FINAL PROGRESS REPORT SUBMITTED TO THE DEPARTMENT OF ENERGY

FOR SUPPORT OF RESEARCH ENTITLED:

OLIGOMER AND MIXED-METAL COMPOUNDS. POTENTIAL MULTIELECTRON TRANSFER CATALYSTS

GRANT NO. DE-FG05-84ER13263

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2/15/93
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DISCLAIMER

Personnel Involved in Research (1990-1992)

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B. Graduate Students

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C. Undergraduate Scholars

- Robert Buelow
- Elaine Hasty
- Whitney Proctor
- Robin Russell

D. Graduate Degree Recipients

- Chuck Blanton, 1990
- Kirk Edwards, 1990
- Randy Shaver, 1991
- June Yao, 1991

List of Publications Resulting From DOE Research (1990-1992)

"Ground State and Excited State Properties of Monometallic and Bimetallic Complexes Based on Rhenium(I) Tricarbonyl Chloride: The Effect of an Insulating vs. a Conducting Bridge," S. Van Wallendael, R. J. Shaver, D. P. Rillema, B. J. Yoblinski, M. Stathis and T. Guarr Inorg. Chem. 1990, 29, 1761.

"Multimetallic Ruthenium(II) Complexes Based on Biimidazole and Bibenzimidazole: The Effect of Dianionic Bridging Ligands on Redox and Spectral Properties," D. P. Rillema, R. Sahai, P. T. Matthews, A. K. Edwards, R. J. Shaver and L. Morgan Inorg. Chem. 1990, 29, 167.

"Highly Luminescing Rhenium(I) Heterocylic Ligand Tetracarbonyl Complexes," R. J. Shaver, D. P. Rillema and C. Woods J. Chem. Soc., Chem. Commun. 1990, 179.

"Crystal and Molecular Structure of the Photocatalyst Tris(2,2'-Bipyrazine) Ruthenium(II) Hexafluorophosphate," H. Li, D. S. Jones, D. C. Schwind and D. P. Rillema J. Cryst. Spectrosc. Res. 1990, 20, 321.

"A Novel Copper(II) Complex Containing the Ligand 1,2-bis(2,2'-bipyridyl-6-yl)ethane: Structural, Magnetic, Redox and Spectral Properties," T. Garber, S. Van Wallendael, D. P. Rillema, M. Kirk, W. E. Hatfield, J. H. Welch and P. Singh Inorg. Chem. 1990, 29, 2863.

"Efficient Preparative Routes to 6,6'-Dibromo-2,2'-Bipyridine and 6-Bromo-2,2'-bipyridine," T. Garber and D. P. Rillema Syn. Commun. 1990, 20, 1233.

"Synthetic Control of Excited-States: Electron Transfer From the $^3\pi$ Level of Biphenyl Coordinated to Platinum(II)," C. B. Blanton and D. P. Rillema Inorg. Chim. Acta 1990, 168, 145.

"Dual Luminescence from a Mixed-Metal Complex Containing Rhenium(I) and Ruthenium(II) Photochromophores," S. Van Wallendael and D. P. Rillema J. Chem. Soc., Chem. Commun. 1990, 1081.

"Carrageenan Hydrogel Immobilization of $[Ru(bpy)_3]^{2+}$ at an Electrode Surface. Electrochemistry and Photocurrents," S. C. Perrine, A. K Edwards, A. L. Crumbliss and D. P. Rillema Inorg. Chem. 1991, 30, 4421.

Photocurrents Derived From $[Ru(bpy)_3]^{2+}$, Oxygen and Triethanolamine in a Hydrogel Matrix," A. K. Edwards and D. P. Rillema J. Electroanal. Chem. 1991, 314, 165.

"A Rapid Method for Degassing Samples," R. Shaver, S. Van Wallendael, and D. P. Rillema J. Chem. Educ. 1991, 68, 604.

"Photoinduced Intramolecular Energy Transfer From One Metal Center to the Other in a Mixed-Metal Ruthenium/Rhenium Complex," S. Van Wallendael and D. P. Rillema Coord. Chem. Reviews 1991, 111, 297.

"Further ESR Studies of Pyrazolato-Bridged Thermochromic Dirhodium Complexes," J. L. E. Burn, C. Woods and D. P. Rillema Inorg. Chim. Acta 1991, 188, 113.

"Characterization of Carrageenan Hydrogel Electrode Coatings with Immobilized Cationic Metal Complex Redox Couples," S. C. Perine, A. K. Edwards, A. L. Crumbliss and D. P. Rillema J. Phys.Chem. 1992, 96, 1388.

"Comparison of the Crystal Structures of Tris Heterocyclic Ligand Complexes of Ruthenium(II)," D. P. Rillema, D. S. Jones, C. Woods and H. Levy Inorg. Chem. 1992, 31, 2935.

"The MLCT-dd Energy Gap in Pyridyl-Pyrimidine and Bis-Pyridine Rutheinum(II) Heterocycles," D. P. Rillema, C. B. Blanton, R. Shaver, D. C. Jackman, M. Boldaji, S. Bundy, L. A. Worl and T. J. Meyer Inorg. Chem. 1992, 31, 1600.

"Ground-State and Excited State Properties of Platinum(II) Complexes Containing Biphenyl as a Ligand: Complexes of the Type (bph)PtX_2, Where X = Monodentate or Saturated Bidentate Ligands," C. B. Blanton, Z. Murtaza, R. Shaver and D. P. Rillema Inorg. Chem. 1992, 31, 3230.

"The Structures and Properties of Copper(II) and Copper(I) Complexes Containing an Ethane-Bridged Dimeric Phenanthroline Ligand," J. Yao, M. W. Perkovic, C. Woods and D. P. Rillema Inorg. Chem. 1992, 31, 3956.

"Physical and Photophysical Properties of Rhenium(I) Tetracarbonyl Complexes," R. J. Shaver and D. P. Rillema Inorg. Chem. 1992, 31, 1401.

"Photoinduced Electron Transfer in Multimetal Transition Metal Complexes, Observations on Electronically Forbidden Back Electron Transfer," T. Buranda, X. Song, Y. Lei, J. F. Endicott, S. Van Wallendael and D. P. Rillema, submitted to J. Phys. Chem.

In Preparation (Work in Progress Resulting From DOE Funded Research)

"Photophysical Properties of Platinum(II) Complexes Containing Biphenyl as Ligand: ^{3}MLCT vs. ^{3}CT Behavior," C. B. Blanton, Z. Murtaza and D. P. Rillema, manuscript in preparation.

"Charge Separation Studies in $[Re(bpm)(CO)_3L]^{n+}$ Complexes, L = CO, CH_3CN, py, MeQ^+ and py-PTZ: Structure, Physical and Photophysical Properties," R. J. Shaver, C. Woods and D. P. Rillema, manuscript in preparation.

"Preparation, Redox and Spectral Properties of a New Series of Ruthenium(II) Complexes Containing the Ligand 1,2-Bis(2,2'-bipyridyl-6-yl)Ethane," A. Macatangay and D. P. Rillema, manuscript in preparation.

"The Photophysical Properties of Rhenium(I) Tricarbonyl Complexes Containing Alkyl and Aryl Substituted Phenanthrolines as Ligands," L. Wallace and D. P. Rillema, manuscript in prepration.

"Photoinduced Energy Transfer in a Ruthenium(II)/Rhenium(I) Bimetallic Complex: A Solvent Effect Study," S. Van Wallendael and D. P. Rillema, manuscript in prepration.

"Photoinduced Electron Transfer in Ruthenium(II)/Rhenium(I) Bimetallic Complexes Containing Electron Donor and Electron Acceptor Ligands," M. W. Perkovic, R. J. Shaver, S. Van Wallendael and D. P. Rillema, manuscript in preparation.

"Redox and Spectral Properties of a Series of Ruthenium(II)/Platinum(II) Heterooligonuclear Complexes: A New Series of Mixed-Metal Complexes," R. J. Shaver, R. Sahai, L. Morgan, C. Woods and D. P. Rillema, manuscript in preparation.

List of Presentations Resulting From DOE Research (1990-1992)

"Oligomer and Mixed-Metal Compounds: Potential Multielectron Transfer Agents," D. P. Rillema, S. Van Wallendael, R. J. Shaver and C. B. Blanton, The Fourteenth DOE Solar Photochemistry Research Conference, Lake Harmony, PA, June, 1990.

"The Excited-State Properties of [Pt(bph)X_2], X = CH_3CN, C_5H_5N, $(C_2H_5)_2S$, bph = Biphenyl, and [Pt((bph)(en)], en = ethylenediammine, Complexes: Electron Transfer and Other Properties," C. B. Blanton and D. P. Rillema, XIIIth IUPAC Symposium on Photochemistry, University of Warwick, Coventry, England, July, 1990.

"Photocurrents Derived from $[Ru(bpy)_3]^{2+}$, Oxygen, and Triethanolamine in a Hydrogel Matrix," A. K. Edwards and D. P. Rillema, The 42nd Southeast/46th Southwest Combined Regional ACS Meeting, New Orleans, LA, December, 1990.

"Rhenium(I) Tetracarbonyl Complexes Containing Bidentate Heterocyclic Ligands," R. J. Shaver and D. P. Rillema, The 201st National ACS Meeting, Atlanta, GA, April, 1991.

"Photophysics of a Heterometallic Ruthenium(II)/Rhenium(I) Complex," S. Van Wallendael and D. P. Rillema, The 201st National ACS Society Meeting, Atlanta, GA, April, 1991.

"Photophysical Properties of MLCT and LC Excited States of Organometallic Complexes of Platinum(II)," Z. Murtaza, C. B. Blanton and D. P. Rillema, The 201st National ACS Meeting, Atlanta, GA, April, 1991.

"Derivatives of $Re(bpm)(CO)_3X^{n+}$, where X = CO, CH_3CN, MeQ^+ and Py-PTZ: Structures, Ground State and Excited State Properties," D. P. Rillema and R. J. Shaver, The 201st National ACS Meeting, Atlanta, GA, April, 1991.

"The Photophysical Properties of Platinum(II) Complexes: Emission From ^{3}MLCT and ^{3}LC States," Z. Murtaza, C. Blanton and D. P. Rillema, The Fifteenth DOE Solar Photochemistry Research Conference, Snowmass Village, CO, June, 1991.

"Photoinduced Intramolecular Energy Transfer From one Metal Center to the Other in a Mixed-Metal Ruthenium/Rhenium Complex," S. Van Wallendael and D. P. Rillema, the 9th International Symposium on the Photochemistry and Photophysics of Coordination Compounds, Fribourg, Switzerland, July, 1991.

"Photoinduced Processes in Covalently Linked Transition Metal Complexes: CT-Perturbations of Electronic Coupling," J. F. Endicott, T. Burande, X. Song, Y. Lei and D. P. Rillema, The 203rd National ACS Meeting, San Francisco, CA, April, 1992.

"The Structures and Properties of Copper(I) and Copper(II) Complexes Containing an Ethane-Bridged Dimeric Phenanthroline Ligand," Y. Yao, M. W. Perkovic, D. P. Rillema and C. Woods, The 203rd National ACS Meeting, San Francisco, CA, April, 1992.

"Physical and Photophysical Properties of Rhenium(I) Tetracarbonyl Complexes," R. J. Shaver and D. P. Rillema, The 14th IUPAC Symposium on Photochemistry, Leuven, Belgium, July, 1992.

"The Photophysical Properties of Rhenium(I) Tricarbonyl Complexes Containing Alkyl and Aryl Substituted Phenanthroline Ligands," L. Wallace and D. P. Rillema, The 44th Southeastern - 26th Middle Atlantic Regional ACS Meeting, Arlington, VA, December, 1992.

"Photoinduced Energy Transfer in a Ruthenium(II)/Rhenium(I) Bimetallic Complex: A Solvent Effect Study," Shawn Van Wallendael and D. P. Rillema, The 44th Southeastern - 26th Middle Atlantic Regional ACS Meeting, Arlington, VA, December, 1992.

"The Photophysical Properties of Heterocyclic Ligand and Carbonyl Complexes of Platinum(II) Coordinated to the Biphenyl Dianion," Z. Murtaza, C B. Blanton and D. P. Rillema, The 44th Southeastern - 26th Middle Atlantic Regional ACS Meeting, Arlington, VA, December, 1992.

"Photoinduced Electron Transfer in Ruthenium(II)/Rhenium(I) Bimetallic Complexes Containing Donor and Acceptor Ligands," M. W. Perkovic, R. J. Shaver, S. Van Wallendael, and D. P. Rillema, The 44th Southeastern - 26th Middle Atlantic Regional ACS Meeting, Arlington, VA, December, 1992.

"Preparation, Redox and Spectral Properties of a New Series of Ruthenium(II) Complexes Containing the Ligand 1,2-Bis(2,2'-bipyridyl-6-yl)ethane," A. Macatangay and D. P. Rillema, The 44th Southeastern - 26th Middle Atlantic Regional ACS Meeting, Arlington, VA, December, 1992.

"Charge Separation Studies in $[Re(bpm)(CO)_3L]^{n+}$ Complexes, L = CO, CH_3CN, Py, MeQ^+ and Py-PTZ: Structure, Physical and Photophysical Properties," R. J. Shaver, M. W. Perkovic and D. P. Rillema, The 44th Southeastern - 26th Middle Atlantic Regional ACS Meeting, Arlington, VA, December, 1992.

Additional Support:

1. The Camille and Henry Dreyfus Foundation funded a proposal entitled, "The Camille and Henry Dreyfus Scholar/Fellow Program." The grant was for $60,000 (plus a $20,000 match by the university) and included a 2 year stipend for the fellow, plus funding for equipment and supplies.

2. The Foundation of the University of North Carolina provided funding to support the research activities of one graduate student during the 1990 summer period. The grant was for $4100.

3. The P.I. used his endowed professorship monies ($8,000) to partially support the work of a postdoctoral student during the 1991-92 year.

4. A proposal to NSF entitled Acquisition of a Nd:YAG laser system is pending. The request is for $96,505 and requires a 50:50 match by the university.

Progress of Project During the Time Period 1/1/90-1/1/93

NARRATIVE

Monometallic Complexes

a) **Ruthenium(II)** i) The crystal structures of $Ru(bpy)_3(PF_6)_2$ (bpy = 2,2'-bipyridine), $Ru(bpm)_3(PF_6)_2{\cdot}CH_3CN$ (bpm = 2,2'-bipyrimidine) and $Ru(bpz)_3(PF_6)_2$ (bpz = 2,2'-bipyrazine) were determined by single crystal x-ray crystallography. The Ru-N bond distances in $Ru(bpy)_3^{2+}$, $Ru(bpm)_3^{2+}$ and $Ru(bpz)_3^{2+}$ were 2.05 - 2.06 Å. Replacement of C by N in the aromatic ring of the ligand caused little variation in the bond length or bond angles nor the bridging C-C bond distance connecting the two aromatic heterocyclic rings. The weaker σ bonding in the series bpy > bpm > bpz was balanced by the stronger π bonding in the series bpz > bpm > bpy such that the interatomic Ru-N distance remained almost constant.

The similarities of the structures has significance for theoretical and photophysical chemists. It may be possible by computational chemistry to theoretically evaluate the degree of σ and π bonding in the complexes and provide a quantitative understanding of the bonding differences that exist among ruthenium(II) heterocycles. For the photophysical chemist, the similarity in bond distance implies that the potential energy surfaces are similar and one is justified in utilizing a common description for their excited-state behavior.

ii) The photophysical and photochemical properties of a series of 2-(2'-pyridyl)pyrimidine (pypm) and bis(pyridine) polypyridyl complexes of ruthenium(II) were determined to identify ligand combinations that would minimize photochemical ligand loss. The order of decreasing quantum yield toward ligand loss was $Ru(bpm)_2(py)_2^{2+}$ > $Ru(pypm)_3^{2+}$ > $Ru(bpy)(pypm)_2^{2+}$ > $Ru(bpy)_2(pypm)^{2+}$ > $Ru(bpy)(bpz)(py)_2^{2+}$. There was extensive suppression of photochemical ligand loss in $Ru(bpy)(bpz)(py)_2^{2+}$ which opens up synthetic opportunities for the preparation of "photostable" light-induced electron transfer chromophores based on "Ru(bpy)(bpz)"$^{2+}$ as the core.

The results of emission curve fitting reinforced earlier observations which had shown that the degree of excited-state distortion depended upon the structure of the chromophoric ligand, and in a series of complexes having the same chromophoric ligand, on the energy gap between the ground and excited state. For the pypm series, E_{00} (the zero-zero energy) fell in the order $Ru(pypm)_3^{2+} > Ru(bpy)(pypm)_2^{2+} > Ru(bpy)_2(pypm)^{2+}$. For $Ru(bpz)_2(py)_2^{2+}$ and $Ru(bpm)_2(py)_2^{2+}$, E_{00} was approximately the same but there was a significant decrease in excited-state distortion for the bpz complexes, as shown by the lower S_m-values (average electron-vibrational coupling constant). The relative low value was shared with $Ru(bpy)(bpz)(py)_2^{2+}$, suggesting that the excited electron resides on the bpz ligand as expected. For the bpm complexes, S_m values were higher indicating a relatively high degree of distortion at bpm in the excited state, indicating more extensive overlap of the vibrational wave functions for ring-stretching acceptor modes between the ground and vibrational states. The greater vibrational overlap led to a larger Frank-Condon factor than for the equivalent bpz complexes, enhanced rate constants for nonradiative decay, and a decreased excited state lifetime.

b) **Rhenium(I)** i) The physical and photophysical properties of a series of rhenium(I) tetracarbonyl complexes $[Re(CO)_4(L\text{-}L)]CF_3SO_3$, where L-L = bpm, bpy, dmb (4,4'-dimethyl-2,2'-bipyridine) and phen (1,10-phenanthroline), were examined as precursors to the more numerous tricarbonyl analogues. The emission quantum yields in methylene chloride at room temperature were near 0.03 for the bpm, bpy and dmb derivatives and 0.008 for the phen analogue. Structured emissions attributed to a ^{3}LC (triplet ligand centered state) were observed near 470 nm for the bpy, dmb and phen derivatives, but nonstructured emission assigned as ^{3}MLCT based (triplet metal-to-ligand charge transfer) was found for the bpm complex. The complexes were photosensitive in methylene chloride expelling one of the CO ligands upon irradiation. It was replaced with the $CF_3SO_3^-$ counter ion. An x-ray structure of $[Re(CO)_4bpm)]^+$ revealed that the two CO ligands attached opposite one another to Re(I) had 0.1 Å longer Re-C bond distances than the two CO ligands coordinated opposite the bpm ligand. Thus, one of the two CO ligands of longer Re-C bond distance most likely was lost upon photolysis, where the photochemical quantum yields for the various complexes ranged from 0.03 to 0.9.

One unique feature of the tetracarbonyl complexes was the observation that photolysis of a highly luminescing complex resulted in a product that had greater luminescence intensity than the parent. This observation was a contradiction of the energy gap law where the nonradiative decay rate constant increases in magnitude as the energy gap between the excited state and the ground state decreases. A second unique feature was related to their electrochemical properties. The complexes displayed only ground state reductions and thereby were shown to behave only as photooxidants. The third unusual property was the ease of CO loss upon photolysis. While this is an undesirable property of a photocatalyst, it does provide an opportunity to utilize the tetracarbonyl complexes as intermediates in the design of uniquely coordinated chromophores in tricarbonyl rhenium(I) complexes.

ii) The physical and photophysical properties of a series of rhenium(I) tricarbonyl pyridine complexes containing various methyl and phenyl substituted phenanthroline ligands were examined with the goal of linking two phenanthroline ligands at the substituent location giving rise to optimum photophysical properties. At room temperature, emission from the complexes in methylene chloride was nonstructured, broad and followed single exponential decay. The emission lifetimes ranged from 3.0 to 12.5 µs. At 77 K in a 4:1 ethanol:methanol glass, the emission behavior fell into two classes. The emission spectra of class A complexes containing the ligands 1,10-phenanthroline and 2,9-dimethyl-, 4,7-diphenyl- and 2,2-dimethyl-4,7-diphenyl-1,10-phenanthroline showed little structure and decayed monoexponentically with emission lifetimes in the 12 - 35 µs range. Class B complexes, on the other hand, which contained the ligands 4,7-dimethyl-, 5,6-dimethyl-, 3,4,7,8-tetramethyl- and 5-phenyl-1,10-phenanthroline, showed structured emission at 77 K which decayed biexponentially. A fast decay with an emission lifetime of approximately

23 μs for all the class B complexes and a slow decay with emission lifetimes that ranged from 100 to 300 μs for individual class B complexes were observed. Time resolved emission spectroscopy revealed that the short-lived emission component was nonstructured while the long-lived emission component was structured. The latter closely resembled the luminescence spectrum of the free ligand. Dual emission was attributed to emission from a ^{3}LC and ^{3}MLCT state populated by partitioning from a single excited state.

Photophysical properties were maximized for the 4,7-dimethyl- and the 5,6-dimethyl-1,10-phenanthroline complexes and, hence, alkyl linkage from one phenanthroline ligand to another at any one of these positions should allow for the possible synthesis of bimetallic species with optimum energy or electron transfer characteristics. These phenanthroline complexes also displayed the unusual property of dual emission from excited states related to the same ligand. This phenomenon appears to occur as more ligand character is blended into the excited-state and results in an increase in emission lifetimes. Such increases are desirable for solar energy photocatalysts, but some of the properties displayed by the complexes were perplexing. First, the emission lifetimes did not follow the energy gap law. Second, emission decay of the short-lived component occurred from a lower energy excited state than that of the longer-lived component which means that the two excited states do not communicate with one another even though they reside on the same ligand. Additional experimentation is underway to further understand the photophysical behavior of the [(xx-phen)Re(CO)$_3$py]$^+$ systems.

iii) Laser flash photolysis of rhenium(I) tricarbonyl bipyrimidine complexes containing the electron acceptor ligand, N-methyl-4,4'-bipyridinium ion (MeQ$^+$), and the electron donor ligand 10-(4-picolyl)phenathiazine (pyPTZ) gave insight into the behavior of charge separation in excited state species. The pyPTZ derivative displayed formation of the pyPTZ$^{\bullet(+)}$ and bpm$^{\bullet(-)}$ radicals within 900 ps after the flash. Back electron transfer (BET), bpm$^{\bullet(-)} \rightarrow$ pyPTZ$^{\bullet(+)}$, occurred with a rate constant of $\sim 3 \times 10^8$ s^{-1}. The transient absorption behavior of [bpmRe(CO)$_3$ MeQ]$^{2+}$ was more complex. Both bpm$^{\bullet(-)}$ and MeQ$^{\bullet}$

radicals were generated within the time frame of the flash and underwent rapid decay. The emission behavior of $[(bpm)Re(CO)_3MeQ]^{2+}$ was identical to that of the control, $[(bpm)Re(CO)_3py]^+$, and by inference suggested that the quenching of $[(bpm^-)Re^{II}(CO)_3MeQ]^{2+}$ by coordinated MeQ^+ did not occur to an appreciable extent. The formation of $[(bpm^{\bullet})Re^{II}(CO)_3MeQ]^{2+*}$ and $[(bpm)Re^{II}(CO)_3MeQ^{\bullet}]^{2+*}$ in the laser flash most likely occurred, then, by partitioning from the singlet excited states of $Re^I \rightarrow$ bpm and $Re^I \rightarrow MeQ^+$ which lie close in energy, and for all intents and purposes may be postulated to be "one excited state."

The results of the study suggest that the procedure for generating long-lived, charge separated species based on transition metal complexes undergoing metal-to-ligand charge transfer may be to have an attached electron donor ligand which transfers an electron to fill the hole generated on the metal upon optical excitation. The electron residing on the heterocyclic ligand can then be channeled to a lower energy acceptor at some other location which, for example, may be another metal center or a chromophore attached to the bipyridine ring.

c) **Platinum(II).** The physical and photophysical properties of $[Pt(bph)(C_2H_5)_2S]_2$, $[Pt(bph)(CH_3CN)_2]$, [Pt(bph)(en)] and $[Pt(bph)(py)_2]$, where bph^{2-} is the dianion of biphenyl, en is ethylenediammine and py is pyridine were investigated. Highly structured emission was observed and attributed to a $^3LC \rightarrow {}^1GS$ (singlet ground state) process. Emission spectral curve fitting using a four mode fit gave E_{00} ~20670 cm^{-1} and vibrational frequencies of 1550, 1150, 715 and 375 cm^{-1} and corresponding S-values (electronic-vibronic coupling constants) of 0.89, 0.60, 0.23 and 0.28 which were nearly independent of the specific complex. Temperature-dependent lifetime data revealed the presence of an energy level above the ^3LC state with an activation energy of 1220 cm^{-1} for $[Pt(bph)(CH_3CN)_2]$, 2280 cm^{-1} for $[Pt(bph)(py)_2]$ and 2490 cm^{-1} for [Pt(bph)(en)]. The nature of this upper energy excited state is still under investigation.

The results of the spectral curve fitting analysis were compared to the vibrational frequencies found for H_2bph and $Hbph^-$ from Raman Spectroscopy. The similarity of the results suggested that the metal center acted as a template and the ligand vibrated almost as if the metal were not present. Apparently, the role of the metal was to increase the intersystem crossing quantum yield which then enhanced the luminescing properties of the attached ligand. An addition feature of importance for $[Pt(bph)L_2]$ complexes was the 2.6 eV energy gap which results in approximately a -1.5V driving force for the $[Pt(bph)L_2^{+/*}$ reduction potential.

While structured emission was observed for the above $Pt(bph)L_2$ complexes, the recently synthesized CO adduct and Pt(bph)(L-L) complexes, where L-L is bpy, dmb, bpm and phenanthroline, displayed nonstructured emission. Like the $Pt(bph)L_2$ complexes, the $Pt(bph)(CO)_2$ adduct luminesced in fluid solution at room temperature. Pt(bph)(L-L) complexes, however, luminesced only in a glass at low temperatures, in the solid state or in a matrix such as such as polymethylmethacrylate at ambient conditions. Luminescence of the CO adduct was attributed to population of a ^{3}MLCT state associated with the Pt(bph) unit; in L-L adducts, it was assigned to a ^{3}MLCT state associated with the Pt(L-L) component, where the $d\pi(Pt) \rightarrow \pi^*(bph)$ transition occurs ~100 nm lower in energy than the analogous $d\pi(Pb) \rightarrow \pi^*(bph)$ transition. Addition of L-L to a solution of $Pt(bph)L_2$ resulted in displacement of both L ligands and replacement with L-L. While an associative substitution mechanism is likely, the kinetics were anomalous and warrant further investigation.

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Rather unusual properties were noted for the CO adduct, $Pt(bph)(CO)_2$. The compound displayed thermochromism in solution changing from green at room temperature to blue at low temperature. Freeze-pump-thaw degassing resulted in formation of a blue species which may be the μ bridged dimer, $[Pt(bph)CO]_2$. These ill characterized systems are currently under investigation, not only for their novelty, but also as potential precursors for multimetallic complexes.

These platinum(II) complexes were synthesized with the goal of affecting two electron oxidation and/or reduction of substrates based on the concept of oxidative addition or reductive elimination reactions. Reductive quenching was demonstrated between Pt(bph)L_2^* and methylviologen, but related studies investigating two electron transfers remain unexplored.

d) Copper(II). Monometallic copper(II) complexes containing the ligands 1,2-bis(2,2'-bipyridyl-6-yl)ethane (O-BPY) and 1,2-bis(9-methyl-1,10-phenanthrolin-2-yl)ethane (Diphen) were synthesized. Single crystal x-ray structures revealed a distorted square planar geometry for $Cu(O\text{-}BPY)^{2+}$ and a trigonal bipyramidal geometry for "$Cu(Diphen)^{2+}$" which contained a water molecule in the fifth coordination site. The shift from square planar geometry for $Cu(O\text{-}BPY)^{2+}$ to trigonal bipyramidal geometry for $[Cu(Diphen)(H_2O)]^{2+}$ was attributed to steric effects related to the presence of the methyl groups located in the 9 position on the phenanthroline rings.

The copper(II) complexes were reduced to copper(I) species with ascorbic acid and the physical and photophysical properties of the copper(I) derivatives were investigated. Both copper(I) complexes displayed a $d\pi \rightarrow \pi^*$ transition near 450 nm in accord with previously studied $[Cu(dmp)_2]^+$, where dmp was 2,9-dimethyl-1,10-phenanthroline, which was reported to luminesce in solution at room temperature and behave as an excited state electron transfer agent upon optical excitation. Of the above two copper(I) complexes, only the Diphen derivative displayed luminescence, and then only at 77 K in a frozen glass. The reason for the lack of luminescence in $Cu(O\text{-}BPY)^+$ (and $Cu(bpy)_2{}^+$) remains open to explanation. However, a crystal structure of copper(I) diphen revealed that it was actually a bimetallic complex containing a CuN_4 core in a distorted tetrahedral arrangement. The CuN_4 core contained two nitrogen atoms from one phen unit of one diphen molecule and two nitrogen atoms from a phen unit of a second diphen molecule. The decrease in luminescence efficiency can then be attributed to the presence of two copper(I) atoms in close proximity which increases nonradiative relaxation pathways. The marked structure change involved in the reaction (1) offers the opportunity to design systems where

$$2\ Cu(Diphen)(H_2O)^{2+} + 2e^- \rightarrow [Cu(Diphen)_2]^{2+} + 2\ H_2O \qquad (1)$$

back electron transfer would be inhibited between an electron donor - $Cu(Diphen)(H_2O)^+$ combination due to a substantial "nuclear gating" effect.

Bimetallic Complexes

a) **Ruthenium(II)-Ruthenium(II) Complexes.** The physical and photophysical properties of a series of ruthenium(II) complexes containing the O-BPY ligand (1,2-bis(2,2'-bipyridyl-6-yl)ethane were compared to a similar series containing the bb ligand (1,2-bis(2,2'-bipyridyl-4-yl)ethane. The O-BPY complexes were $[Ru(bpy)_2(O\text{-}BPY)]^{2+}$, $[Ru(bpy)(O\text{-}BPY)]^{2+}$ and $\{[Ru(bpy)_2]_2O\text{-}BPY\}^{4+}$; the bb complexes were $[Ru(bpy)_2bb]^{2+}$ and $\{[Ru(bpy)_2]_2bb\}^{4+}$. The data are compared in Table I.

From the results in solution at room temperature, one notes that the emission maxima remain nearly at the same energy. The emission quantum yield of $Ru(bpy)_3{}^{2+}$. $Ru(bpy)_2bb^{2+}$ and $\{[Ru(bpy)_2]_2bb\}^{4+}$ remain approximately the same, but those of the O-BPY complexes are less and decrease in the order $[Ru(bpy)(O\text{-}BPY)]^{2+} > [Ru(bpy)_2O\text{-}BPY]^{2+} > \{[Ru(bpy)_2]_2O\text{-}BPY\}^{4+}$. The emission lifetimes range from 800 - 900 ns, with the exceptions of $\{[Ru(bpy)_2]_2bb\}^{4+}$ and $\{[Ru(bpy)_2O\text{-}BPY\}^{4+}$. The effect, however, is small for $\{[Ru(bpy)_2]_2bb\}^{4+}$ (473 ns) compared to $\{[Ru(bpy)_2]_2O\text{-}BPY\}^{4+}$ (~1 ns).

Clearly, the presence of the ethane linker in the 2 position effects the photophysical properties in a more substantial way than attachment in the 4 position. The extreme case noted is for the emission lifetime of $\{[Ru(bpy)_2]_2O\text{-}BPY\}^{4+}$ which has decreased by almost three orders of magnitude, presumably due to quenching by the adjacent ruthenium component. The data indicate that attachment of the linker in the 4 position results in excited state behavior that emulates $Ru(bpy)_3{}^{2+}$. Attachment in the 2 position leads to

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Table I. Emission Maxima, Emission Lifetimes and Emission Quantum Yields for a Series of Ruthenium(II) Complexes with O-BPY and bb Ligands.

Complexes	λ_{em}, nm	τ_o, ns	Φ_{em}
$[Ru(bpy)_3]^{2+}$[a]	615	860	0.062
$[Ru(bpy)_2O\text{-}BPY]^{2+}$[b]	618	842	$1.3 (\pm 0.2) \times 10^{-3}$
$[Ru(bpy)(O\text{-}BPY)]^{2+}$[b]	616	869	$6.3 (\pm 0.4) \times 10^{-3}$
$\{[Ru(bpy)_2]_2O\text{-}BPY\}^{4+}$[b]	620	~1[e]	$1.4 (\pm 0.04) \times 10^{-4}$
[Ru(bpy)2bb]2+ c	617	915	7.5 (±0.002) x 10-2
$\{[Ru(bpy)_2]_2bb\}^{4+}$[b]	624	473	$6.5 (\pm 0.001) \times 10^{-2}$

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a. B. Durham, J. V. Caspar, J. K. Nagle, T. J. Meyer. J. Am. Chem. Soc. 104 (1982) 4803-10.

b. In acetonitrile; $\lambda_{ex} = 436$ nm; 298 K; degassed; Φ_{em} relative to $Ru(bpy)_3{}^{2+}$.

c. In acetonitrile; $\lambda_{ex} = 355$; 298 K; degassed; Φ_{em} relative to $Ru(bpy)_3{}^{2+}$.

marked quenching which may be desirable for designing highly efficient electron transfer donor-acceptor systems.

b) **Ruthenium(II)-Cobalt(III).** The photophysical behavior of the $[(bpy)_2RubbCo(bpy)_2]^{5+}$ ion was investigated. The molecule contained the $Ru(bpy)_2^{2+}$ electron donor and a low spin (or singlet) $Co(bpy)_2^{3+}$ electron acceptor bridged by 1,2-bis(4'-methyl-2,2'-bipyridyl-4-yl)ethane (bb). Light absorption by the $Ru(bpy)_2^{2+}$ moiety of the complex led to generation of a bb bridged intermediate containing $Ru(bpy)_2^{3+}$ and high spin (or quartet) $Co(bpy)_2^{2+}$ centers. The bb ligand was selected because the ethane linkage was expected to result in weak donor-acceptor coupling and because the bidentate ligand would be difficult to displace from labile cobalt(II) and ruthenium(III). The $Ru(bpy)_2^{2+}$ unit was chosen due to its good light absorbing characteristics and its well characterized photophysical behavior. $Co(bpy)_2^{3+}$ was selected as the electron acceptor because the large bond length changes accompanying its reduction usually lead to slow electron transfer rates, and because relaxation to the ground state of the expected high spin ($^4T_2$ in O_h symmetry) product is electronically forbidden, so the rate of electron transfer might be further inhibited.

The results of the work permitted some unique insights into details of electronically forbidden electron transfer processors. The separation of the $Co(bpy)_2^{2+}$ electron donor and the $Ru(bpy)_2^{3+}$ electron acceptor by the ethane linker resulted in an electron transfer rate between 0.1 and 1% of the rate predicted based on the electron transfer properties of the component couples. These differences in electronic coupling were examined by a simple spectroscopic, donor-acceptor model. The evidence indicated that the $Co(bpy)_3^{3+/2+}$ electron self exchange occurs through thermal population of the ^2E state of $Co(bpy)_3^{2+}$ (preequilibrium constant $\sim10^{-3}$) while the cross reaction with $Ru(bpy)_3^{3+}$ probably occurs through the $^4T_2$ state. The only significant electronic coupling in either case was super exchange coupling mediated by the polypyridyl ligands.

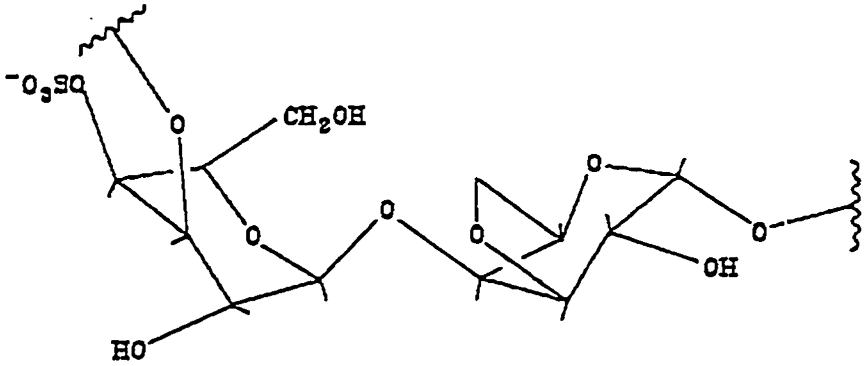
c) **Ruthenium(II)-Rhenium(I).** The physical and photophysical properties of $[(\mathrm{bpy})_2\mathrm{RubbRe(CO)_3py}]^{3+}$ were investigated. The bb ligand, 1,2-bis(4'-methyl-2,2'-bipyridyl-4-yl)ethane, served as an ethane bridged linker between what would otherwise be described as two independent bipyridine mixed ligand complexes, $\mathrm{Ru(bpy)_2(dmb)}^{2+}$ and $\mathrm{(dmb)Re(CO)_3py}^{+}$, where dmb is 4,4'-dimethyl-2,2'-bipyridine. The separated monomers, $\mathrm{Ru(bpy)_2bb}^{2+}$ and $\mathrm{bbRe(CO)_3py}^{+}$ had well characterized light absorbing and emission properties of their own. However, the emission occurred at higher energy (552 nm) for $\mathrm{bbRe(CO)_3py}^{+}$ than for $\mathrm{Ru(bpy)_2bb}^{2+}$ (610 nm). Since the emission quantum yield of $\mathrm{bbRe(CO)_3py}^{+}$ ($\Phi_{em} = 0.179$) was greater than for $\mathrm{Ru(bpy)bb}^{2+}$ ($\Phi_{em} = 0.080$), irradiation of $[(\mathrm{bpy})\mathrm{RubbRe(CO)_3py}]^{+}$ to produce $[(\mathrm{bpy})_2\mathrm{RubbRe^{*}(CO)_3py}]^{3+}$ was expected to form $[(\mathrm{bpy})_2\mathrm{Ru^{*}bbRe(CO)_3py}]^{3+}$ by energy transfer and result in an increased emission quantum yield from the ruthenium portion of $[(\mathrm{bpy})_2\mathrm{RubbRe(CO)_3py}]^{3+}$. Indeed the emission quantum yield was found to increase from 0.080 for $\mathrm{Ru(bpy)_2bb}^{2+*}$ to 0.16 for $[(\mathrm{bpy})_2\mathrm{Ru^{*}bbRe(CO)_3py}]^{3+}$ when excited at 355 nm in methylene chloride at room temperature. There was also no residual emission from the rhenium position of the molecule indicating the energy transfer process was very efficient.

The results of the energy transfer prompted an investigation into the mechanism of the process. The two leading possibilities were energy transfer by dipole-dipole intercharge (Förster) or electron interchange (Dexter). The latter mechanism would result in large dipole charges in the molecule and would then be very solvent dependent. The results of a solvent dependency study revealed little difference between the emission behavior of $[(\mathrm{bpy})_2\mathrm{RubbRe(CO)_3py}]^{3+*}$ and those found for $[\mathrm{Ru(bpy)_2bb}]^{2+*}$ and $[\mathrm{bbRe(CO)_3py}]^{+*}$. The results were in accord with the Förster mechanism where energy transfer can occur with up to 100 Å separation between donor and acceptor.

The results of this study are encouraging for designing energy transfer systems which not only are highly efficient, but also allow one to enhance the photophysical properties of a potential solar energy catalyst. New systems are being proposed to exploit this important discovery.

Applications

Surface Modified Electrodes-Hydrogels. Platinum and gold working electrodes were modified with the hydrogel kappa-carrageenan shown below. This hydrogel is an anionic polysaccharide extracted from seaweed. The hydrogel was cured on the electrode surface with ruthenium(II) trisbipyridine and methyl viologen. In the presence of triethanolamine (TEOA), the following sequence of reactions were postulated to occur upon illumination of the modified electrode with light. Photolysis at 436 nm gave rise to a significant photocurrent which depended on the concentration of $Ru(bpy)_3{}^{2+}$, MV^{2+} and



D–galactose–4–sulfate   3,6–anhydro–D–galactose

$$[Ru(bpy)_3]^{2+} \xrightarrow{h\upsilon} [Ru(bpy)_3]^{2+*} \qquad (2)$$

$$[Ru(bpy)_3]^{2+*} + MV^{2+} \rightarrow [Ru(bpy)_3]^{3+} + MV^{+} \qquad (3)$$

$$[Ru(bpy)_3]^{3+} + TEOA \rightarrow [Ru(bpy)_3]^{2+} + \text{Oxidation Prod.} \qquad (4)$$

$$MV^{+} \xrightarrow[electrode]{} MV^{2+} + e^{-} \qquad (5)$$

triethanolamine. The maximum photocurrent obtained was 12 μa.cm^2.

The behavior of the modified electrode was also examined in water with MV^{2+} replaced by O_2. The type of photocurrent (oxidative or reductive) depended on the pH of the solution and the offset potential of the working electrode. The maximum photocurrent of 12 μa/cm^2 was obtained with a 4% carrageenan hydrogel cured with 5 mM $[Ru(bpy)_3]^{2+}$ in 50 mM KNO_3, $PO_2 = 1$ atm, an electrolyte solution containing 1 M TEOA in 0.1 M KNO_3 and an excitation wavelength of 436 nm. The mechanism that accounted for the observations is outlined as follows.

$$[Ru(bpy)_3]^{2+}\ h\upsilon \xrightarrow{I_a} [Ru(bpy)_3]^{2+*} \qquad (6)$$

$$[Ru(bpy)_3]^{2+*} + \xrightarrow{k_0} \begin{cases} \xrightarrow{k_r} [Ru(bpy)_3]^{2+} + h\nu' \\ \xrightarrow{k_{nr}} [Ru(bpy)_3]^{2+} + \text{heat} \end{cases} \qquad (7)$$

$$[Ru(bpy)_3]^{2+*} + O_2^- \xrightarrow{k_q} [Ru(bpy)_3]^{3+} + O_2^- \qquad (8)$$

$$[Ru(bpy)_3]^{2+*} + O_2^- \xrightarrow[H_2O]{k'_q} [Ru(bpy)_3]^{3+} + HO_2^- \qquad (9)$$

$$2\ O_2^- + 2\ H_2O \xrightarrow{k_d} O_2 + H_2O_2 + 2\ OH^- \qquad (10)$$

$$[Ru(bpy)_3]^{3+} + TEOA \xrightarrow{k_{irr}} [Ru(bpy)_3]^{2+} + \text{oxidation products} \qquad (11)$$

$$H_2O_2 \xrightarrow{K_a} HO_2^- + H^+ \qquad (12)$$

$$HO_2^- + OH^- \xrightarrow[electrode]{} O_2 + H_2O + 2e^- \quad (13)$$

The E° values for the redox couple in eq. 13 is 0.076 V in 1 M OH^- and the pKa of H_2O_2 is 11.6. Superimposed on the photocurrent is a background current due to the process represented in eq. 13 (reduction of O_2) which becomes less important as the offset potential of the working electrode becomes more positive.

The relationship between the observed photocurrent and offset potential was consistent with the proposed mechanism. As the offset potential of the working electrode became more positive, the oxidative photocurrent produced by the system increased due to the fact that the background current produced at the electrode became less significant. The opposite is true as the offset potential became more negative. More O_2^- oxidatively quenches the excited state of $[Ru(bpy)_3]^{2+*}$ according to eq. 9 resulting in the observed reductive photocurrent.

The fact that the photocurrent increased as the partial pressure of O_2 increased in the system was also consistent with the proposed mechanism. The rate of O_2^- excited state quenching of $[Ru(bpy)_3]^{2+*}$ or its rate of reaction at the electrode surface to give O_2^- was enhanced by an increase in the concentration of O_2.

Perhaps the most revealing evidence supporting the proposed mechanism was the dependence of the photocurrent on pH. A plot of the photocurrent vs. pH was sigmoidal much like an acid-base titration curve. The change in slope of its derivative occurred at pH = 11.5 which is approximately equal to the pK_a of H_2O_2. Thus, the oxidative photocurrent depended on the concentration of HO_2^- in solution. At low HO_2^- concentrations, reductive photocurrent was observed due to preferential reduction of O_2 at the electrode surface to form O_2^- which then quenched the excited $Ru(bpy)_3^{2+*}$ according to eq. 9 resulting in the observed reductive photocurrent.