

METAL-TO-LIGAND CHARGE TRANSFER EXCITED STATES ON SURFACES AND IN RIGID MEDIA. APPLICATION TO ENERGY CONVERSION

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Objectives

- *To investigate systematically MLCT excited state properties and reactions on surfaces and in rigid media including electron and energy transfer.*
- *To use fundamental knowledge to design new molecular-composite or molecular-surface assemblies in molecular-level composite devices for photovoltaic and solar fuel applications.*

Technical Barriers

- *Significant challenges exist from a lack of fundamental knowledge of electron and energy transfer at interfaces and in rigid media and then, how to couple light absorption-excited state formation to long-range, directed electron and energy transfer (photovoltaics) or to catalysts for solar fuel formation.*

Abstract, Progress Report and Future Direction

I. Photophysical and photochemical studies of MLCT excited states in polymer films and on oxide surfaces.

Processing PEG-DMA (polyethylene glycol dimethacrylate) to make ~1 mm thick films has been developed as an alternative rigid medium to PMMA (polymethylmethacrylate). PEG-DMA films are ~10 times faster to synthesize, and have improved uniformity compared to PMMA. The rigidity of the polymerized PEG-DMA film is determined by the size of the PEG monomers. Emission measurements for Ru(phen)₃pTos₂ in various PEG films showed an expected rigidity dependence of increased emission energies and lengthened lifetimes with increasing rigidity.

Nanosecond transient absorption and emission data were collected for PEG-DMA films doped with Ru(phen)₃pTos₂ and various concentrations of TMBD (tetramethylbenzidine), an electron donor ($E^0=0.43$ V). Reductive quenching of the Ru(phen)₃²⁺ MLCT excited state was observed on the nanosecond time scale. The quenched emission is consistent with a random distribution of quenchers throughout the film. Analysis of the data will parameterize the effect of the medium on the distance dependence of electron transfer rate constants.

Both time-resolved and steady-state emission measurements provide evidence for excited state interactions for $\text{Ru}(\text{bpy})_2(4,4'-(\text{PO}_3\text{H}_2)_2\text{bpy})(\text{PF}_6)_2$ adsorbed to nanocrystalline 10 – 20 nm diameter nanostructured ZrO_2 and TiO_2 thin films of ~ 10 micron thicknesses. These interactions include a contribution from triplet-triplet annihilation. Photophysical measurements on Ru^{II} loaded ZrO_2 films with coadsorbed MV-COOH have shown that oxidative excited state quenching occurs followed by cross-surface back electron transfer. More complex surface structures are currently under investigation which contain: adsorbed reductive quenchers, adsorbed reductants and oxidants, and ion-paired oxidants and reductants.

II. Electrochemical and Photocatalytic Oxidation of Water by Adsorbed Ru Complexes on Metal Oxide Surfaces

Kinetic and mechanistic studies have been conducted on water oxidation by the “blue dimer” diruthenium catalyst $[(\text{bpy})_2(\text{H}_2\text{O})\text{RuORu}(\text{OH}_2)(\text{bpy})_2]^{4+}$ (bpy is 2,2'-bipyridine) in acidic aqueous solutions by using Ce^{IV} as a sacrificial oxidant. These results indicate that the mechanism of water oxidation by the blue dimer strongly depends on the nature of the acid as well as its concentration. For example, in 0.1 M HNO_3 the rate determining step is oxidation of a peroxidic intermediate $((\text{HO}_2)\text{Ru}^{\text{III}}\text{ORu}^{\text{V}}(\text{O})^{3+})$ that we have characterized by redox and acid-base titrations. In 1.0 M HNO_3 the rate determining step is oxidation of the V,IV form of the dimer, $(\text{O})\text{Ru}^{\text{V}}\text{ORu}^{\text{IV}}(\text{O})^{3+}$. Under these high anion concentration conditions, $\text{Ce}(\text{IV})$ depletion leads to the appearance of anated species, $(\text{O}_2\text{NO})\text{Ru}^{\text{V}}\text{ORu}^{\text{III}}(\text{OH}_2)^{5+}$. The anated species have also been characterized by redox and acid-base titrations.

Mechanistic results have led to a new approach to water oxidation to overcome the slow step in the overall catalytic cycle. This strategy for enhancing catalytic rate is based on the addition of the kinetically facile redox mediators $\text{Ru}(\text{bpy})_2(\text{L-L})^{2+}$ (L-L is 2,2'-bipyridine (bpy), 2,2'-bipyrazine (bpz) and 2,2'-bipyrimidine (bpm)) and $[\text{Ru}(\text{bpm})_3]^{2+}$. With this approach, rate enhancements for water oxidation by factors of up to ~ 25 have been achieved.

These results open the door for future catalyst design to maximize rates of catalytic water oxidation. Electrochemical rather than chemical oxidation of the blue dimer catalyst should reduce the degree of over-oxidation and allow fundamental studies over a wide pH range. We have also begun studies on the generation of oxidizing equivalents with light by photo injection from the complex $\text{Ru}(\text{pbpy})(\text{bpy})_2^{2+}$ (pbpy is 4,4'-(PO_3Et_2)₂bpy) to nanocrystalline TiO_2 films. To this end, we have begun emission and ns transient absorption studies of $\text{Ru}(\text{pbpy})(\text{bpy})_2^{2+}$ on TiO_2 in aqueous solutions. Our future work in this scheme for photochemical water splitting includes integrated photon-to-current efficiency (IPCE) measurements and direct monitoring of oxygen evolution by these films in the presence of catalyst.

Publications

Published

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- (3) Excited State Intervalence Transfer in a Rigid Polymeric Film. Fleming, C. N.; Dattelbaum, D. M.; Thompson, D. W.; Ershov, A. Y.; Meyer, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 9622-9630. (DOE DE-FG02-06ER15788, LANL and NSERC)
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- (5) Vibrational and Structural Mapping of $[\text{Os}(\text{bpy})_3]^{3+/2+}$ and $[\text{Os}(\text{phen})_3]^{3+/2+}$. Demadis, K. D.; Dattelbaum, D. M.; Kober, E. M.; Concepcion, J. J.; Paul, J. J.; Meyer, T. J.; White, P. S. *Inorg. Chim. Acta* **2007**, *360*, 1143–1153. (DOE-BE-FG02-06ER15788)
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