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**INTRAMOLECULAR ENERGY- AND ELECTRON-
TRANSFER REACTIONS IN POLYMETALLIC COMPLEXES**

Annual Progress Report

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A. PROGRESS REPORT**1. Excited-State Energy Transfer**

We have prepared and studied the photochemistry of $(\text{tpy})\text{Ru}^{\text{II}}(\text{tpp})\text{Co}^{\text{III}}(\text{PPhEt}_2)\text{H}_2^{3+}$, $(\text{NC})_3\text{Fe}^{\text{II}}(\text{tpp})\text{Co}^{\text{III}}(\text{PPhEt}_2)\text{H}_2$ and $(\text{NC})_3\text{Fe}^{\text{II}}(\text{tpp})\text{Co}^{\text{III}}(\text{PPh}_3)\text{H}_2$ (where tpp = 2,3,5,6-tetrakis(2'-pyridyl)pyrazine). All three compounds undergo photoinduced reductive elimination of molecular hydrogen when irradiated at 365 nm and one of the compounds gives a small amount of H_2 at 577 nm. Table I displays the quantum yield values observed for this photochemical process.

TABLE I.

Complex	λ_{irr} , nm	Φ_{H_2}
$(\text{tpy})\text{Ru}(\text{tpp})\text{Co}(\text{PPhEt}_2)\text{H}_2^{3+}$	365	8.4×10^{-2}
$(\text{NC})_3\text{Fe}(\text{tpp})\text{Co}(\text{PPhEt}_2)\text{H}_2$	365	1.9×10^{-3}
	577	1.3×10^{-3}
$(\text{NC})_3\text{Fe}(\text{tpp})\text{Co}(\text{PPh}_3)\text{H}_2$	365	1.4×10^{-2}

The low quantum yields for these systems are possibly due to the non-planarity of the bridging ligand which may present problems with the metal-metal communication in the excited state. In addition, the presence of only one phosphine ligand to stabilize the dihydride system, might contribute to the long-term thermal instability of these compounds.

To address the possibility that lack of bridging ligand planarity is responsible for low quantum yields, the following transformation is currently underway:

There is also the possibility that the low quantum yields in these systems are not due to the lack of bridge planarity but to the stability of the complex. This possibility will be described in the plans for next year.

2. Charge Separation

A series of complexes is currently under preparation consisting of the following general formula:

where bpy = 2,2'-bipyridine; tpy = 2,2':6',2''-terpyridine and

BL and BL' can be 2,2'-bipyrimidine (bpm), 2,3-bis(2'-pyridyl)pyrazine (dpp) or 2,3-bis(2'-pyridyl)quinoxaline (dpq)

MQ⁺ = N-methyl-4,4'-bipyridinium

The projected role of each of the portions of this molecule are photon absorber ((BL)Ru(bpy)(BL')), electron acceptor (MQ⁺), and electron donor ((NC)₄Fe(BL)). The synthesis of the complexes is outlined in the following equations for the complex where BL=dpp and BL'=bpm.

II

Complex I does not undergo emission at room temperature in fluid solution. The quenching of the typically luminescent Ru(II) center could be due to the presence, in general, of the second metal center which supplies additional relaxation pathways into the ground state; it could arise from the presence of the Cl^- ligands and the effect that lower excited state energies has on the lifetime; or hopefully it is due to electron transfer quenching of the Ru(II) MLCT excited state by the MQ^+ ligand. Transient absorption studies are planned to look for the formation and lifetime of MQ^* .

Work on the modification of the spacer in the charge separation species has involved the use of Cu(II) polymers as bridges between donor and acceptor systems. Two of the polymeric Cu(II) systems which have been prepared, $[\text{Cu}_2(\text{bpm})(\text{OH})_2(\text{H}_2\text{O})_4]_x (\text{ClO}_4)_2$ and $[\text{Cu}_x(\text{bpm})_{x+1}(\text{H}_2\text{O})_{2x}](\text{ClO}_4)_{2x}$, displayed conductivities of $\sim 5 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ as powdered samples. The former complex is proposed as a spacer in the target molecule below:

At this point, the Ru/Cu system displayed in Figure 1 has been prepared and also a complex with Cu(II) and tetrahydroxyquinone. (This latter species is interesting in that it undergoes facile proton and electron gains and losses to give species that vary all the way from a hexaketone to a hexahydroxo species).

FIGURE I.

1. Intramolecular Energy Transfer

The image displays two chemical structures. The structure on the left is 1,1'-bis(2-methyl-4-pyridyl)-2,2'-bis(methylene)ethane, which consists of two 2-methyl-4-pyridyl rings connected at their 1-positions by a -CH₂-CH₂- bridge. Each ring has a methyl group (CH₃) at the 2-position and a nitrogen atom at the 4-position. The structure on the right is 2,2'-bipyridine, which consists of two pyridine rings connected at their 2-positions by a single bond, with nitrogen atoms at the 1-positions of each ring.

dtbi

Now that the tridentate ligand, bpd, has been prepared, it will be used as a link between Ru(II) and Co(III) centers. The first complex which will be studied is $(\text{tpy})\text{Ru}(\text{bpd})\text{Co}(\text{PR}_3)\text{H}_2^{3+}$. If this complex is not thermally stable, attempts will be made to use the diphosphine, monohydride complex, $(\text{tpy})\text{Ru}(\text{bpd})\text{Co}(\text{PR}_3)_2\text{H}^{4+}$, in acidic solution to generate molecular hydrogen. This process should be more facile toward production of H_2 , but regeneration of the starting complex could be more difficult in homogeneous solution. If this hydrogen generation system works, then it may be necessary to bind the metal system to an electrode so that charge and protons can come from different locations.

Two additional energy transfer systems will be studied this next year. Preliminary experiments on a small sample of $(\text{NC})_4\text{Fe}(\text{dpp})\text{Co}(\text{PEt}_2\text{Ph})_2\text{H}_2$ display photoinduced production of H_2 ($\lambda_{\text{irr}} = 577 \text{ nm}$) with a quantum yield approaching 10^{-1} mol/ein . This complex has been difficult to make but the initial result has been encouraging and we will continue to pursue this system.

2. Charge Separation

A number of systems will be studied this year in the area of photoinduced charge separation. The ruthenium/copper system mentioned in the progress report will continue to be a focus of our efforts. We have bound $\text{Cu}(\text{II})$ to $\text{Ru}(\text{II})$ through a bpm bridge and $\text{Cu}(\text{II})$ to a quinone. What remains is to complex the polymeric backbone of $\text{Cu}(\text{II})$, alternately bridged by bpm and two OH^- ligands, to connect the pieces. The ability of this polymer to function as a semiconductor will hopefully enable efficient charge separation between the two terminal functionalities.

A major effort will be to finish the synthesis of the series of complexes, $[(\text{NC})_4\text{Fe}^{\text{II}}(\text{BL})\text{Ru}^{\text{II}}(\text{bpy})(\text{BL}')\text{Rh}^{\text{III}}(\text{tpy})(\text{MQ}^+)]^{4+}$, described earlier. Electronic communication between the various components should be very dependent on whether or not BL and/or BL' are bpm, dpp or dpq. Once a significant number of these supramolecules are prepared, we will be going to other laboratories (either Notre Dame, Bowling Green or Santa Barbara) to make transient absorbance measurements. The desired result would be the presence and the long lifetime of the methyl viologen radical, $\text{MQ}^\bullet$.

A parallel system, that hasn't been studied as yet, can be generated by substituting dmbpz for MQ⁺. This electron acceptor has a slightly less

dmbpz

negative reduction potential than MQ⁺ so it should afford more flexibility for these systems.

Lastly, the formation of a ruthenium(II) polymer with the tridentate bpd ligand has not yet been explored. The extensive π^* -network of the ligand should give a small band gap for the Ru(II) $\rightarrow$ bpd MLCT transition. Preliminary studies will involve the formation of this polymer, which should be highly colored, followed by the characterization of ground- and excited-state properties through electrochemistry, emission spectroscopy and lifetime measurements. Emission in this system may require an infrared detector.

Emphasis on these various projects will depend upon the successes observed. There will be one postdoctoral fellow and at least three graduate students working on this study (only two graduate students supported by DOE on this grant and an additional graduate student with a DOE Traineeship).

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