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INTRAMOLECULAR ENERGY TRANSFER REACTIONS IN POLYMETALLIC COMPLEXES

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ABSTRACT

A series of polymetallic complexes are being developed for use in converting solar radiation to usable chemical potential energy. The system is made up of three components: 1) A highly-absorbing (antenna) metal center which absorbs visible light but is photochemically unreactive; 2) A second metal center which undergoes a useful chemical reaction from a non-spectroscopic excited state; and 3) A bridging ligand which couples the two metal fragments and facilitates intramolecular energy transfer from the antenna to the reactive fragment. This paper will focus on optimizing the three components of the system.

INTRODUCTION

Transition metal complexes have been of interest as potential catalysts for the photodissociation of water by visible light.[1-3] In developing systems that will convert solar energy to usable chemical potential energy, there are many constraints that limit system selection. In order to undergo a photochemical reaction, light must first be absorbed. Since the portion of the solar radiation that reaches the earth's surface is mainly in the visible spectral region, this greatly reduces the number of usable systems. In order to use a photochemical reaction of a non-absorbing system, energy must be transferred from the absorbing molecule to the reacting molecule through some energy or electron transfer reaction. Traditionally, this process of sensitization has been bimolecular and, thus, not efficient. Our intentions are to expand the number of potential systems that would be useful for solar energy conversion by preparing polynuclear metal complexes where both the absorbing and reacting centers are present in the same molecule. The advantages of these systems over the more typical bimolecular approach are that the donor lifetime does not have to be extraordinarily long and the concentration of acceptor does not have to be large in order to have efficient sensitization.

Over the last ten years, many researchers have studied the photochemical,[4-6] bimolecular energy transfer,[7] and electron transfer[8-13] reactions of Ru(II) complexes of various nitrogen heterocyclic ligands such as substituted pyridines(py-X) and pyrazine (pz). This work has precipitated because of the in-

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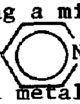
tense metal-to-ligand charge transfer (MLCT) bands these complexes display in the visible region of the spectrum, and the ease of oxidation or reduction and substitutional inertness of the corresponding intermediates or products. The role of the MLCT excited state in photosubstitution reactions of $L_5M(py-X)$ complexes (py-X is a substituted pyridine (also pyrazine or organonitrile)) has been studied by Malouf and Ford[4] for $L_5M = (NH_3)_5Ru^{II}$ and by our group for $L_5M = (CN)_5Fe^{II}$.[14] The results are similar in that the quantum yield for photosubstitution of py-X is dependent on the relative energies of MLCT and ligand field (LF) excited states. The ordering of the excited states can be tuned by appropriate choice of py-X, since the MLCT absorption maxima are very sensitive to the energy of the π* orbitals in this ligand. When the LF state is lower in energy than the MLCT state, substantial photosubstitution is observed. However, tuning the MLCT state energy to a point lower than the corresponding LF excited state vastly reduces the substitutional reactivity of the molecule. It is this latter case of a highly absorbing but non-reacting metal center which we wish to develop.

In 1979,[15] we reported the first example of an intramolecular energy transfer reaction using a mixed-metal bimetallic complex. The complex, $(NH_3)_5Ru^{II}NC-$$N-Rh^{III}(NH_3)_5^{5+}$, has an absorption maximum at 488 nm which is assigned as a metal-to-ligand charge transfer (MLCT) from Ru(II) to 4-cyanopyridine (4-CNpy). The reaction observed is cleavage of the Rh(III)-4-CNpy bond, which is a characteristic process of the triplet ligand field excited state associated with Rh(III). The advantage to this system is not in generating new chemistry, but driving old chemistry with lower energy irradiation. Figure 1 points out the generality of using this intramolecular energy transfer approach any time the desired photochemical reactivity arises from a non-spectroscopically observed state.

In a follow up study on the 1979 communication,[16] a variety of pentaammineruthenium(II) and pentacyanoferrate(II) systems were explored. These antenna fragments were coupled through monodentate bridging ligands like pyrazine (pz), 4,4'-bipyridine(4,4'-bpy) and 4-CNpy to pentaamminerhodium(III) and pentacyanocobaltate(III) reactive fragment. Although energy transfer reactions were observed in some of the ruthenium(II)rhodium(III) systems, a major complication (especially in the Fe(II) system) was the thermal and photochemical resiliency of the metal-ligand-metal bridge. These preliminary studies suggested the use of chelating bridging ligands to maintain the integrity of the complex during the photon absorption/energy transfer/remote reaction sequence.

BRIDGING LIGANDS

Previous studies[17] in our laboratories on the thermal stability and the

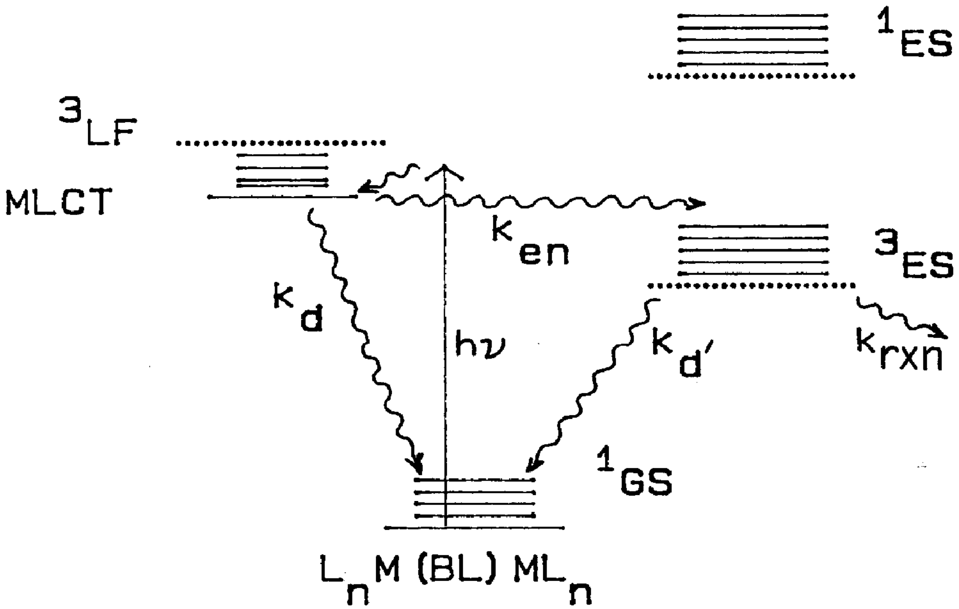


Figure 1. Energy Level Diagram for a Bimetallic System. L_nM-B represents highly absorbing metal fragment while B-M'L'_n represents the reactive fragment. Dotted lines signify non-spectroscopic states.

electrochemistry of bimetallic complexes illustrated that additional considerations, besides metal-bridging ligand-metal resiliency through chelation, need to be addressed. In addition to the sites of attachment, another factor in complex stability is the overall charge on the polymetallic unit. In situations where large positive charges build up, there is a tendency for the complex to decompose to the monometallic fragments. Charge reduction can take place through the addition of anionic ligands. These anionic ligands can either be terminal ligands on one of the metal centers, or be designed into the bridging ligand. A second point is that metal-metal communication must be maximized so that energy transfer (k_{et} in Fig. 1) can successfully compete with excited state relaxation (k_d in Fig. 1). With the points raised above taken into account, Figure 2 illustrates the bridging ligands we are currently using. We will discuss various methods for analysis of this communicative ability later in this paper.

All of the proposed bridging ligands form chelates with two metal centers, have short metal-metal distances, and have highly unsaturated aromatic π-systems. The communicative ability of the bridging ligands will be discussed in the following sections dealing with the antenna fragments.

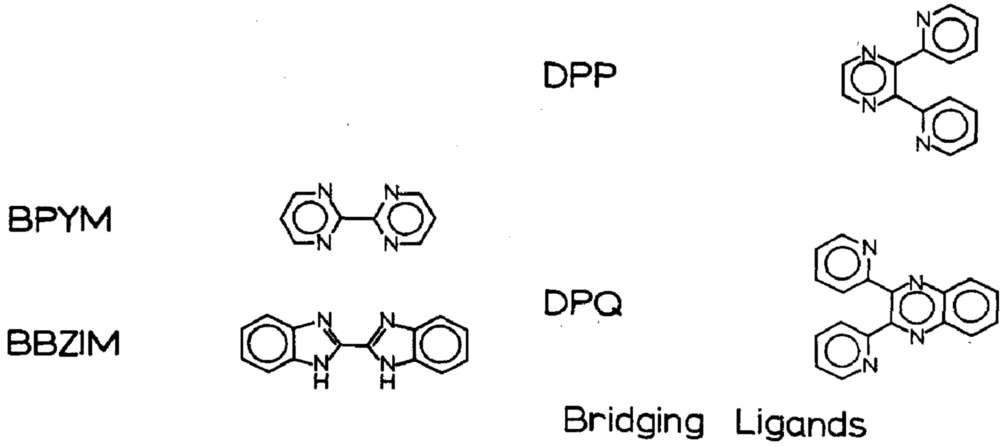


Figure 2. Bridging Ligands - 2,2'-bipyrimidine (bpym), bibenzeneimidazolate ($bbzimH_2$), 2,3-(2'-pyridyl)pyrazine (dpp) and 2,3-bis(2'-pyridyl)-quinoxaline (dpq).

ANTENNA FRAGMENTS

In developing highly absorbing but non-photochemically reactive metal centers, the low-valent d^6 complexes of Fe(II),[18] Ru(II),[19] W(0),[20] and Cr(0)[20] were used. These systems were selected because of the thermal stability and intense MLCT transitions associated with complexes of these metals containing aromatic, nitrogen heterocyclic ligands. Table I summarizes the electronic absorption spectra of a number of the antenna fragments.

Electronic Spectra

The various antenna fragments listed in Table 1 encompass anionic, neutral, and cationic systems which are soluble in aqueous solution as well as the Group VI zero-valent carbonyl complexes of chromium and tungsten which are soluble in most organic solvents. Therefore, a wide range of solution conditions, reactive fragments and desired photochemical reactions can be coupled in to the specific systems best suited as an antenna fragment in this list.

With the exception of the carbonyl complexes, the quantum yield for degradation of these antenna fragments is less than 10^{-5} mol/ein.[20] For $Cr(CO)_4(bpym)$ and $W(CO)_4(bpym)$, loss of CO occurs with an efficiency of $2.0x10^{-2}$ and $6.0x10^{-4}$ mol/ein, respectively, with 405nm irradiation. However, the bimetallic species, $[W(CO)_4]_2(bpym)$, which is probably a better measure of the photochemical

TABLE 1.

Electronic Absorption Spectra of the Antenna Fragments and Corresponding Homobimetallic Complexes.

Complex	λ_{max}, nm	ε_{max}, $M^{-1}cm^{-1}$	Ref.
$Fe(CN)_4(bpym)^{2-}$	533	1790	
	403	4690	18
$[Fe(CN)_4]_2(bpym)^{4-}$	648	--	
	597	--	
	425	--	21
$Fe(bpym)_2(CN)_2$	545	3380	
	380	6140	
$Fe(bpym)_3^{2+}$	530 sh	2700	
	481	3000	
	363	5000	
$[Fe(bpy)_2]_2(bpym)^{4+}$	521	9590	21
	349	7350	
$Ru(NH_3)_4(bpym)^{2+}$	567	2000	
	402	8400	19
$[Ru(NH_3)_4]_2(bpym)^{4+}$	697	4000	
	428	18000	
$Ru(bpy)_2(bpym)^{2+}$	475 sh	--	22, 23
	415	11300	
$[Ru(bpy)_2]_2(bpym)^{4+}$	606	7600	22, 23
	560 sh		
	408	31000	
$[Ru(bpy)Cl_2]_2(bpym)$	657	6500	
	447	14800	
$[Ru(tpy)Cl]_2(bpym)^{2+}$	625	--	
	465	--	
	410	--	
$Ru(NH_3)_4(biimH_2)^{2+}$	407	2700	24
$Ru(bpy)_2(bbzim)$	~540	~10000	
$[Ru(bpy)_2]_2(bbzim)^{2+}$	712	1700	25
$Cr(CO)_4(bpym)$	499	2401	20
	389	5630	
$W(CO)_4(bpym)$	478	3973	
	371	6940	
$[W(CO)_4]_2(bpym)$	610	6076	
	421	13200	
	385	12506	

reactivity of the antenna fragment under antenna fragment/reactive fragment conditions, has a decomposition quantum yield less than 10^{-5} mol/ein.

Some generalities can be observed in Table 1. In comparing analogous monometallic and bimetallic systems, e.g., $Ru(NH_3)_4(bpym)^{2+}$ and $[Ru(NH_3)_4]_2(bpym)^{4+}$, the bimetallic complex displays an additional band at the low energy end of the

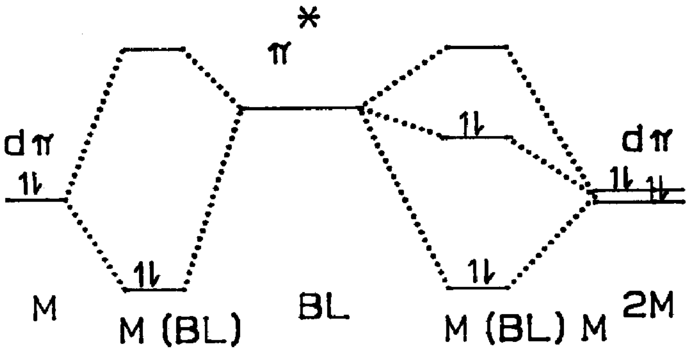


Figure 3. Partial Molecular Orbital Diagram for the Monometallic and Symmetrical Bimetallic Species.

spectrum which extends the absorption spectrum of the antenna fragment when it is bound to another metal center. The source of this transition is outlined in Figure 3.

The variation in charge observed in Table 1 can have a significant effect on the stability of bimetallic complexes formed from these antenna systems. In our preliminary work using monodentate bridging ligands,[17] the formation constant of electronically similar complexes shows three orders of magnitude difference depending on the charge of the bimetallic system, $4\times10^{3}M^{-1}$ and $3.5\times10^{6}M^{-1}$ for $Fe(CN)_5pzCo(CN)_5{}^{5-}$ and $Fe(CN)_5pzRh(NH_3)_5$, respectively. Thus, having a series of antenna fragments of varying charge and solubility characteristics is of use in developing flexible systems.

In comparing the tetraammineruthenium(II) complexes to bis(2,2'-bipyridine) systems, a trend in absorption maximum is observed. The absorption maxima for both $[Ru(NH_3)_4]_{1,2}(bpym)^{2+,4+}$ occur at a lower energy than the corresponding $(bpy)_2$ complexes. This result is due to the ability of the bpy π* orbitals to participate in π-backbonding with the Ru(II). This results in an additional stabilization of the Ru(II) d_π orbitals. In the case of the $(NH_3)_4$ system, only bpym effectively backbonds with the Ru(II).

Electrochemistry

Cyclic voltammograms have been recorded on a number of the monometallic and homobimetallic systems. The information obtained from these studies indicate the degree of communication possible between the antenna and reactive fragment mediated by the bridging ligand. Table 2 summarizes these data. In all cases, for both mono- and homobimetallic systems, M(III)/M(II) reduction potentials are more positive for bpym complexes than the analogous bpy complexes. This observation is consistent with the better π-acceptor ability of bpym vs. bpy and is manifested in the lower energy electronic transitions for the bpym analogs as well.[18,19]

The cyclic voltammograms of the mixed-ligand complexes of Fe(II) with CN^- and bpym show an increasing Fe(III)/Fe(II) reduction potential as more bpym ligands appear in the coordination sphere.[18] In the Ru(II) complexes,[19] the same type of behavior is observed for the RuL_4(bpym) complexes. The greater the π-acceptor ability of the L_4 ligands, the more positive the Ru(III)/Ru(II) couple.

In comparing the difference between the M(III)/M(II) couple in the monometallic system to the corresponding M(III),M(II)/M(II),M(II) couple in the bimetallic system, an interesting trend emerges (column $E_{1/2}^{d-m}$ in Table 2). When the complex is anionic, as is the case with $Fe(CN)_4(bpym)^{1-/2-}$ and $[Fe(CN)_4]_2(bpym)^{3-/4-}$, the value for $E_{1/2}^{d-m}$ is negative, or indicating that the bimetallic complex is more easily oxidized. The cationic species show the reverse trend with oxidation occurring less readily for the bimetallic species. In both types of complexes, oxidation occurs more readily for the lower positively (or greater negatively) charged ion.

A better way to see how ionic charge affects metal-metal communication in the bimetallic species is to compare the differences ($\Delta E_{1/2}$) observed in the M(III),M(II)/M(II),M(II) ($E_{1/2}^{1}$) and M(III),M(III)/M(III),M(II) ($E_{1/2}^{2}$) couples for each species. This $\Delta E_{1/2}$ value ranges from 120 to 310mV for various bpym bridged systems. The larger values for $\Delta E_{1/2}$ correspond to greater stability of the mixed valence complex vs. the isovalent complexes and reflect a degree of metal-metal communication through the bridging ligand. Experimentally, the $\Delta E_{1/2}$ values are larger when the charge on the complex are closest to zero. The largest $\Delta E_{1/2}$ value of 310mV is observed for the $[Ru(bpy)Cl_2]_2(bpym)^{2+/+/0}$ series. These results, in conjunction with the previous studies on complex stability as a function of the charge on the bimetallic unit, suggest that the more stable (and probably most highly communicative) bimetallic complexes will be those in which the combination of the antenna and reactive fragments gives a small ionic charge on the system.

Reduction of the ionic charge on the antenna fragment can be accomplished in

TABLE 2.

Electrochemical Data of the Mono- and Homobimetallic Complexes of the Antenna Fragment with Various Bridging Ligands.

		E, in Volts vs. SCE		
Complex	$E_{1/2}{}^{1}$	$E_{1/2}{}^{2}$	$E_{1/2}{}^{d-m}$	$\Delta E_{1/2}$
$Fe(CN)_4bpym)^{3-/2-}$	0.482			
$[Fe(CN)_4]_2(bpym)^{2-/3-/4-}$	0.34	0.49	-0.14	0.150
$Fe(CN)_2(bpym)_2{}^{+/0}$	0.876			
$Fe(bpym)_3{}^{3+/2+}$	1.33			
$Fe(bpy)_3{}^{3+/2+}$	0.825			
$[Fe(bpy)_2]_2(bpym)^{6+/5+/4+}$	1.01	1.13	---	0.120
$Ru(NH_3)_4(bpym)^{3+/2+}$	0.52			
$[Ru(NH_3)_4]_2(bpym)^{6+/5+/4+}$	0.59	0.78	0.07	0.190
$Ru(bpy)_2(bpym)^{2+/2+}$ [23]	1.40			
$[Ru(bpy)_2]_2(bpym)^{6+/5+/4+}$ [23]	1.44	1.52	0.04	0.180
$Ru(bpy)_2Cl_2{}^{+/0}$ [26]	0.31			
$[Ru(bpy)Cl_2]_2(bpym)^{2+/+/0}$	0.85	1.17	---	0.310
$Ru(tpy)Cl(bpym)^{2+/+}$	0.92			
$[Ru(tpy)Cl]_2(bpym)^{4+/3+/2+}$	1.00	1.16	0.09	0.15
$Ru(NH_3)_4(biimH_2)^{3+/2+}$	-0.12			
$Ru(bpy)_2(bbzimH_2)^{3+/2+}$ [25]	1.11			
$[Ru(bpy)_2]_2(bbzim)^{4+/3+/2+}$ [25]	0.74	1.04	---	0.30
$Cr(CO)_4(bpym)^{+/0}$	0.59			
$W(CO)_4(bpym)^{+/0}$	∿0.5			
$[W(CO)_4]_2(bpym)^{2+/+/0}$	0.47	0.74	∿0	0.27

$E_{1/2}{}^{1}$ = Oxidation potential of monomer or 1st oxidation of the dimer

$E_{1/2}{}^{2}$ = 2nd oxidation potential of dimer

$E^{d-m} = E_{1/2}{}^{1}$ (dimer) $- E_{1/2}$ (monomer)

$\Delta E_{1/2} = E_{1/2}{}^{2}$ (dimer) $- E_{1/2}{}^{1}$ (dimer) three ways: 1) Use of zero-valent metals such as Cr(0) and W(0), 2) Use of anionic terminal ligands such as CN^- in $Fe(CN)_2(bpym)_2$, and 3) Use of anionic bridging ligands such as 2,2'-biimidazolate derivatives. In this latter area, a 310mV value for $\Delta E_{1/2}$ is observed for $[Ru(bpy)_2]_2(bbzim)^{4+/3+/2+}$ [25] which is larger than the 180mV observed for the analogous $[Ru(bpy)_2]_2(bpym)^{6+/5+/4+}$.[22,23] The problem with ligands such as 2,2'-bibenzeneimidazole is that the hydrogens bound to nitrogen are not very acidic.[24] In fact, the $[Ru(bpy)_2]_2(bbzim)^{2+}$ bimetallic complex could only be made by reacting $Ru(bpy)_2(bbzimH_2)^{2+}$ with $Ru(bpy)_2Cl_2$ in the presence of methoxide ion.[25] The analogous tetraammine complexes, $Ru(NH_3)_4(biimH_2)^{2+}$ and $Ru(NH_3)_4(bbzimH_2)^{2+}$ maintain both hydrogen atoms bound to nitrogen to at least pH 11. The pH dependent profile of the cyclic voltammograms of $Ru(NH_3)_4(biimH_2)^{3+/2+}$ shows a pH independent redox couple at 0.12 V (*vs.* SCE) from $0 < pH \leq 5.8$. For the pH range of 5.8 to at least 13, the plot of $E_{1/2}$ *vs.* pH has a slope of 59.0 mV/pH unit. This behavior is due to the proton coupled redox process described in the following equations:

$$Ru(NH_3)_4(biimH_2)^{3+} + e^- \rightleftharpoons Ru(NH_3)_4(biimH_2)^{2+}$$

$$0 < pH \leq 5.8$$

$$Ru(NH_3)_4(biimH)^{2+} + H^+ \ e^- \rightleftharpoons Ru(NH_3)_4(biimH_2)^{2+}$$

$$5.8 \leq pH < 13$$

$$Ru(NH_3)_4(biimH_2)^{3+} \rightleftharpoons Ru(NH_3)_4(biimH)^{2+} + H^+$$

$$pK_a = 5.8$$

The analogous $bbzimH_2$ complex has a pK_a value of approximately 4.30 but also undergoes a decomposition reaction at $pH < 3.4$. While the dianionic bridging ligand appears to help couple the metal centers by reducing the positive charge in the complex, the difficulty in deprotonating the amine nitrogen atoms suggests that other biimidazolate derivatives might prove more successful in preparing bimetallic complexes.

Cyclic voltammetry, while being a very helpful technique for studying communication between metal centers in polymetallic species, does suffer from the problem that it is a ground state technique. A more appropriate probe would be to look at the interactions of the metal center or remote ligands on the reactive fragment during the excitation event at the antenna fragment. Preliminary studies in our laboratories using resonance Raman spectroscopy show promise in this area.

REACTIVE FRAGMENT

Most of our effort to date has concentrated on the reactive fragment, $Co(bpy)(PR_3)_2H_2^+$. The qualitative photochemistry of the diethylphenylphosphine derivative of this complex was originally reported by Camus *et al.*[27]

Irradiation of 436nm or shorter wavelengths resulted in a spectral change that was at least partially or totally reversed by bubbling H_2 back into the solution. We chose to study this system as a potential reactive fragment for the following reasons: 1) Since cobalt is a first row transition metal, the excited states have a tendency to be lower in energy and more easily sensitized than second and third row congenitors; 2) The complex contains a bpy ligand, which is structurally similar to the bpym and biim bridging ligands used in our studies; and 3) The complex is known to undergo the photoelimination of H_2.

The quantitative photochemistry of $Co(bpy)(PEt_2Ph)_2H_2^+$ confirms the preliminary observations of H_2 production. At the longer wavelengths, (405 and 436nm), the efficiency for H_2 evolution is greater than 10% as determined by changes in absorption spectra and direct measurement of evolved hydrogen by gas chromatography. The 436nm irradiation leads to the formation of H_2 and $Co(bpy)(PEt_2Ph)_2^+$ with a quantum yield of 0.12 mol/ein and can be totally reversed by addition of H_2.

At an irradiation wavelength of 577nm, no photochemistry is observed for the cobalt dihydride complex. However, 577nm light will generate H_2 from $Co(bpy)(PEt_2Ph)_2H_2^+$ when $Ru(bpy)_3^{2+}$ or $Fe(bpy)_2(CN)_2$ are present in the solution. The efficiency of the sensitization reaction is similar for the two systems when they are at equal concentrations. The $Ru(bpy)_3^{2+}$ complex does not absorb as much light at 577nm as $Fe(bpy)_2(CN)_2$, but the long lifetime of $Ru(bpy)_3^{2+}$ assists in the bimolecular quenching process.

Stern-Volmer kinetics on solutions containing $Fe(bpy)_2(CN)_2$ and various concentrations of $Co(bpy)(PEt_2Ph)_2H_2^+$ result in linear plots for H_2 production. The limiting quantum yield for H_2 production is 0.13 mol/ein ($K_Q = 680M^{-1}$) which is remarkably similar to the quantum yield obtained for direct irradiation of the cobalt dihydride complex at 436nm. These data suggest that conversion of a spectroscopically accessible Co(III) state to the reactive excited state occurs with approximately unitary efficiency. The reactive state populated through intersystem crossing or sensitization then partitions ∿13% to products and ∿87% to ground state starting material.

The fact that $Fe(bpy)_2(CN)_2$ sensitizes the photoelimination of H_2 from $Co(bpy)(PEt_2Ph)_2H_2^+$ is a positive result. The inefficiency of this intermolecular process, due to the relatively short lifetime of the Fe(II) complex, should be circumvented when the two metal centers are covalently coupled and the energy transfer process is intramolecular in nature. We have prepared the bpym analog of both the Fe(II) and Co(III) systems. Spectroscopically, $Co(bpym)(PEt_2Ph)_2H_2^+$ is similar to the bpy analog. The bpym complexes of the antenna fragments (including $Fe(bpym)_2(CN)_2$) all have intense MLCT transitions in the visible region of the spectrum and are red-shifted with respect to the bpy analogs.

Current and future studies involve the preparation of the mixed-metal bimetallic complexes. Further development of the cobalt dihydride reactive fragment, along with other systems such as $Rh(bpym)_2H_2^+$, will enable us to couple our various antenna fragments with any suitable reactive fragment. The electrochemical, Mossbauer, resonance Raman, and nuclear magnetic resonance studies on the various antenna fragments have supplied valuable information in the design of polymetallic complexes capable of driving useful photochemical reactions with visible light.

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