

Final Report

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Energy, Electron Transfer and Photocatalytic Reactions of Visible Light Absorbing  
Transition Metal Complexes

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Research over the past four and a half year period has focused on a variety of areas both locally and collaboratively. Projects under investigation include (A) the detailed mechanistic analysis of photochemical systems for production of hydrogen, (B) use of photoinduced electron transfer to generate metallic nanoparticles, (C) the development of Pt(II) complexes as sensitizers for photoredox reactions and the development of new methods for the synthesis of N<sup>+</sup>C<sup>-</sup>N ligands and their associated Pt(II) complexes, (D) photophysical and photoredox studies of Sn(IV) chromophores, (E) the synthesis of metal complex block copolymers using RAFT methods, (F) the study of pH control of excited state energy and intramolecular energy transfer in covalently linked Ru(II)/ pyrene complexes (G) the investigation of intramolecular charge transfer in Re(I) complexes via ultrafast IR with Igor Rubtsov (Tulane) and (H) photoredox reactions of Re(II) phosphine complexes in collaboration with Dean Roddick (U. Wyoming). The report will also provide an update on training and personnel in the group (I). Manuscripts published, under review or in preparation during the reporting period are presented at the end of the report (J). Also included are presentations made by group members at scientific conferences since June 2011 (K).

(A) **Mechanistic analysis of homogeneous photochemical systems for hydrogen generation**. This portion of the work was motivated by the fact that many reports of new catalysts for photochemical reduction of water to hydrogen lack information on the overall photochemical efficiency of the system. Since studies of the examination of photochemical systems for hydrogen generation, mostly sacrificial, have been carried out for many years, the recent trend to focus entirely on turnover numbers and turnover frequencies for the catalyst served to provide numerous literature accounts that are of limited use in assessing the true utility of a particular catalyst for water reduction. Related to this is the question of whether assessments of catalyst efficiency by faradaic analysis are comparable to efficiencies for the catalyst under photochemical conditions, particularly at the relatively low light intensities associated with solar irradiation. The issue is that water reduction is a two electron process and intermediate catalyst species formed in the reduction process may undergo unproductive side reactions in the absence of a high concentration of reducing equivalents.

Our objectives were twofold: (1) to explore the comparison of faradic vs. photochemical efficiencies for water reduction catalysts and (2) to provide a simple photochemical system for use by the community of synthetic and mechanistic chemists involved in development of water reduction catalysts that would allow them to directly determine efficiencies for catalyst performance under controlled irradiation conditions. The first system we employed was not of our own design, but a simple system, with commercially available reagents, that needed thorough characterization. The chromophore used was [Ru(bpy)<sub>3</sub>](Cl)<sub>2</sub>, the excited state quencher and “sacrificial” electron donor was sodium ascorbate and the system was buffered with acetate. The initial catalyst we studied was a Co(III) complex homogeneous catalyst reported in *Angewandte Chemie* in 2012 by Xuan Zhao’s group at the University of Memphis (fig.1). The work reported the efficiencies for all the pertinent steps in the photochemical system, including the intersystem crossing efficiency (literature value), rate constants for the quenching process in a variety of buffer solutions, charge

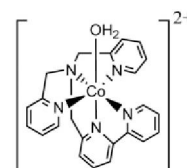
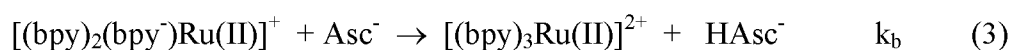
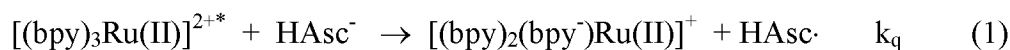


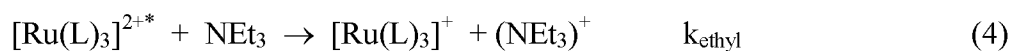
Fig. 1

separation yields in various buffers, and a measure of the fraction of  $[\text{Ru}(\text{bpy})_3]^+$  that reacts with the Co(II) complex. This last value would have to be assumed to be unity by others making use of the system to evaluate other catalysts. Measurement of the overall quantum yield for hydrogen generation allows determination of the hydrogen generation efficiency by the reduced catalyst. This work was published in *Inorg. Chem.* in 2013.

A part of the above clearly indicated that the one electron oxidized form of the ascorbate ion, in the absence of a secondary electron acceptor to react with the photoreduced Ru complex, back reacts at diffusion limited rates (eq. 3). In an effort



to generate very strong reducing agents through photoinduced reductive electron transfer reactions that do not undergo competitive back electron transfer, we explored the possibility of using a known irreversible reductant, such as triethylamine ( $\text{NEt}_3$ ) with chromophores that absorb in the visible and have very negative one electron reduction potentials, such as  $[\text{Ru}(\text{bpy})_3]^{2+}$ . Of course, it has been known for many years that  $\text{NEt}_3$  and related reductive quenchers react with photoexcited  $[\text{Ru}(\text{bpy})_3]^{2+}$  at rates that are too slow to be useful and that  $\text{NEt}_3$  is only effective with Ru(II) complex chromophores with significantly more positive one electron reduction potentials ( $E^0([\text{RuL}_3]^{2+}/[\text{Ru}(\text{L})_3]^+) > -1.1 \text{ V vs. SCE}$ ). To get around this problem, we explored the possibility of using other reductive quenchers for  $[\text{Ru}(\text{L})_3]^{2+}$  complexes that have  $E^0(\text{R}_3\text{N}^+/\text{R}_3\text{N})$  values close to that of  $\text{NEt}_3$ , but react with the photoexcited Ru complex with much higher rate constants (eq. 4-6). In this way, even if the back electron transfer reaction between  $[\text{Ru}(\text{L})_3]^+$  and



$(\text{NR}_3)^+$  is diffusion limited, as long as  $k_{\text{cross}}$  is somewhat competitive, enough  $\text{NEt}_3$  can be added so that reduction of  $(\text{NR}_3)^+$  by  $\text{NEt}_3$  dominates over back electron transfer. Since the  $[(\text{NR}_3)^+]$  formed even in laser flash photolysis experiments is generally  $< 10 \mu\text{M}$ , the half life for the back electron transfer reaction is typically 50 - 100  $\mu\text{s}$  and, thus, with  $k_{\text{cross}}$  of around  $10^6 \text{ M}^{-1}\text{s}^{-1}$ , it is possible to trap the majority of  $(\text{NR}_3)^+$  with a high (1M), but manageable concentration of  $\text{NEt}_3$  (eq. 6). Figure 2 illustrates such a case in which  $[\text{Ru}(\text{bpy})_3]^{2+}$  serves as the chromophore with tritolyamine (TTA) as the reductive quencher and triethylamine as sacrificial electron donor. The initial photoproducts,  $[\text{Ru}(\text{bpy})_3]^+$  and  $\text{TTA}^+$  form in high yield (the charge separation yield is nearly 100 %) and the transient spectrum of Fig. 2 shows the  $[\text{Ru}(\text{bpy})_3]^+$  absorption maximum at 510

nm and the TTA<sup>+</sup> maximum at 670 nm. In the absence of NEt<sub>3</sub> (TEA in Fig. 2) these species back react at near diffusion limited rates. In the presence of TEA the 670 nm absorption disappears while the [Ru(bpy)<sub>3</sub>]<sup>+</sup> persists. If TEA had been used without TTA

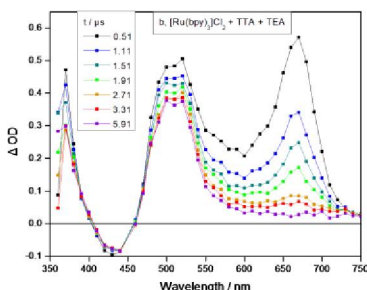


Figure 2

as the quencher *no* photoredox products would have formed since the rate constant for quenching of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> by TEA is orders of magnitude less than that of TTA. Thus, this mediated electron transfer, requiring cross reaction of the cation radical of an aromatic amine with an alkyl amine ( $\Delta G \sim 0$ ), provides an approach for making strongly reducing species ( $E^0([Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^+ = -1.4 \text{ V vs. SCE})$  in high yields in solution with visible light excitation. Unlike the system employing ascorbate as a sacrificial reductant, the [Ru(LL)<sub>3</sub>]<sup>2+</sup>, TTA, TEA system functions only in a variety of nonaqueous solvents. The system, however, serves to generate high yields of very strong reductants ( $\Phi_{\text{overall}} \sim 0.5 - 0.6$ ) and our intent is to use it for investigation of mechanistic aspects for water reduction catalysts and the generation of nanoparticulate metal particles (as potential catalysts for water reduction). This work was done by Bing Shan, who recently finished her Ph.D. and this work was published in the *Journal of Physical Chemistry* in 2014.

#### (B) Use of Photoinduced Electron Transfer to Generate Metal Nanoparticles:

One use of the photoreduction system discussed above is in the reduction of metal ions in solution to nanoparticulate metals. Such systems allow for *in situ* generation of nanoparticulate metals that may serve as functional catalysts for a variety of reduction reactions, including reduction of water to hydrogen. Initial work focused on reduction of Cu(II) and Ni(II) in nonaqueous conditions employing [Ru(5-Clphen)<sub>3</sub>]<sup>2+</sup> as chromophore, TTA as the reductive quencher and oleylamine as the sacrificial electron donor and solvent (buffered with oleic acid). Figure 3 shows the spectrophotometric changes observed during photolysis of the sacrificial reduction system containing

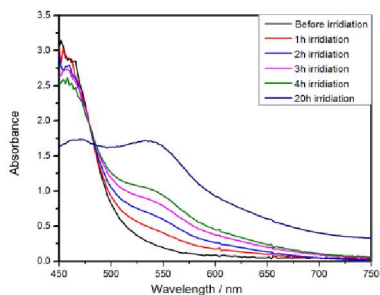


Figure 3: Changes upon irradiation of [Ru(5-Clphen)<sub>3</sub>]<sup>2+</sup>, TTA, oleylamine and oleic acid.

[Cu(acac)<sub>2</sub>] (acac = acetylacetonate ion). Upon irradiation of a deaerated solution, a new absorption feature develops around 530 nm and the solution takes on a visibly reddish hue (Fig. 4) while maintaining optical transparency. Following prolonged irradiation ( $\sim 20 \text{ hrs}$ ), the solution was exposed to air and the yellow color returned within a few minutes as the reduced Cu was oxidized. Following literature reports for stabilization of nanoparticles formed via thermal reduction of [Cu(acac)<sub>2</sub>] by addition of small quantities of Au(III) solution, nanoparticles were isolated in air and shown to form spherical particles of approximately 10 nm diameter (after prolonged photolysis) as shown by TEM (Fig. 4). The particles contained both Au and Cu and the

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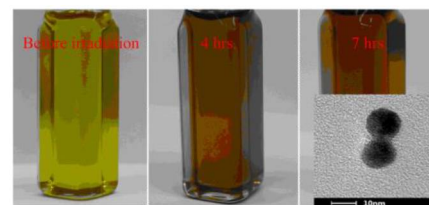


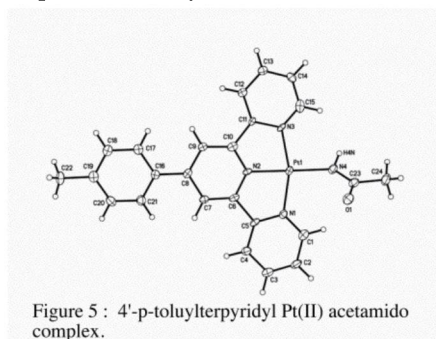
Figure 4

stability is attributed to the formation of Cu core / Au shell particles, though we have only EDX to support this assumption. Irradiation in the presence of Ni(II) salts indicated that evidence for particle formation was only obtained when water was rigorously excluded from the photolysis solutions. Under no circumstances were the particles stable in air, so no TEM data has been obtained. Thus far we have published nothing on this and we plan to continue to investigate this area further over the next three years. This work was also done by Bing Shan and is as yet unpublished.

(C) **Square planar Pt(II) complex sensitizers and their photoredox reactivity:**

For the past five years we have studied the photophysical behavior and photoredox reactivity of two specific groups of Pt(II) complexes: various terpyridyl Pt(II) hydroxo complexes and a group of bis-pyridylbenzene Pt(II) chloro systems. The result of this work is a mass of data with no publications resulting, generally because of ambiguities in the data that remain unresolved. We have persisted with this work and recent activities are presented here.

The terpyridyl Pt(II) hydroxo derivatives are fascinating and unique luminescent Pt(II) species. Unlike most other Pt(II) terpyridyl derivatives other than the acetylides, the hydroxo complexes are strongly luminescent with red emission and lifetimes on the order of 700 ns in acetonitrile at room temperature. A difficulty we faced in looking at various complexes in this series (including terpyridyl, 4'-phenyl-terpyridyl and 4'-chloro-terpyridyl) in acetonitrile was that the luminescence diminished and the absorption spectrum changed over a period of 2-4 hours following solution preparation. Thus, efforts to examine processes such as the acidity of the hydroxyl proton for the photoexcited complex or the possible dissociation of the hydroxyl proton from the one electron oxidized complex, were always complicated by net (photo) chemistry taking place. After extended efforts we managed to obtain crystals from CH<sub>3</sub>CN and, to our surprise, the crystals showed formation of an acetamido complex (Fig. 5) from the 4'-p-



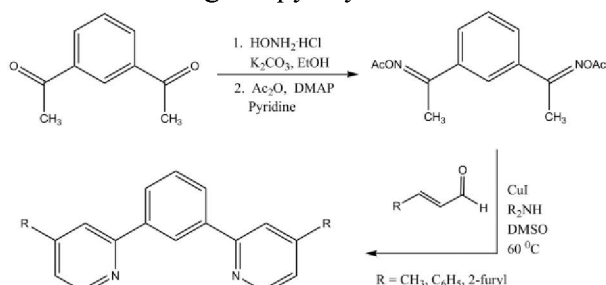
tolylterpyridyl complex; the coordinated hydroxide is quite a good nucleophile. ESI mass spectral results had shown this to be the case in earlier experiments, but we misinterpreted the ESI to represent a loosely coordinated acetonitrile solvent rather than the acetamido complex. There are a few reports of Pt(II) amido complexes, but none result from reaction of a coordinated hydroxide with a nitrile. This discovery was made while the student working on the project, Amelia Neuberger, was

beginning to write her dissertation. Loose ends remain, but a new student working on Pt(II) complex chemistry will hopefully bring this work to fruition. We still are no closer to understanding the acidity of the excited state of the hydroxo complex, but at least we will do the work in an aprotic solvent that is not susceptible to nucleophilic attack (DMF, propylene carbonate, etc.)!

A second area of research for us revolved around bis-pyridylbenzene complexes of Pt(II) involving an ortho-metallated benzene. The complexes were prepared in Garreth Williams lab (Durham, U.K.) and our focus was to explore light induced redox reactions of the complexes in solution. The complexes are particularly appealing for

studies of photoredox reactions because even the chloro complexes have microsecond excited state lifetimes in solution. Our initial work with these complexes illustrated that they do undergo photoredox reactions with both one electron donors and acceptors and the reactions are reversible (back electron transfer on the 100  $\mu$ s time scale competes effectively with back electron transfer).

While we made significant progress with the samples sent to us by the Williams lab, we were limited in what we could do by the limited amounts of complex in hand. We thus decided to learn how to make these ligands and the associated complexes on our own so that we could make complexes other than the chloro derivatives. We began this effort more than two years ago and, a rookie graduate student interested in synthesis, Aditya Kulkarni, agreed to take this on. We had very limited success with the published methods and only recently did we cross the threshold for making the ligands by variation of a method that was inspired by a phenyl pyridine synthesis reported in JACS in early 2013 (Scheme 1). The acetyloxime derivatives can be prepared in two steps in high yield and the resulting bis-pyridylbenzene derivatives obtained offer a variety that is limited



Scheme 1: acetyloxime synthesis of  $N^C^N$  Ligands

only by the vinyl aldehydes available. The approach does not involve highly reactive intermediate species or extreme temperatures and provides the desired product in multi-hundred milligram quantities in reasonable overall yields.

Having these ligands in hand we have now prepared the Pt(II) complexes of each of them and are in the process of

characterizing the complexes. We have done Rehm-Weller free energy dependence for oxidative quenching of the long lived excited states. The work has allowed us to determine the Pt(III/II) ground state potential which is kinetically irreversible electrochemically and therefore inaccessible. We are in the process of preparing a manuscript on this research.

(D) **Photophysical and Photoredox studies of Sn(IV) Chromophores.** Over the past two years we have begun an investigation of the triplet state photochemistry of Schiff base complexes of Sn(IV). The work is a part of an initiative to develop new transition metal complex photosensitizers that have good visible light absorption, high intersystem crossing efficiencies, reversible excited state electron transfer chemistry and are composed of earth abundant metals. Since Sn has a very high spin-orbit coupling matrix element, we decided to begin by examining Sn coordination complexes that had reported singlet state photochemistry. This led us to the group of Sn(IV) Schiff base complexes shown in the figure below. The literature reports for the complexes are for the tri-halo species (for “detection” of Sn by luminescence), but we found that complexes with similar luminescence behavior could be prepared from reaction of the Schiff base ligand (or the component arylamine and aldehyde) with  $[\text{Sn}(\text{Ph})_2\text{Cl}_2]$  to yield the *trans*- $[(N^N^O)\text{Sn}(\text{Ph})\text{Cl}_2]$  complex as an orange crystalline solid (Fig. 6). The absorption

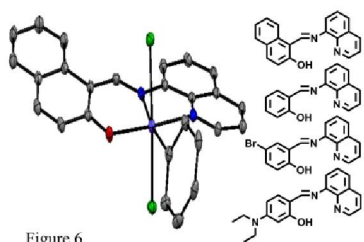


Figure 6

spectra of the complexes have maxima around 450 nm and all exhibit green fluorescence. Transient absorption spectroscopy of solutions of the complexes have transients with lifetimes between 8 and 20  $\mu\text{s}$  and spectra that have absorbance throughout the visible; one example transient spectrum is shown in figure 7. The complexes of this series meet some of the criteria listed above, but those prepared thus far undergo partial degradation upon prolonged laser spectroscopic analysis. In addition, the intersystem crossing yields range between 0.04 and 0.4, far below useful levels. The combined spectroscopic data, including ultrafast transient absorption and determination of triplet energies from energy transfer quenching experiments, indicate that the excited state is a ligand localized triplet. The triplet is not observed for the free ligand, but this may be largely due to excited state proton transfer processes of the ligand rather than the absence of spin-orbit coupling effects of the Sn. We are just beginning study of photoredox reactions of these complexes and have clearly established that the excited triplets of the Sn complexes serve as good one electron acceptors, reacting reversibly with N-methylphenothiazine ( $k_b \sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ). The work was done completely by Tod Grusenmeyer, a 2015 Ph.D. graduate, and has been published in *Dalton Transactions*.

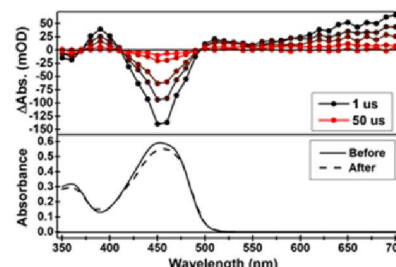


Figure 7. (top) Transient absorption spectrum of [(N,N'-Onap)-Sn(Ph)Cl<sub>2</sub>] in deaerated acetonitrile. (bottom) Uv-vis spectrum before and after transient spectral analysis.

(E) **Synthesis of metal complex block copolymers using RAFT methods** For the past five years we have explored the possibility of using block copolymers of transition metal complex polymers for light harvesting purposes. Toward this end, we began by preparing

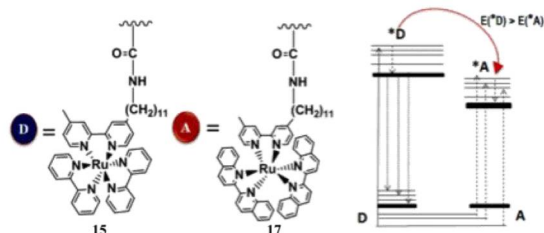


Figure 8. Donor and acceptor monomers used in both ATRP and RAFT polymerization reactions.

the two chromophore/monomer complexes and using them in preparing the acrylamide polymers of figure 8. Each monomer has a bipyridine ligand with an undecyl chain linking the chromophore and the backbone of the polymer. With significantly shorter chain lengths, no polymer or oligomer was formed via the

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ATRP or RAFT methods. ATRP is known to be of limited effectiveness in polymerizing acrylamides and, after repeated efforts, we abandoned efforts to make oligomers via ATRP. The RAFT initiator and associated reagents are shown in Figure 9. The process

served to yield oligomers of 5-10

monomer units. We prepared oligomers of each of the two monomers, one a tris-bipyridyl complex and the other a bis-2,2'-biquinoline bipyridyl complex to serve as an energy acceptor.

Attempts to use either of the product oligomers as starting material for

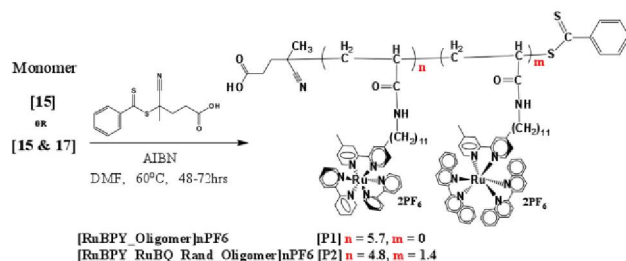


Figure 9: RAFT polymerization of the Ru acrylamide monomers.

generation of a block copolymer resulted in no identifiable product. However, copolymers prepared by reaction of the mixed monomers under RAFT conditions did



yield an oligomeric product. The products were characterized by ESI and MALDI-TOF mass spectrometry,  $^1\text{H}$  NMR, spectrophotometry and electroanalytical methods. The results of each experiment allowed determination of the ratio of the tris-bipyridyl and the bis-biquinoline monomers in the oligomer to be approximately 2:1.

Photophysical characterization of the monomers, homo-chromophoric oligomers and the mixed oligomer revealed that (a) no self-quenching occurred in the homo-chromophoric oligomers and (b) no energy transfer was evident in the mixed oligomer. Photoreduction of the mixed oligomer with N-methylphenothiazine resulted in electron localization on the biquinoline containing complexes in the oligomer (the biquinoline complex reduction potential in the monomer is  $\sim 0.4$  V less negative than that of the tris-bipyridyl complex). Transient laser spectroscopic studies indicated that the intramolecular reduction of the biquinoline complex in the mixed oligomer was complete in a few microseconds. The behavior is entirely different from the observed photoreduction in solutions containing an equivalent concentration of the two monomers. These observations were documented and published in a polymer preprint and presented at a national ACS meeting in 2012; a copy of the preprint is appended to this report. The work was done by Gilbert Kosgei, a 2013 Ph.D. who is now a postdoctoral associate at the University of New Mexico.

**(F) pH control of excited state energy and intramolecular energy transfer in covalently linked Ru(II)/ pyrene complexes** In a follow up on earlier work involving energy transfer in Ru(II) diimine / pyrene donor/acceptor system, we were able to illustrate the control of excited state energy transfer processes via variation of pH. In these systems a Ru(II) complex having two carboxylated bipyridyl ligands is covalently linked to pyrene via one of two different pyrene derivitized bipyridyl ligands (fig 10).

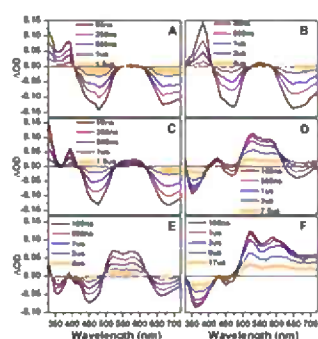


Fig. 9: . Nanosecond transient absorption spectra for each of the chromophores at pH 0 (A,C and E) and pH 8 (B, D and F). (A)  $[(\text{dcbH}_2)_2\text{Ru}(\text{bpy})]^{2+}$ , (B)  $[(\text{dcbH}_2)_2\text{Ru}(\text{bpy})]^{2-}$ , (C)  $[(\text{dcbH}_2)_2\text{Ru}(\text{pyr-ph-bpy})]^{2+}$ , (D)  $[(\text{dcbH}_2)_2\text{Ru}(\text{pyr-ph-bpy})]^{2-}$ , (E)  $[(\text{dcbH}_2)_2\text{Ru}(\text{pyr-bpy})]^{2+}$ , (F)  $[(\text{dcbH}_2)_2\text{Ru}(\text{pyr-bpy})]^{2-}$ .

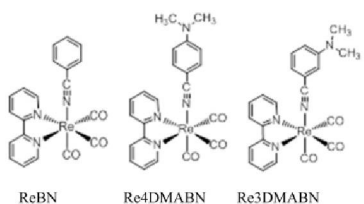
The energy of the Ru to carboxy-bipyridine  $^3\text{MLCT}$  state is pH dependent while the pyrene triplet energy remains unchanged with solution acidity. At pH 0 the  $^3\text{MLCT}$  state is the lowest energy state and, as the pH is raised and the carboxy-bipyridyl ligands are successively deprotonated, the energy of the  $^3\text{MLCT}$  state rises above that of the pyrene triplet, resulting in a significant increase in the lifetime of the observed emission. Detailed analysis of ultrafast and microsecond time resolved excited state decays, carried out in collaboration with Jeff Rack (Ohio University) results in a description of excited state decay that involves initial equilibration of the  $^3\text{MLCT}$  and pyrene triplet states followed by relaxation to the ground state. The lifetime of excited state decay is defined by the position of the equilibrium, going from  $2\mu\text{s}$  at pH 0 to  $>10\mu\text{s}$  at higher pH as the equilibrium favors the pyrene triplet. The ns transient absorption spectra clearly indicate the difference between the  $^3\text{MLCT}$  state and the  $^3\text{IL}$  (or ligand involved) excited state (fig. 9). The work serves as a very clear demonstration of systematic control of subtle energetics between states separated in energy by less than  $800\text{ cm}^{-1}$  and, in the case of the pyr-ph-bpy complex, a complete reversal in the localization of excitation energy. A coupled observation is that the oxygen quenching of the excited state increases dramatically in more basic solution. The effect is due solely to a change in the



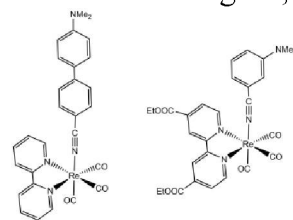
luminescence lifetime of the chromophores and not to a change in the rate constant for oxygen quenching. This work was done by Tod Grusenmeyer and was published in the *Journal of the American Chemical Society* in 2012.

**(G) Intramolecular charge transfer in Re(I) complexes via ultrafast IR (with Igor Rubtsov; Tulane)**

This work involved a detailed examination of the photophysical behavior of three Re(I) bipyridyl carbonyl complexes, shown below. By using time resolved infrared

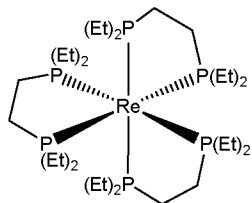


spectroscopy on the ps time scale, it was possible to follow electron density changes on the CO ligands, the CN ligand and the phenyl of the nitrile ligand. The luminescence behavior of the DMABN complexes indicated nearly complete quenching of the Re4DMABN complex emission upon changing the solvent from CH<sub>2</sub>Cl<sub>2</sub> (MC) to CH<sub>3</sub>CN (AN). The Re3DMABN complex is only weakly luminescent in either solvent, but the excited state lifetime decreases from ~ 20 μs in MC to only a few ns in AN. The luminescence and transient absorbance results suggest that the excited state initially formed is of MLCT origin and that, in the more polar solvent (AN), intramolecular electron transfer occurs to generate a species having an oxidized amine moiety ([ (bpy-)Re(I)(DMABN<sup>+</sup>) ]). However, transient infrared data indicate a more complex picture involving coupling of the Re to bpy MLCT state and an interligand, DMABN to bpy, ILCT state. The portion of the work done by our group was managed by Tod Grusenmeyer. The results were published in late 2013 in the *Journal of Physical Chemistry, B*. and in two subsequent publications, one in the *Journal of Physical Chemistry, A* and the other in *Dalton Transactions* in 2015.



**(H) Photoredox reactions of Re(II) phosphine complexes (with Dean Roddick ;U. Wyoming)**

Since 2011 we have worked in collaboration with Dean Roddick (U. Wyoming) continuing the work of the late B.P. Sullivan on the investigation of Re(II) phosphine complex chromophores that have excited state energies around 2 eV and very low one electron oxidation potentials and, therefore, are very strong excited state oxidants.



Sullivan termed these chromophores HOES (highly oxidizing excited states) and demonstrated, via the free energy dependence of excited state quenching rate constants, that the systems were effectively quenched by relatively hard to oxidize aromatic hydrocarbons (xylenes, toluene). Our objective was to use nanosecond transient absorption spectroscopy to identify the organic radical ion products (or the deprotonated radicals; for example the toluene cation radical or the benzyl radical) and examine the fate of these species ( recombination or following reactions such as radical coupling). In initial experiments with mesitylene as

the electron donating quencher of the excited state NO radical ions were observed upon photolysis of the Re complex ( $[\text{Re}(\text{depe})_3]^{2+}$ ; depe = bis-diethylphosphino ethane). With this surprising result, we examined laser flash photolysis of the Re(II) complex with N-methylphenothiazine and dimethylaniline, two quenchers that yield radical ions in solution with a wide variety of electron accepting chromophores. In these and other closely related cases the radical cation of the electron donor was observed. We are exploring the limit to which we can push the oxidizing ability of the amine cation radical and then explore use of the photochemically generated cation radical to oxidize hydrocarbons such as mesitylene or durene (tetramethylbenzene). Because of the stability of the Re(II) and Re(I) complexes, and the ease of oxidation of the Re(I) complex, it may be possible to develop photochemical systems for doing highly endergonic oxidations of organics (for example, toluene to benzyl alcohol). We have also explored the spectroscopy of these complexes in low temperature matrices and have come to understand that the ground state of the complex is split into two different doublet states that give rise to structure in low temperature luminescence. For complexes having varying degrees of aryl and alkyl phosphine ligand contributions to the coordination sphere, correlation of the ground state redox potentials and luminescence energies provides an excited state picture consistent with a phosphine to metal charge transfer excited state. The work was published in *Inorganic Chemistry* in 2015.

#### **(I) Update on training and personnel in the group**

Five students have finished Ph.D. degrees while working at least in part on DOE related projects over the past four years. One, Jing Gu, finished in 2011, spent a period working with Andy Bocarsly (Princeton) and has now moved on to a second postdoctoral position at NREL. A second, Amelia Neuberger, completed her Ph.D. in the summer of 2012 and spent the past two years as a Visiting Assistant Professor at Loyola University of New Orleans. Gilbert Kosgei, finished in December of 2013 and worked with Karen Brewer (VPI) until she passed away in November of 2014; he then moved to Ohio University to work with Jeff Rack and has helped the Rack group move to the University of New Mexico. Tod Grusenmeyer completed his Ph. D. in December of 2014, spent six months working as a postdoc in my group and then obtained an NRC Fellowship and moved to Wright Patterson AFB to work with Tom Cooper. In July of 2015 Bing Shan completed her Ph.D. and took a postdoctoral position at the UNC EFRC with Tom Meyer.

At present there are five graduate students and a postdoctoral associate in the group. Of these, three worked on DOE related research prior to the closeout of the grant. . Aditya Kulkarni (5<sup>th</sup> year) is working on the synthesis and photophysical characterization of Pt(II)  $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$  complexes. After two years of synthetic struggle, he is now ready to prepare significant quantities of the complexes and begin investigation of possible one photon-two electron processes and, possibly, light induced proton coupled electron transfer reactions of hydroxo complexes. He has worked as a Teaching Assistant at Tulane for his entire career. Patricia Fontenot came to Tulane after undergraduate work at UL Lafayette in the fall of 2012. She is working jointly with Jim Donahue and myself and her efforts have been focused on making molybdenum sulfur complexes as potential catalysts for hydrogen generation from water. Her support has been largely from working

as a Teaching Assistant at Tulane. Finally, Rebecca Adams, a third year graduate student with a B.S. from Nicholls State (LA) has worked on a range of projects including interfacial electron transfer/ charge separation, photoredox reactions of Os(II) phenanthroline hydride complexes and charge recombination kinetics associated with dye sensitized solar cells.

Undergraduates in the lab:

Brian Hubig, 2011-12, Tulane Junior/ Senior, Cell Biology major

Tri Pham, 2012-2013, Tulane Sophomore/Junior, Cell Biology major

Kristina Martinez, summer 2013, Loyola University Senior.

Aquiel Warner, summer 2013, Yale University Junior (Astronomy major).

Alexander Kulik, summer 2014, Tulane University Sophomore, Chemistry Major

**(J) Manuscripts Published, in press or submitted during this period.**

Grusenmeyer, Tod A.; Chen; Jin, Jin, Yuhuan; Nguyen, Jonathan; Rack, Jeffrey J. ; Schmehl, Russell H. "*pH Control of Intramolecular Energy Transfer and Oxygen Quenching in Ru(II) Complexes Having Coupled Electronic Excited States*" J. Am. Chem. Soc., **2012**, 134, 7497–7506. DOI: **10.1021/ja300866s**

Shan, Bing; Baine, T; Ma, X.A. N.; Zhao, X; Schmehl, Russell "*Mechanistic Details for Cobalt Catalyzed Photochemical Hydrogen Production in Aqueous Solution: Efficiencies of the Non-Photochemical Steps*" Inorg. Chem., **2013**, 52, 4853-59. DOI: 10.1021/ic302381w

Yue, Yuankai; Grusenmeyer, Tod; Ma, Zheng; Zhang, Peng; Pham, Tri Tat; Mague, Joel T.; Donahue, James P.; Schmehl, Russell H.; Beratan, David and Rubtsov, Igor V. " *Evaluating the Extent of Intramolecular Charge Transfer in the Excited States of Rhenium(I) Donor–Acceptor Complexes with Time-Resolved Vibrational Spectroscopy*" J. Phys. Chem., B., **2013**, ASAP. DOI: 10.1021/jp409628e

Shan, Bing and Schmehl, Russell "Photochemical Generation of Strong One-Electron Reductants via Light Induced Electron Transfer with Reversible Donors Followed by Cross Reaction with Sacrificial Donors" J. Phys. Chem. A, **2014**, 118, 10400-10406. DOI: 10.1021/jp503901v.

Yue, Yuankai; Grusenmeyer, Tod; Ma, Zheng; Zhang, Peng; Schmehl, Russell H.; Beratan, David N.; Rubtsov, Igor V. Full-Electron Ligand-to-Ligand Charge Transfer in a Compact Re(I) Complex. J. Phys. Chem., A, **2014**, 118, 10407-10415. DOI: 10.1021/jp5039877

Grusenmeyer, Tod; King, Albert; Mague, Joel T.; Rack, Jeff; Schmehl, Russell H. "*Sn(IV) Schiff Base Complexes: a New Class of Triplet Photosensitizer for Photoredox Reactions*". Dalton Transactions, **2014**, 43 (47), 17754-17765. DOI: 10.1039/c4dt01427h.

Gu, Jing; Yan, Yong; Helbig, Brian J.; Huang, Zhuangqun; Lian, Tianquan; Schmehl, Russell H. The influence of ligand localized excited states on the photophysics of second and third row transition metal terpyridyl complexes: recent examples and a case study *Coord. Chem. Rev.*, **2015**, 282, 100-109. DOI: 10.1016/j.ccr.2014.06.028.

Yue, Yuankai; Grusenmeyer, Tod; Ma, Zheng; Zhang, Peng; Schmehl, Russell H.; Beratan, David N.; Rubtsov, Igor V. Electron transfer rate modulation in a compact Re(I) donor-acceptor complex. *Dalton Transactions*, **2015**, 44 (18), 8609-16. DOI: 10.1039/C4DT02145B

Adams, J. J.; Arulsamy, N.; Sullivan, B. P.; Roddick, Dean M.; Neuberger, Amelia; Schmehl, Russell H. Homoleptic Tris-Diphosphine Re(I) and Re(II) Complexes and Re(II) Photophysics and Photochemistry. *Inorg. Chem.*, **2015**, 54, 11136- 49. DOI: 10.1021/acs.inorgchem.5b01395.

#### (I) Presentations of Group Members at Scientific Conferences since June 2011.

1. Kosgei, G.; Schmehl, R. H., Ru(II) complex polymers for light harvesting: ATRP synthesis and photophysical characterization. In *Abstracts of Papers of the American Chemical Society*, 2011; Vol. 242; Denver, CO.
2. Lebkowsky, K.; Shan, B.; Schmehl, R. H., Nanoparticulate Ni colloids as catalysts for photochemically induced reduction of water to hydrogen. In *Abstracts of Papers of the Amer. Chemical Society*, 2011; Vol. 242; Denver, CO.
3. Schmehl, R. H.; Gu, J., Development of black Ru(II) complexes as chromophores for photoredox reactions. In *Abstracts of Papers of the American Chemical Society*, 2011; Vol. 242, Denver, CO.
4. Schmehl, R.; Shan, B., Development of a photochemical system for determining quantum yields for water reduction to hydrogen. In *Abstracts of Papers of the American Chemical Society*, 2012; Vol. 244, Philadelphia, PA.
5. Draggich, Jeff; Neuberger, Amelia; Grills, David and Schmehl, Russell, *Photophysical Behavior And Photoredox Reactions Of Square Planar Pt(II) Complexes In Solution : One Electron Oxidation Processes*. XXIV IUPAC Symposium on Photochemistry, Coimbra, Portugal, July, 2012
6. T. A. Grusenmeyer, J. T. Mague, R. H. Schmehl *Sn(IV) Schiff base complexes: A new class of photosensitizer for photoredox reactions*, SE Regional ACS Meeting, Raleigh, N.C., Nov., 2012.
7. B. Shan, R. Schmehl, Evaluation of catalysts for hydrogen production: The importance of extracting the efficiencies for each reaction in photochemical water reduction systems. SE Regional ACS Meeting, Raleigh, N.C., Nov., 2012.
8. Schmehl, R. , Another lap for [Ru(bpy)<sub>3</sub>]<sup>2+</sup> derivatives: reversible energy transfer, oxygen sensing and reporting reactions of singlet oxygen with substrates. 22nd Winter Meeting, Inter-American Photochemical Society, Sarasota, Fl., Jan. 2013.
9. Tod A. Grusenmeyer, Joel T. Mague, and Russell H. Schmehl, Sn(IV) Schiff Base Complexes: A new Class of Photosensitizer for Photoredox reactions, 22nd

10. Winter Meeting, Inter-American Photochemical Society, Sarasota, Fl., Jan. 2013.  
Schmehl, R.; Grusenmeyer, T.; Yue, Y., Beretan, D; Rubtsov, I. , Use of Time Resolved Infrared to Evaluate Charge Transfer Excited States and Intramolecular Electron Transfer in Re(I) Dimethylaminobenzonitrile Complexes" 20th International Symposium on the Photochemistry and Photophysics of Coordination Complexes, Traverse City, MI, July, 2013.
11. Grusenmeyer, T. A.; Pham, T. T.; Mague, J. T.; Schmehl, R. H., Sn(IV) Schiff base complexes as photosensitizers for photoredox reactions. In *Abstracts of Papers of the American Chemical Society*, 2013; Vol. 245, New Orleans, LA.
12. Kosgei, G. K.; Schmehl, R. H., Metal complexes containing aryl-phenylene-vinylene bipyridine ligands for reverse saturable absorbers. In *Abstracts of Papers of the American Chemical Society*, 2013; Vol. 245, New Orleans, LA.
13. Schmehl, R. H.; Rubtsov, I. V.; Grusenmeyer, T. A.; Yue, Y.; Pham, J., Photoinduced intramolecular electron transfer vs. interligand charge transfer in Re(I) diimine carbonyl complexes with electron donating monodentate ligands: Observations from ultrafast infrared results. In *Abstracts of Papers of the American Chemical Society*, 2013; Vol. 245, New Orleans, LA.
14. Shan, B.; Schmehl, R., Photocatalytic reductive systems using Ru(II) diimine complex chromophores and kinetically adventitious amine donors. In *Abstracts of Papers of the American Chemical Society*, 2013; Vol. 245, New Orleans, LA.
15. Xu, Z.; Zhang, N.; Zhang, H.; Jayawickramarajah, J.; Sulkes, M.; Schmehl, R.; Mitchell, B. S.; Fink, M. J., Energy transfer between silicon nanoparticle and a covalently attached porphyrin. In *Abstracts of Papers of the American Chemical Society*, 2013; Vol. 245, New Orleans, LA.
16. Yue, Y.; Grusenmeyer, T. A.; Schmehl, R. H.; Rubtsov, I. V., Photoinduced charge separation in [(bpy)Re(CO)(3)DMABN] complex. In *Abstracts of Papers of the American Chemical Society*, 2013; Vol. 245, New Orleans, LA.
17. Grusenmeyer, T. An investigation of the excited state properties of a series of Sn(IV) Schiff Base complexes: the observation of long-lived, photoredox active excited states. Closs Award Address, 23<sup>rd</sup> Inter-American Photochemical Society Meeting, Sarasota, Fl. , January 2014.
18. Shan, B.; Schmehl, R.H. Visible light induced electron transfer system for high yield of reducing equivalents. , 23<sup>rd</sup> Inter-American Photochemical Society Meeting, Sarasota, Fl. , January 2014.
19. Yue, Y.; Grusenmeyer, T.A.; Schmehl, R. H.; Rubtsov, I.V. Full electron ligand-to-ligand charge transfer in Re(I) Complexes. , 23<sup>rd</sup> Inter-American Photochemical Society Meeting, Sarasota, Fl. , January 2014.
20. Shan, B.; Adams, R.; Schmehl, R. H. Simple photochemical systems for the detailed evaluation of homogeneous water reduction catalysts. 20<sup>th</sup> International Conference on Photochemical Conversion and Storage of Solar Energy, Berlin Germany, August 2014.
21. Shan, B.; Adams, R.; Schmehl, R. H., Photoinduced generation of strong reducing agents for the production of metallic nanoparticles as catalysts for in situ generation of H-2 . In *Abstracts Of Papers of the American Chemical Society* , 2014 Volume: 247 , Dallas, TX., August 2014.

22. Yue, Y., Grusenmeyer, I. V.; Rubtsov, I. V.; Schmehl, R. H. Time resolved IR of Rhenium diimine tricarbonyl donor-acceptor complexes: Tracking events in intramolecular energy and electron transfer reactions. In *Abstracts of Papers of the 71<sup>st</sup> SWRM/67<sup>th</sup> SERMACS*, Memphis, TN, November 2015.
23. Kulkarni, A. D.; Schmehl, R. H. Hydrogen generation using single component Pt(II) NCN system. In *Abstracts of Papers of the 71<sup>st</sup> SWRM/67<sup>th</sup> SERMACS*, Memphis, TN, November 2015.
24. Shan, B.; Fontenot, P.R.; Donahue, J. P.; Schmehl, R. H. Tracking catalyst intermediates in photoinduced generation of hydrogen with transient spectroscopic and mass spectral methods. In *Abstracts of Papers of the 71<sup>st</sup> SWRM/67<sup>th</sup> SERMACS*, Memphis, TN, November 2015.
25. Adams, R. E.; Schmehl, R. H. Micellar effects on photoinduced electron transfer in aqueous solutions: Dramatic enhancement of cage escape yields in surfactant Ru(II) diimine complex /  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  systems. In *Abstracts of Papers of the 71<sup>st</sup> SWRM/67<sup>th</sup> SERMACS*, Memphis, TN, November 2015.