

WEDNESDAY, JANUARY 3, 2024

Fundamental Excitations in Porphyrin Supermolecules

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Modulation of the nature and dynamics of fundamental excitations in highly conjugated structures is central to the design of the new materials for specialized emission, imaging, frequency doubling, optical limiting, photon upconversion, solar energy conversion, charge and spin transport, and quantum information science. Supermolecular chromophores – conjugated structures based on combinations of simple chromophoric building blocks that feature exceptionally strong electronic and excitonic interactions between these units – enable exquisite control over of the lifetimes, dynamics, delocalization, dephasing, and migration of excitons, polarons, and spins. This presentation will broadly cover the development of porphyrin-based supermolecules, and discuss how molecular design can be leveraged to control (i) the photophysics of these compositions, (ii) the natures and relative energies of their ground, electronically excited singlet, and electronically excited triplet states, and (iii) charge and spin transport, delocalization, and polarization in these systems.

THURSDAY, JANUARY 4, 2024

With a Great Help from my Friends: from Ru(II) Polypyridine Complexes to Luminescent Dendrimers as Artificial Antennas, Excited-state Equilibration and Photo-driven Water Oxidation

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Within the framework of supramolecular photochemistry, the build up of structurally-organized and functionally-integrated multicomponent molecular architectures capable to exhibit photoinduced energy and electron transfer is pivotal to the preparation of supramolecular species behaving as light-harvesting antenna species and charge separation molecular devices, fundamental components for artificial photosynthesis. We prepared and studied several multicomponent metal complexes of dendritic shape, made of Ru(II) and Os(II) polypyridine components. These species exhibit made-to-order photophysical and redox properties, which indicate them as efficient antennas. For specific purposes, it is quite important to increase the luminescence lifetimes of metal chromophores: excited-state equilibration, taking advantage of equilibria between excited states of different chromophores covalently linked one another in multicomponent structures, has been explored. Finally, the use of luminescent dendrimers for photoinduced water oxidation is reported and commented.

Structural Insights into Metal Ion Linked Molecular Multilayers Using Polarized Spectroscopy

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Metal ion linked multilayers on metal oxide surfaces have emerged as an intriguing scaffolding to control interfacial electron and energy transfer events. Here we will briefly recount the history and utility of these multilayer films in catalysis, sensing, and solar energy conversion, as well as the structural insights that have been gained along the way. Then we will highlight our recent efforts using polarized spectroscopic techniques to determine the structure of these multicomponent assemblies. More specifically the use of 1) visible polarized attenuated total reflectance to determine the orientation of the chromophores relative to the surface and 2) energy transfer combined with emission anisotropy to determine the orientation of the chromophores relative to each other. These measurements enable the determination of the structure of the multilayer assembly which is a crucial first step towards controlling the structure, and structurally dependent energy and electron transfer events, and realize the full potential of metal ion-linked multilayers.

Charge Transfer, Dipoles and Solvation

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Charge transfer (CT) is of fundamental importance for sustaining life on Earth and for making our modern ways of living possible. CT governs the optical properties of chromophores comprising electron-rich and electron-deficient components. Factors affecting the CT thermodynamics, reorganization energy and the donor-acceptor electronic coupling allow emergence of some unprecedented photophysical behavior. In complex chromophores with an acceptor-donor-acceptor (A-D-A) or donor-acceptor-donor architecture, for example, CT breaks the quadrupolar symmetry upon photoexcitation. Counterintuitively, a decrease in donor-acceptor electronic coupling enhances the CT rates and leads to simultaneous fluorescence from the donor and acceptor locally excited states along with the CT emission. Tuning this anti-Kasha behavior with solvent polarity presents a means for achieving white fluorescence, i.e., emission that spreads through the whole visible spectral region¹. The ubiquitous nature of dipoles and the strong effects they have on CT warrant a close look at dipolar structures that generate localized electric fields. Molecular electrets, possessing ordered electric dipoles, can serve as an indispensable platform for understanding the dynamics of such localized fields. As expected, when the electret macrodipoles are averaged over sub-nanosecond timescales, they show a nice linear dependence on the size of these dipolar structures, reaching magnitudes of 100 and 200 D. Nevertheless, analyzing the dynamics at high temporal resolution shows fluctuation of the molecular dipoles that vary between 50% and 300% of their average values. The electret geometry does not show such drastic variations. Further analysis reveals that the solvent dynamics, via the solvent-generated Onsager reaction fields, is responsible for the enormous picosecond spikes in the dipole magnitude². These findings suggest drastic differences between the solvent effects on picosecond processes vs. slower ones. While the impotence of CT cannot be overstated, the unexplored complexity of condensed media in broad spatial and temporal scales offers a wealth of opportunities for molecular photonics and optoelectronics.

1. *Chem. Sci.* 2023, 14, 13537-13550
2. *J. Am. Chem. Soc.* 2024, DOI: 10.1021/jacs.3c10525

Molecular Photoswitch Designs Inspired By Popular Organic Solar Cell Materials

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Acceptor-donor-acceptor (A-D-A) type π -conjugated push-pull oligomers have been widely used in organic photovoltaic (OPV) applications. 2-(1,1-Dicyanomethylene)rhodamine, or RCN, has been a mainstay component since 2011 in this regard, specifically serving as a popular terminating unit of non-fullerene acceptors (NFAs). In 2020, our group reported RCN-functionalized thiophenes are susceptible to photo-induced Z/E isomerization in solution. The thermodynamically stable Z isomer can isomerize to the metastable E isomer upon UV or visible-light irradiation. Given that small changes in structure can alter the morphology of the organic solar cell active layer we followed up this work and showed somewhat surprising consequences of Z/E photoisomerization on the optoelectronic properties of thin films. We have more recently demonstrated the well-controlled photochemical behavior of donor-acceptor molecules functionalized with 1,1-dicyanomethylene-3-indanone (INCN), a state-of-the-art NFA component, upon selective photoirradiation spanning the UV and visible regions. Facile Z/E isomerization is found with visible light for a series of INCN model compounds, with one exception, a case where 454 nm excitation selectively secures a tandem electrocyclization and sigmatropic rearrangement pathway. The results lend clarity to two recent literature reports of photoisomerization-related photodegradation of INCN molecules using broad spectrum irradiation sources. With inspiration from these systems, we are now developing RCN-containing molecules to achieve more efficient and practical photoswitching. Here, visible-light-induced quantitative switching is observed in both directions in solution, in large part due to inter- and intramolecular hydrogen bonding interactions present in the Z and E isomers, respectively, that contribute to their mutual stability.

Cooperative Supramolecular Polymerization of Triphenylamine Bis-Urea Macrocycles

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Porous organic crystals have applications as nanocontainers for reactions, in sensing, and for molecular separations.¹ The Shimizu group has explored the assembly of triphenylamine (TPA) bis-urea macrocycles into pillars and columns to afford porous molecular crystals. The TPA framework of these materials can undergo electron transfer with electron accepting guests loaded in their nanochannels.² Herein, we examine soluble derivatives of the TPA bis-urea macrocycle, probing the mechanism of assembly in solution to supramolecular polymers and gels.³ The macrocycle exhibits concentration-dependent aggregate formation in THF and THF/H₂O mixtures as characterized by ¹H NMR and DOSY experiments. Its assembly and disassembly processes were further probed by temperature-dependent UV/vis and fluorescence spectroscopy. Thermodynamic analysis of the emission spectra indicates a cooperative self-assembly pathway with distinct nucleation and elongation regimes. In addition, the assembly/disassembly process was examined in the presence of guests, known to fit inside the columnar channels, as well as chain stoppers. Our goals are to develop reliable strategies to control the size and functionality of these systems and employ them as nanocontainers for reactions.\n\n

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3. Prakash, R.; Islam, M. F., Kothalawala, R. M.; Hossain, M. S.; Smith, M. D.; Shimizu, L. S. *Chem.-Eur. J.* 2023, 29, e202300698.

Dual-Linker Design of Perylenes for Interfacial Electron Transfer Studies

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Molecular-based approaches to interfacial charge transfer are important for solar fuels production, solar energy capture and conversion at interfaces. Although these interfaces have been studied for decades, the ability to address the sensitization process at the molecular level remains a challenge, due to the complexity and heterogeneity of the interface. We will illustrate our results towards dual linker-design for perylene chromophores and show how substitution pattern, conformational and binding effects influences charge separation.

Structure and Environmental Control of Radical Intermediates from Naphthalene Imide Excited States

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The photochemical generation of free radicals is useful for initiating polymer formation and peptide/protein covalent labeling. Photoinduced intramolecular electron transfer (PIET), followed by decarboxylation, rapidly produces biradicals in certain 1,4,5,8-naphthalene diimides (NDIs). The biradical undergoes competitive intramolecular rearrangement, radical-radical recombination and hydrogen-atom abstraction useful to labeling peptides and proteins. Using transient absorption, the partitioning between triplet state and radical production was found to depend on the number of intervening methylene groups.¹ Asymmetric compounds (R = -CH₂CH₂CH₂OH) were found to deactivate alcohol dehydrogenase upon UV irradiation, providing evidence for site-specific enzyme modification.² Molecules that produce a large change in dipole moment upon electronic excitation may also react via redox or atom abstraction processes. ANIs photoinitiate tissue welding and protein cross-linking processes, though the mechanism remains unknown. The implications of tuning the structure and environment of ANIs for specific photochemical outcomes remain largely unexplored. Specifically, the interconversion between singlet, triplet and CT excited states is governed by solvent polarity. The spectroscopies of ANIs reveal dark radical states that are quantified by a redox trap. Interestingly, porcine arteries are most efficiently modified by these dark states, suggesting that protein cross-linking likely occurs via atom abstraction and/or redox processes.

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Improving Photocages for Biological Applications

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New tools are needed that will provide spatial and temporal control over biology for both basic research purposes and for application as potential therapies. We have a long-standing interest in using light to break existing bonds and create new interactions, with the goal of regulating biological function and dysfunction. Coordination chemistry provides a convenient platform for the rapid generation of libraries of compounds, where the photochemistry, biological compatibility, and downstream biological effects of the systems can be rationally manipulated through utilization of individual structural elements. We will present our approach to the development of Ru(II) “prodrugs” as photocages, with the unmasking of a biologically active organic ligand. To create improved photocages, both the metal center and the organic components of the coordination complex can be modified to optimize the photochemistry and biocompatibility of the system. We will share how these features are all combined to create red light activated cytochrome P450 (CYP) inhibitors and Proteolysis Targeting Chimeras (PROTACs) with unprecedented photocontrol for treatment-resistant cancers.

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Energy Transfer Steps Essential to Photoredox Catalysis

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Photocatalyzed cross-coupling reactions transform small molecules into value-added products. The presumed mechanism for C(sp³)-C(sp²) cross-coupling proceeds by nucleophilic reductive quenching of an Ir(III) photosensitizer, which subsequently reduces Ni(II)/0. Stern-Volmer analysis and transient absorption spectroscopy experiments reveal dominant energy transfer mechanisms in both cross-electrophile coupling and C(sp³)-C(sp²) coupling with an alkyl borate nucleophile. In C(sp³)-C(sp²) coupling with a carboxylic acid nucleophile, reductive quenching by the base initiates the catalytic cycle. A competitive energy transfer step forms the C(sp²)-O coupled product. Pulse radiolysis experiments reveal an energy transfer rate constant that is an order of magnitude greater than the electron transfer rate constant.

Thionated Compounds for Photodynamic Therapy

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Photodynamic therapy (PDT) is a clinically approved, noninvasive cancer treatment that involves administering a photosensitizer (PS) and light to the affected area. However, the current range of photodynamic therapy agents is limited, and there is a pressing need for a diverse alternative that can offer improved efficacy under multiple photosensitization mechanisms. In this talk, I will present the recent advances made by our group in developing biocompatible all-organic PSs that exhibit tunable absorption spectra from the ultraviolet-A (UVA) to the near-infrared (IR) regions of the electromagnetic spectrum. These PSs have been found to exhibit excellent PDT efficacy against monolayers of human epidermoid carcinoma, melanoma, cervical, and human epithelium cancer cells, regardless of the oxygenation status (i.e., under both normoxic and hypoxic conditions), when applied *in vitro* with a low dose of light.

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Photo-induced Membrane Leakage and the Intracellular Electrophiles: Perspectives for PDT and for Sun Care Technology

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Irreversible membrane damage is key to the efficiency of photo-induced cell death induced either by photosensitizers (PS) used in Photodynamic Therapy (PDT) or by PS naturally present in skin cells.[1,2] Processes depending on direct-contact reactions between photosensitizers and lipids were revealed to be essential for the progress of peroxidation, aldehyde formation, and membrane leakage, providing a molecular-level explanation of why membrane binding is so well correlated with the efficiency of the PS.[3] Besides the formation of transmembrane pores, lipid aldehydes have key roles as redox signaling molecules.[4] Membrane leakages correlate with PS photobleaching, suggesting that PS regeneration should be exploited as an effective tool to the development of improved PDT PS.[5] Upon sun exposure, electrophiles formed by the photosensitized oxidation reactions accumulate in skin cells and induce the formation of lipofuscin, which increases substantially the sensitivity of skin cells to visible light.[6] Indeed, redox regulation is involved in the accumulation of several oxidation-end products that are correlated with skin disorders.[3] I will also discuss recent unpublished data proposing novel strategies for sun protection.

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Stretching Golden Chains from Molecule to Molecule

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Photoredox catalysis is transforming modern synthetic chemistry. Expensive, hard to handle stoichiometric reagents can be replaced by short-lived excited states using a visible light absorbing photocatalyst. However, a fundamental challenge in moving photoredox catalysis from the bench to scale is achieving efficient light utilization through high quantum yields. Mechanistic and kinetic studies are key to achieving this goal, however, these studies have lagged compared to the development of new methods. An overarching goal of research in the Swierk group is to provide a solid mechanistic foundation for reactions that are successful but poorly understood. This talk will describe how a combination of transient absorption spectroscopy, electrochemical methods, steady state photochemical measurements, and kinetic modeling can be used to map out the reaction mechanisms and kinetics of chain photoredox reactions. The importance of quantum yield and, by extension mechanistic studies, will be discussed and highlighted.

Friday, JANUARY 5, 2024

Photophysics and Electron Transfer Reactivity of Organic Ion Radicals

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There has been recent increased interest in the excited state properties and electron transfer reactions of doublet excited states of ion radicals.[1-4] This interest is driven in part by the recognition that excited states of anion and cation radicals can serve as “super-reductants” and “super-oxidants” in photocatalytic schemes with difficult to oxidize or reduce substrates. This concept is illustrated conceptually in Fig. 1 where the excited state of an anion radical ($^*PC^-$) is shown to serve as a powerful reducing agent. In principle, through careful design of ion-radical chromophores it is possible to attain super-redox sensitizers with excited state potentials as positive as $E(^+ / 0) = +3.0$ or as negative as $E(^- / 0) = -3.0$ V vs. SCE. Given their powerful redox reactivity, ion-radical sensitizers are thermodynamically capable of driving important redox reactions in solar conversion (e.g., CO_2 reduction or water oxidation).

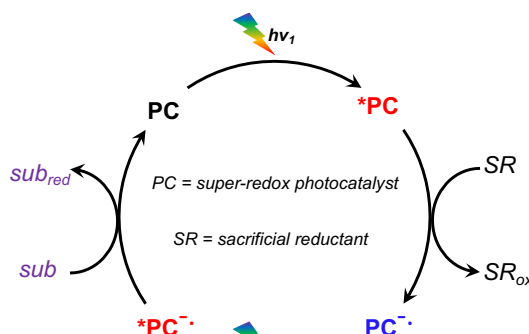


Figure 1. Photocatalytic cycle involving an anion radical doublet excited state ($^*PC^-$) as a reducing agent.

We recently demonstrated reduction of difficult to reduce aryl halides by the diffusion-controlled reduction by the excited state of perylene diimide anion radical, which has $E(^- / 0) = -1.8$ V vs SCE and a lifetime of 180 ps.[5] The talk will highlight recent results concerning the excited states of ion radicals of a variety of structures, including imides and diimides, organic conjugated heterocycles and oligomer systems. In some cases the doublet excited states of the ion radicals are fluorescent and have lifetimes greater than 500 ps. Factors that control the lifetime of the doublet excited state ion radicals will be discussed.

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Designing and probing exciton quantum phase transitions in atomically-thin semiconductors

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Designing and harnessing quantum phases of matter is a central goal in modern physical sciences and information technologies. Quantum phases of matter are predominantly characterized as interacting many-body electronic systems. They often feature intricate interplay between strong correlation, magnetism, and topology, which are underpinned by charge, spin, and orbital interactions. In this talk, I will present examples from our recent research efforts in realizing exciton (H-atom-like electron-hole pair) quantum phase transitions. Particularly, the crystallization of dipolar and quadrupolar excitons in 2D van der Waals heterostructures of transition metal dichalcogenide will be discussed. The goal is to understand how the fundamental factors, such as Coulomb interactions, kinetic energies, Fermionic exchange interactions, and quantum fluctuations, drive the formation of ordered ground states. Along this line, we further aim to develop “quantum knobs” that tune charge, spin, and orbital degrees of freedom by controlling interfacial interactions amongst molecular-to-nanoscale material entities and map the resultant emergent quantum effects using spectro-microscopies under cryogenic and magnetic conditions. I will survey a number of recently observed exotic quantum phases of matter based on 2D materials and hint the future opportunities in this area of research.

Structural and functional heterogeneity in light-harvesting materials

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Functional materials that fall outside the realm of traditional solid-state physics are promising platforms for optoelectronic applications in a variety of arenas – from photocatalysis to solar energy conversion to quantum information. While promising, these “disordered” materials pose an enormous challenge to those seeking to understand and ultimately exploit their electronic structure. Because these materials are often soft and have strong molecular-like character, their electronic structure, and therefore their functionality, is highly sensitive to both static and dynamic structural disorder. On the other hand, this sensitivity to the local electronic structure means that synthetic chemistry can provide a powerful approach for tuning material function. I’ll discuss recent work in my group utilizing time-resolved spectroscopies and microscopies to disentangle the effects of structural and compositional disorder in complex materials that lie somewhere between the molecular and semiconductor limits. In particular, I’ll describe efforts that use time resolved microscopy to determine how disorder affects the excited state relaxation and transport in single porphyrinic MOF microcrystals. I’ll also discuss some recent work elucidating how morphology affects exciton delocalization and transport in solid-state materials derived from organic perylene diimide assemblies. Both systems are intrinsically heterogeneous, and an accurate understanding of their photochemical functionality requires approaches that can directly probe this heterogeneity.

Perovskite-Sensitized Photon Upconversion: Replacing Rubrene

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Triplet generation at a hybrid inorganic/organic semiconductor interface is a promising approach to increase the (photo-)excited state recombination lifetime, and thus, facilitate solar energy harvesting. By exploiting photon upconversion in solid-state devices via triplet-triplet annihilation, where two low energy triplet states are combined to form one high energy singlet state, it is possible to harness a greater portion of the solar spectrum and e.g., increase solar cell efficiencies. While substantial UC efficiencies have been demonstrated for solution-based inorganic/organic hybrid UC systems, the required performance in their solid-state counterparts has not been achieved. Typically, excimer formation or intermolecular interactions result in an unfavorable singlet and triplet energy surface, disallowing efficient TTA. Since the direct optical excitation of triplet states is spin-forbidden, sensitizers are required to efficiently populate the triplet state. Currently, triplet sensitizers span a broad range of material classes including metal-organic complexes, nanomaterials, and bulk perovskite films. Understanding the fundamental energy transfer mechanism at the interface is crucial for the advancement of future optoelectronic devices. Here, I will present the current understanding of triplet generation at the bulk perovskite/organic interface and discuss the role of molecular aggregation and intermolecular coupling on the energy landscape underlying the upconversion process.

Reusable molecular platforms for photochemical dihydrogen production

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Reusable solid or liquid materials that store hydrogen indefinitely at ambient temperature and pressure and release it on demand are critical to facilitate the expansion of the renewable hydrogen economy. Chemically reduced molecular platforms can potentially provide simple, safe, and volumetrically efficient means of storing and transporting hydrogen, but recyclability, price, and ease of storage/release remain significant challenges for existing materials. We have recently discovered that simple, shelf-stable derivatives of anthracene undergo a photochemical reaction upon absorption of visible light that results in the release of hydrogen gas with excellent selectivity and good quantum yield. Specifically, hydroxymethyl groups appended to the dyes undergo photooxidative dihydrogen elimination to give their corresponding aldehydes. We have also found similar transformations to occur in several other hydroxymethyl-substituted organic dyes, suggesting that this photochemistry may be common to a broad range of chromophores bearing suitably reduced functional groups. In this talk, I will present the results of our mechanistic investigations, which include isotopic substitution experiments, transient absorption spectroscopy measurements, and TD-DFT calculations. I will also discuss the progress we have made in a parallel synthetic effort toward improving both the storage capacity and efficiency of these molecular hydrogen storage materials.

Probing Dynamics of Chemical Bonds in Organic Chromophores by X-ray Spectroscopies

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Chemical bonding patterns fundamentally change when molecules dynamically evolve in electronically excited states created by optical excitations. These dynamics give rise to many useful properties and functionalities, and can be resolved in space and time at modern XFEL facilities. In this talk I will overview some applications of Non-adiabatic EXcited-state Molecular Dynamics (NEXMD) framework developed at several institutions and released to public. The NEXMD code is able to simulate tens of picoseconds photoinduced dynamics in large molecular systems and dense manifold of interacting and crossing excited states. In the first example, we use dynamical simulations to compute X-ray Raman signals, which are able to monitor the coherence evolution. The observed coherences have vibronic nature that may survive multiple conical intersection passages for several hundred femtoseconds at room temperature. In the second example, we use dynamical simulations to compute X-ray Raman signals, which are able to monitor the coherence evolution in molecular photoswitches. Finally, potential energy surfaces and chemical reactivity of molecules can be modified by strong interactions with quantum light in a cavity. As such, photochemical reactions (such as photoisomerization) can be controlled by specially designed photonic or plasmonic cavities.

Extracting Energy from Singlet Fission Materials

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Singlet exciton fission (SF) is a unique energy conversion process that generates a pair of spin-triplet excitons from a single spin-singlet exciton. SF can potentially be harnessed to produce high-efficiency photovoltaic devices and new materials for quantum computing and sensing applications, but an improved understanding of how excitons move in SF materials and how these materials can be interfaced with modern electronics is needed. In this presentation, I will highlight methods employed by my group to track exciton transport within SF materials. Using transient absorption microscopy, we have quantified rates of exciton diffusion within single perylene-3,4,9,10-tetracarboxylic diimide crystals that undergo SF. We find that equilibration between SF and its inverse process, triplet fusion, plays a critical role in driving triplet exciton transport as it allows triplets to effectively diffuse by converting into singlet excitons that can more rapidly diffuse. Such singlet-mediated triplet diffusion has previously been observed in acene single crystals, but our work highlights that this mechanism is likely generalizable to a wider variety of SF materials. We have also observed that SF rates can vary in their value at different points within single crystals due to the presence of strain that alters the intermolecular arrangement of molecules within the crystal, suggesting a potential pathway by which SF can be actively controlled within molecular solids.

Reflection on 5+ Decades of Curiosity-Driven Photochemistry

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Our photochemical research has largely focused on fundamental mechanisms of transition metal complex excited states and the resulting reactive intermediates. This presentation will reflect upon past and recent studies (and the people involved) that addressed the following:

- Photosubstitution reactions of pentaammine ruthenium(II) and rhodium(III) complexes $M(NH_3)_5Ln^+$ and reactivity "tuning" with ligand substituents, solvent and pressure.
- Applying flash photolysis to probe the reactive intermediates of relevance to organometallic and bioinorganic catalysis reactions.
- Strategies for photo-uncaging of the bioregulatory molecules NO and CO.
- Photoluminescence of cuprous iodide clusters leading to our recent investigation of the time-resolved radioluminescence of these materials.

Saturday, JANUARY 6, 2024

En Route to Photo-Glycosylation: Light-induced SN1 and SN2 Reactions

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The absolute majority of photo-labile protecting groups release nucleophilic substrate (e.g., alcohol, carboxylic acid, amine, etc.). The development of photo-glycosylation procedure requires an efficient method for the photochemical generation of electrophilic glycosyl donors. Two novel strategies for the photochemical induction of nucleophilic substitution will be presented. The first, i.e., photo-SN1, relies on the photo-heterolysis of the bond between anomeric carbon and the “onium” heteroatom (N or P) with the generation of oxocarbenium ion (Scheme below). The alternative photo-SN2 approach employs light-induced rearrangements to activate the leaving group. The latter strategy allows for the control of the reactivity-selectivity properties of the glycosyl donor. In addition, we explore concurrent generation of fluoride ion as a potential activator of glycosyl acceptor. The exploration of the scope of these photoreactions, as well as their potential utility for the photo-glycosylation will be discussed.

Photoreductive CO₂ Capture

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Carbon dioxide is an abundant and inexpensive reagent that, if captured from the air, can serve as a source of value-added chemicals. However, efficient approaches toward direct-air capture of CO₂ rely on the formation of strong chemical bonds with the capturing reagent, which require prohibitively large energy inputs when CO₂ release is needed, rendering the overall capture process impractical. To circumvent this challenge, we investigate a photoreactive capture approach that combines the DAC of CO₂ with its direct conversion into value-added chemicals, such as formate or carbon monoxide, using visible light as an energy input. Light-responsive MOFs are explored as scaffolds for photochemical upgrading of CO₂, while transition metal complexes with pendant groups are investigated for reductive CO₂ capture. Here, we report our recent findings on photo-reductive CO₂ capture that include: (i) the discovery of light-responsive nanographene MOFs whose bandgaps can be tuned throughout UV/Vis/near-IR ranges using a simple post-synthetic oxidation reaction; (ii) the discovery of reactive CO₂ capture via CO₂ insertion into Zr-OH bond, Ru-H bond or via reaction of CO₂ with alkoxide ions from the secondary coordination sphere. These studies have provided us with novel chemical approaches that combine capture and conversion of CO₂.

Using Organic Photochemistry to Help Solve Problems in Photomedicine and Photobiology

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My focus today will be on fundamental and applied aspects in the photosciences. First, a photoconversion of heptamethine cyanine to trimethine cyanine will be described that involves singlet oxygen and subsequent 4-carbon truncation through a retro-Diels-Alder process for a potentially useful photobluing optical tool (Δ of ~200 nm). Secondly, the development of a hand-held fiber device will be described which delivers singlet oxygen but not sensitizer by a superhydrophobic-tip. Red light emitted by the fiber tip is transmitted through the backside of a polydimethylsiloxane strip before irradiating a verteporfin coating facing a biofilm-covered tooth or gingival surface. The device shows promising results based on a Wistar rat model of periodontitis. Results will be highlighted from our collaborations with the groups of Martin J. Schnermann (National Cancer Institute), Alan Lyons (College of Staten Island), and Tayyaba Hasan (Harvard Medical School).

Capturing Sunlight with Earth-Abundant Materials

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Solar photocatalysis offers a mechanism to harness the sun's energy and store it in chemical bonds, creating new fuels. While there are many known fuel-forming catalysts based on first-row transition metals, there are few examples of earth-abundant photosensitizers. Metal complexes of dipyrromethene (dipyrin) ligands have potential as sensitizers for photocatalysis. These ligands possess the intense visible absorption properties of the related porphyrins, while being more synthetically accessible. First row transition metal complexes of dipyrin ligands are known, but the photophysical properties of these complexes are generally unexplored. In zinc dipyrin complexes the tetrahedral geometry allows for interligand charge transfer, forming a charge separated (CS) state. In polar environments the CS state is stabilized and quenches the S_1 fluorescence. It is theorized that the CS state also enhances the intersystem crossing (ISC) to the long lived T_1 state. This presentation will quantify the triplet extinction coefficient and quantum yield for a series of zinc dipyrin complexes in both polar and non-polar solvents to determine if increased CS state formation (as determined by fluorescence quenching) does lead to increased triplet state formation.

Monitoring Faecal Matter Presence in Water Through Faecal Pigment Fluorescence

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Faecal contamination of water has significant health impact on the population of developing countries as Faecal Matter (FM) contain a variety of pathogens.¹ Currently used methods for detecting the presence of FM in surface water are time-consuming and expensive. The presence of Faecal Pigments (FP) in water, particularly urobilin (UB) and stercobilin (SB), is considered as indicator of FM presence.¹ The weak fluorescence of UB and SB get enhanced in their Zn-complexes in alcoholic media, which is the basis of their detection/estimation, using the existing Schlesinger's Method.² However, this method is associated with limitations, as the fluorescence of Zn(II) complexes of UB and SB in water (i) is weak, (ii) show time dependent loss of intensity and (iii) has strong interference from the fluorescence of dissolved organic matter (DOM) in surface water. We have carried out a detailed photophysical investigation of the FPs and FP-Zn(II) complexes towards developing efficient fluorescence based analytical methods for monitoring FM in water. Spectroscopic analysis of FPs and FP-Zn(II) complexes in aqueous and mixed aqueous media confirmed their aggregation behaviour.^{2,3} Various spectroscopic, thermodynamic and computational techniques were used to investigate the possibility of 1:1 and 1:2 stoichiometry of FP-Zn(II) complexes. Understanding the fluorescence behaviour of FP-Zn(II) helped us to propose an efficient extraction based method using 1-hexanol as extractant, that enhances fluorescence intensity and minimizes DOM fluorescence interference.⁵ By using a solid matrix containing Zn salt, we developed a rapid analytical method for naked-eye detection of FM in water under 365 nm UV illumination.^{6,7} The identification of two binding sites of different sizes in FP prompted us to investigate the possibility of bimetallic complexation towards efficient lowering of nonradiative decay routes, thereby further enhancing the fluorescence intensity. We found that maximum fluorescence enhancement occurs at Zn(II):Gd(III) stoichiometry 3:2.⁸ This enabled achieving the detection limit up to nanomolar concentration range, in addition to reducing HA fluorescence interference.

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