and attenuation of plasmons . Further, these changes were reversible upon sequential redox treatment. We also present how temperature and ligand environment controls this plasmon. The results presented here serve as a precedent for fabricating $Cu_{3-x}P$ based electrochromic devices and monitoring activity of these materials in different applications.

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PP015

Tracking Heterogeneous Photochemical Reaction in Photoresponsive Crystals with Low-Frequency Raman Microscopy

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Photomechanical crystals are one of materials that directly convert the light energy into the mechanical motion by the change of the shape of assemblies through the photochemical reactions accompanied with the geometrical change at the molecular level. Photoreactions in these crystals often proceed heterogeneously due to interactions with neighboring molecules, leading to specific reaction behaviors. In the present work, to clarify the heterogeneous kinetics in photomechanical crystals, we analyzed the photopolymerization reaction of a distyrylpyrazine derivative[1] (DSP, Figure 1a) in the crystalline phase using low-frequency Raman microscopy, which enables us to detect not only molecular-level vibrations but also mesoscale changes in crystal structure.

Figure 1b shows a series of Raman spectra of a single DSP crystal recorded during ultraviolet irradiation at 365 nm. The spectrum at 0 second is characterized by several Raman peaks, which are ascribable to vibrational modes of the DSP monomer. Upon the irradiation, this spectral pattern decreases in several tens of seconds, and other Raman peaks show up at distinct wavenumber from the monomer. These Raman bands are attributable to the DSP polymer produced by the photopolymerization reaction in the crystal. To track the reaction kinetics in heterogeneous environments, we analyzed temporal changes of Raman intensity. Interestingly, the intensity due to the monomer more rapidly decreases at the edge of the crystal, indicating that the monomer at the edge has higher reactivity than at the center. This specific reactivity was confirmed by difference in the Raman frequency between the edge and center, and mesoscopic elasticity detected by atomic force microscopy (Figure 1c). In the conference site, we also discuss the reaction behaviors of photomechanical crystals detected by time-resolved fluorescence spectroscopy.

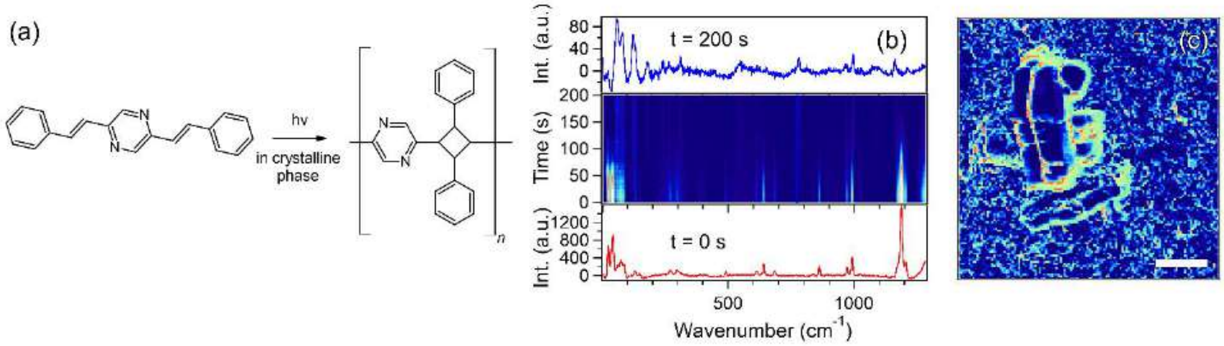

Figure 1. (a) Photopolymerization reaction of DSP in the crystalline phase. (b) Time evolution of Raman spectra of DSP crystals under irradiation. (c) AFM phase image. Scale bar: 500 nm.

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PP016

Surprising Temperature-Enhanced Fluorescence in Dye-Doped Porous Materials

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This study investigates the intriguing photophysical behaviour of acridine yellow (AY), when doped into the porous framework of magnesium aluminophosphate-11 (MgAPO-11). Utilizing hyper-imager microscopy and spectral analysis, we observed unusual photophysical phenomena upon heating our sample: a significant increase in fluorescence intensity, which deviates from conventional photophysical responses. This anomaly suggests the occurrence of reversed intersystem crossing (RISC), a process rarely observed in such systems. An Arrhenius plot of the system revealed two distinct slopes, indicating a potential transition point suggestive of significant changes within the system. This transition could be attributed to changes in the molecular structure of the AY, alterations in the framework of MgAPO-11, or possibly aggregation or disaggregation events within the sample. Other plausible explanations include the expulsion of water molecules from the crystalline structure or the initiation of proton transfers or other catalytic mechanisms.

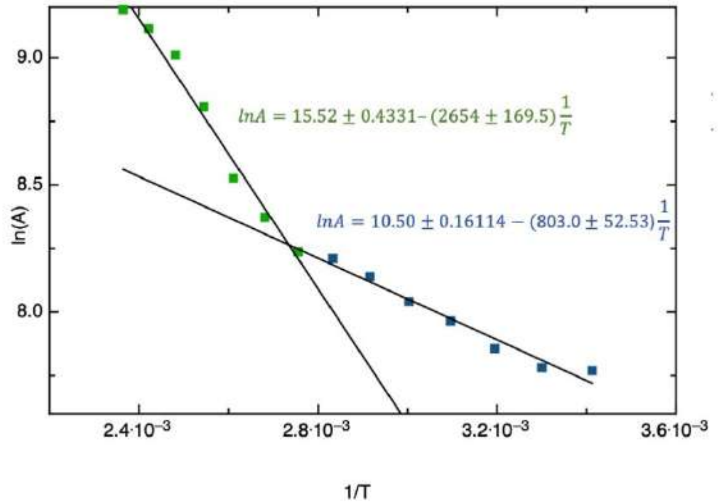

Figure 1: 1/T vs ln(A), where T is the temperature and A is the intensity

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PP017

The Formation of Water on Surfaces of Photocatalytic Water Splitting

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Photocatalytic water splitting is an appealing approach for using solar energy to produce and store hydrogen, which can be an environmentally friendly renewable fuel. However, only a few semiconductor materials can be efficiently employed for the water splitting process. One of the semiconductors that has shown great potential to be used in photocatalytic water splitting is $SrTiO_3$ (1). It was demonstrated that the photocatalytic activity of the prepared materials could be increased by applying noble metals and metal oxides as co-catalysts for the hydrogen and oxygen evolution reactions (H_2 and O_2) and metals oxide as overlayer to avoid the recombination of H_2O(2, 3). In this project, we have applied several strategies to study the water dissociation when adsorbing onto these materials. The co-catalyst decorated materials were prepared by sputtering and annealing in an ultra-high vacuum (UHV) to keep the samples clean. To achieve the objectives of this work, two main techniques based on electron spectroscopy were employed. They have been used to investigate the formation of the samples with or without water adsorption. Firstly, X-ray Photo-electron Emission Spectroscopy (XPS) was employed as a common technique to investigate the chemical compositions of the surfaces including the adsorbates. Secondly, Metastable Induced Electron Spectroscopy (MIES), the most surface-sensitive technology for analyzing the surface, have been used to measure the electronic structure of the material and to determine the molecular orientation on the outermost layer. This study examined the effects of water exposure on two samples. $SrTiO_3$ (100) single crystals and CrO_3 photodeposited on $SrTiO_3$ (100) single crystals have been studied to investigate the water dissociation. The XPS and MIES provided evidence of hydroxide OH and H_2O form the water dissection for both samples.

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PP018

Environmental controls reveal trap exciton dynamics in quantum dots

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One major challenge in nanoscience is understanding the complex physics and chemistry at the surface, especially for quantum dots (QDs) with a high surface-area-to-volume ratio. Surface traps formed by uncoordinated atoms on QDs can significantly affect carrier generation, transportation, and recombination.[1,2] These traps quench the QD's emission and generate low-energy fluorescence known as "trap emission". However, the mechanism behind trap emission is not well understood. In this study, we investigate the surface trap emission of a CdSe QD film under the modulation of oxygen pressure and we identify two types of traps.

As shown in Fig.1(a), increasing pressure in the presence of oxygen leads to oxygen adsorption, which passivates surface traps, resulting in increased core emission and decreased trap emission. Conversely, when pressure decreases and oxygen desorbs, more traps remain unpassivated, causing a decrease in core emission and an increase in trap emission. This aligns with a simple trap emission model illustrated in Fig. 1(b). However, the rates of change in core and trap emission are inconsistent with this model. When pressure increases, trap emission rapidly decreases while core emission only increases slowly. To explain it, we propose a modified model shown in Fig.1(c). In this model, there are two types of traps that provide nonradiative and radiative pathways, respectively. When pressure increases, oxygen immediately passivates the radiative channel, i.e., trap state 2, and thus suppresses trap emission. However, it takes a while to passivate the nonradative channel, trap state 1. Therefore, core exciton can still decay nonradiatively through trap state 1 before complete passivation. To validate the model, we also investigate temperature dependence of trap emission and the role of oxygen and light in trap passivation.

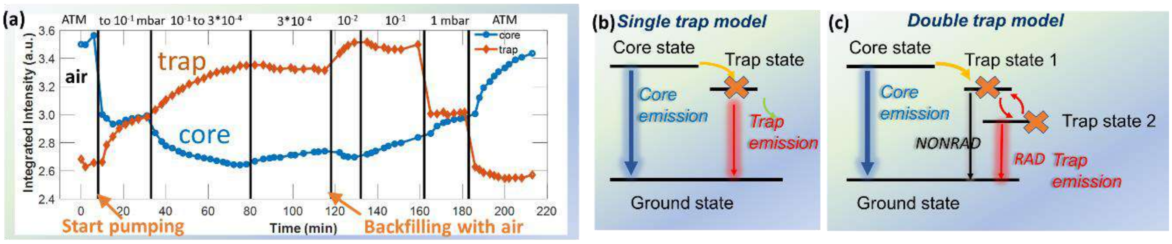

Fig. 1 Trap emission model: (a) Core and trap emission vs air pressure. Vertical black lines indicate the change of pressure. (b) Simple trap model. (c) Double trap model.

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PP019

Improving the visible absorption of photoactive iridium complexes

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Luminescent iridium(III) based complexes have gained lot of attention in the past two decades due to their wide applicability in many fields such as light emitting diodes, oxygen sensing, photocatalysis, bioimaging and electrochemiluminescence[1] as a result of possessing unique properties such as relatively long-lived excited states and great photo- and redox stability. Furthermore, iridium(III) complexes can accommodate up to three cyclometalated (Ir-C) bonds which allows the tunability of the optoelectronic properties, due to destabilization of the metal-centered antibonding orbitals by strong σ-donating carbanions of the cyclometalating ligands.[2] Therefore, by substituting different cyclometalating ligand systems, the HOMO-LUMO energy gap can be tuned to achieve interesting photochemical and photophysical properties. Despite the unprecedented control of emission properties in cyclometalated iridium(III) complexes, many (particularly high energy emitters) exhibit poor absorption in the visible region which can limit their utility.[3]

Coumarin is a naturally occurring molecule found in many plants with a rigid structure containing a fused α-pyrone and benzene ring. Unsubstituted coumarin shows no fluorescence, whereas the addition of different functional groups can result in highly conjugated systems that display high fluorescence.[4] In this work, we synthesized a series of heteroleptic iridium(III) complexes incorporating coumarin derivatives, with different electron donating and electron withdrawing functional groups, into the cyclometalated ligands (Figure 1). Synthesized complexes were fully characterized using a range of experimental techniques and optical spectroscopy revealed considerably improved absorption of visible light (Figure 2).

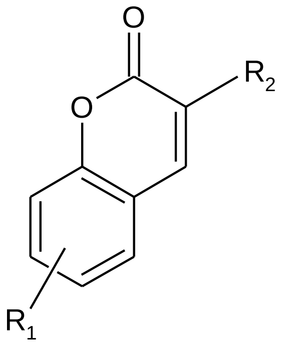

Figure 1 – General structure of cyclometalating coumarin derived ligands

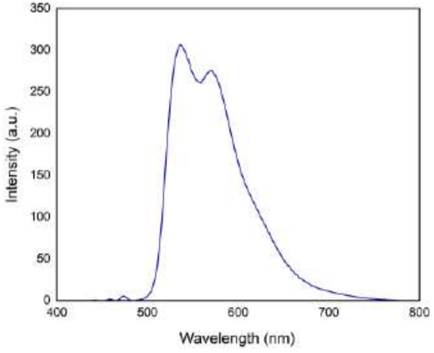

Figure 2 – Emission spectrum of a synthesized novel Iridium(III) Complex

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PP020

High-sensitivity fluorescence-detected multidimensional electronic spectroscopy through continuous pump-probe delay scan

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Multidimensional electronic spectroscopy (MES) is a state-of-art spectroscopic tool that resolves femtosecond quantum dynamics as 2D contour maps along excitation (w_1) and detection frequency (w_3) axes as a function of pump-probe delay (T) axis. However, existing methods rely on interferometric detection, do not provide spatial resolution, and are prone to sample scatter[1]. Fluorescence-detected MES has made recent strides by combining MES with a microscope for an objective-limited spatial resolution[2], with a promise of high-sensitivity fluorescence detection prevailing over the slow nature of experiments arising from the requirement of scanning an additional time delay.

We report an alternative fMES approach that addresses the above challenges regarding experimental throughput and systematically establishes the sensitivity of fMES compared to existing MES approaches. We present[3] a visible white-light continuum-based fMES spectrometer with 15 fs temporal resolution, system-limited spectral resolution, and microscope-objective limited spatial resolution. As a departure from existing approaches, we scan the continuous pump-probe delay T for each (t1,t3) grid point, further enabling 1/f suppression of experimental noise. Such an approach allows for free optimization of scan speed and choice of grid points to sample while substantially minimizing the continuous sample exposure window, a vital advantage for spatially resolved measurements. Together, these innovations allow us to demonstrate fMES sensitivity by measuring the high SNR 2D spectra, as well as room temperature vibrational coherence maps(CMs) at an optical density of ~1.4mOD, which is 300x lower than the conventional approach[3](Fig1).

The observed narrow diagonal lineshapes in CM were also reported earlier for a BChla monomer[4] and perplexed with the diagonal nodal lineshapes observed in multichromophoric CMs. In our later study[5], we resolved this by showing a precise connection between microscopic interference as wavemixing signal pathways to macroscopic observables such as 2D lineshapes.

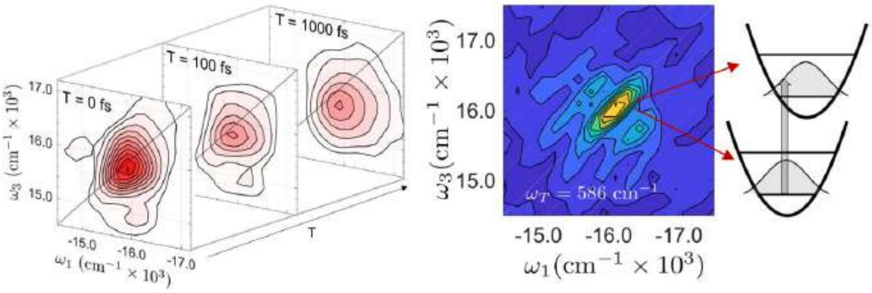

Fig1: (left) Absorptive 2D spectra at pump-probe waiting time T = 0,100, and 1000 fs, showing evolving femtosecond polar solvation dynamics. (middle) Real rephasing coherence map of a laser dye Oxazine 720 measured at room temperature. (right)Node-like lineshapes in coherence maps arise from destructive interference of ground and excited state vibrational coherences.

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PP021

Flexible polaritonics

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This presentation will discuss our recent work towards incorporating strong light-matter coupling and polaritonic effects into wearable devices – in other words, wearable polaritonics.

Conventional optical cavities are constructed using rigid materials like glass where the flexibility of the optical cavity is limited. To overcome this challenge, we have been investigating free-standing, commercially available and flexible materials for optical cavity fabrication. This should provide a route to polaritonics with the advantages of cost-effectiveness and responsivity.

Particularly we will present results on fabricating flexible optical cavities using polyethylene terephthalate (PET) films, and using stretching to tune the cavity thickness, and thereby the light-matter coupling strength. We show that tensile stress applied to the PET Fabry-Perot optical cavities enables the tuning of cavity mode energy by a remarkable 200 cm^{-1}, which can take the system from 'on' to 'off' resonance with a material absorption in the infrared.

Additionally, the effects of folding, twisting, and stacking of these flexible optical cavities is being investigated, adding flexibility and versatility to the design process. This research can help pave the way for innovative and perhaps even wearable optoelectronic devices featuring polaritonic effects.

PP022

Electrochemiluminescence of $[Ir(df(CF_3)ppy)_2(N^\wedge N)]^+$ complexes

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Iridium(III) complexes play a significant role in the design and development of numerous smart technologies involving the interconversion of light and chemical energy, including light emitting devices, photoredox catalysis systems, and electrochemiluminescence (ECL) based sensors.[1, 2] However, only a small number of Ir(III) chelates have been found to be effective as ECL luminophores.[3]

This research aims to synthesize and compare the ECL properties of four heteroleptic Ir(III) complexes with $df(CF_3)ppy$ cyclometallated (C^N) and polypyridine (N^N) ancillary ligands. The structures of the complexes were confirmed by nuclear magnetic resonance (NMR) spectroscopy and X-ray crystallography. UV-Visible absorption, ambient, and low (85 K) temperature photoluminescence spectroscopy were performed. The redox potentials of the complexes were measured against a ferrocene internal standard and reported against the saturated calomel reference electrode. Importantly, it was found that the ECL intensity of the best-performing Ir(III) complex was greater than that of the conventional $[Ru(bpy)_3]^{2+}$ luminophore, with tri-*n*-propylamine (TPrA) as co-reactant. Thus, this ECL data in conjunction with the assessment of the respective Ir(III) complex photophysical and electrochemical properties will be evaluated and compared to $[Ru(bpy)_3]^{2+}$ by reference to the energetically feasible light-producing reaction pathways using TPrA as co-reactant.

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PP023

Remarkable luminescence enhancement of alkaloid dyes in aqueous solution by using clay nanosheets

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Layered compounds are a type of material widely used in our daily lives. For example, advanced photoenergy conversion materials, drug delivery systems, materials to pencil and so on. Layered compounds have an atomically smooth two-dimensional surface and can adsorb various ions and molecules on their surfaces. Among various layered compounds, we have focused on synthetic saponite and reported unique photophysical properties of its host-guest complexes. Synthetic saponite is a type of clay mineral, as a host compound and adsorbing various dyes on the surface. For example, cationic porphyrins were adsorbed on clay without aggregation even at high density adsorption conditions. This phenomenon was named "size-matching effect" [1,2] . In addition, the luminescence enhancement via the motion control of molecules adsorbed on clay minerals has been named as Surface-Fixation Induced Emission (S-FIE) [3,4]. The phenomena of S-FIE by using clay minerals is expected to be applied to bio-imaging materials because it can be used as a luminescent material in an aqueous system.

In this study, the S-FIE behavior for Berberine (Fig. 1 (a)), a type of alkaloid dye, was investigated. Figure 1(b) shows the absolute quantum yield spectra of Berberine on the exfoliated clay surface in water . The loading level of Berberine was 0.05% of the cation exchange capacity (CEC) of the clay. As a result, the drastic fluorescence enhancement was observed for Berberine adsorbed on the clay surface. The fluorescence quantum yield (Φ_f) of Berberine on the clay surface is 0.47, while that in bulk water is < 0.001 (Fig. 1 (c)).

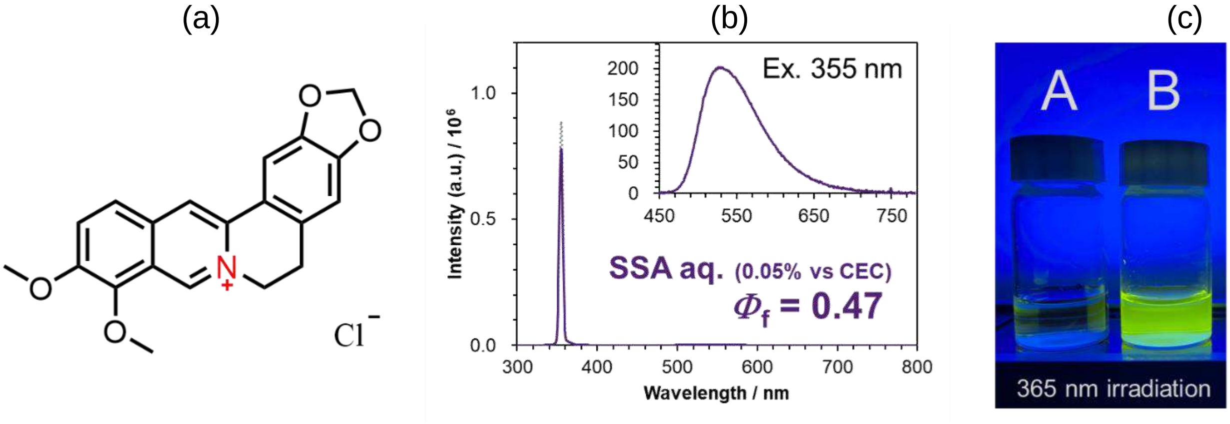

Fig. 1. (a) The structure of Berberine. (b) Absolute quantum yield spectra for Berberine in clay dispersion (0.05% vs CEC). (c) The picture of Berberine fluorescence excited by black light (l = 365 nm) (A : without clay in water, B : in aqueous clay dispersion).

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PP024

Development of a new red-shifted photosensitizer for near-infrared photoimmunotherapy

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[Introduction] Near-infrared photoimmunotherapy (NIR-PIT) is a new type of cancer therapy that utilizes antibody-conjugated phthalocyanine photosensitizer (Ab-IR700) and NIR light at 690 nm. In NIR-PIT, hydrophilic axial ligands of IR700 are cleaved by light irradiation[1]. Then aggregation of Ab-IR700 is formed on plasma membrane, causing cell death. Compared to light at 690 nm, longer-wavelength light penetrates deeper in tissue, and thus, preferable NIR-PIT would be achieved using longer-wavelength light. In this study, we developed a red-shifted photosensitizer for NIR-PIT, KA800, which is introduced with ethoxy groups to phthalocyanine ring of IR700.

[Methods] KA800 was conjugated to an antibody, trastuzumab, to obtain Ab-KA800. In vitro cytotoxicity of Ab-KA800 was investigated using 3T3-HER2 cells, and in vivo therapeutic effect was examined using tumor-bearing mice. In NIR-PIT with Ab-IR700, aggregation is a main factor of cytotoxicity, whereas photo-excited IR700 could produce cytotoxic singlet oxygen ($^1O_2$).[2] To evaluate contribution of $^1O_2$ to cytotoxicity of Ab-KA800, sodium azide (NaN_3) was used as a quencher of $^1O_2$. In addition, efficiency of axial ligand cleavage reaction of KA800 was investigated.

[Results and discussion] Absorption maximum of KA800 was 84 nm longer than IR700. In vitro studies showed phototoxicity of Ab-KA800. However, Ab-KA800 showed no therapeutic effect in vivo. In the presence of NaN_3, in vitro cytotoxicity of Ab-KA800 was almost completely suppressed, suggesting that Ab-KA800 induced cell death not via aggregation but by $^1O_2$. Thus, aggregate formation would be important for in vivo therapeutic effect of NIR-PIT. The efficiency of axial ligand cleavage was lower in KA800 than in IR700, which explains KA800 was less likely to form aggregation compared to IR700. We need to develop a new red-shifted photosensitizer which is more efficient in axial ligand cleavage reaction.

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PP025

Silver Nanocubes Produced by Pulsed Laser Ablation in Liquid: Structural and Optical Properties

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This study describes a simple approach for producing silver (Ag) nanocubes using pulsed laser ablation in a water medium. The surface morphological analysis, which was performed using field-emission scanning electron microscopy (FESEM), showed that the Ag nanocubes have been successfully created. The surface morphological images clearly reveal the formation of good quality and densely packed Ag nanocubes with edge lengths from 150 nm to 250 nm. The UV-Vis spectroscopy demonstrates that the concentration of Ag nanostructures, evidenced by the characteristic localized surface plasmon resonance band around 400 nm, in the colloidal solution containing Ag nanoparticles increased with the increasing laser ablation time from 5 min to 20 minutes as shown in Fig.1[1]. The morphology of Ag nanoparticles was transformed from spherical to cube-like as laser ablation times increased. The growth mechanism for Ag nanocubes can be easily understood with the change in laser ablation time from 5 minutes to 10 minutes, 15 minutes, and then 20 minutes. The Ag sheets or tiny particles with no specific shape start to develop after 5 minutes of laser ablation, and after 10 minutes, larger particles begin to form. Then, after 15 minutes of laser ablation, we obtained small number of cube-like nanostructures with rough and uneven edges. At the end of 20 minutes, a full cubic form with fine and distinct edges and a very large amount of nanocubes was obtained as illustrated in Fig. 2[2,3]. The EDS spectrum confirms the presence of elemental silver signal in Ag nanocubes as displayed in Fig.3. The obtained Ag nanocubes have the ability to build nanocomposites with two-dimensional materials which have practical applications in the electrical, optoelectronic, electrochemical, and biological fields.

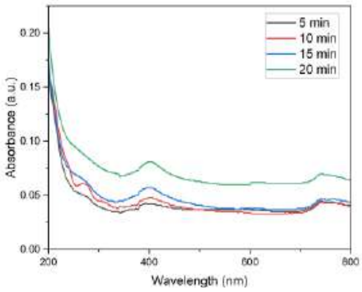

Fig 1. UV spectra of Ag nanocubes

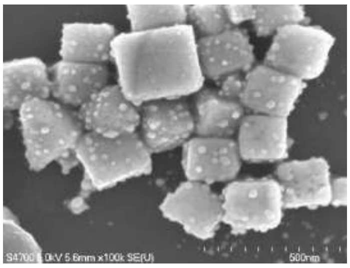

Fig 2. SEM image of Ag nanocubes (20 min)

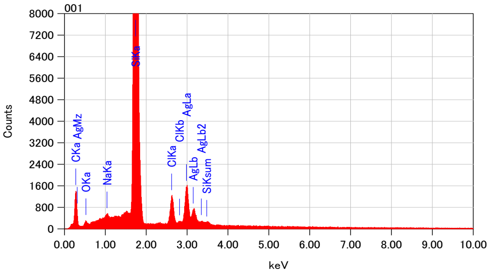

Fig 3. EDS spectrum of Ag nanocubes (20 min)

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PP026

Towards catalytic redox-active Iridium polypyridyl complex by *in situ* photosubstitution

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Iridium (III) complexes are widely used in photocatalysis to participate in electron transfer processes upon photoexcitation. These complexes typically undergo oxidative quenching where it donates an electron to a substrate to promote bond cleavage or reductive quenching, where it accepts an electron in its excited state to before transferring an electron to the substrate. In our study, heteroleptic $[Ir(dF(CF_3)ppy)_2(dtbbpy)]^+$ complex is used to catalyse the hydrodehalogenation of aryl halides via reductive quenching by an amine salt. However, this reaction is deemed thermodynamically unfavorable, with an overall positive Gibbs free energy of electron transfer from the reduced Iridium complex to an aryl halide. The covalent addition of □-amino radicals to both the ancillary N^N and cyclometallating C^N ligands on the Ir(III) complex was observed to occur in situ along with the displacement of fluorine atoms. Interestingly, the introduction of electronically rich amine groups on the ligands destabilises the HOMO metal orbital, reducing the HOMO-LUMO energy gap. This, leads to a bathochromatic shift in the emission spectrum as well as the decrease of the catalyst's oxidation potential.

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PP027

Bioluminescent Sensors for Tyrosinase and NQO1 Detection

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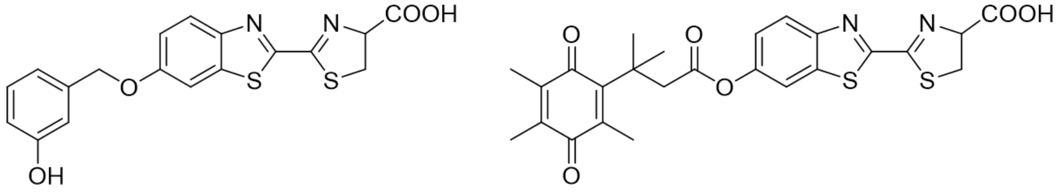
Bioluminescence exhibit high potential in biosensing because of its low background, high stability and quantum yield. Herein, two sensors based on bioluminescence mechanism are reported. TYR-LH2[1] was applied to detecting tyrosinase, which is a biological marker of melanoma. In the presence of tyrosinase, the caging group 3-hydroxybenzyl was released, revealing luciferin, which then exhibited emission in the Luciferase-ATP-Mg^{2+} environment. High sensitivity was achieved. The detection limit was as low as 0.11 U/ml. NQO1-Luc[2] was used to detect another tumor marker NAD(P)H quinone oxidoreductase 1 (NQO1). Upon treatment with NQO1, the tetramethylbenzoquinone group was oxidized and cleaved. Then the generated D-luciferin emitted orange-red light in the Luciferase-ATP-Mg^{2+} system. TYR-LH2 was applied to B16-Luc, Hela-Luc and NIH/3T3-Luc cells, and NQO1-Luc was applied to A549-Luc cells. Both sensors could be used for in vivo imaging of tumors overexpressing the responding analytes.



TYR-LH2 **NQO1-Luc**

Figure. Bioluminescent sensor TYR-LH2 and NQO1-Luc

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PP028

Single nanoparticle arrays of quantum rods using surface templated electrophoretic deposition

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When ordered into arrays, fluorescent nanoparticles (NPs) in the 1-100 nm size regime have numerous applications. This includes optical displays, single molecule sensors, catalysis, and molecular logic gates. However, the precise placement of NPs into arbitrary configurations presents a significant challenge. Surface templated electrophoretic deposition (STEPD) is shown to be a powerful technique for single nanoparticle deposition,[1] which forms the basis of the research described herein.

We have fabricated fluorescent nanoparticle arrays consisting of CdSe@CdS semiconductor quantum rods using STEPD. The fluorescence emission confirms the deposition of quantum rods within the arrays. The presence of ordered single quantum rods, as well as their relative orientation within the template is then discerned. This is achieved through several imaging techniques including atomic force microscopy (AFM) and scanning electron microscopy (SEM). Future studies, such as investigations into the polarization dependence on nanorod emission intensity, the effect of nanorod orientation on FRET efficiency, and the modulation of the fluorescence emission in single nanoparticles under an applied electric field (due to the Stark effect) are then outlined.

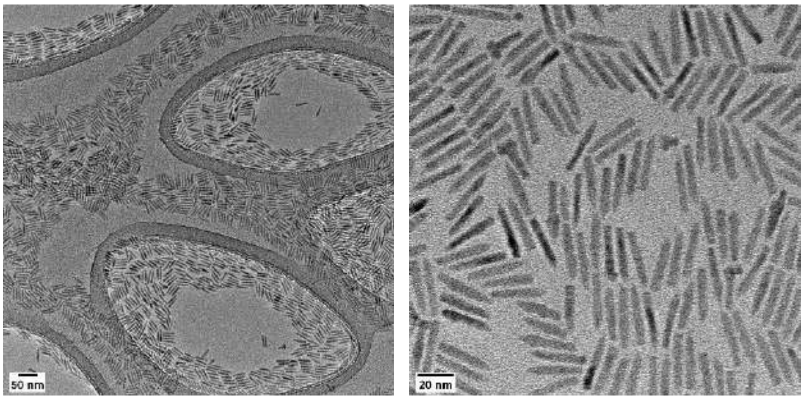

Figure 1: Scanning electron microscopy images of CdSe@CdS nanorods used in surface templated electrophoretic deposition experiments.

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PP029

Photothermal Spectroscopy of CBNP Nanofluids under Femtosecond Pulsed Excitations

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Nanofluids are the suspensions of nanoparticles in a base fluid, and they have been of immense research interest due to their unique thermal characteristics[1]. We studied the photothermal dynamics of carbon-based nanofluids under femtosecond pulsed excitations to explore the potential of these materials for photothermal conversion and energy storage applications. Dual-beam Z-Scan measurements[2] were performed on Carbon black nanoparticles on four different base fluids viz. Methanol, Water, DMSO, and DMF. We observed that the inclusion of the carbon black nanoparticle in the base fluids significantly enhances the thermal load in the system. However, the heat transfer characteristics of these systems rely entirely on the solvent-nanoparticle interaction. We also noticed that the presence of nanoparticles in the host fluid leads to a convective heat transfer in certain cases which therefore plays a critical role in their photothermal characteristics and heat dissipation dynamics.

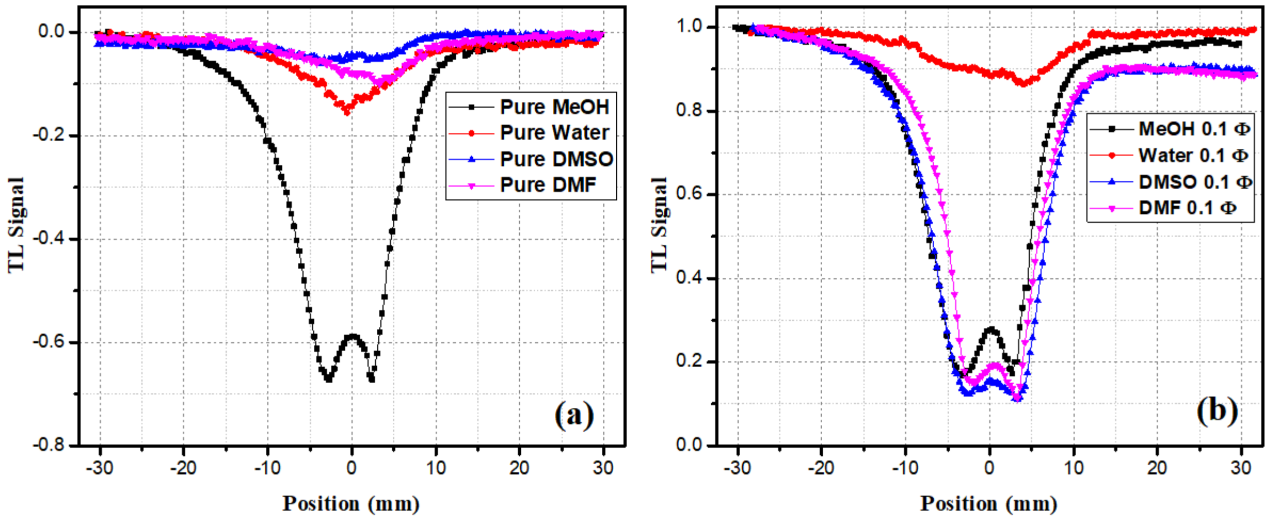

Fig. 1. (a) TL Signatures of Pure base fluids, (b) TL Signature of CBNP Nanofluids at 0.1 ϕ loading concentrations.

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PP030

Charge transfer-mediated multi-exciton mechanisms in weakly coupled perylene dimers

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Multi-exciton processes have recently gained momentum as an approach to surpass the single-junction Shockley-Queisser limit[1], via one of two pathways. The first is where a high energy singlet exciton is cleaved into two low energy triplet excitons (singlet fission), both capable of charge separation, and the second process, whereby two low energy triplet excitons come together and fuse into a high energy singlet exciton (triplet-triplet annihilation). The role of charge transfer states in multi-exciton mechanisms has recently become a point of discussion due to the difficulty associated with modelling their contributions accurately. The have been shown to participate via multiple mechanisms[2], and while not always prevalent with respect to a direct pathway[3], they have been identified as optimum pathways for many extended systems, especially in the case of SF[4,5].

As the growing energy crisis begins to loom, the need for an optimisation methodology increases. Unfortunately, there is yet to be a definitive method to calculate this complex coupling between dimer components for charge-transfer mediated multi-exciton mechanisms. In this talk, we take two commonly used methods[6-8] to model the coupling between the bright and correlated triplet ^{1}TT states as a function of relative displacement, calculated at different levels of theory, and compare the resulting rate constants for both singlet fission and triplet-triplet annihilation, yielding rates in the femtosecond and nanosecond range, respectively. Following this, the decoherence of the ^{1}TT into two individual triplets is also examined. We show that the decorrelation time scale depends on the nature of the relative molecular motion, ranging from picoseconds for fluctuations in the monomer orientations, to microseconds, for coplanar fluctuations.

This work is currently under review; the current draft may be obtained by contacting the author.

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PP031

Fabrication and Analysis of Femtosecond-Laser Ablated THz Band-Pass Filters for Polarization-Sensitive Measurements

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The spectral range available on the synchrotron THz/Far-IR beamline is extremely broad, spanning from 1 µm to 1 mm in wavelength, necessitating the use of various spectral filters and optical elements to manipulate the polarization behaviors, including spin angular momentum (SAM) and orbital angular momentum (OAM), of this broadband radiation. In this study, we focused on the fabrication and analysis of THz band-pass filters using femtosecond-laser ablation of stainless steel and Kapton film micro-foils, aiming to develop high-transmission filters for polarization-sensitive measurements. Through femtosecond-laser ablation and subsequent metal coating with a film thickness of approximately 70 nm, the filters were fabricated to match the skin depth of the THz spectral window. Testing their spectral performance at the Australian Synchrotron's THz beamline in transmission and reflection modes, we observed distinct transmission peaks at specific frequencies, indicating the selective transmission of certain THz wavelengths. The filters' performance was found to be polarization-dependent, with the Kapton film filters exhibiting Fabry-Pérot etalon behavior, offering tunability, finesse, and a free spectral range within a specific wavelength range. To account for the complexities associated with the THz beam's polarization, wavelength, and position distribution, careful normalization of measurements was performed for each linear polarization orientation. This allowed accurate polarization-sensitive measurements in both transmission and reflection modes, enabling reliable characterization of the filters' spectral properties and beam profiles. Overall, our research contributes to the advancement of THz optical elements and narrow band filters, providing insights into their design, fabrication, and performance in polarization-sensitive measurements. These findings hold promise for biomedical applications requiring precise discrimination within the THz-IR spectral range and offer potential for further exploration of THz-based research in diverse scientific disciplines.

PP032

Strong coupling and recombination in organic photovoltaic blends

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Embedding molecules in optical cavities is an emerging method of controlling excited-state processes of optoelectronic materials without synthetic modification. An application in which this has potential benefit is organic photovoltaics, where the strong light-matter coupling achieved in optical cavities could be used to assist charge formation and mitigate loss pathways. Here we investigate the effect of strong coupling on such loss pathways: the bimolecular annihilation and recombination of excitons and charges in organic photovoltaic blends. We establish strong light-matter coupling in photovoltaic blend films and devices of PTB7-Th:PC$_{71}$BM, and measure device performance. External quantum efficiency measurements show that the lower polariton generated from strong-light matter coupling contributes to charge formation. Transient absorption measurements are used to investigate the lifetime and fluence dependence of these generated charges. We find that fluence dependence, and thus bimolecular processes, are affected by strong coupling, and investigate the origins of these changes.

PP033

TDDFT Study on Excited States of Metal-Adsorbed Dimethyl Disulfide

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The near field refers to a localized light field near a material's surface that can induce photochemical phenomena such as dipole-forbidden transitions. Recently, the photodissociation of the S–S bond of dimethyl disulfide (DMDS) was investigated using a scanning tunneling microscope with far- and near-field light.[1] This reaction is thought to be initiated by the lowest-energy highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) transition of the DMDS molecule under far-field light. In near-field light, photodissociation proceeds at lower photon energies than in far-field light.

To gain insight into the underlying mechanism, we theoretically investigated the excited states of DMDS adsorbed on Cu and Ag surfaces modeled by a tetrahedral 20-atom cluster as shown in Figure 1, by means of time-dependent density functional theory (TDDFT) calculations. The frontier orbitals of the molecule were delocalized by the interaction with the metal, resulting in narrowing of the HOMO–LUMO gap energy. The excited-state distribution was analyzed using the Mulliken population analysis, decomposing molecular orbitals into metal and DMDS fragments. The excited states of the intra-DMDS transitions were found over a wider energy range, but at low energies, their oscillator strengths were negligible, which is consistent with the experimental results. Sparse modeling analysis showed that typical electronic transitions differed between the higher and lower excited states. If these low-lying excited states are efficiently excited by near-field light with different selection rules, the S–S bond dissociation reaction can proceed.[2]

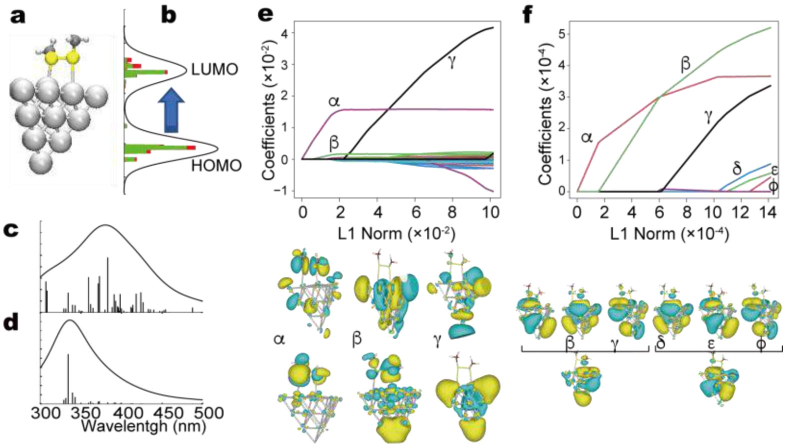

Figure 1. (a) Computational model for DMDS adsorbed on a 20-atom metal cluster, (b) HOMO and LUMO of adsorbed DMDS, the (c) fractions and (d) oscillator strength of intramolecular electronic excitations, and Lasso analyses using (e) oscillator strength and (f) fractional rate of excited states of intra DMDS excitations as objective variables.

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PP034

CZTSSe grain growth and all solution process of CZTSSe solar cell

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CZTSSe is a p-type doping, holes concentrated, semiconductor material. The band gap of CZTSSe is 1.1 eV. It is a green, cheap material[1-2]. Nowadays, the record of the power conversional efficiency of CZTSSe is 13.8%[3]. In my research project, the goal is to control the grain growth of the CZTSSe via selenization process. During the selenization process, selenium vapour can attach on the surface of the CZTS precursor film. It boosts the grain growth because the selenium can bond with copper in the film. Therefore, selenization time and temperatures optimization is necessary for studying the grain. Different sets of selenization process were developed in my research to observe the morphology of the CZTSSe absorber layer. Selenization at 550°C for 600s is the best methodology that is found to receive less voids and large grain absorber layer.

When the CZTSSe absorber layer was constructed, n-type doping, which is electrons concentrated, material can be generated on the top of the CZTSSe layer. CdS is the n-type doping semiconductor material that is used for growing on the top of the CZTSSe to form p-n junction. The method that we use is chemical bath deposition. On the top of the CdS, CdZnS is deposited for reducing the recombination of holes and electrons. After CdZnS layer, AgNWs and Ag electrode were fabricated. AgNWs is used for replacing ITO because Indium is a rare earth metal. Therefore, the CZTSSe solar cell was achieve all-solution process. This fabrication type is easy and cheap.

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PP041

Synthesis of *N*-methylated chlorophyll derivatives having various substituents and comparison of their optical properties

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Chlorophyll(Chl)-*a* is the most abundant pigment in photosynthetic oxygenic organisms, and one of the porphyrinoids possessing a π-conjugated cyclic tetrapyrrole skeleton, called a chlorin. Substitution at the inner nitrogen atom in various porphyrins has been reported so far, but the related *N*-alkyl-chlorins are limited to structurally simple species. Here we report the synthesis of *N*-methylated Chl-*a* derivatives and their photophysical properties in a solution.

Chl-*a* obtained from cyanobacterial cells was chemically modified to methyl pyropheophorbide-*a* (**1**, R = $CH{=}CH_2$ in the upper left drawing of Fig. 1). Synthetic Chl-*a* derivative **1** was reacted with methyl fluorosulfonate and treated with an aqueous solution of sodium hexafluorophosphate to produce N22-methylated Chl-*a* derivative **2** (R = $CH{=}CH_2$ in the center drawing of Fig. 1).[1,2] The other eight N22-methylated C3-substituted Chl-*a* derivatives **2** (Fig. 1, upper right) were synthesized and measured photophysical properties in dichloromethane. The Soret and Qy absorption bands of **2** were blue- and red-shifted, respectively, comparing with those of **1** (Fig. 1, lower). Optical properties of **2** in dichloromethane were dependent on the C3-substituents (R in Fig. 1, upper right). Quantum yields and lifetimes of their fluorescence emission decreased by the *N*-methylation except for the 3^2-nitro substitute.

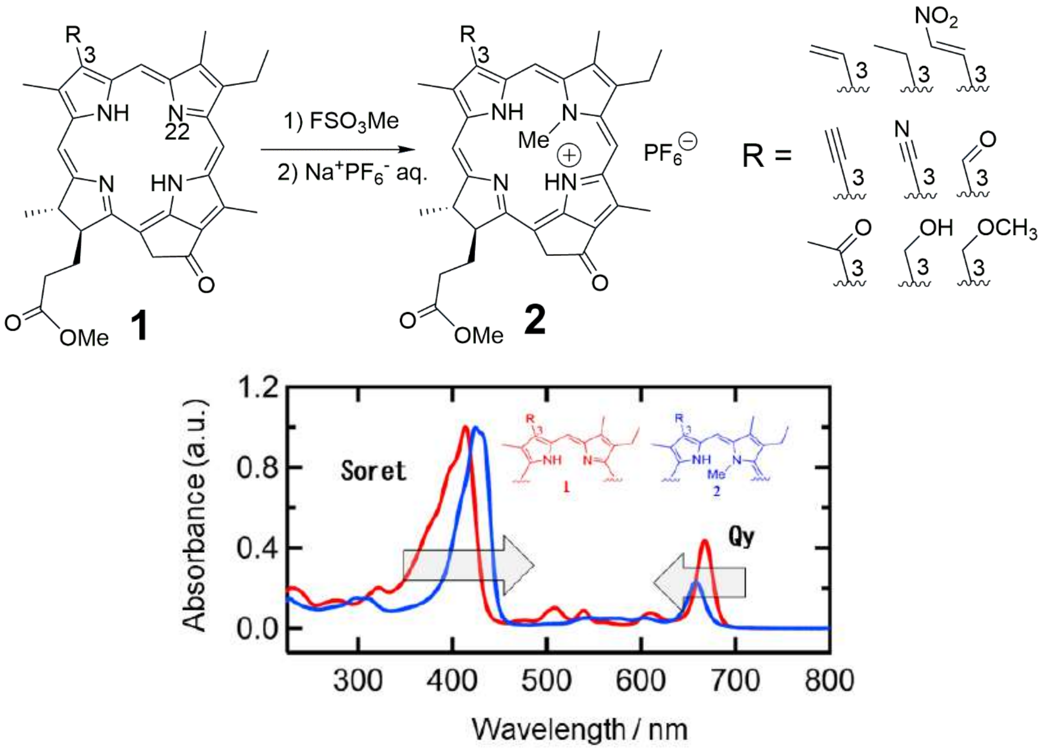

Fig. 1. Synthesis of N22-methyl-Chl-*a* derivatives **2** possessing various C3-substituents (upper) and their UV-visible absorption spectra in dichloromethane (lower).

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PP042

Se-incorporation in CZTSSe precursor inks for printable, large-scale CZTSSe thin films

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The highest efficiency CZTSSe absorbers are made via spin-coating in a glovebox – a deposition technique incompatible with low-cost and high-throughput production methods. Thus, deposition of high-efficiency thin films based on scalable printing methods is critical if CZTSSe is to realise its potential as a low-cost thin film solar cell material.

In traditional selenization, selenium (Se) vapour diffuses from the surface to the bottom of the CZTSSe precursor. Due to large molecular chains, the diffusion distance of Se is limited, and it's a challenge for Se to be distributed sufficiently and evenly throughout the film[1]. The growth of large-scale CZTSSe films with uniform composition and ideal grain growth has thus been especially difficult. Insufficient Se diffusion and chemical activity leads to the formation of secondary phases, fine grains, voids and other intrinsic defects responsible for the poor carrier transport near the back contact and hence limiting photovoltaic efficiencies of CZTSSe[2].

To overcome secondary phase formation, precursors need to be annealed or selenized at temperatures of 550 °C or higher. However, selenization at such high temperatures precludes the use of flexible plastic substrates such as polyethylene terephthalate (PET) and polyimide (PI).

In this work, a homogeneous CZTSSe molecular precursor solution is prepared. Unlike typical precursor inks, all the necessary elements are incorporated, with Se being added through an NaHSe solution. The direct addition of Se in the precursor along with Se vapour ensures ample supply of Se, enabling the bidirectional diffusion of Se, which may enable the growth of high-quality large-scale films. In addition, Na+ can act as a surfactant, promoting the preferential growth of grains along the (112) plane[3].

In preliminary tests, despite selenisation of the CZTSSe films at lower temperatures (<500 °C), the formation of undesired secondary phases is avoided, and densely packed large crystalline grains are able to form.

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PP043

Photoluminescence enhancement on ordered packing of Gold clusters with carboxylate ligands and Zinc atoms

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Gold clusters are nanoparticles with less than 200 atoms or smaller than 2 nm. They are considered as alternatives to quantum dots due to their ultrafine structure, good stability and low toxicity. Compared with gold nanoparticles, many of their properties are fundamentally altered. Significant quantization will occur to the continuous conduction band, and it will break into discrete energy levels, which show multiple electronic transition peaks in the visible region. However, the quantum yield of gold clusters is found to be very low. Recently, researchers discovered the aggregation-induced emission enhancement of these clusters, the quantum yield of the poor or non-emissive gold clusters can go up to 90% after aggregating with Zinc atoms.[1, 2] The caboxylated gold clusters are synthesized first, then mixed with Zn salt, where the negative carboxylate group can electrostatically link to the positive Zn atoms to form the superlattice. Such property was observed in Au4 clusters and Au25 clusters, however, they all lack crystallinity, which limits the study of this kind of material. Here, we are trying to make single crystal with carboxylated gold clusters and Zn atoms, and then explore the structure of the crystal and study the PL enhancement mechanism.

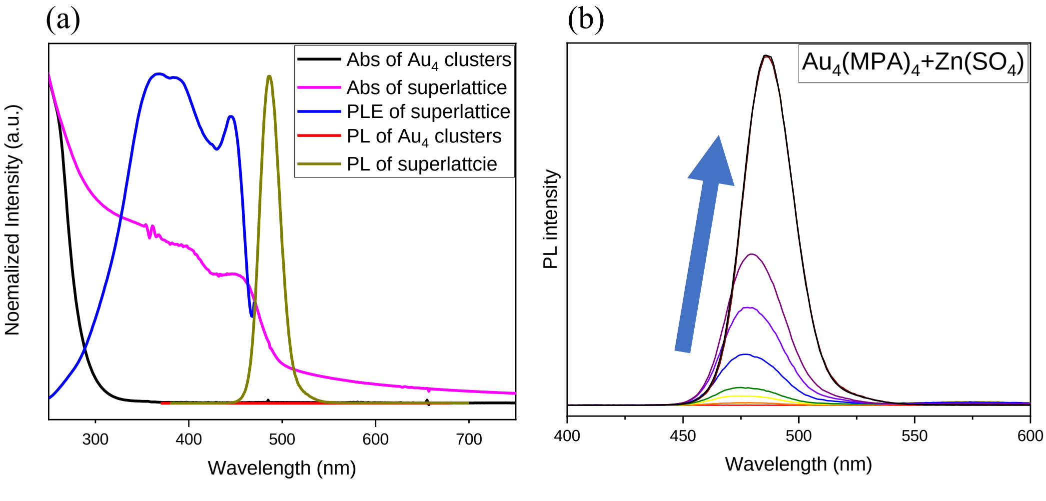

Figure 1. (a) UV-vis and PL spectra of Au4 clusters and aggregates, PLE spectra of assembly. (b) Increasing PL intensity of aggregates after adding Zn salts.

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PP044

Molecular Ordering-Dependent Hydrogen Evolution by Organic Semiconducting Nanoparticles

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Hydrogen (H_2) is a crucial industrial feedstock that can also be a clean alternative to fossil fuels. To achieve the widespread use of H_2, it must be generated using renewable resources and energy. One such approach is to harness solar energy by using organic semiconducting nanoparticles (NPs), which exhibit strong visible light absorption and the ability to generate charges under photoexcitation. Several groups have thus far demonstrated the use of organic semiconducting NPs for photocatalytic H_2 evolution. However, the effects of molecular order and disorder within organic semiconducting NPs on photocatalytic H_2 evolution have yet to be determined. An increase in molecular ordering has been predicted to improve photocatalytic H_2 evolution due to enhanced charge mobility, whereas molecular disorder facilitates charge generation.[1]

In this work, a well-studied polymer electron donor (P3HT) and the non-fullerene acceptor Y6 are prepared as intermixed NPs to mimic the bulk heterojunctions in P3HT:Y6 thin films utilised in photovoltaic studies. We demonstrate control over the molecular ordering within the organic semiconducting NPs through temperature control during NP preparation. Spectral differences between NP samples were attributed to changes in molecular ordering resulting in changes in vibronic peak intensity. We show that disordered NPs demonstrated significantly higher photocatalytic H_2 evolution rates than ordered NPs, suggesting that molecular disorder is more important than molecular order for the photocatalytic H_2 evolution performance of P3HT:Y6 organic semiconducting NPs. This work points to the role of molecular disorder in organic semiconducting NPs and its effect in enhancing photocatalytic H_2 evolution.

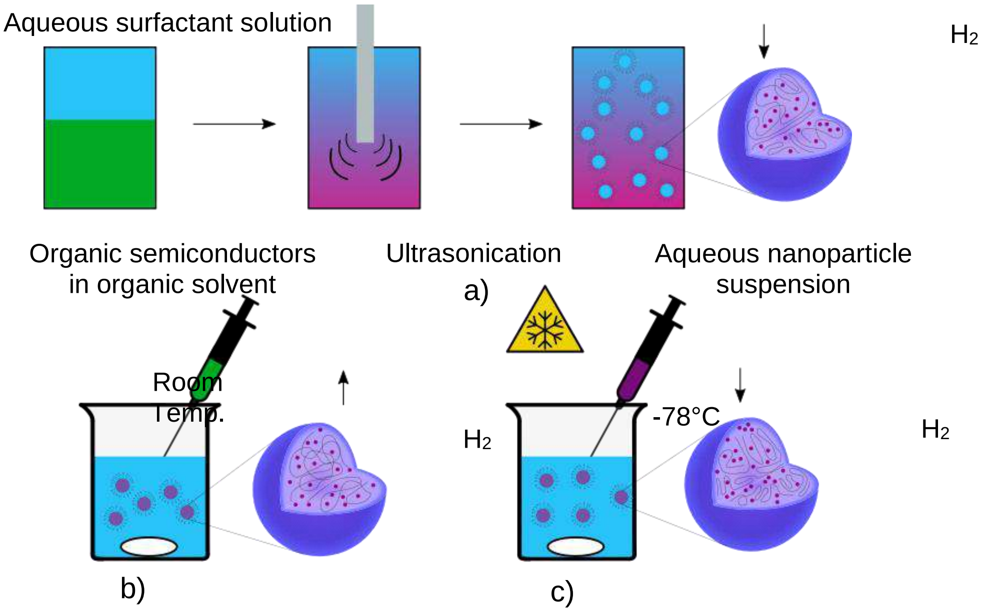

Figure 1: Graphical representation of the molecular ordering present in organic semiconductor nanoparticles synthesized by a) mini-emulsion, b) nanoprecipitation, and c) cold nanoprecipitation method.

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PP045

Prediction of the photoelectrochemical performance of hematite electrodes using analytical data

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As for a promising energy-harvesting material, photoelectrodes have been studied as a means for the generation of hydrogen and oxygen. Hematite as one of the promising photoanodes,[1] has a drawback on the reproducibility of the performance, and the underlying reasons for it are often unclear. To clarify the origin only from dozens of actually prepared samples, we attempted to identify the determining factors that affect the photocurrent by using machine learning (ML) based on the features derived from various analytical data of UV/Vis spectra, Raman spectra and X-ray diffraction pattern (XRD), such as peak intensities and positions. The dominant features in the analytical data were determined by the stepwise regression, and finally the prediction function was refined using a gaussian process regression model. Figure 1 shows a scatter plot, where the predicted photocurrents by the model function prepared by ML were plotted to the target values. The model was accurate enough to predict the target values only by the features of analytical data.[2] The identified determining factors were two UV/Vis, four Raman and five XRD peaks, which included reasonable and unexpected factors. This will lead the photocurrent enhancement by inductive searching and tuning the experimental parameters affecting the descriptors, and it is now under progress.

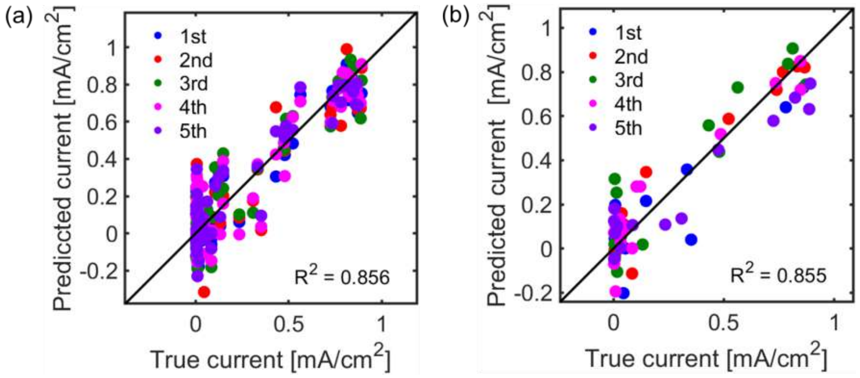

Figure 1 The scatter plots of the true photocurrents vs the predicted values; a) training and b) test dataset

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PP046

Colloidal Nanoparticle “Molecules”: Towards Self Assembled Plexitonic Heteroparticle Nanostructures Using Oligonucleotide Hybridisation

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The optical properties of metal and semiconductor nanoparticles can be enhanced when they are made to interact and couple to one another. Systems where these particles interact with one another have been explored for applications including nanoscale lasers and LEDs, photonic circuitry, single photon sources, and thin film solar cells. However, efficient coupling between plasmonic and excitonic states in these systems is fundamentally dependant on their interparticle separation and relative positioning. Yet one of the key challenges when it comes to fabricating coupled structures is the ability to reproducibly assemble different colloidally synthesised nanoparticles with a given assembly geometry and with small interparticle separations. This is further complicated if the targeted assemblies contain components that differ in morphology or in composition.

Presented here is a comprehensive method for the formation of heteroparticle assemblies consisting of gold nanoparticles and photoluminescent cadmium selenide quantum dots using single DNA strand hybridisation. We demonstrate a workflow and methodology for attaching complementary single stranded DNA to both metal and semiconductor nanoparticles. Furthermore, an electrophoresis-based procedure is described which allows for the separation of particles based on the number of DNA strands attached to them. Samples are formed with high yields of particles functionalised with discrete numbers of DNA strands. The result of this is the ability to selectively form the desired heteroparticle dimer, trimer or more complex assemblies. The versatility of this method to assemble nanoparticles that have vastly different geometries is demonstrated. Finally, assemblies with small interparticle separations are presented, allowing for strong optical and polaritonic coupling.

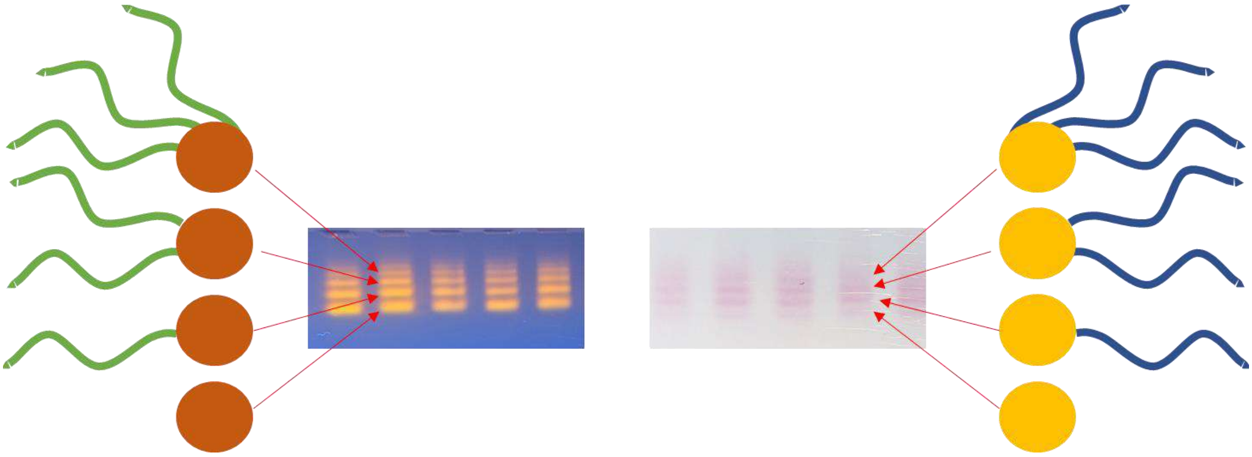

Figure 8:Two agarose gels depicting the separation of CdSe/CdS quantum dots (left) and gold nanoparticles (right) functionalized with a different number of complementary DNA strands to one another.

PP047

The Impact of Surface Termination of Perovskite on the Electronic Structure at Interface with Rubrene

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Photon upconversion presents itself as a valuable prospect in increasing the efficiency of photovoltaics by overcoming the detailed balance limit via harvesting sub-bandgap photons [1]. Upconversion via Triplet-triplet annihilation (TTA), where two triplet (spin-1) excitons interact to become one higher energy singlet (spin-0) exciton, is of great interest due to being efficient at low powers since energy is stored in long-lived triplet excitons as recombination is spin-forbidden.[1] Whilst efficient TTA upconversion has remained elusive in the solid state, an exciting new system is based on a perovskite sensitizer with an adjacent organic-semiconductor film as an annihilator, first demonstrated in 2019.[2] Questions remain however over how the interfacial properties of the perovskite sensitizer affect the formation of triplet excitons in the organic annihilator.

In this work the electronic interaction between interfaces of rubrene and the perovskite MAPbI3, with various MAPbI3 surface terminations are probed by means of density functional theory. The results show that different surface terminations of the perovskite film greatly affect the density of electrons in the supercells. Namely, for a PbI2 terminated system a strong interfacial dipole ($E_{dip} \approx 830$ meV) is formed between the $MAPbI_3$ and rubrene slabs. Contrastingly, almost no interaction is seen between a MAI terminated perovskite and rubrene, likely due to the lower density of states in the MAI layers for the rubrene to interact with. As the sensitization mechanism of triplet excitons is theorized to be via sequential charge-transfer across the perovskite/rubrene interface [2], the existence of an interfacial dipole between the sensitizer and the annihilator would have a significant impact on the efficiency of the upconverting system and presents itself as a crucial factor to control during the fabrication of these heterostructures.

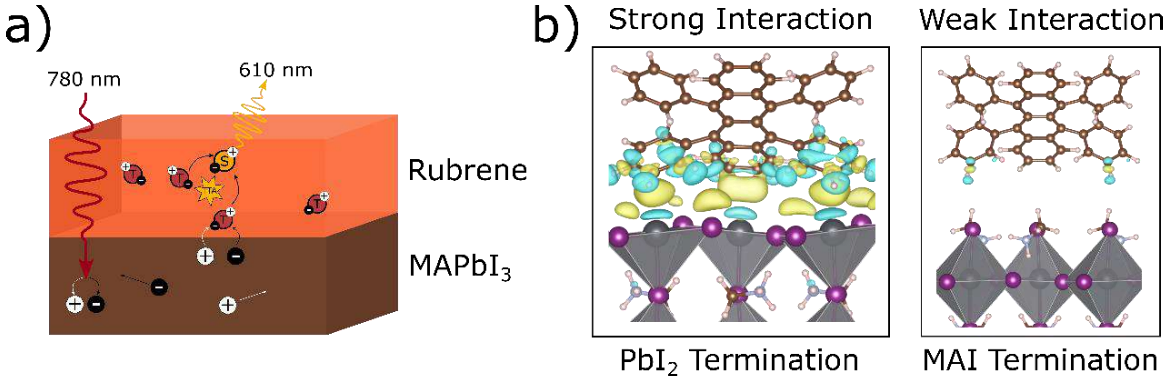

Figure 1: *a) Heterostructure consisting of a MAPbI3 sensitizer and rubrene annihilator. b) Interfacial electron density change observed for different surface terminations of the perovskite film in the contact with rubrene.*

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PP048

Composite Nanostructures of Dipole and Quadrupole Surface Plasmons Optimal for Metal-Enhanced Fluorescence of Bioimaging Dyes

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Metal-enhanced fluorescence (MEF) has been considered one of the emerging technologies in biomedicine, optoelectronics, *etc*., due to the improvements in photostability and quantum yields of fluorescent dyes.[1] The combination of increased excitation and radiative decay rates of dyes by the induced local electric field and plasmon-coupled emission of metal nanoparticles, respectively, has been explained as the MEF mechanisms.[1] In addition, the spectral overlap of dipole (DSPR) or quadrupole surface plasmon resonance (QSPR) bands of metal nanoparticles with the emission bands of dyes has been reported as one of the crucial factors for strong MEF.[2,3] Recently, we have observed larger MEF of dyes with composite nanofilms showing combined SPR bands of small (DSPR) and large (QSPR) nanoparticles overlapped with dyes' emission bands than those with nanofilms composed of small or large nanoparticles only.[4]

In this study, we explore optimal MEF of *in vivo* bioimaging dyes such as Alexa Fluor with composite silver colloidal films (SCFs) prepared homogeneously by small and large silver nanoparticles. Several Alexa Fluor dyes exhibit low quantum yields in an aqueous solution in spite of their selective binding capability to active sites and high photostability. Average particle sizes of small and large silver nanoparticles showing efficient DSPR and QSPR for strong MEF of various Alexa Fluor dyes, respectively, are determined (Fig. 1(a)). Then, the combination of DSPR and QSPR of small and large silver nanoparticles, respectively, for optimal MEF of Alexa Fluor dyes is investigated. Alexa Fluor dyes show larger fluorescence enhancements and shorter emission lifetimes with composite SCFs than those with SCFs of one particle size, as shown in Figs. 1(b) and 1(c). It clearly indicates that the stronger MEF of Alexa Fluor dyes originates from the more significant plasmon-coupled emission of the composite SCFs accompanying the energy transfer between the dyes and silver nanoparticles.

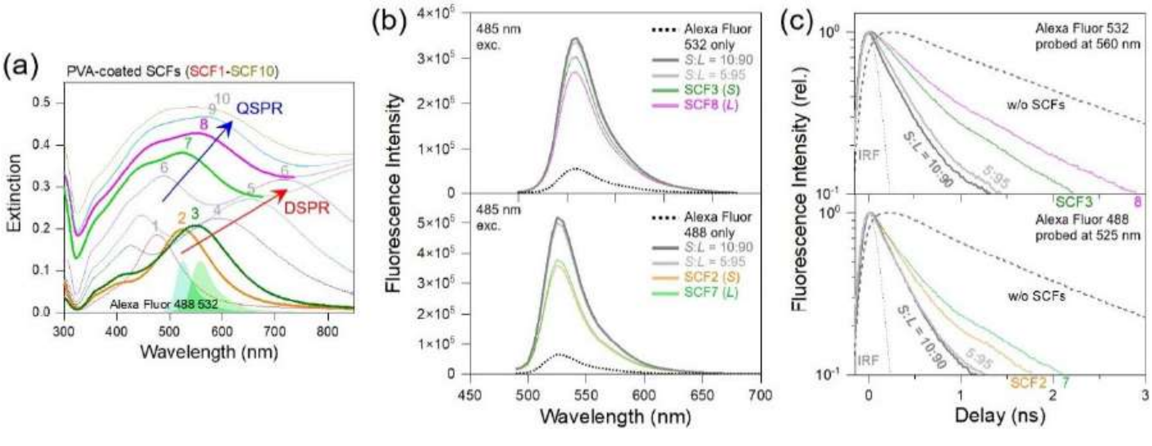

Figure 1. (a) Extinction spectra of the SCFs overlapped with the fluorescence spectra of Alexa Fluor dyes in PVA films, and (b) fluorescence enhancements and emission kinetics of the Alexa Fluor dyes with the SCFs and composite SCFs. *S* and *L* represent the small and large silver nanoparticles, respectively.

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PP049

Visible-Light Induced Decomposition of PFAS by Semiconductor Nanocrystals

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Per- and polyfluoroalkyl substances (PFAS) are practically used in various industrial fields, while their extremely high stability causes serious environmental persistence. Different decomposition methods such as heat and irradiation of deep ultraviolet light have been reported, however, decompositions under more mild conditions are desired for realizing sustainable fluorine recycling. Here, we report that PFAS can be decomposed into fluoride ions using irradiation of visible LED light to aqueous nanocrystals (NCs) at room temperature under atmospheric pressure. The decomposition reaction is induced by the stepwise two-photon absorption processes of NCs,[1] i.e., the decomposition of PFAS such as perfluorooctanesulfonic acid (PFOS) and polytetrafluoroethylene (PTFE) is induced by electrons of higher excited states and hydrated electrons generated by Auger recombination.

Laser flash photolysis measurements show that hydrated electrons are formed upon irradiation of a 355-nm nanosecond laser (Figure 1a). The signal associated with the hydrated electrons nonlinearly depends on the excitation intensity (Figure 1b). It indicates that the hydrated electrons are generated by the stepwise two-photon processes such as Auger recombination. Hydrated electrons (and higher excited states) have enough reduction potential to reduce the PFOS and even PTFE.

The decomposition of PFOS was investigated by fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectroscopy and fluoride ion sensors by prolonged irradiation of 405-nm LEDs. After irradiation with 405-nm light (890 mW/cm^2) for 6 hours, the signals associated with PFOS largely decreased and a new sharp peak ascribable to the fluoride ion was observed at 122 ppm (Figure 1c). It clearly shows that PFOS can be decomposed to fluoride ions by visible light irradiation. After 24 h irradiation, the efficiency for the C−F bond breaking (it is noted that a PFOS has 17 C−F bonds) is 85% after 24-hours irradiation.

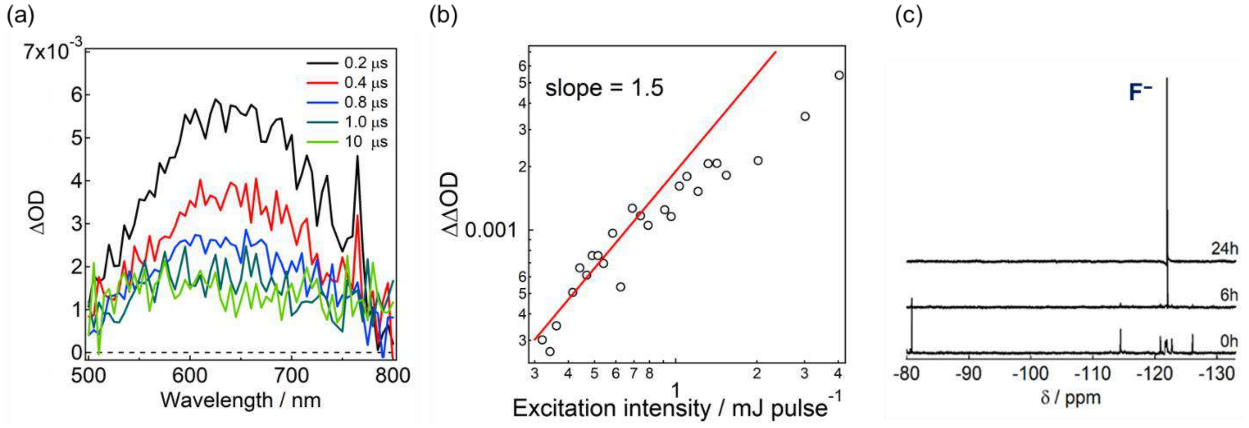

Figure 1. (a) Transient absorption spectra of 12% Cu-doped CdS NCs exited with a 355-nm nanosecond laser pulse (15 mJ/cm^2). (b) The signal associated with the hydrated electron (ΔΔOD) as a function of excitation intensity. (c) ^{19}F NMR spectra of PFOS in D_2O in the presence of semiconductor NCs upon visible-light irradiation (890 mW/cm^2).

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PP050

Photodoping of Semiconductor Nanocrystals Controlled by Supramolecular Gel

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Photodoping is the phenomenon that electrons are accumulated in the conduction band of semiconductor nanocrystals (NCs) by light irradiation.[1] This phenomenon is expected to be applied to solar energy storage and photochromic materials.[2] However, photodoping works generally only under an inert atmosphere because the accumulated electrons react with oxygen.

In this study, we focused on the sol-gel transition of a supramolecular gel to control oxygen supply. We successfully controlled photodoping of semiconductor NCs under air based on on-demand oxygen supply using sol-gel transition. In the gel state, photodoping occurs because oxygen transfer from the air is suppressed. Whereas, after the thermally induced gel-to-sol transition, oxygen easily permeates the sol sample and reacts with the doped electrons to return the NCs to the initial undoped state.

We synthesized alkyl-capped semiconductor NCs and dissolved the NCs in toluene containing a hole scavenger. A supramolecular gelator was also dissolved in this solution and the sample was gelated by cooling. When this gel was irradiated with UV light, the sample was changed from colorless to blue by plasmon resonance of free electrons at the conduction band of the NCs (Figure 1). In the N_2-purged gel, electrons started to be accumulated immediately after the beginning of UV light irradiation. On the other hand, the air-saturated gel exhibited an induction period of around 15 minutes until photodoping occurred after UV irradiation is started. This induction period was considered as the duration until the dissolved oxygen was consumed by reaction with electrons in the conduction band and subsequent decomposition. After the gel-to-sol transition by heating, the sol changed from blue to colorless because the electrons in the conduction band of the NCs reacted with oxygen supplied from the air. Moreover, coloration by photodoping and decoloration by gel-to-sol transition were successfully repeated. These results show that supramolecular gel is useful to control photochromism by photodoping.

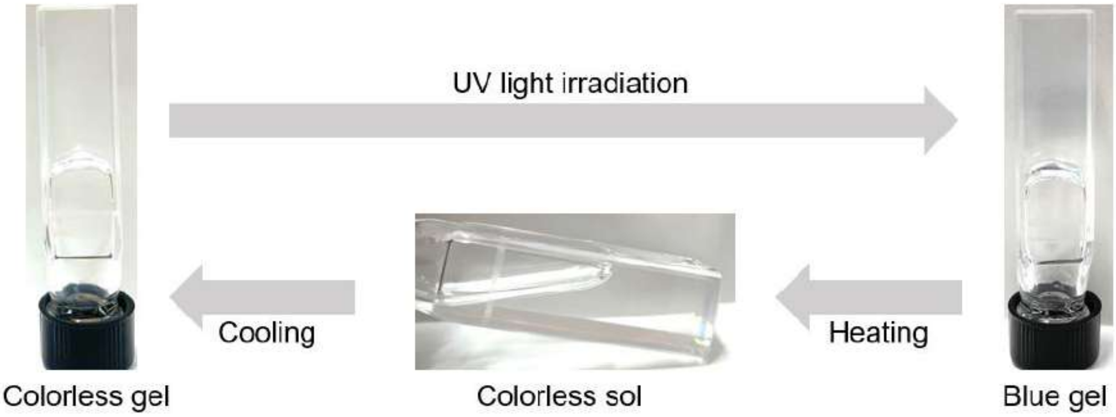

Figure 1. Color change of the sample by UV irradiation and sol-gel transition.

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PP051

New Pyridinium Phenolate Dyes

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Reichardt's Dye (also known as Betaine 30), reported by Reichardt and Dimroth in 1963, is the benchmark solvatochromic dye and is used as a solvent polarity indicator, being the basis of the $E_T(30)$ scale. Although numerous derivatives of **Reichardt's Dye** have been previously reported (figure 1, structures 1-4), there has been no report of the effect of π-extension. Pyridinium phenolates have been synthesised with a phenyl ring separating the pyridinium and phenolate moieties. They have demonstrated negative solvatochromism, with **Extended Reichardt's Dye** (figure 1) shifting in wavelength from 479 nm in methanol to 711 nm in pyridine.

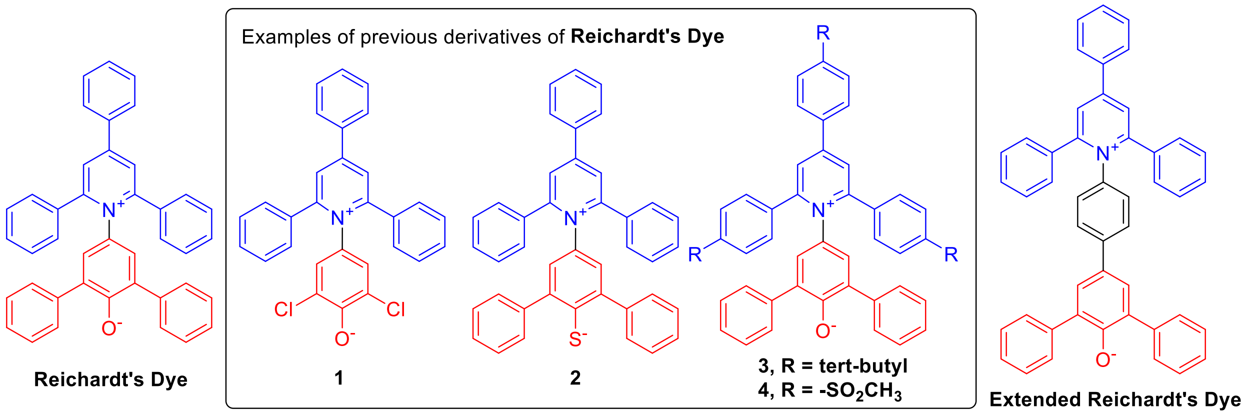

Figure 1. Structures of Reichardt's Dye, derivatives of Reichardt's Dye from previous works and Extended Reichardt's Dye

PP052

Panchromatic Light Harvesting in Luminescent Solar Concentrators

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Luminescent solar concentrators (LSCs) are solar harvesting devices that utilize luminescent materials embedded within a waveguide to capture solar energy. Multi-dye systems using energy transfer strategy can be used to maximize the light harvesting performance of LSCs.[1-2] In our work, we use a 3-dye combination, two energy donors naphthalene diimide (NDI) and perylene diimide (PDI) and an energy acceptor/emitter LR305 (Fig.1). By varying the concentration of the dyes in a polymer matrix, we can achieve light harvesting films that display efficient energy transfer and high photoluminescence quantum yield. To further investigate the behavior of these multi-dye systems, we compare the two NDI and two PDI energy donors, which possess sidechains with varying steric bulk. This comparison enables us to examine the impact of hindered and unhindered donors on energy transfer characteristics and ultimately, how these molecular structure variations affect LSC device performance.

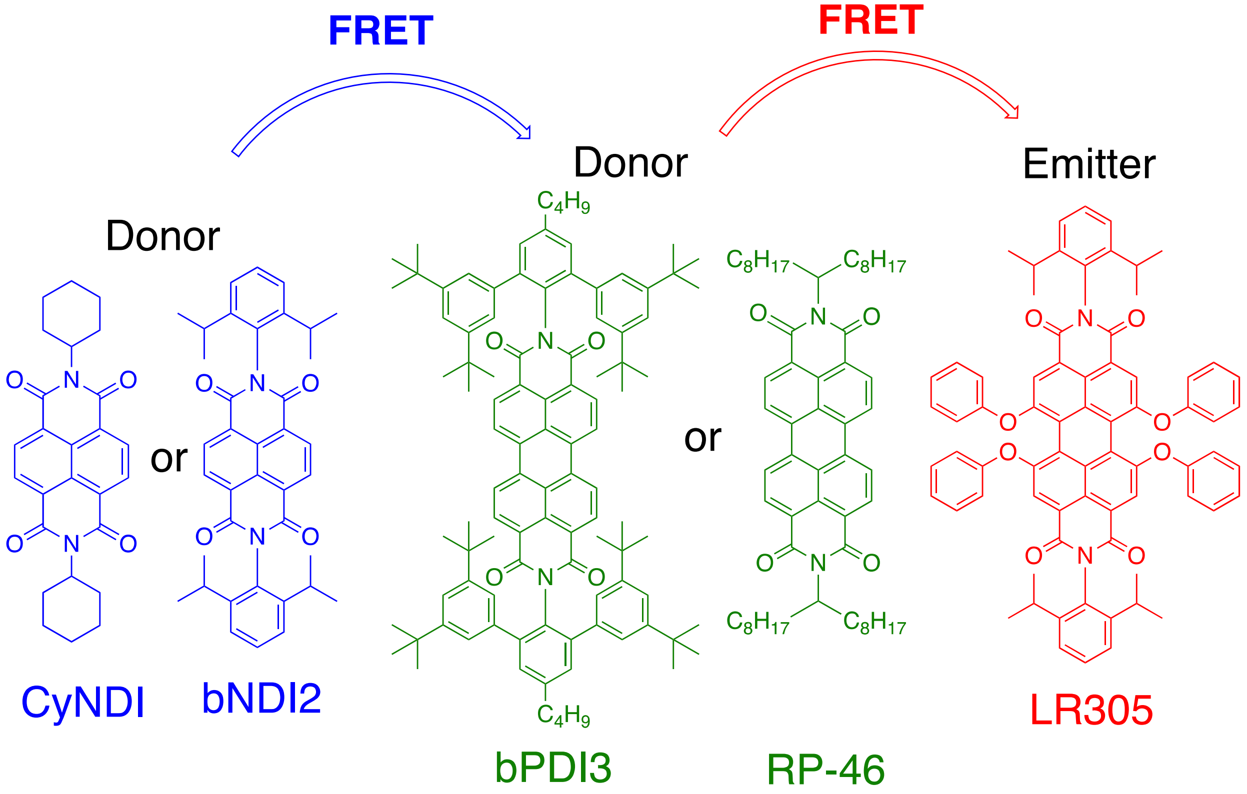

Figure.1 Simplified representation of the multi luminophores FRET energy transfer system and structures of CyNDI, bNDI-2, bPDI-3, RP-46 and LR305.

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PP053

Raman spectroscopy of MAPbBr₃ under hydrostatic pressures: Organic vibrational modes sense internal pressure and phase transitions

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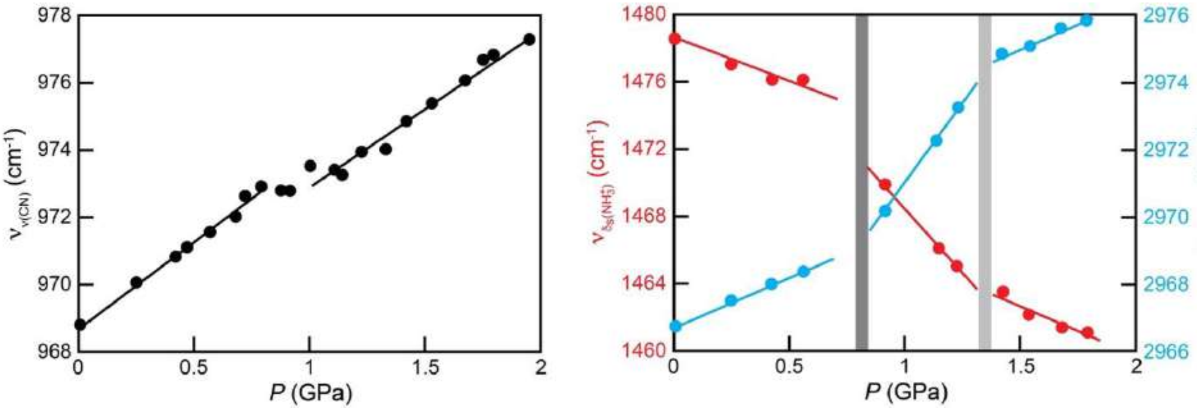
Methylammonium lead halides (MAPbX$_3$, X = Cl, Br and I) have attracted immense attention to their optoelectronic properties that are governed by their PbX_6^{4-} octahedron frameworks and are perturbed by the interaction with the caged MA^+ cation. Depending on the sites and the directions of atoms in motion, the frequency shifts of the vibrational modes of MA^+ would reflect the internal force and the inorganic framework geometry induced by externally applied pressure. Despite several pressure-dependent Raman studies,[1] controversy remains because of poor spectral resolution and non-hydrostatic pressure applied. In this study, we investigated the interaction in cubic MAPbBr$_3$ lattice by revealing how the vibrational modes obtained with high-precision Raman spectroscopy are varied with external pressure.

Our Raman setup bore a spectral accuracy within 0.1 cm^{-1}, while the pressure *P* was calibrated to 0.1 GPa in accuracy. The three prominent Raman peaks, H_3C-NH_3 stretch $\nu_{\nu(CN)}$, NH_3^+ umbrella bend $\nu_{\delta_s(NH_3^+)}$ and CH_3 symmetric stretch $\nu_{\nu_s(CH_3)}$, show different pressure dependences (see the figure below): with the increment of *P*, $\nu_{\nu(CN)}$ increases virtually linearly, $\nu_{\delta_s(NH_3^+)}$ decreases and $\nu_{\nu_s(CH_3)}$ increases stepwise. The linear $\nu_{\nu(CN)}-P$ relation indicates that $\nu_{\nu(CN)}$ can serve as an internal pressure gauge. Since cubic MAPbBr$_3$ lattice undertakes a $Pm\bar{3}m$-to-$Im\bar{3}$ transition at 0.8 GPa (marked by the dark gray column) where the $PbBr_6^{4-}$ octahedron assumes different deformations,[2] the alternated interactions between the methyl-ammonium group and the octahedra would induce different frequency shifts. In fact, beyond 1.3 GPa (marked by the light gray column), new $\nu_{\delta_s(NH_3^+)}-P$ and $\nu_{\nu_s(CH_3)}-P$ relations emerge, suggesting a new phase unrecognized before. A liquid-crystal-like transition around that pressure suggested recently[3] supports our observation.



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PP054

Two Tales of Energy Harvesting

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Natural photosynthesis involves a series of highly efficient energy transfer processes wherein the light energy absorbed by the chromophore bound light-harvesting complexes is guided to the photosynthetic reaction centre, and the excitation energy is converted into chemical energy.[1] Fabrication of functional nanomaterials capable of harvesting and transferring energy is of great interest. In this poster, two methods for the down conversion of higher energy light to lower energy red light using (i) one-dimensionally grown CdS on CdSe seeds (CdSe–CdS)[2] and (ii) coupled quantum dots (QDs) with different band-gaps within dimer and core-satellite systems are discussed. The photophysical properties of CdSe–CdS, which have a tapered end, are investigated as a function of shell length. The CdS segment in the CdSe-CdS acts as a light-absorbing antenna because of its large absorption cross section and funnels charge carriers to CdSe before radiative recombination. Single-particle photoluminescence of CdSe-CdS revealed a decrease in the ON-to-OFF ratio upon elongation, and established the occurrence of trap-induced Auger processes arising from the stacking faults. In the second method, the donor QD absorbs energy and transfers it non-radiatively to an acceptor QD (red-emitting) via very-weak dipolar coupling, is known as Förster resonance energy transfer.[3] We have developed an approach for the self-assembly of QDs through the hybridization of single-stranded DNA attached to the QD.[4] DNA-mediated self-assembly offers precise control over the distance between the constituent particle and the number of particles attached. This approach enables the selection of QDs with absorption in the different regions of the visible spectrum, facilitating efficient energy transfer to the acceptor QD. The synthesis and investigation of the optical properties of these functional nanoassemblies will be discussed.

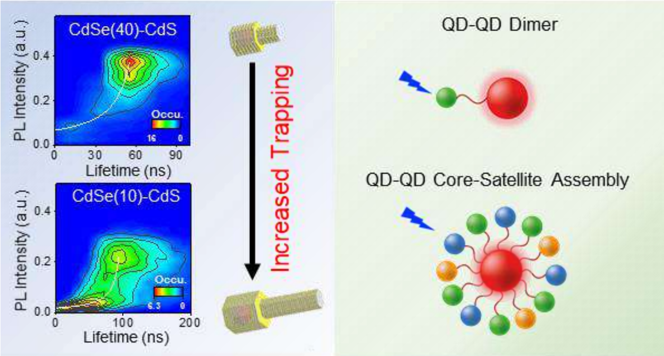

Figure 1, (Left) Fluorescence lifetime intensity distribution of CdSe-CdS with increasing length of the nanostructure, (Right) illustration of QD nanoassembly for energy transfer.

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PP055

Ensemble and Single Particle Photoluminescence of Quantum Dots in Plasmonic Field

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The undesirable trapping of photogenerated charge carriers in semiconductor quantum dots (QDs) to the mid-gap states detrimentally affects their brightness and color purity. The phenomenon of charge carrier trapping in QDs leads to trap state mediated photoluminescence (PL) and blinking. This inhibits the use of QDs as photon sources for various applications. While a plethora of chemical methods has already been devised to eliminate the trap states, these methods often involve tedious synthesis pathways.

Alternatively, modification in the photonic environment of the emitter can be achieved by physical methods[1] and the poster will demonstrate two examples of this concept. A physical approach for the selective enhancement of band edge PL of CdSe QDs over trap state PL by controlling the local photonic environment through the plasmonic coupling at the ensemble level will be presented in the first part. Frequency-specific plasmon resonance coupling selectively enhances the band edge PL and alters the spectral profile of the QDs.[2] The second example is based on single-particle investigations, wherein the intrinsic PL blinking of CdSe/CdS heteronanostructures is greatly suppressed by keeping them in the proximity of a plasmonic field.[3] A large increase in the radiative rate of the heteronanostructures along with their reduction in the Auger recombination significantly suppresses their blinking.

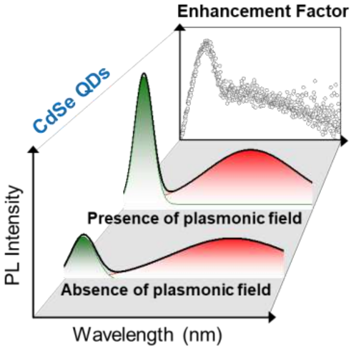

Figure 1. PL spectra of CdSe QDs in the absence and presence of plasmonic field along with the enhancement factor.

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PP056

Exploring novel luminescent iridium(III) complexes

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Luminescent iridium(III) complexes have numerous applications, including biological imaging, photocatalysis, luminophores for organic light-emitting diodes (OLEDs), and chemical and biological detection using electrochemiluminescence (ECL). This study focuses on the synthesis and characterization of a series of novel, highly emissive Ir(III) complexes, as well as the investigation of their electrochemical and photophysical properties that would be beneficial for the advancement of these applications.

Due to having higher ligand field stabilisation energy (LFSE), Ir complexes have shown tunable redox and optical properties by altering the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).[2] This can be achieved by the modification of the coordinated ligands resulting in a red/blue shift in the emission maxima.[2] In this work, the functional group attached to the cyclometalated ligand is changed as shown in the figure 1. Moreover, full structural characterization, absorption and emission spectroscopy, cyclic voltammetry, and ECL properties are being explored.

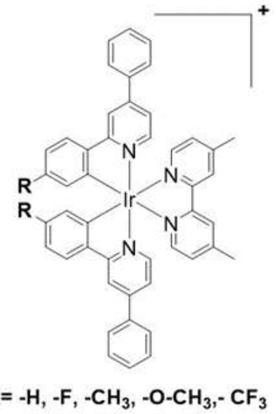

Figure 1: Structure of the synthesized cyclometalated heteroleptic Ir(III) complexes.

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PP057

Rapid Scan White Light Two-dimensional Electronic Spectroscopy with 100 kHz Shot-to-Shot Detection

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Two-dimensional Electronic Spectroscopy (2DES) enables mechanistic insights into the ultrafast dynamics of condensed phase phenomenon by resolving the system dynamics along the excitation and detection frequency as a function of delay without compromising the spectral or temporal resolution. Extensions towards micro-spectroscopy have recently led to the development of high-repetition rate 2DES, where programmable acousto-optic pulse shaping (AOPS) technology[1] for pulse-pair generation has proven highly effective for high-repetition rate shot-to-shot 2DES. However significant cost and complexity of AOPS, along with limited time aperture–RF band-width product and the RF waveform update rate poses fundamental challenges in terms of its repetition rate scalability.

Here we present a 2DES spectrometer which takes white-light continuum (WLC) as input, and combines the advantages[2] of high repetition rate rapid scan shot-to-shot detection with the simplicity of a broadband WLC and traditional birefringent optical elements instead of AOPS. of our approach is only limited by the CCD line rate. A *final averaged* 2DES absorptive spectrum is generated in as fast as 7 seconds at 100 kHz repetition rate, with signal-to-noise ratio (SNR) of 6.81 for optical densities down to 0.05. This throughput and SNR of our spectrometer is comparable to the state-of-the-art AOPS based 2DES, hence providing a viable repetition-rate scalable and cost-effective alternative to high repetition rate WLC- 2D electronic spectroscopy.

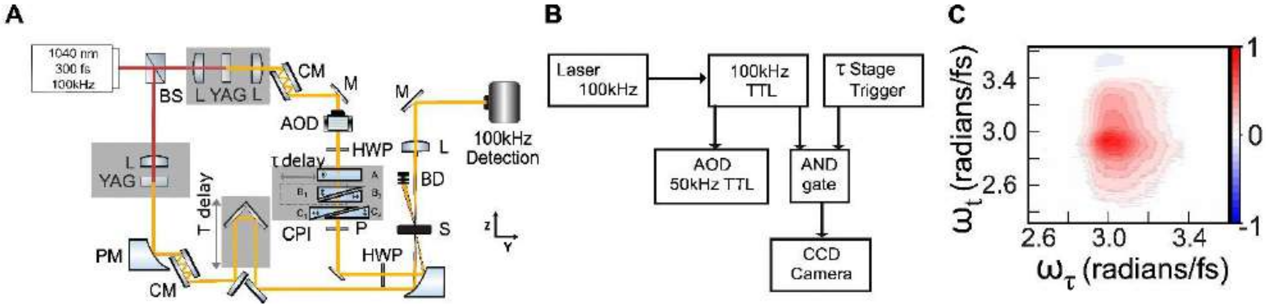

Figure 1. (A) Schematic of the WLC 2DES setup. (B) Electronics synchronization which enables 100kHz shot-to-shot detection. (C) Representative experimental 2D spectrum for a laser dye Oxazine720 in MeOH collected using the 100kHz shot-to-shot rapid scan data collection scheme.

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PP058

Harvesting Near-infrared Photons by Perovskite Quantum Dots and 3D Display via Photochemical Upconversion

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Coupling organic light-harvesting materials and lead halide perovskite quantum dots (LHP QDs) is an attractive goal that could provide great potential in optoelectronic applications owing to the diversity of organic materials and the intriguing optical and electronic properties of LHP QDs.[1,2] Here we demonstrate efficient energy collection by $CsPbI_3$ QDs from a light-harvesting upconversion system which consists of Pd-tetrakis-5,10,15,20-(p-methoxycarbonylphenyl)-tetraanthraporphyrin (PdTAP) as the sensitizer to harvest near-infrared photons and rubrene as the annihilator to generate upconverted photons via triplet-triplet annihilation (TTA). Our study successfully achieved near-infrared photon harvesting at low power density by perovskite quantum dots. Steady-state and time-resolved photoluminescence spectra reveal that the $CsPbI_3$ QDs are energized via radiative energy transfer from the singlet excited rubrene with photophysics fidelity of respective components. Moreover, we constructed a three-dimensional display device relying on $CsPbI_3$ QDs as light emitters using photochemical upconversion, showing excellent monochromaticity. These results present the feasibility of merging organic light-harvesting systems and lead halide perovskite quantum dots, enabling diverse energy harvesting and activating perovskite materials for optoelectronic applications.

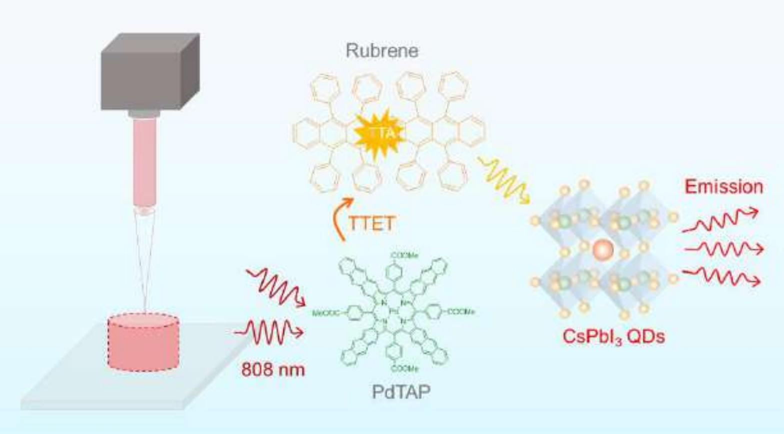

Fig. 1 Schematic diagram of 3D display based on perovskite via photochemical upconversion.

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PP059

Development of Scalable Luminescent Solar Concentrator Fabrication Techniques

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Luminescent solar concentrators (LSCs) are an emerging technology in the area of building integrated photovoltaics (BIPV) due to the ability to control appearance, color and transparency and are a candidate for solar harvesting windows[1]. Solar energy is absorbed by luminescent compounds coated on or embedded within a transparent substrate and the luminescence is subsequently guided to the edges of the substrate by total internal reflection where it can be collected by photovoltaic (PV) cells[2]. At lab scale, there is a wide range of available fabrication techniques, such as spin coating or drop casting, to deposit luminescent compounds onto substrates which are not appropriate for fabrication of large scale. As a result, there is a need for scalable LSC fabrication techniques which are compatible with existing industrial processes. Our approach is to integrate LSC materials into the glass lamination process in order to develop solar harvesting windows that can be substituted into existing applications in the building construction industry. We are investigating three approaches to scalable fabrication, coating luminophores onto window glass prior to lamination, coating luminophores onto standard window lamination interlayers and coating luminophores onto a flexible substate which can be integrated into window interlayers. Initial testing has shown that scalable roll-to-roll printing methods can coat consistent layers of organic dyes and polymers onto flexible substates. The flexible substrates where then successfully laminated between two sheets of glass and was achieved using industry standard adhesive layers. Further work is being undertaken in order to adapt this method for a wide range of LSC candidate materials.

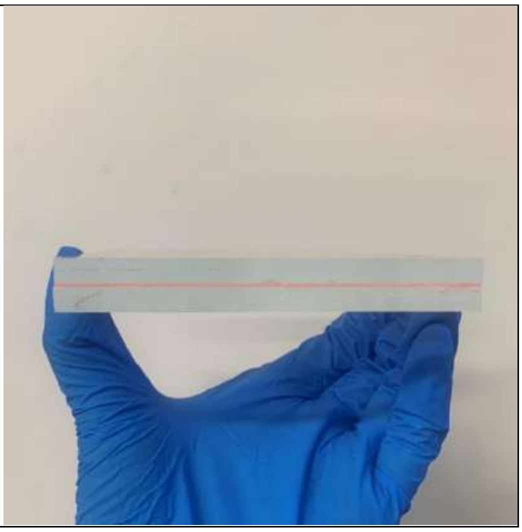

Figure 1 Fabricated LSC samples showing flexible substrate laminated between two sheets of low-iron glass

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PP060

Room Temperature and Cryogenic Transient Absorption of Helicate and Mesocate Forms of Double-stranded Di-nuclear Ru(II) Complexes

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The excited-state kinetics of two double-stranded Ru(II) complexes of helicate and mesocate conformations were investigated at 294 K and 77 K with transient absorption spectroscopy (TAS). Both isomers are non-luminescent at room temperature because the emitting states are in thermal equilibrium with an energetically proximal metal-centered state (^{3}MC) as well as a triplet metal-ligand charge transfer (^{3}MLCT) state with greater singlet character. The mesocate showed a five-fold decrease in the excited lifetime compared to the helicate due to a slight geometric distortion near the ligand bridge which stabilizes the ^{3}MC state. The energies of the ^{3}MC and the ^{3}MLCT states calculated by density functional theory (DFT) were in qualitative agreement with the observed kinetics. At 77K, the kinetics of the two complexes are similar. Cryogenic TA with long pump-probe delays up to ~ 20 µs uncoupled energetically proximal ^{3}MLCT states with varying singlet characters and decay rates of ~ 10^6 s^{-1} and ~ 10^5 s^{-1}.

PP061

Electronic Spectroscopy of Astrophysically Relevant Closed-Shell Cations

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The interstellar medium (ISM) describes the region of space between stars and is comprised of gas molecules and dust particles and accounts for approximately 15% of the milky way. Molecules within the ISM absorb and scatter light throughout the visible and near-infrared regions of the electromagnetic spectrum. However, the species responsible for interstellar spectroscopic absorption features are largely unidentified and await laboratory spectra to confirm assignment. [1] The absorption bands have been collectively named the diffuse interstellar bands (DIBs) and the identity of their carriers have eluded scientists for over 100 years. There have been many suggestions for groups that are responsible for these bands including fullerenes, hydrocarbon chains and polycyclic aromatic hydrocarbons (PAHs). It wasn't until 2015, when Campbell et al., confirmed by laboratory experiments the existence of buckminsterfullerene cation (C60+) as a carrier in the ISM.[2]

Further evidence of the abundance of PAHs in the ISM comes from the aromatic infrared bands (AIBs) of star forming regions and pro-planetary nebulae that account for approximately 15% of energy emitted in space and 20% of all cosmic carbon.[3] An important class of PAHs, that is lacking in experimental data, is closed-shell cations. Closed – shell PAHs have their lowest electronic excitation in the visible region and can come in the form of resonance stabilised cations that would be easily energised in the ISM. They are also unlikely to be ionized by the interstellar radiation field which would deplete most neutral species.

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PP062

Monolayer modification of spherical amorphous silica by clay nanosheets

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Clay nanosheets have been studied as ideal host materials for the construction of unique assembly of dyes, especially under the exfoliated conditions in water. Because clay nanosheets have high aspect ratio, nanosheets tend to stack in the solid state. Therefore, the properties of the sheet surface cannot be utilized efficiently, especially in the solid state. Dyes between the stacked nanosheets exhibit different photophysical properties than those on the exfoliated nanosheet. For example, the absorption behavior and excited lifetime are different[1]. The purpose of this study is to maintain the photophysics of the dyes on the exfoliated nanosheet even when the nanosheet is in the solid state to avoid the stacking of nanosheets. In this study, we examined compositing clay nanosheets with silica spheres (Fig.1, left). If clay nanosheets are fixed on the silica spheres, the properties of the exfoliated state can be maintained even in the solid state (Fig.1, right). This is expected to expand the range of applications of clay nanosheet-dye composites as photo-functional materials such as luminescent materials.

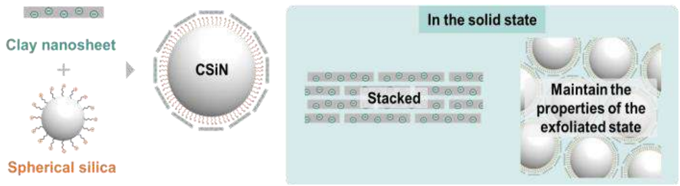

Fig. 1 Image of the clay-silica nanocomposite material (CSiN).

At first, poreless spherical silica (Seahoster®KE-W10) with a particle size of 0.1 μm was organically modified with the silane coupling agent [3-(*N,N*-dimethylamino)propyl]trimethoxysilane. Then it was methylated at the amino group to produce silica spheres with the cationized surface. Clay-silica nanocomposite materials (CSiN) were prepared by electrostatic interaction between negatively charged clay nanosheets and positively charged spherical silica.

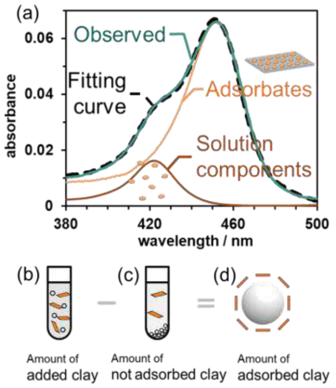

Fig. 2 Measurement of adsorption of clay nanosheets on silica spheres.

To examine the surface coverage ratio of silica surface by nanosheets, we investigated the effect of the particle size of clay nanosheets. The adsorption amount of clay nanosheets on cationic silica was quantified by the method shown in Fig. 2. First, clay nanosheets complexed with cationic silica (from b to c) were precipitated by centrifugation. In the supernatant of the solution after centrifugation, only clay nanosheets that were not adsorbed on silica spheres were present (c). Next, the amount of clay nanosheets in bulk water (c) was calculated by measuring the absorption spectrum (a) using cationic porphyrins where the adsorption amount is known on clay nanosheets. Finally, the amount of clay nanosheets adsorbed on silica spheres was calculated by subtracting the amount of clay nanosheets not adsorbed on silica spheres from the amount of clay nanosheets added. This hybrid is a promising material for the photo-functional materials.

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PP063

Induced Self-assembly of Nanocrystals for Luminescent Solar Concentrators

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Luminescent Solar Concentrators (LSCs) are vital for renewable energy technology, especially in areas where traditional solar cells face limitations. While crystalline silicon solar cells have higher efficiency, this technology is limited by the large surface area, required direct sunlight exposure, and high energy cost to produce. LSCs have the distinct advantage of being able to adsorb ambient and non-direct light, allowing for efficient energy harvesting without direct sunlight. However, challenges that still need to be addressed are dye photobleaching, limited absorption, and energy losses due to unoriented light cones. A proposed solution to these challenges is the use of luminescent nanocrystalline semiconductor rods (nanorods) due to their high stability and potential for efficient solar harvesting when properly aligned.

This research aims to develop a novel method for controlling the self-assembly of nanorods to deposit monolayers on a large area. The proposed method involves the self-assembly of metallic tipped nanorods through a depletion of attraction mechanism on a substrate. The anisotropic attractive force between the tip of the nanorods and the substrate results in perpendicular monolayer nucleation, facilitating side-by-side alignment. This alignment is crucial for minimising light escape from the LSCs and enhancing light collection efficiency. Due to the spontaneous nature of this method, it is more scalable and suitable for large-scale applications like solar energy harvesting than traditional crystalline silicon solar cells.

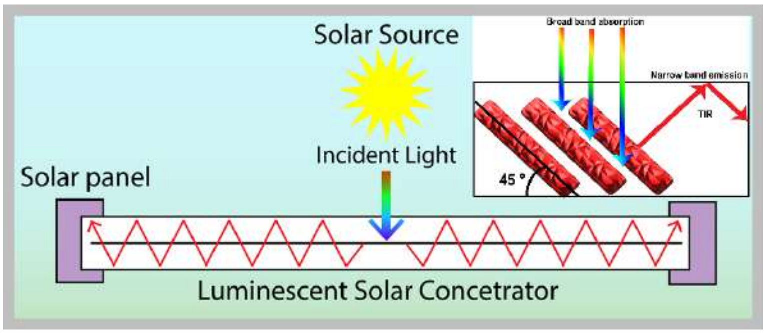

Figure 9 The schematic illustrates the functioning of LSCs, which capture both diffuse and direct light and subsequently re-emit the light towards the edges for harvesting. The inset shows that the emission dipole of nanorods provides precise control over the direction of emitted light.

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PP064

Electronic and optical properties of [3]radialenes and related molecules

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[3]Radialene is the smallest omni-conjugated[1] molecule – so-called because all of its exocyclic substituents are linearly conjugated to one another, allowing for electronic communication along three different pathways. [3]Radialenes can be used as three-way conjugated linkers to build topologically interesting circuits. They have been employed in metallosupramolecular coordination chemistry[2] and in molecular electronics, and they feature heavily in patent literature as organic superconductors for OLED[3] devices. Despite these exciting advances, the fundamental nature of electron delocalization across the [3]radialene core is not well understood. This research explores the electronic and photophysical properties of [3]radialene and p-extended analogues, including triquino[3]radialenes,[4,5] which exhibit strong transitions in the visible part of the spectrum owing to their extreme conjugation (Figure 1).

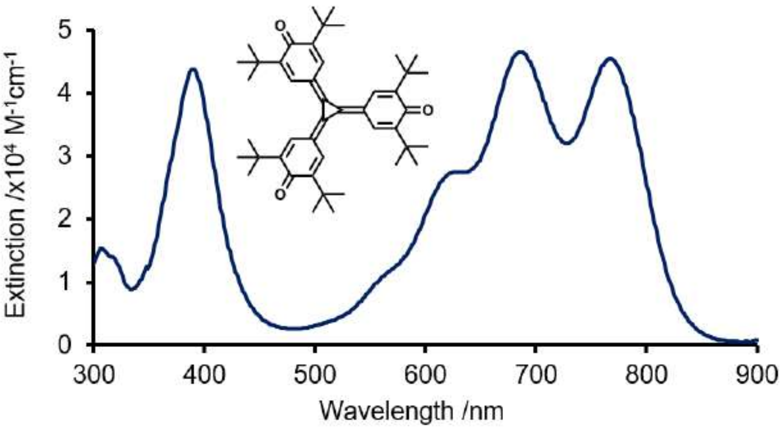

Figure 1: UV-visible absorption spectrum of triquino[3]radialene

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PP065

Sustainable and biodegradable polaritonics: Inspirations from the Australian Christmas Beetle

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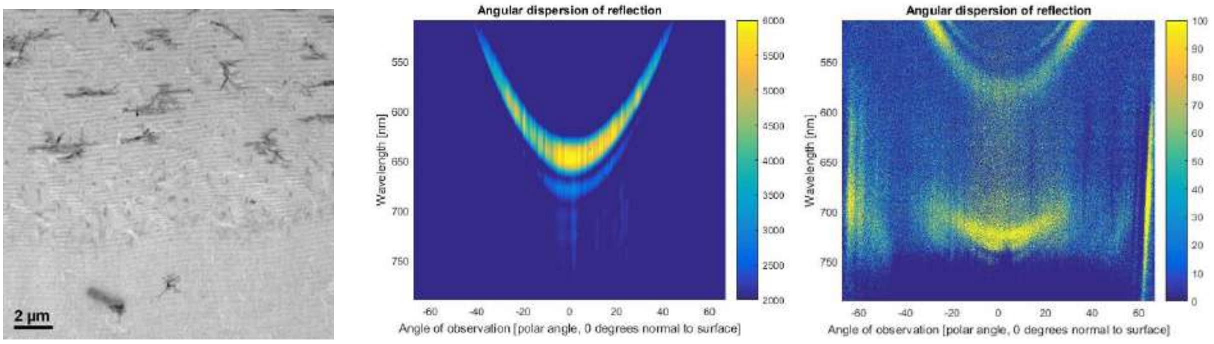
This presentation will discuss our recent work towards developing sustainable and bio-inspired optical cavities for strong light-matter coupling and polaritonics.

In Nature many species use nano/microstructures to control light, not least of them being the beetles. Beetles have two pairs of wings, the first pair hardened by chitin into elytra (protective wing cases without veins), while the second pair is membranous, used for flying[1]. The elytra can feature a multilayered structure[2] (shown in Figure 1(a)). The elytra of Australian Christmas beetles are iridescent, indicating that optical interference effects occur in the multilayer structure, potentially making them of interest as optical cavities for strong light-matter coupling. This work will discuss the interaction of organic dyes with these elytra (and their synthetic analogues) as a proof-of-principle towards sustainable polaritonics.

The iridescent reflectance of the elytra was investigated using microscopic back focal plane imaging (shown in Figure 1(b)). At normal incidence, red light is reflected (around 650 nm) which is near-resonant with the absorption peak of the dye methylene blue. After absorbing methylene blue into the elytra, the characteristic signatures of polariton formation are revealed, including a splitting of the optical mode and reduction in iridescence (increased effective mass, see Figure 1(c)). The fabrication of artificial synthetic structures to mimic the elytra structure is underway and may point the way towards sustainable and biodegradable polaritonics.



(a) (b) (c)

Figure 1: (a) Electron microscopy cross-section of the Christmas beetle elytra (thanks to Laura Ospina-Rozo, Biosciences, Uni. Melbourne); (b) Angular dispersion of percent reflectance for the Christmas beetle elytra; (c) Angular dispersion of percent reflectance for the Christmas beetle elytra after absorbing methylene blue dye.

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PP066

Effect of varying dimensions of CdSe/CdS dot-in-rod donors in energy transfer to molecular dye acceptors

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Donor-acceptor energy transfer (ET) systems find application in optoelectronics, biotechnology, and energy conversion. Semiconductor nanocrystals (NCs) are extensively used as donors, as they exhibit many favourable characteristics such as broad absorption profiles, high absorption coefficients, photostability, long lifetimes, narrow emission spectra, and high PLQYs. In addition to these, CdSe/CdS dot-in-rod structures (DiRs) with inherently larger Stokes shifts, can mitigate reabsorption losses following ET, making them more promising candidates as donors in ET systems.

In this study, we investigate the energy transfer between CdSe/CdS DiRs of varying dimensions and molecular organic dyes. The CdSe/CdS DiRs are synthesized using a well-established solution-based method, with precise control over their dimensions and optical properties. ET efficiencies are quantified by measuring the photoluminescence intensities and lifetimes of the DiRs upon interaction with the dye, through steady-state and time-resolved spectroscopic techniques.The rate and efficiency of ET typically depend on the PLQYs, donor-acceptor distance, exciton lifetimes (τ), dipole orientations, polarization, spectral overlap, and the acceptor loading on the donor. The dimensions of the DiRs were systematically varied to probe the interplay and influence of PLQY, distance, τ, and acceptor loading on ET rate and efficiency.

Compared to CdSe QD-Molecular dye ET systems[1,2], the ET efficiency of DiRs proved to be low. Our experiments revealed the shorter DiRs exhibit higher ET efficiencies compared to longer ones. We also compare DiR donors to quantum confined CdSe rod donors to test material and structural effects.

CdSe/CdS DiRs are known to spontaneously self-assemble on substrates[3,4] forming ordered arrays over large areas, have excellent air-stability and linearly polarized emission, desirable traits for fabricating large scale devices such as, LEDs, light concentrators, and solar cells. These traits, along with an in-depth understanding of the underlying mechanisms of ET from DiR donors, pave the way to tune and enhance efficiency for different applications.

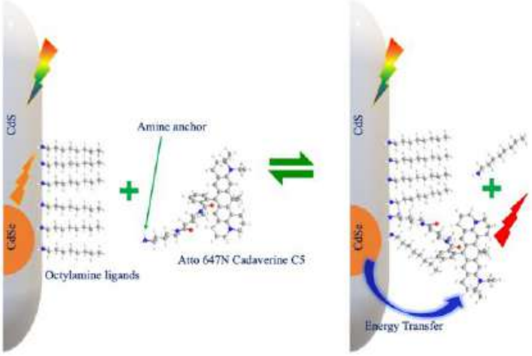

Figure 10: Energy transfer system of CdSe/CdS DiR donors and Atto 647N Cadaverine C5 molecular dye acceptor

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PP067

Optical Studies of Anti-microbial Nanostructured Materials

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Dental implants and hip replacements improve the quality of human life. However bacterial infection can lead to the failure of these surgeries and subsequent complicated, expensive, and dangerous resection. Traditional antibiotics are not an effective solution for implant infection as the blood supply to bones tends to decrease with age, causing problems for drug delivery. Inspired by the structure of the wings of cicadas, there has been much recent interest in using multi-wall carbon nanotubes (MWCNT) as a novel antibacterial weapon. MWCNTs show potential for physically damaging bacteria without inducing bacterial resistance as happens for chemical antibiotics. Previously, arrays of MWCNTs were produced by expensive and time-consuming lithography methods. Recently, a new lithography-free, self-assembly method has been developed that lowers the fabrication cost and time.[1]

This presentation will discuss recent work in our laboratories using fluorescence microscopy and hyperspectral imaging to determine the bactericidal ability of these lithography-free MWCNT substrates towards gram-negative (E.coli) and gram-positive bacteria (Bacillus subtilis and Staphylococcus). We observe that the structure with 360 nm separation between MWCNTs, with 130 nm diameter nanotubes, and with a plasma-etch post-treatment, exhibited the highest bactericidal ability against the gram-negative bacterium E. coli, killing with 94% effectiveness. Conversely, for the gram-positive bacterium Bacillus subtilis, MWCNT arrays with 70 nm diameter displayed the highest antibacterial ability, at 77%. However, for staphylococcus, smaller bacteria with a round shape, the MWCNT arrays exhibited very low antibacterial efficacy.

These findings show the great potential of these MWCNTs arrays to become a powerful anti-bacterial coating with potential applications for dental and hip replacements, and more. Currently, our focus is on enhancing the bactericidal properties of MWCNTs against Staphylococcus by functionalizing the nanotubes with acid or other chemicals and analyzing the shape and array of MWCNTs to optimize the best antimicrobial MWCNT structure for different bacteria.

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PP068

Ultrafast Broadband Time-resolved Study on the Excitation Dynamic of Bimolecular Human Telomeric RNA (TERRA) G-quadruplex

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Human telomeric RNA (TERRA) is an inhibitor of making telomere,[1] which plays an important role on DNA protection, while cell division in human. As the telomeric sequences are guanine (G)-rich sequences, they can form a special conformation, the G-quadruplex (GQ). Human telomeric GQ also is a well-known material for the targeting of cancer and the probing technique. The excitation dynamics of the human telomeric DNA has been examined in the past few years.[2]

However, there is no discussion on the optical properties of the bimolecular TERRA G-quadruplex before latest publishment.[3] By using the femtosecond broadband time resolved fluorescence (fs-TRF) and transient absorption (fs-TA), I find that there are one monomeric like π-π* state and two charge transfer states. The two different charge transfer states corresponding to excimer state from GQ core and exciplex state from the loop region. This is the first direct observation of the excited state spectra and dynamics for the G-quadruplexes formed from TERRA sequences.

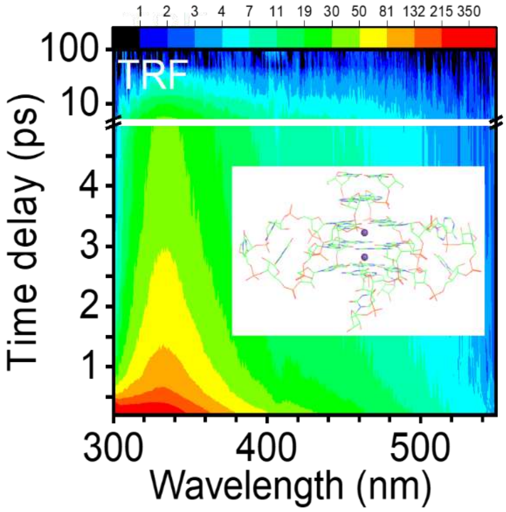

Figure 11 The 3D TRF spectrum of the bimolecular TERRA with inserted the crystal structure.

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PP069

Blending Low-Frequency Vibrations and Push–Pull Effects Affords Superior Photoacoustic Imaging Agents

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Photoacoustic imaging (PAI) is a state-of-the-art noninvasive in vivo imaging technique.[1-3] Constructing photoacoustic (PA) images requires contrast agents (or PAI agents) that generate ultrasonic emissions upon the irradiations of non-ionizing laser pulses. Owing to the merits of high optical resolution (~100 µm) and large penetration depth of ultrasound (~10 cm), the advances of PAI have improved the landscapes of high spatial resolution imaging in deep tissues, allowing clinical diagnosis of many diseases (such as scleroderma,[4] breast cancer,[5] thyroid cancer[6] as well as inflammatory arthritis[7]).

However, the design of high-performance PAI agents with three key characteristics, i.e., near-infrared (NIR) absorption (λ_{abs}>800 nm), intense PA signals, and excellent photostability, remains a challenging goal. Herein, we present a facile but effective approach for engineering PAI agents by amplifying intramolecular low-frequency vibrations and enhancing the push-pull effect.[1] As a demonstration of this blended approach, we constructed a PAI agent (BDP1-NEt2) based on the boron-dipyrromethene (BODIPY) scaffold. Compared with indocyanine green (ICG, an FDA-approved organic dye widely utilized in PAI studies; λ_{abs}=788 nm), BDP1-NEt2 exhibited a UV/Vis-NIR spectrum peaked at 825 nm, superior in vivo PA signal intensity and outstanding stability to offer improved tumor diagnostics. We believe this work provides a promising strategy to develop the next generation of PAI agents.[8]

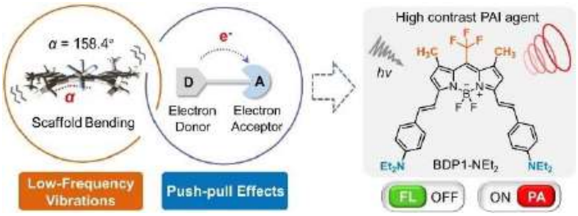

Figure 1: The combination of low frequency vibrations and push-pull effects helped create a novel photoacoustic agent design.

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PP070

The Effects of the Metal-Semiconductor Interface on Surface Plasmon induced Photocatalysis with Gold Nanorods

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This study explores the potential of utilizing gold nanorod (AuNR) coated with a shell of titanium dioxide (TiO_2) for the effective production of hydrogen through photocatalytic water-splitting. Recognizing the urgent need for transitioning from fossil fuels to more sustainable alternatives, this research taps into hydrogen's inherent properties as an abundant, clean, and less toxic energy source[1,2]. The designed AuNR@TiO_2 core-shell structure harnesses the localized surface plasmon resonance (LSPR) of AuNR for light absorption in the visible-Near Infrared (NIR) range, as shown below in figure 1(a)[3]. Concurrently, the interface of AuNR and TiO_2 shell functions as a hub for photocatalytic redox reactions as shown below in figure 1(b)[4]. The optimal dimensions of the core-shell structure were computationally simulated before the actual synthesis[5]. Characterization of the synthesized AuNR@TiO_2 was conducted using spectroscopic analysis, while its photocatalytic performance was assessed using a dye-degradation model. The study also investigated the influence of shell thickness and crystallinity on the catalyst's performance. The observed high photocatalytic activity indicates that AuNR@TiO_2 could be a promising system for future large-scale hydrogen production.

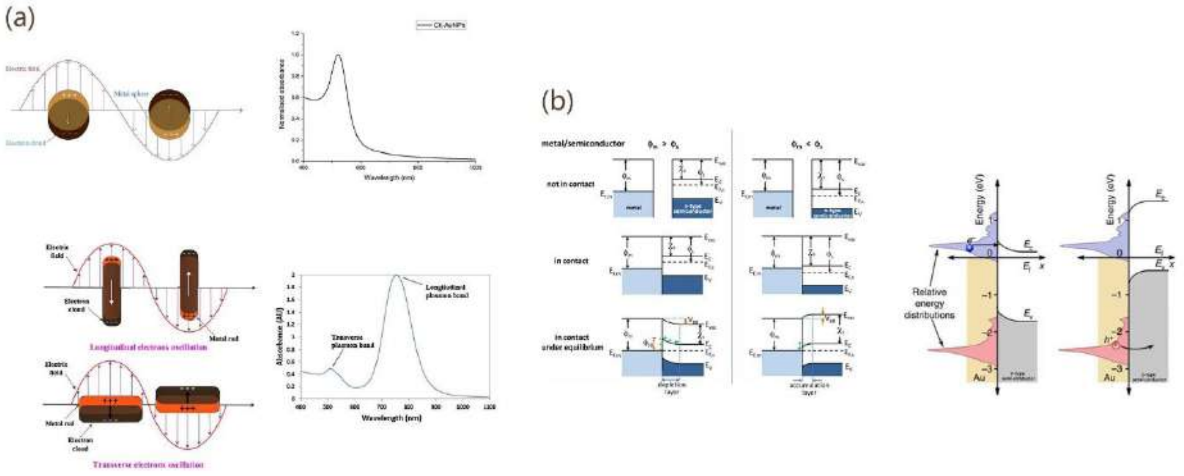

Figure 1: (a) Illustration of LSPR bands with dependence on shape and size; (b) Illustration of band bending and charge separation at metal-semiconductor interface.

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PP071

Synthesis of Magnetic Nanoparticles and Size Control

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The fundamental method of synthesizing magnetic nanoparticles (Fe_3O_4) and controlling their size to achieve varied various size-related functions. The solvothermal polyol synthesis method is utilized to generate magnetite nanoparticles[1], which is both scalable and results in discrete particles with high degree of monodispersity.

The solutes used in the reaction include anhydrous $FeCl_3$, sodium acetate (CH_3COONa), and sodium citrate ($Na_3C_6H_5O_7$), while ethylene glycol ($C_2H_6O_2$) and diethylene glycol ($C_4H_{10}O_3$) serve as the polyols. Sodium acetate maintains the reaction environment's basicity, and sodium citrate acts as a surfactant or stabilizer to modify the nanoparticle surfaces for enhanced stability and reduced aggregation.

My poster will show how to control the magnetite nanoparticle size by adjusting the citrate, base and water content in the reaction. Previous research indicates that the amount of sodium citrate used directly affects the nanocluster size, and the nanoparticles tend to agglomerate over time.[2] To address this issue, silica coating has been applied to the particles. My poster will demonstrate size control and silica coating of magnetite nanoclusters, as well as explore methods to convert the particles from liquid to solid while maintaining stability.

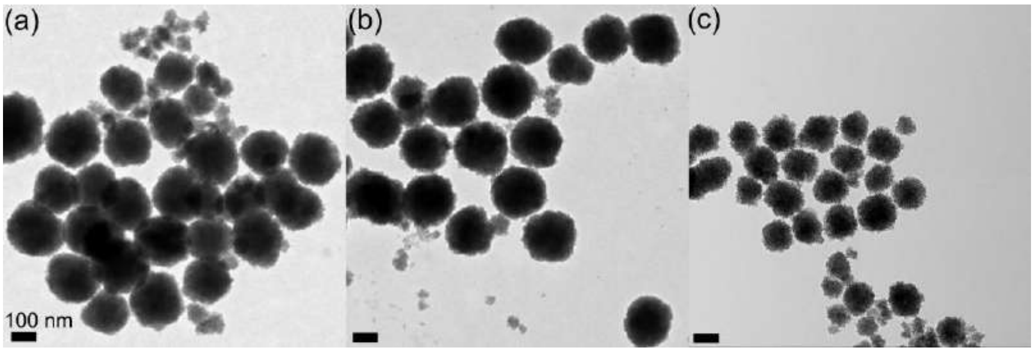

Figure 1: TEM images of MNPs synthesized with different concentrations of H_2O (a) 1 M, (b) 1.39 M, (c) 1.77 M. The corresponding particle sizes were 215 ± 23 nm, 189 ± 26 nm and 138 ± 22 nm respectively. The scale bar in the images represents 100 nm.[2]

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PP072

Colloidal Indium Antimonide Nanocrystals

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Indium antimonide (InSb) is a III-V semiconductor material with a super small bulk band gap of 0.17 eV (7300 nm), and a very large exciton Bohr radius of 65 nm. It is a key material in infrared (IR) photodetectors that can operate in the mid-wavelength IR (MWIR) region. However, solution synthesis of InSb nanocrystals in the literature remained sparse and showed limited size tuning range, yielding small nanocrystals with effective band gaps in the near-IR region.[1] Here, we propose a new solution synthesis route to monodisperse colloidal InSb nanocrystals with a much larger size tuning range, with the largest size up to 120 nm, pushing the band gap to the MWIR region. We also demonstrate the fabrication of photoconductors by solution processing of the as-synthesized InSb nanocrystals and achieved the first ever photoresponse in the MWIR region for colloidal nanocrystal based InSb photodetectors.

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PP073

Visualising the Process of Hg^{2+} and MeHg Bioaccumulation & Biomagnification in Water Flea Daphnia carinata by Aggregation-Induced Emission Luminogen

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Mercury ion (Hg^{2+}) is a toxic heavy metal ion and Hg^{2+} is convertible to methylmercury (MeHg) by many aquatic microorganisms. Both toxins lead to bioaccumulation and biomagnification in aquatic organisms, which can interfere with brain development and function in humans [1]. This study employs a newly developed aggregation-induced emission fluorogen (AIEgen) [2] to quantify and visualise the process of Hg^{2+} and MeHg bioaccumulation in vivo on the species of water flea *Daphnia carinata*. Two approaches to Hg^{2+} or MeHg absorption were taken, either by direct incubation in a Hg^{2+} or MeHg solution or by indirect consumption of algae contaminated with Hg^{2+} or MeHg. We analysed the relationship between the ratio of photoluminescence (PL) intensities (I_{585}/I_{480}) and Hg^{2+} or MeHg concentration (C_{Hg} or C_{MeHg}) and generated a master curve for determining Hg^{2+} or MeHg concentration based on the measurement of PL intensities. Fluorescent image analysis showed the occurrence of Hg^{2+} or MeHg in *D. carinata* to be mainly in the compound eyes, optic nerve and carapace. This study indicates that Hg^{2+} or MeHg absorption can be quantified and visualised in the body of zooplankton. The *D. carinata* showed higher mortality by direct Hg^{2+} or MeHg immersion than via food ingestion. The reason for the high mortality after Hg^{2+} immersion was possibly due to carapace deformity after chemical reaction between chitin and mercury [3]. The accumulation of MeHg in the eye and the nervous system could be the cause of the high mortality of *D. carinata* exposed to MeHg in water [4].

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AUTHOR INDEX