Photoinitiated Electron Collection in Mixed--Metal Supramolecular Complexes: Development of Photocatalysts for Hydrogen Production

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I. Summary of Progress since 2015

Increased Water Reduction Efficiency of Polyelectrolyte Bound Ru,Rh,Ru Photocatalysts in Air-Saturated Aqueous Solutions. The groundbreaking use of polyelectrolytes to increase efficiency of supramolecular photocatalysts in solar H_2 production schemes under aqueous aerobic conditions is reported. Supramolecular photocatalysts of the architecture $[\{(TL)_2Ru(BL)\}_2RhX_2]^{5+}$ (BL=bridging ligand, TL=terminal ligand, X=halide) demonstrate high efficiencies in deoxygenated organic solvents but do not function in air-saturated aqueous solution due to quenching of the metal-to-ligand charge transfer (MLCT) excited state under these conditions. The new photocatalytic system incorporates poly(4-styrenesulfonate) (PSS) into aqueous solutions containing $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ (bpy=2,2'-bipyridine, dpp=2,3-bis(2-pyridyl)pyrazine). PSS has a profound impact on photocatalyst efficiency, increasing H_2 production over three times that of deoxygenated aqueous solutions alone. H_2 photocatalysis proceeds even under aerobic conditions for PSS containing aqueous solutions, unprecedented for this structural motif.

Early studies of Ru(II) polypyridyl complexes demonstrated that the addition of PSS to aqueous solutions increased the luminescence and excited state lifetime in both Ar purged and air-saturated solutions. PSS is a low-cost, water-soluble polymer commonly used as an ion exchange medium (**Figure 1A**). The polyelectrolyte contains a hydrophobic backbone and a negatively charged hydrophilic side group that interacts strongly with postively charged photocatalysts. Herein we report groundbreaking use of PSS to increase efficiency of Ru,Rh,Ru supramolecular water reduction photocatalysts in aqueous solutions, including H_2 production under aerobic conditions.

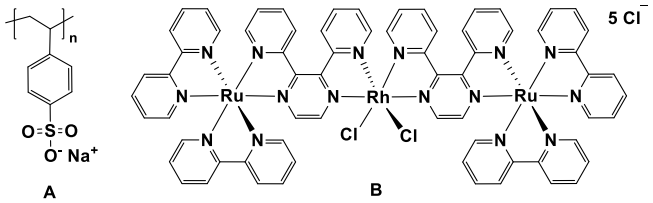

Figure 1. Structure of poly(styrenesulfonate) (**A**) and $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]Cl_5$ (**B**).

The previously reported trimetallic complex $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]Cl_5$ (**Ru,Rh,Ru**) (**Figure 1B**) was synthesized using a building block approach. Electrochemical analyses (Figure S1) for the photocatalyst give evidence for a Ru-based highest occupied molecular orbital (HOMO) and Rh-based lowest unoccupied molecular orbital (LUMO). The Rh(III) undergoes two overlapping one-electron reductions to generate a Rh(I) species that functions as the water reduction catalyst.

The **Ru,Rh,Ru** complex is an efficient light absorber in the UV and visible (Figure S2). Electronic absorption transitions in the UV are assigned to dpp($\pi\rightarrow\pi^*$) and bpy($\pi\rightarrow\pi^*$) intraligand (IL) transitions with Ru($d\pi$)$\rightarrow$dpp(π^*) and Ru($d\pi$)$\rightarrow$bpy(π^*) MLCT transitions dominating in the visible. These spectral transitions are unperturbed in the presence of PSS.

Steady-state emission spectroscopy (**Figure 2**) provides insight into the excited state dynamics of the complex in the presence and absence of polyelectrolytes. In organic solvent, CH_3CN, emission from the ^{3}MLCT excited state of **Ru,Rh,Ru** (λ_{em} = 780 nm, quantum yield of emission, $\Phi^{em} = 2.8 \times 10^{-4}$) is greatly quenched compared to the $[\{(bpy)_2Ru\}_2(dpp)]^{4+}$ model

complex ($\Phi^{em} = 1.4 \times 10^{-3}$) due to the presence of low-lying Rh(dσ)-based acceptor orbitals in **Ru,Rh,Ru** that allow for electron collection on the catalytic center through a metal-to-metal charge transfer (MMCT) excited state. In deoxygenated aqueous solution the ^{3}MLCT excited state is further quenched ($\Phi^{em} = 1.4 \times 10^{-5}$).

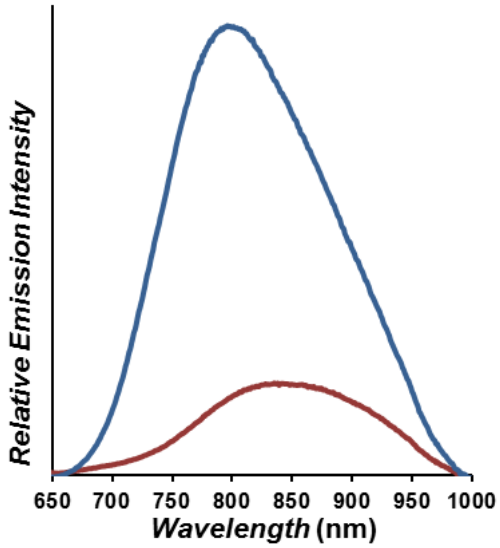

Figure 2. Emission profile of **Ru,Rh,Ru** (10 μM) in (red) aqueous solution and (blue) 2.5 mM poly(4-styrenesulfonate). Spectra corrected for PMT response. Measured in pH = 7 deoxygenated aqueous solutions at 23 C^0.

Addition of PSS (M_w = 68,300, PDI = 1.18) to aqueous solutions of **Ru,Rh,Ru** dramatically increases the emission intensity from the ^{3}MLCT excited state ($\Phi^{em} = 1.7 \times 10^{-4}$). Consistent with previous studies on Ru chromophores, addition of poly(vinyl sulfonate) (PVS) , without a hydrophobic sidegroup, does not alter the excited state dynamics of the Ru,Rh,Ru motif (Figure S3) attributing the increased Φ^{em} in the presence of PSS to strong interaction of the chromophore with the hydrophobic polymer backbone which decreases vibrational non-radiative decay (k_{nr}) thus increasing radiative decay (k_r). The emission energy (λ_{max}^{em}) for the **Ru,Rh,Ru** photocatalyst shows a hypsochromic shift in PSS (λ_{em} = 798 nm) consistent with decreased solvent reorganization following excitation. The lifetime (τ) of the ^{3}MLCT excited state for the photocatalyst in aqueous solution is short-lived (τ = 14 ns) which increases (35 ns) and becomes bi-exponential in the presence of 2.5 mM PSS, suggesting the complex resides in multiple microenvironments in PSS solutions. (Figure S5). The increased ^{3}MLCT excited state lifetime for the photocatalyst in the presence of PSS is a promising result as the lifetime of the excited state plays a major role in electron transfer to the reactive metal center and photocatalytic efficiency.

Addition of PSS to deoxygenated aqueous solutions of **Ru,Rh,Ru** results in the formation of aggregates, which are not observed for the individual components. Morphology of the aggregates was investigated using cryogenic-transmission electron microscopy (Cryo-TEM). The findings indicate that globules of approximately 20 nm in diameter aggregate to form larger structures on the order of 1-2 microns (**Figure 3**), similar to porphyrin:PSS assemblies. Dynamic light scattering experiments were used to confirm aggregate dimensions. Aggregate size and structure has been shown to play an important role in electron transfer efficiency and could greatly impact quenching of the photocatalyst in solution.

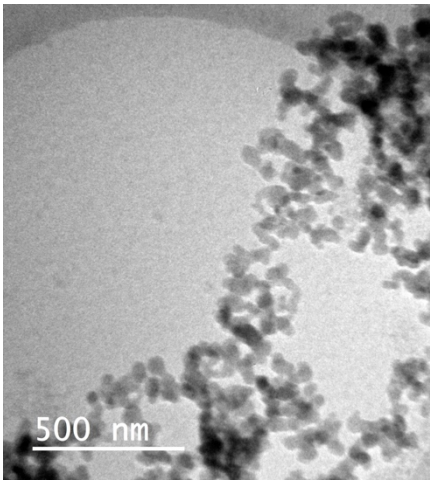

Figure 3. Cryo-TEM of aggregate formation between PSS (0.5 mM) and **Ru,Rh,Ru** (120 μM) in aqueous solution.

Photolysis of **Ru,Rh,Ru** solutions using ascorbate buffer (**H_2A/HA^-**) as sacrificial electron donor affords $[\{(bpy)_2Ru(dpp)\}_2Rh^{I}]^{5+}$, consistent with previous studies.[4e] A hypsochromic shift of the low energy Ru(dπ)→dpp(π*) transition is observed, consistent with photoreduction of the reactive metal center from Rh(III)-Rh(I) (**Figure 4**).

Interestingly, in deoxygenated solutions, complete photoreduction to the active Rh(I) species in the absence of PSS requires 4.5 h but decreases to only 2 h in the presence of 2.5 mM PSS. Photolysis in air-saturated aqueous solutions greatly increases the photoreduction time to 20 h in the absence of the polyanion but only requires 4 h to reach completion in the presence of PSS. The increased photoreduction rate to the active Rh(I) species in PSS solutions is a promising result and may provide insight into H_2 photocatalysis for these systems.

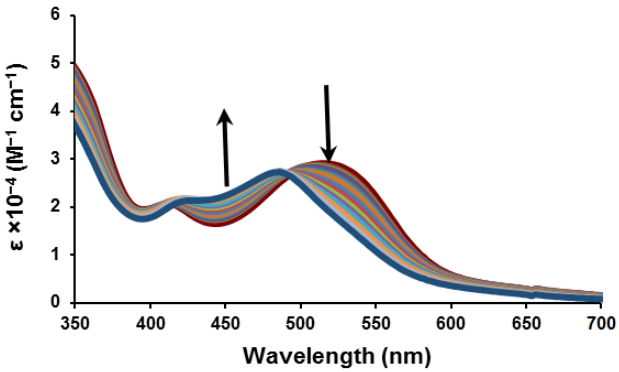

Figure 4. Electronic absorbance of **Ru,Rh,Ru** (65 μM) during photoreduction in deoxygenated aqueous solutions containing 1.1 M H_2A/HA^-. Spectra measured in 15 min intervals over 4 h

In pH 4 **H_2A/HA^-** (1.1 M), **Ru,Rh,Ru** functions as a photocatalyst to produce H_2 from water upon photolysis with visible light (470 nm). The catalytic efficiency of the complex is greatly reduced in deoxygenated aqueous solutions, achieving only 15 TON compared to 30 TON in

CH_3CN using *N*,*N*-dimethylaniline (DMA) as sacrificial reductant.[4c] Upon the addition of PSS to deoxygenated aqueous solutions, substantially enhanced photocatalytic activity is observed, achieving up to 46 TON after 10 h of irradiation (**Figure 5**). H_2 production in the presence of 2.5 mM sodium *p*-toluenesulfonate (TS) was similar to aqueous solutions without PSS, indicating that the styrene sulfonate unit must be in the polymeric form to impact catalyst efficiency. Control experiments confirmed H_2 production was only achieved in the presence of the photocatalyst.

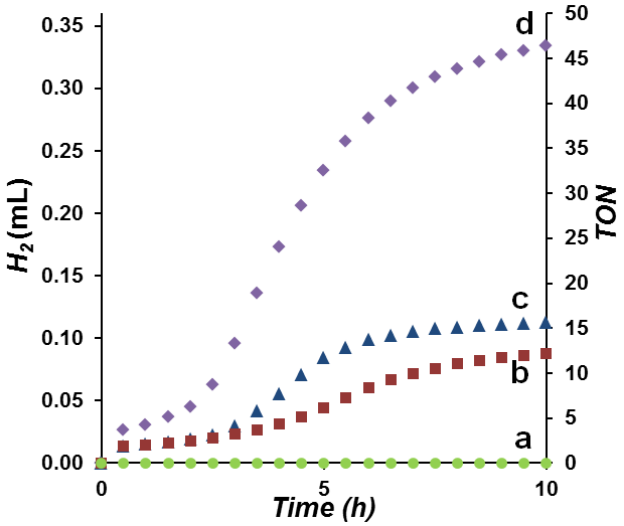

Figure 5. H_2 production of **Ru,Rh,Ru** in deoxygenated pH 4 H_2A/HA^- a) without catalyst b) [catalyst] = 65μM c) [catalyst] = 65 μM [TS] = 2.5 mM d) [catalyst] = 65 μM [PSS] = 2.5 mM

The addition of PSS to aqueous solutions of Ru,Rh,Ru has a profound impact on the photophysics and H_2 production of the supramolecule. Quenching of the ^{3}MLCT excited state is greatly decreased in PSS solutions due to the strong interaction between the polypyridyl ligands and the hydrophobic backbone of the polymer resulting in an increased Φ^{em} and τ for the supramolecule, favorable for photocatalyst functioning. Cryo-TEM studies show evidence for aggregate formation between the photocatalyst and PSS which may greatly impact electron transfer efficiency as well as quenching of the ^{3}MLCT excited state. An unprecedented increase in photocatalyst activity was observed in aqueous solutions containing PSS, producing over three times as much H_2 fuel as that without PSS. A photocatalytic system resistant to high levels of O_2 has also been achieved with addition of PSS, taking advantage of the decreased O_2 solubility due to high local ionic strength near the polyanion. The increased efficiency and O_2 resistance observed with the addition of a low cost, abundant polyelectrolyte is a promising method to optimize hydrogen evolving catalysts is easily incorporated into many other photocatalytic schemes. Current work is focused on investigating electron transfer processes using transient absorption techniques.

Probing Co-Assembly of Supramolecular Photocatalysts and Polyelectrolytes using Isothermal Titration Calorimetry. Synthesis of renewable fuels to replace dwindling natural resources is one of the greatest challenges facing the scientific community. Generating H_2 fuel from water is a carbon-neutral strategy that has demonstrated great promise. Supramolecular

photocatalysts of the molecular architecture $[\{(TL)_2Ru(BL)\}_2RhX_2]^{5+}$ (BL=bridging ligand, TL=terminal ligand, X=halide) produce H_2 in organic solvents under anaerobic conditions, but are limited by poor performance in air-saturated aqueous solutions. The use of low cost, abundant, water-soluble polyelectrolytes is a promising new method to increase stability and efficiency of water reduction photocatalysts in air-saturated aqueous solutions. Herein, we investigate intermolecular interactions between Ru,Rh,Ru photocatalysts and water soluble polyelectrolytes using isothermal titration calorimetry (ITC). Application of ITC reveals the thermodynamic forces driving self-assembly, providing new insight into the intermolecular forces leading to increased photocatalytic efficiency.

Increasing ligand hydrophobicity was found to increase the impact of added PSS on excited-state properties of Ru,Rh,Ru photocatalysts (**Figure 6**). Terminal ligand variation from 2,2'-bipyridine to 1,10-phenanthroline or 4,7-diphenylphenanthroline resulted in even larger changes in emission quantum yield and excited-state lifetime of the photocatalysts . Increasing I/I_0 with increasing terminal ligand hydrophobicity is the result of increased hydrophobic interactions between the photocatalyst and PSS, which agrees with previous reports for Ru monometallic analogs.

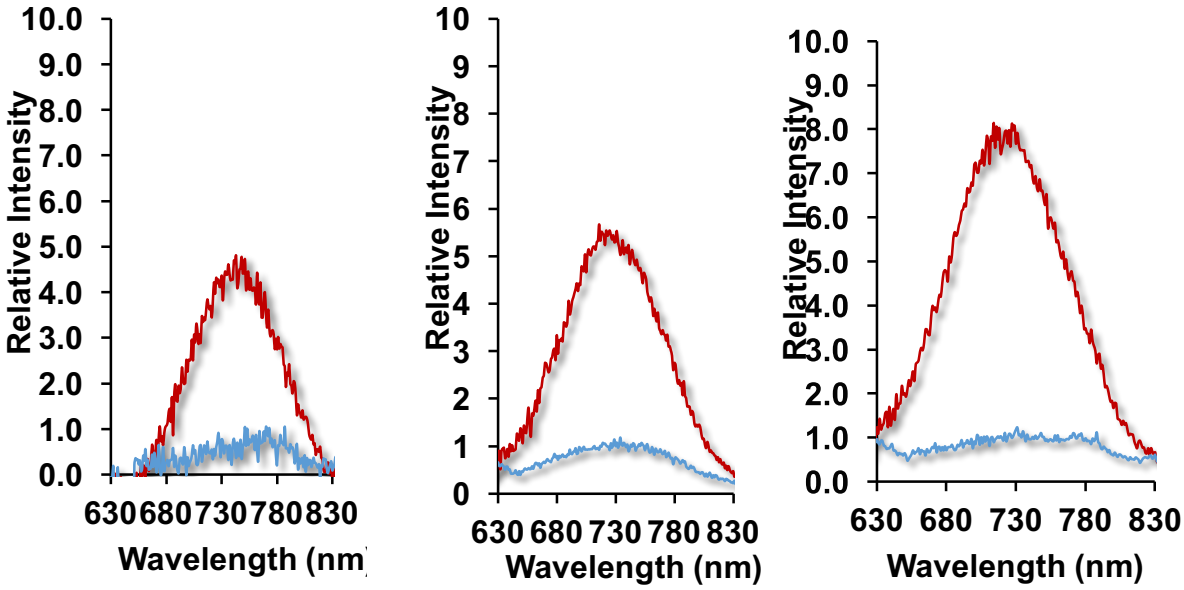

Figure 6. Relative emission spectra of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]Cl_5$ (**a**) $\{(phen)_2Ru(dpp)\}_2RhCl_2]Cl_5$ (**b**), and $\{(Ph_2phen)_2Ru(dpp)\}_2RhCl_2]Cl_5$ (**c**) in the absence (blue) and presence (red) of poly(4-styrenesulfonate) (PSS). Measured in deoxygenated ultrapure water, corrected for PMT response. bpy = 2,2'-Bipyridine, dpp = 2,3-Bis(2-pyridyl)pyrazine, phen=1,10-phenanthroline, Ph2phen = 4,7-diphenyl-1,10-phenanthroline

As expected, thermograms for the isothermal titration of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]Cl_5$ into solutions containing PSS are similar to $[Ru(bpy)_3]Cl_2$ with added endothermic heat changes at high concentration of complex (**Figure 7**). At the start of the titration, when the concentration of PSS was much greater than that of the photocatalyst, large exothermic heat changes were observed. The large heat release is the result of combined electrostatic and hydrophobic interactions, which drive the aromatic groups to within close proximity and allows for additional aromatic-aromatic interactions. Beyond the equilibrium point of the titration, conformation changes of the polyanion due to charge neutralization results in aggregation of PSS-photocatalyst assemblies and a switch from exothermic to endothermic heat changes, not observed with $[Ru(bpy)_3]Cl_2$. After all binding sites were occupied, heat changes returned to the baseline. Fitting of the thermogram (**Figure 4.14**) was performed using a two-stage model developed for the study of Co complexes binding to DNA, which also displayed sequential binding and aggregation. The model assumes the two sequential binding events can be fit separately using an independent site model with a correction to the stoichiometry of the second binding event.[61] Binding of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]Cl_5$ to PSS was found to be largely enthalpic in nature, having a binding enthalpy of −29 ± 1 kJ/mol and stoichiometry of 6.5 ± 0.3 polymer repeat units per photocatalyst, slightly greater than charge balance. Binding affinity for PSS-photocatalyst interactions ($K_a = 1.3 \pm 0.4 \times 10^6\ M^{-1}$) is increased compared to $[Ru(bpy)_3]Cl_2$, a result of greater coulombic and hydrophobic interactions between the supramolecular complex and the sulfonated polymer.

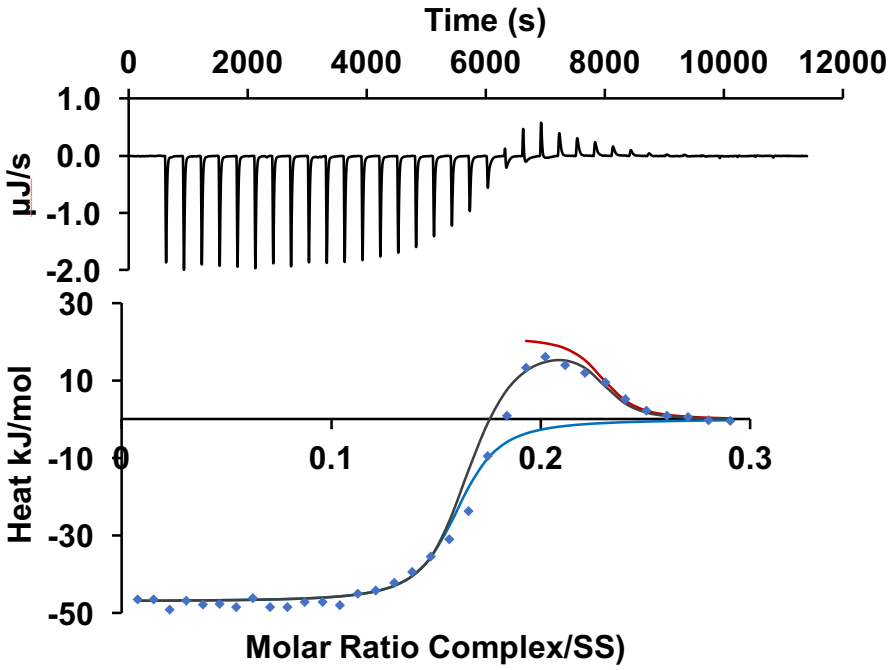

Figure 7. Thermogram of raw heat (top) and enthalpy change (bottom) with first stage independent fit (blue), second stage independent fit (red) and sum of fits (black) for the isothermal titration of 1.18 mM $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]Cl_5$ into 1.31 mM poly(4-styrenesulfonate) (PSS). Measured in ultrapure water, corrected for dilution response. Mole ratio = number of Ru,Rh,Ru per PSS repeat unit. bpy = 2,2'-Bipyridine, dpp = 2,3-Bis(2-pyridyl)pyrazine)

ITC and NMR studies of the model complex $[Ru(bpy)_3]Cl_2$ reveal intermolecular forces between Ru photocatalysts and PSS are the result of combined electrostatic and hydrophobic interactions. Electrostatic and hydrophobic interactions drive the molecules into close proximity and allows for strong aromatic-aromatic interactions between the chromophore and sulfonated polymer to occur, resulting in large exothermic heat changes in solution. Titration of the photocatalyst $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]Cl_5$ into PSS displayed a sizable increase in exothermic heat changes compared to $[Ru(bpy)_3]Cl_2$ owing to increased coulombic and hydrophobic interactions, not detected for the monomeric model TS or the non-aromatic polyelectrolyte PVS. Moreover, PVS and TS were not found to greatly impact the excited-state properties of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]Cl_5$ while PSS significantly decreased vibrational quenching of the ^{3}MLCT excited-state, previously reported to increase photocatalytic efficiency of the H_2 evolving complex. Therefore, a link between the thermodynamics of co-assembly, excited-state properties, and H_2 production efficiency was shown by this novel application of ITC in the study of photocatalyst-polyelectrolyte assemblies. The impact of PSS on the excited-state properties of Ru,Rh,Ru photocatalysts was found to increase with increasing terminal ligand hydrophobicity with little dependence on polymer molecular weight above 1,440 g/mol, a result of increased hydrophobic interactions between the complexes and PSS. ITC and scattering studies with added salt were found to display a shift in aggregation molar ratio to lower concentrations of photocatalyst. Reverse titrations, where the polyelectrolyte was titrated into solutions containing the metal complexes, demonstrated overlapping endothermic and exothermic events at the start of the titrations at low concentrations of the polyelectrolyte. The overlapping heat changes at high mole ratio of photocatalyst are similar to classic titrations and are the result of aggregate formation between the photocatalyst and sulfonated polymer. Fitting of ITC data for the most hydrophobic complexes proved complicated due to overlapping endothermic and exothermic heat changes but fitting of the data near the equivalence point allowed for comparison of binding stoichiometry and binding affinity for the reverse titrations. Increased binding affinity with increasing terminal ligand hydrophobicity agrees well with increased emission intensity for more hydrophobic complexes in the presence of PSS.

II. Summary of Progress FY 2015 and prior

This project is aimed at developing and studying a class of mixed-metal supramolecular complexes with promising redox and excited state properties. These systems couple charge transfer light absorbing metals to reactive metals that will allow these systems to undergo photoinitiated electron collection (PEC) while possessing reactive metal sites capable of delivering collected electrons to a substrate such as H_2O to facilitate the production of H_2. **Figure 8** shows the two lowest lying triplet states that are thought to be engaged in the excited state electron transfer leading to reduction of the photocatalyst and the functioning of one example photocatalyst. This project period has uncovered much about the factors impacting multi-electron photochemistry and the reduction of water to produce H_2.

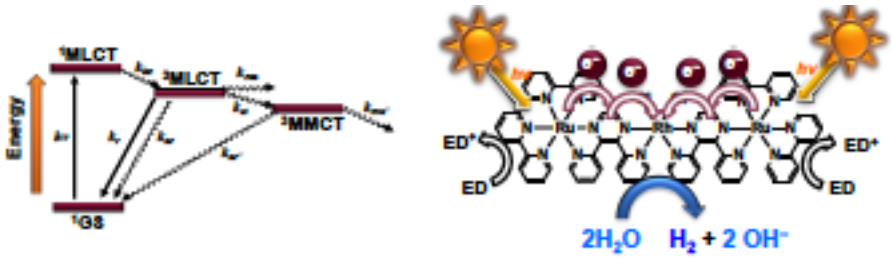

Figure 8. Excited state diagram for Rh centered supramolecules and a representative single component photocatalyst for water reduction to produce hydrogen.

A number of recent successes have been published and others are in preparation providing considerable insight into the mechanism of functioning of our supramolecular photocatalysts. We recently explored electrocatalysis by our Ru,Rh,Ru complexes demonstrating efficient catalysis and allowing the study of catalytic intermediates that provide information on the functioning of the photocatalytic system, manuscript in preparation. Interestingly, the electrocatalytic studies demonstrate a new mechanism of electrocatalysis with the Rh metal being reduced, halide loss, and one dpp bridging ligand (BL) reduced to generate the active H_2 generating species, $[(Ph_2phen)_2Ru(dpp^-)RhI(dpp)Ru(Ph_2phen)_2]^{3+}$. The development of a new Ru(II),Rh(I) complex provides unusual reactivity with an equilibrium of species in coordinating solvents that provides insight into the role of solvent on catalysis (Inorg. Chem.). The development of Ru3 extended light absorbers produces interesting complexes that violate Kasha's rule for population of the lowest lying emissive state (Inorg. Chem.) and generates lowest lying 3CS states that recently have been observed in transient absorption studies in collaboration with Prof. Meyer at UNC, manuscript in preparation. A series of Ru,Rh bimetallic complexes have unprecedented electrochemical mechanisms for Rh complexes and highlight the design constraints for production of active water reduction photocatalysts (Chem. Eur. J.). A new bimetallic supramolecule with nonchromophoric Br− ligands on Rh was synthesized to compare to the reported Cl− analogue, and H2 generation experiments within this series of complexes provides evidence for ion pairing serving to deactivate the catalyst (Inorg. Chem.).

New Ru,Rh bimetallic supramolecular architectures incorporating electron withdrawing and donating substituents on the terminal ligand (TL) on Rh has a significant effect on the orbital energetics with the RhIII,II reduction shifting to more positive potential when electron withdrawing substituents are present, manuscript in preparation. A new Ru,Rh complex with a single halide and a tridentate TL at Rh allows assessment of the need for two labile halides t provide for active catalysts and to assist in the determination of the mechanistic steps involved in the final steps of photocatalytic H_2 generation, manuscript in preparation. Selective deuteration of BLs and TLs in this structural motif allows characterization of the coordination environment about the Rh metal center upon reduction. The nature of excited states important in the photochemistry is identified upon deuteration of the acceptor ligand, which provides for lengthened excited state lifetimes and enhanced emission quantum yields in ^{3}MLCT excited states (submitted). This selective deuteration also allows the implementation of ^{1}H NMR spectroscopy in systems that have not been amenable to this technique due to the formerly large number of equivalent aromatic protons in these complex molecular architectures. Enantiomerically pure isomers of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ have been synthesized. Subunit chirality impacts electronic circular dichroism (ECD) properties, while maintaining redox and

excited state properties, with observed ellipticity signals being equal in magnitude but opposite in sign for enantiomers and with no observed ellipticity signals for racemic mixtures, **Figure 9**, of chiral subunits affords an additional spectroscopic handle for the study of the excited state degradation pathways for supramolecular complexes under catalytic conditions.

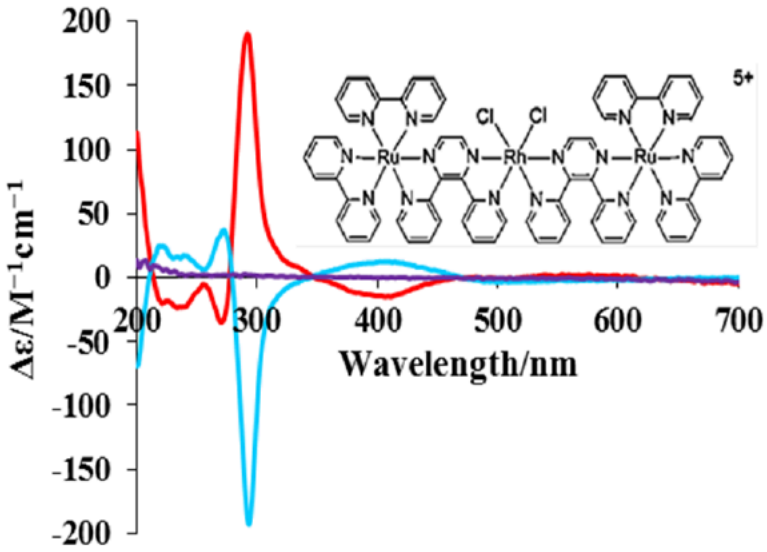

Figure 9. Ru,Rh,Ru complex containing enantiomerically pure Ru(II) light absorbing units; Purple line indicates a racemic mixture of light absorbers.

A remarkable halide-free Ru(II),Rh(III),Ru(II) photocatalyst with OH^- ions coordinated to Rh has been synthesized and provides a pH probe at the catalytic Rh center, manuscript in preparation. A Pourbaix diagram constructed from electrochemical data at various pH values provides evidence for proton-coupled electron transfer (PCET) and gives information about catalyst stability as pH varies, **Figure 10**. A new Ru,Rh,Ru complex possessing heteroleptic TLs on the Ru chromophore reinforces the necessity of the light absorbing capabilities to achieve a more efficient photocatalyst, manuscript in preparation. New tetra and heptametallic Ru(II),Rh(III) systems having Ru3 light absorbing antennae demonstrate surprising electron transfer phenomena, manuscript in preparation.

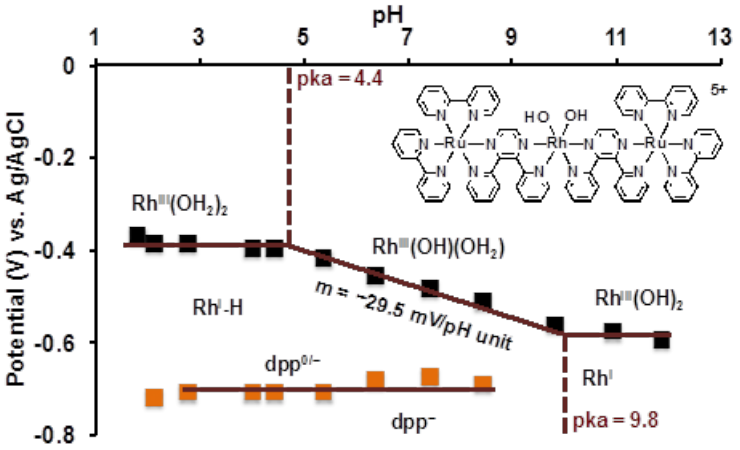

Figure 3: Porbaix diagram in aqueous buffer solution for a Ru,Rh,Ru complex with hydroxide ligands coordinated at Rh.

Figure 10. Porbaix diagram in aqueous buffer solution for a Ru,Rh,Ru complex with hydroxide ligands coordinated at Rh.

Progress Report from Previous Grant Period

This project is aimed at developing mixed-metal complexes for photoinitiated electron collection and the establishment of this approach to design photocatalysts for water reduction for solar hydrogen production. The project has been successful in achieving these goals as well as the overriding goal of developing a knowledge base of the excited state and photocatalytic properties of supramolecular complexes and how they are impacted by sub-unit variation. A number of surprising discoveries have modified hypotheses about structure property relationships in these motifs, and new and unusual properties have been uncovered that can be exploited to design new systems for light and redox activated applications. Many of these results have been published (listed below) and highlights of significant studies focusing on unexpected results and preliminary results are summarized here. The excited state diagram for Rh complexes and the mechanism of photoinitiated electron collection and site of catalysis are highlighted in **Figure 8**.

We have recently explored electrocatalysis by our Ru,Rh,Ru complexes, demonstrating efficient catalysis and allowing the study of the intermediates in catalysis that provide information on the functioning of the photocatalytic system (submitted). The development of a Ru(II),Rh(I) complex provides unusual reactivity with an equilibrium of species in coordinating solvents that provides insight into the role of solvent on catalysis (Inorg. Chem.). The development of Ru_3 extended light absorbers produces interesting complexes that violate Kasha's rule for population of the lowest lying emissive state (Inorg. Chem.) and generate lowest lying ^{3}CS states that recently have been observed in collaboration with Prof. Meyer at UNC (manuscript in preparation). Bimetallic systems for PEC that are not photocatalysts (Chem. Comm) and that are photocatalysts (J. Am. Chem. Soc.) have been uncovered, demonstrating that minor changes lead to orbital inversion in these systems and that sterics are important in generation of active photocatalysts. Much more highly efficient photocatalysts (Angew. Chem.) that demonstrate the TL is more critical to functioning than hypothesized given the Ru→BL ^{3}MLCT and Ru→Rh ^{3}MMCT photoactive states for these motifs have been studied. It has become very clear that cycling of the Rh center from Rh(III) to Rh(II) to Rh(I) and the complexation of solvent when Rh(I) oxidizes to Rh(III) is important in efficient cycling of the photocatalyst. Also highlighted is the role of halide

solubility in the product of Rh reduction as a function of halide identity (Cl^- vs. Br^-) and solvent (CH_3CN vs. DMF vs. H_2O). An Angew. Chem. paper reports the production of a photocatalyst that displays a 7% initial efficiency for absorption of light, collection of electrons, and delivery of the electrons to water to produce H_2. This system also provided for 1300 moles H /mole catalyst, a very large increase in turnover.

Interestingly, we have discovered new electrochemical mechanisms for bimetallic Ru,Rh complexes in contrast to all known Rh diimine complexes which display ECEC mechanisms. The Ru,Rh bimetallics have complex new mechanisms that vary with minor substituent addition on the TL with multipathway reductive chemistry observed for all systems (submitted). New synthetic methods have been designed to prepare three metal systems with control of each metal and ligand to produce $(TL)_2M(BL)M'(TL')(BL')RM(TL'')$ motifs with M and M′ = Ru(II) or Os(II), RM = Pt(II) or Rh(III). Initial members of this series violate Kasha's rule (unity population of the lowest lying ^{3}MLCT state) and display lowest lying ^{3}CS states important in catalysis (manuscript in preparation). Related Ru_3Pt systems (Inorg. Chem.) have demonstrated lowest lying ^{3}CS states providing for charge flow towards the reactive metal and systems that violate Kasha's rule and display complex excited state dynamics. The Rh-based systems are part of the proposed work as preliminary studies demonstrate longer lived ^{3}MLCT states, part of the design of the remote M, but BL′(π^*) orbitals can be inverted to fall below the Rh($d\sigma^*$) orbitals, providing a barrier to intramolecular electron transfer and therefore photocatalysis. These discoveries highlight the unexpected outcomes still seen in this field given the small number of mixed-metal complexes coupling reactive metals into supramolecular architectures with varied sub-units and the close energetic proximity of frontier orbitals in these motifs. Understanding and controlling these unexpected new properties can lead to many applications of these and related molecules in light and redox activated forums and is critical to application of supramolecules in solar energy conversion and catalysis (Coord. Chem. Rev. and Encyclopedia of Sustainability Science and Technology).

Enhanced Photocatalysis by Sub-unit Variation and Solvent Providing Insight into Mechanism of Catalysis. An Angew. Chem. paper reports the production of a photocatalyst that displays a 7% initial efficiency for absorption of light, collection of electrons, and delivery of the electrons to water to produce H_2. This system, $[\{(Ph_2phen)_2Ru(dpp)\}_2RhBr_2]^{5+}$, also provided for 1300 moles H_2/mole catalyst, a very large increase in turnover. This system illustrates the role of TL on the formally Ru→BL ^{3}MLCT and Ru→Rh ^{3}MMCT photoactive states for these motifs. This was unexpected and likely results from electronic and steric influences of the phenyl substituent on the phen ligand in these complexes. Even though the ^{3}MLCT excited state is only slightly changed by the addition of the phenyl groups and the rate of intramolecular electron transfer and electron transfer quenching are similar for the phen and Ph_2phen system, the Ph_2phen system is a superior photocatalyst with dramatically enhanced quantum efficiency and stability illustrating much remains to be learned about these mixed-metal systems. We hypothesized that a balance of steric and electronic factors lead to the observed enhanced photocatalysis including steric direction of isomerization by the sterically demanding Ph_2phen TL, steric protection of the photogenerated Rh(I) site by the bulky TL, electronic contributions of Ph_2phen to the formally Ru($d\pi$) donor orbital in the excited state operative in this motif, and resultant reduced back electron transfer from the reduced metal complex to the oxidized electron donor. In addition, the use of DMF provides for enhanced catalyst stability, quantum efficiency, and TON as does the incorporation of bromide instead of chloride on the Rh center. The higher solubility of bromide vs. chloride likely drives the reaction towards halide loss upon Rh(I) generation, supported by

electrocatalytic studies. The electrochemical mechanism for the Ru,Rh,Ru trimetallics can be influenced by solvent and halide in dry solvents displaying an EEC mechanism leading to formation of a Rh(I) halide bound complex when chloride is bound to Rh and dry CH_3CN is the solvent, likely due to poor solvation of free chloride in this solvent system (submitted for publication). The use of DMF will also enhance halide solvation and loss upon Rh(I) generation as does water.

Electrocatalysis and Mechanistic Insight. The electrocatalytic study of the trimetallic Ru,Rh,Ru systems demonstrate that the efficient photocatalysts for water reduction to H_2, $[\{(Ph_2phen)_2Ru(dpp)\}_2RhX_2](PF_6)_5$, are particularly active and efficient electrocatalysts for H_2 production. The onset of catalytic current as measured by cyclic voltammetry (CV) occurs at −0.29 V vs. Ag/AgCl for CF_3SO_3H, −0.75 V for CF_3CO_2H, and −1.03 V for CH_3CO_2H, representing very low overpotentials of 0.08, 0.3, and 0.03 V, respectively. An irreversible wave at −0.75 V is assigned as the Rh^{III}-H/Rh^{II}-H couple. A mechanism where a reduced dpp facilitates hydride protonation and H_2 formation is observed, **Figure 11**.

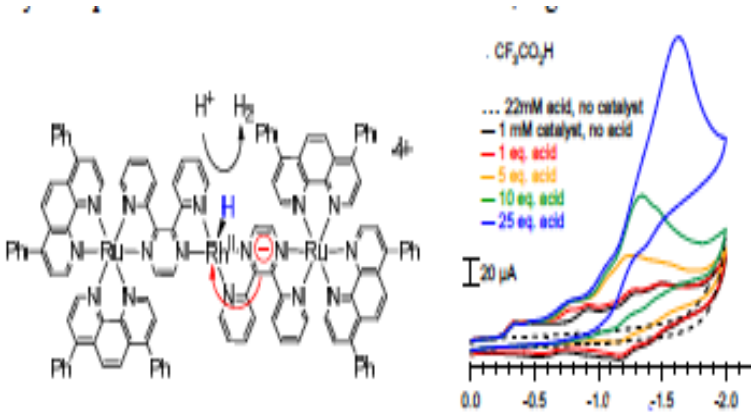

Figure 11. *Electrocatalysis by Ru,Rh,Ru complex in CF_3CO_2H and new mechanism of hydride loss with reduced dpp facilitating hydride protonation and H_2 formation.*

Bulk electrolysis experiments generate H_2 with 72-85% Faradaic yields and 95-116 turnovers after 2 h. The turnover number after 10 h was 435 with quantitative charge efficiency. In contrast to widely reported dissociation of halides upon reduction of *cis*-RhX_2 complexes, the amount of halide loss depends on solvent and water content. In dry CH_3CN, in which Cl^- is poorly solvated, $[(Ph_2phen)_2Ru(dpp)Rh^ICl_2]^+$ and $[(Ph_2phen)_2Ru(dpp)]^{2+}$ are formed upon Rh reduction: $[(Ph_2phen)Ru(dpp)RhCl_2(dpp)Ru(bpy)_2]^{5+} + 2e^- \rightarrow [(Ph_2phen)Ru(dpp)RhCl_2]^{2+} + [(dpp)Ru(bpy)_2]^{5+}$ In contrast, for X = Br^-, the major product of reduction is the intact Rh(I) trimetallic $[\{(Ph_2phen)_2Ru(dpp)\}_2Rh^I]^{5+}$. Chloride dissociation is facilitated in 3M H_2O/CH_3CN. In DMF, the primary reduction product is $[\{(Ph_2phen)_2Ru(dpp)\}_2Rh^I]^{5+}$ regardless of X = Cl^- or Br^-.

Ru,Rh Bimetallics: A New Structural Motif for PEC Providing Insight Into Photocatalysis by Rh Centered Trimetallics. We have prepared and studied a series of Ru,Rh

bimetallic complexes of the general form $[(TL)_2Ru(BL)RhCl_2(TL')](PF_6)_3$. These complexes are synthetically more challenging due to the tendency of $RhCl_3{\cdot}3H_2O$ to react with NN chelates to form cis-$[Rh(NN)_2Cl_2]^+$ coordination motifs. We have nonetheless been able to prepare these complexes and reported their basic chemical, redox, and photophysical properties as well as photocatalytic abilities. The complexes display rather complicated electrochemistry, indicative of the close energetic proximity of the BL(π^*) and Rh($d\sigma^*$) orbitals in our structural motifs. The bimetallic complexes can be designed to have low lying ^{3}MLCT states with lower lying ^{3}MMCT states. The emission from the ^{3}MLCT state is quenched by the low lying ^{3}MMCT state in manner quite similar to that seen for our trimetallic H_2 photocatalysts. These bimetallic complexes provide an interesting forum to explore the role of the second LA-BL unit on the photocatalysis by the trimetallic complexes and a less complex system to study mechanistic details should the bimetallic complexes function as photocatalysts, proposed herein. Recent studies indicate the bimetallic complexes undergo PEC providing a new structural motif for PEC. The study of the Rh(I) form of this bimetallic via ESI-MS shows that the Rh(I) species dimerizes to produce $2[(phen)_2Ru(dpp)Rh(bpy)]+2Na+4PF_6]^{2+}$ Variation of the substituent on the TL′ leads to orbital inversion with ^{t}Bu$_2$bpy having a dpp(π^*) LUMO while bpy and Ph$_2$phen have Rh($d\sigma^*$) LUMOs. This series provides for a system that does not undergo PEC (^{t}Bu$_2$bpy), undergoes PEC (bpy) but not photocatalysis, or undergoes PEC and is a photocatalyst (Ph$_2$phen) (J. Am. Chem. Soc.). These Ru,Rh bimetallics display new electrochemical mechanisms in stark contrast to the ECEC mechanism for all the widely studied cis-$Rh(NN)_2X_2$ and even $Rh(NN)_3$ motifs studied to date (submitted for publication), **Figure 12**. For these complexes, four mechanisms are operative with two simultaneous pathways occurring for even one complex leading to non-integer electron transfer in the first two reductive couples.

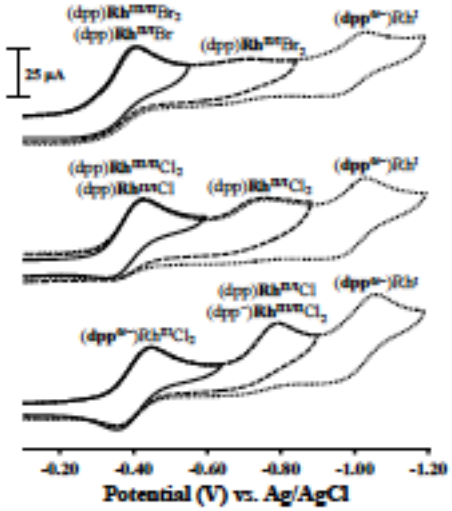

Figure 12. Cyclic voltammograms of 1 mM $[(Ph_2phen)_2Ru(dpp)RhBr_2(Ph_2phen)]^{3+}$ (top), $[(Ph_2phen)_2Ru(dpp)RhCl_2(Ph_2phen)]^{3+}$ (middle), and $[(Ph_2phen)_2Ru(dpp)RhCl_2(^tBu_2bpy)]^{3+}$ (bottom).

Charge Separation in Supramolecular Complexes with Unusual Excited State Dyanmics. The expansion of the light absorbers to include the Ru_3 systems moves the lowest lying ^{3}MLCT state away from the reactive metal to enhance the excited state lifetime by a factor

of 3-4 and provides for lowest lying ^{3}CS states. These systems violate Kasha's rule, displaying a wavelength dependence of the population of the emissive ^{3}MLCT state, displaying complex photophysics (Inorg. Chem.), and functioning as photocatalysts for H_2 production (ChemSusChem). These surprising photophysics highlight again the need to prepare and study these complexes to exploit the unusual properties displayed by new motifs. This new knowledge was used to design a new Ru,Ru,RM motif that we hypothesized would maintain these unusual properties. We have developed synthetic methods to prepare these new Ru,Ru,RM systems proposed herein that do have these same unusual photophysics but allow variation of all sub-units individually and are amenable to transient absorption spectroscopy. The state diagram showing the unusual photophysics for these systems is shown in **Figure 13**. Applying these new chromophores to the Rh- based systems has uncovered some expected results that provide considerable insight into the functioning of this motif in photocatalysis for H_2O reduction to produce H_2.

Transient Absorbance Spectroscopy. We have conducted some preliminary transient absorbance studies of our photocatalysts in conjunction with Prof. Meyer at UNC, Figure 8. These studies show population of a Ru→BL CT state occurs quickly. This state decays in a time consistent with the emission quenching. The transient signal for our complexes is quite strong and we hope to continue the study of our system using this proposed method. Study of our new Ru,Ru,Pt systems designed for this study demonstrate the population of a ^{3}CS state as well as showing the wavelength dependence photophysics characteristic of systems that violate Kasha's rule (manuscript in preparation).

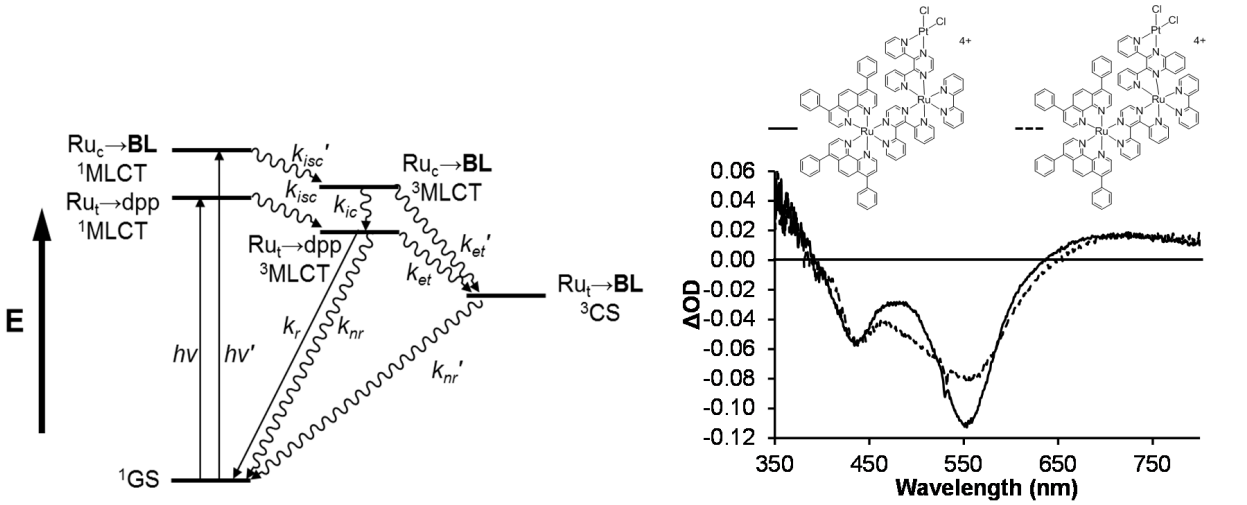

Figure 13. State diagram for new RuRuPt systems with lowest lying ^{3}CS states that violate Kasha's rule and transient absorbance spectra of these systems 20 ns following 532 nm excitation displaying varied signals as a function of BL′.

Summary. The funding from DOE BES has led to significant research results that have been disseminated through publication and presentation of our results. Key publications and those not available electronically are included with this proposal. A number of other recent developments are important to the proposed work. We have implemented the selective deuteration of BLs and TLs. This has allowed for support of the nature of excited states important in the photochemistry as deuteration of the acceptor ligand provides for lengthened excited state lifetimes and enhanced

emission quantum yields in ^{3}MLCT excited states. This selective deuteration also provides for the implementation of ^{1}H NMR spectroscopy in systems that have not been amenable to this technique do to the large number of equivalent aromatic protons in many of these motifs. We have recently used this method to study the Rh(I) product of reduction of the synthesized Rh(III) complexes. This highlights the proposed application of this technique to study reactions of these supramolecular complexes using NMR spectroscopy. We have studied a new Ru_3Rh motif that is analogous to the described Ru_3Pt systems. This motif was designed to exploit the dramatically enhanced ^{3}MLCT excited state of these complexes produced by design by moving the chromophore away from the reactive metal site as well as the charge separated state possible in this motif. In contrast to the Ru_3Pt complexes, the Ru_3Rh systems are not photocatalysts for H_2 production. This is an exciting result that highlights the need to carefully and precisely control intramolecular electron transfer in these systems. Preliminary studies indicate that electron transfer from the terminal BL of the photoactive ^{3}MLCT state is uphill to the terminal dpp bound to the Rh leading to a barrier to electron transfer to the Rh center. This is a very interesting result that bears exploration and is part of the proposed work. Calculations support this hypothesis about the photochemical properties of these systems, as does a preliminary study showing that extension of the architecture to a Ru_3RhRu_3 system provides for stabilization of the Rh orbital leading to an interesting and active heptametallic system. Proposed work includes the modification of the sub-units in the Ru_3Rh motif to tune the orbital energetics as well as TA spectroscopy studies to probe the properties of these molecules in more detail.

Publications and Dissemination of Results

Results of our studies have and will be disseminated. This includes the presentation of our preliminary results at meetings including regional and national meetings as well as manuscripts. The PI has given a number of invited talks including 22nd Winter Inter-American Photochemical Society Meeting, Gordon Research Conference on Electron Transfer, SERMAC and SERC Annual Meeting, ACS National Meetings, Canadian Chemical Society Annual Meeting, and Solar Fuels Symposium. We have also been invited to prepare book chapters for a number of forums.

List of Publications Attributable to the Grant

- "Mechanistic Insight into the Electronic Influences Imposed by Substituent Variation in Polyazine-Bridged Ru(II),Rh(III) Supramolecules," White, Travis A.; Mallalieu, Hannah E.; Wang, Jing; Brewer, Karen J. **2014**, submitted for publication.
- "New Structural Motif for Electrocatalytic H_2 Production Elucidating Mechanistic Details of Ru(II),Rh(III),Ru(II) Water Reduction Photocatalysts: Importance of Reduced Speciation and Ligands as Electron Reservoirs," Manbeck, Gerald F.; Canterbury, Theodore; Zhou, Rongwei; King, Skye; Nam, Geewoo; Brewer, Karen J. **2013**, submitted for publication.
- "Polyatomic Bridging Ligands," *Elsevier Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, Editor-in-Chief, Jan Reedijk, **2013**, in press.
- "New Supramolecular Structural Motif Coupling a Ruthenium(II) Polyazine Light Absorber to a Rhodium(I) Center," Zhou, Rongwei; Sedai, Baburam; Manbeck, Gerald F.; Brewer, Karen J. *Inorg. Chem*. **2013,** *52(23)*, 13314-13324.
- "Subunit Variation to Uncover Properties of Polyazine-Bridged Ru(II), Pt(II) Supramolecules with Low Lying Charge Separated States Providing Insight into the Functioning as H_2O Reduction Photocatalysts to Produce H_2." Knoll, Jessica D.; Higgins,

S. L. H.; White, T. A.; Brewer, K. J. *Inorg. Chem*. **2013**, *52*, 9749-9760.

- "Water reduction in Nafion membranes with Ru-Rh-Ru mixed-metal complexes." Naughton, Elise M.; Moore, Robert B.; Brewer, Karen J. *From Preprints – American Chemical Society, Division of Energy and Fuels*, **2013**, 58(1), 472.
- "Photoinitiated electron collection in polyazine chromophores couple to water reduction catalysts for solar H_2 production." Manbeck, G. F.; Brewer, K. J. *Coord. Chem. Rev*. **2013**, *257*, 1660-1675.
- "Supramolecular Complexes as Photochemical Molecular Devices for Solar Energy Conversion via Water Reduction to Produce Hydrogen Fuel," Brewer, Karen J.; White, Travis; Arachchige, Shamindri; Tsui, Hei-Man; Knoll, Jessica; Gardner, Paige; Shaw, Ryan *ASES National Solar Conference*, 40th, Raleigh, NC, United States, May 17-20, 2011 **2012**, 538-545.
- "Supramolecular complexes as photochemical molecular devices for solar energy conversion via water reduction to produce hydrogen." White, Travis A.; Manbeck, Gerald; Whitaker, Brittany; Quinn, Kevan; Zhou, Rongwei; Dent, Evan; Knoll, Jessica; Wang, Jing; Higgins, Samantha; Arachchige, Shamindri; Brewer, Karen J. *From Preprints of Symposia – American Chemical Society, Division of Fuel Chemistry*, **2012**, 57(1), 581–582.
- "Hydrogen via Direct Solar Production," Arachchige, Shamindri; Brewer, Karen J., Edited by Robert A. Meyers, *Encyclopedia of Sustainability Science and Technology*, Springer Reference, Springer-Verlag Berlin Heidelberg, **2013**.
- "A series of supramolecular complexes for solar energy conversion via water reduction to produce hydrogen: an excited state kinetic analysis of Ru(II),Rh(III),Ru(II) photoinitiated electron collectors." White, Travis A.; Knoll, Jessica D.; Arachchige, Shamindri M.; Brewer, Karen J. *Materials* **2012**, *5*, 27-46. Invited Paper.
- "Supramolecular Complex Design and Function for Photodynamic Therapy and Solar Energy Conversion via Hydrogen Production. Common Requirements for Molecular Architectures for Varied Light-Activated Processes," Jing Wang, Shamindri Arachchige, Karen
- J, Brewer, Edited by Schneider, Hans-Joerg From *Applications of Supramolecular Chemistry*
- CRC Press, Boca Raton, Fla **2012**, 255-300, ISBN: 978-1-4398-4014-6, Invited Book Chapter.
- "Efficient photocatalytic hydrogen production in a single-component system using Ru,Rh,Ru supramolecules containing 4,7-diphenyl-1,10-phenanthroline," White, Travis A.; Higgins, Samantha L. H.; Arachchige, Shamindri M.; Brewer, Karen J. *Angew. Chem., Int. Ed*. **2011**, *50*(51), 12209-12213.
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- "Electrochemical, spectroscopic, and photophysical properties of structurally diverse polyazine-bridged Ru(II),Pt(II) and Os(II),Ru(II),Pt(II) supramolecular motifs," Knoll Jessica D; Arachchige Shamindri M; Wang Guangbin; Rangan Krishnan; Miao Ran; Higgins Samantha L H; Okyere Benjamin; Zhao Meihua; Croasdale Paul; Magruder Katherine; Brewer, Karen J. *Inorg. Chem*. **2011**, *50*(18), 8850-8860.
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- "A New Structural Motif for Photoinitiated Electron Collection: Ru,Rh Bimetallics Providing Insight into H_2 Production via Photocatalysis of Water Reduction by Ru,Rh,Ru Supramolecules," Travis A. White, Jing Wang, Shamindri M. Arachchige, Karen J. Brewer *Chem. Comm*. **2011**, *47*, 4451-4453.
- "Emission Spectroscopy as a Probe into Photoinduced Intramolecular Electron Transfer in Polyazine Bridged Ru(II),Rh(III) Supramolecular Complexes," Travis A. White, Shamindri Arachchige, Karen J. Brewer, *Materials* **2010**, *3*, 4328-4354.
- "Synthesis, Characterization, and Study of the Photophysics and Photocatalytic Properties of the Photoinitiated Electron Collector $[\{(phen)_2Ru(dpp)\}_2RhBr_2](PF_6)_5$," Travis A. White, Krishnan Rangan, Karen J. Brewer, *J. Photochem. Photobiol. A: Chem*. **2010**, *209*, 203- 209.
- "Photocatalytic Hydrogen Production from Water," Shamindri M. Arachchige, Karen J. Brewer, *Energy Production and Storage-Inorganic Chemical Strategies for a Warming World, Encyclopedia of Inorganic Chemistry,* Robert Crabtree Editor, John Wiley and Sons, **2010**, 143- 172.
- "Supramolecular Complexes as Photoinitiated Electron Collectors: Applications in Solar Hydrogen Production ," Shamindri M. Arachchige, Karen J. Brewer, *On Solar Hydrogen and Nanotechnology*, Lionel Vayssieres Editor, John Wiley and Sons, **2010**, 589-617.

Recent Publications Attributable to the Grant

- "Tuning the photophysical properties of Ru(II) monometallic and Ru(II),Rh(III) bimetallic supramolecular complexes by selective ligand deuteration." Wagner, Alec T.; Zhou, Rongwei; Quinn, Kevin S.; White, Travis A.; Wang, Jing; Hale, Michael L.; Brewer, Karen. J. *J. Phys. Chem. A,* **2015***,*submitted*.*
- "Nonchromophoric halide ligand variation in polyazine-bridged Ru(II),Rh(III) bimetallic supramolecules offering new insight into photocatalytic hydrogen production from water." Rogers, Hannah. M.; White, Travis A.; Stone, Brittany N.; Arachchige, Shamindri M.; Brewer, Karen J. *Inorg. Chem.* **2015***, in press*.
- "Mechanistic insight into the electronic influences imposed by substituent variation in polyazine-bridged Ru(II),Rh(III) supramolecules." White, Travis. A.; Mallalieu, Hannah. E.; Wang, Jing.; Brewer, Karen J. *Chemistry – A Eur. J.* **2014,** *20* (27), 8221-8221.
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- "New supramolecular structural motif coupling a Ru(II) polyazine light absorber to a Rh(I) center." Zhou, Rongwei; Manbeck, Gerald; Sedai, Baburam; Brewer, Karen J. *Inorg. Chem.* **2013***, 52,* 13314-13324*.*
- "Subunit variation to uncover properties of polyazine-bridged Ru(II),Pt(II) supramolecules with low lying charge separated states providing insight into the functioning as H_2O reduction photocatalysts to produce H_2." Knoll, Jessica D.; Higgins, Samantha L. H.; White, Travis A.; Brewer, Karen J. *Inorg. Chem*. **2013**, *52* (17), 9749-

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- "Water reduction in Nafion membranes with Ru-Rh-Ru mixed-metal complexes." Naughton, Elise M.; Moore, Robert B.; Brewer, Karen J. *Preprints - ACS, Division of Energy & Fuels* **2013**, *58(1),* 472.

Recent Presentations Attributable to Grant

- "Mechanistic insight into water reduction provided by labile ligand variation at Rh(III) in Ru(II),Rh(III),Ru(II) supramolecular photocatalysts." Rogers, Hannah M.; Brewer, Karen
- J. 249th American Chemical Society National Meeting and Expositions, Denver, Colorado, United States, March **2015**, CATL 6.
- "Synthesis and photostability of mixed-metal supramolecular catalysts containing enantiomerically pure light absorbing sub-units." Wagner, Alec T.; Brewer, Karen J. **2015** Winter I-APS Conference; Sarasota, FL.
- "Heteroleptic mixed-metal Ru(II),Rh(III),Ru(II) supramolecular complexes as photocatalysts for the reduction of water to hydrogen." Kosgei, Gilbert; Rogers, Hannah M.; Canterbury, Theodore; Brewer, Karen J. **2015** Winter I-APS Conference; Sarasota, FL
- "Tuning the photophysical properties of Ru(II) monometallic and Ru(II),Rh(III) bimetallic supramolecular complexes by selective ligand deuteration." Wagner, Alec. T.; Zhou, Rongwei.; Quinn, Kevin. S.; White, T. A.; Wang, Jing.; Hale, Michael. L.; Brewer, Karen. J. American Chemical Society Meeting **2014**.
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- "New Ru(II),Rh(III) bimetallic motif with tridentate ligand on the Rh(III) center." Zhou, Rongwei; Wimer, Dexter G.; Manbeck Gerald F.; White Travis A.; Wang, Jing; Brewer, Karen J. 22nd Winter Inter-American Photochemical Society Meeting **2013**.
- "Intricate balance of steric and electronic factors with reactivity to allow directed charge transfer, photoinitiated electron collection and development of molecular devices as single component photocatalysts for hydrogen production." Manbeck, Gerald F.; White, Travis; Knoll, Jessica, Mallalieu, Hannah, King, Skye, Whitaker, Brittany, Brewer, Karen. J. 22nd Winter Inter-American Photochemical Society Meeting **2013**. Invited Presentation.