**Understanding Structure-Property Relationships in Phosphorescent Materials**

The effortless color tunability of cationic, luminescent Ir(III) complexes increased their popularity in contemporary research tremendously. These luminophores have seen widespread use as dyes in biological applications, light emitting electrochemical cells, photocatalytic hydrogen generation, photoredox catalytic organic transformations and more. The current work in the Bernhard lab aims to understand and predict structure activity relationships in the aforementioned application arenas. The modular nature of [Ir(C^N)2(N^N)]+ complexes allows the exploration of unprecedented molecular diversity. However, targeted synthetic approaches, such as chiral hemi-cage ligands, are also being explored.

First Image: SternVolmer.jpg

Parallel screening of the oxygen-quenching properties of 96 Ir(III) luminophores

Second Image: HemiCage.jpg

A chiral hemicage complex was synthesized using pinene-decorated bipyridine ligands

**Solar Fuels**

Solar-generated fuels show promise as a renewable energy carriers for the future. In the Bernhard lab, our research in this area focuses on searching for new catalysts for photolytic water splitting, light-driven reduction of metal ions, and photo-induced dehydrogenation reactions of bio-molecules. By creating novel inorganic compounds and organometallic ligand architectures, we are able to tune the electro-chemistry of our complexes and build supramolecular structures. This approach allows us to arrange molecular components energetically and spatially in order to optimize the fuel producing reactions. Reduction catalysts are studied individually, with sacrificial species replacing the opposing oxidation reaction, in order to scientifically determine the structure-property relationships significant to the creation of a full solar fuel system. New catalytic systems are evaluated in our home-built photoreactors, which enable us to monitor the kinetics of fuel evolution for many reactions simultaneously and in real time.

Two top images identical.

Bottom Image will be new: Hydrogen.jpg

Photocatalytic hydrogen production using 1920 structurally diverse Ir(III) photosensitizers as photosensitizers.

**Water Oxidation**

In order to develop a complete solar fuel system, it is necessary to replace the sacrificial reductant used in photocatalytic reductions with an efficient water oxidation catalysis process. Our recent efforts have very successfully investigated cyclometalated Ir(III) aquo complexes as robust water oxidation catalysts. By substitution of the cyclometalating 2-phenylpyridine ligands of these complexes, it has been shown that a broad range of oxidation potentials can be achieved. A new collaboration with Martin Albrecht (University of Bern) targets families of Ir-based water oxidation catalysts that use strongly bound carbene ligands. An initial publication in Angewandte Chemie highlighted the robustness of these catalysts with the documentation of turn-over numbers approaching 10,000. Currently, follow-up work using similar catalysts is being performed to analyze the catalytic mechanism of these aquo complexes carefully. UV-Vis spectroscopy is employed in combination with oxygen evolution studies to pinpoint reactive intermediates. Dynamic light scattering ruled the presence of colloidal materials out and documented that gas bubbles can easily be mistaken for nano-particulate matter in the reaction solutions. Immobilization of the catalysts on photoelectrodes was used as a stepping stone towards the implementation of a full water splitting system.

Two other catalyst designs were discovered in the Bernhard group. A collaboration with Marcella Bonchio (University of Padova) on polyoxometalates (POMs) yielded a novel, efficient Ruthenium-based catalyst. Later, work on Fe-TAML complexes and their water oxidation capacity was started in collaboration with the Collins group at Carnegie Mellon. The catalyst exhibits unprecedented turnover frequencies of 1 per second.

Same Images

**Automated Science**

The overarching goal of our research in this field facilitates the transition from the traditional, linear approach to chemical discovery to highly parallelized, computer-guided procedures. The work aims to overcome the fundamental limitation of modern chemistry: its inability to precisely describe and predict the construction and deconstruction of chemical bonds and the behavior of energetically excited states of molecules. Our efforts are aided by machine learning and artificial intelligence, which appear to be well positioned to address the currently insurmountable computational task of accurately treating the many-body correlated electron systems which govern the structure, properties and dynamics of functional molecules. In pursuing this goal, we focus on *light-to-chemical-energy transformations* suited for the production of solar fuels. So far, the primary candidate for solar fuels has been hydrogen generated by photocatalytic water splitting (“unburning”). To overcome the challenges associated with hydrogen handling and storage, our work extends to alternative solar fuel system like metals (e.g. Zn, Al) or small organic molecules generated from CO2.

Picture 1: Parallel.jpg

Greatly parallelized reactors are custom-made to investigate the kinetics of highly complex photochemical processes relevant to renewable energy solutions.

Picture 2: Prediction.jpg

Correlation of photoredox reaction rates with rates predicted from QM calculations (with Yaron group).