Coordination Chemistry Reviews, 111 (1991) 319–324
Elsevier Science Publishers B.V., Amsterdam

Excited-State Energy- and Electron-Transfer Reactions in Multimetal Systems

John D. Petersen*, Larry W. Morgan, Iyun Hsu, Mark A. Billadeau and Silvia E. Ronco

Department of Chemistry, Clemson University, Clemson, South Carolina, 29634-1905, USA

1. INTRODUCTION

The ability of scientists to convert light into stored chemical potential energy has increased over the past ten years.[1] A critical component of this development has been the sophistication of the synthesis of multi metal systems.[1,2] Conceptually, the design of individual, but coupled, components in supramolecular systems with specific properties such as light absorption, light emission, chemical reaction, charge storage and conductivity are now possible through elaborate synthetic schemes.[2] However, little is known about the coupling of these components. Extensive electronic coupling may perturb the desired characteristics of the mononuclear fragments. On the other hand, minimal coupling may preclude energy- or electron-transfer processes within the lifetime of the excited state of the molecular ensemble. Our goal in this paper is to outline some of the design constraints present in supramolecular systems in terms of the coupling of metal centers in excited-state, energy- and electron-transfer processes.

Metal azine systems have been used extensively in the design of multimetal complexes.[1,2] One reason for this extensive use in the long-lived excited state of complexes such as $Ru(bpy)_3^{2+}$, where bpy = 2,2'-bipyridine. Another reason is that polyazaaromatic ligands form stable, chelating, bridging ligands. The azines used as bridging and terminal ligands in this work are pictured in Figure 1.

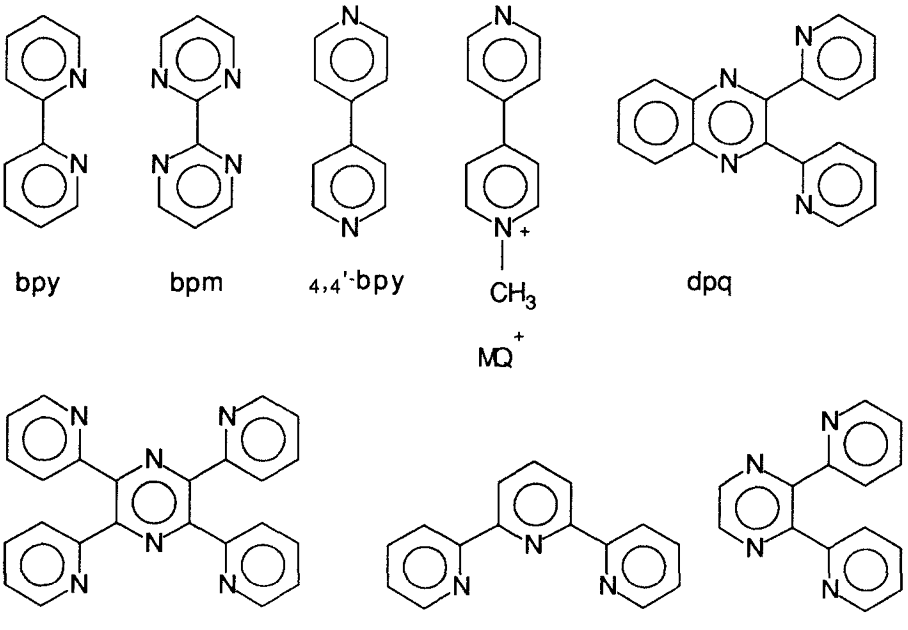
2. ENERGY TRANSFER

Previous studies in our laboratories have indicated that the energy of the bridging ligand orbitals are critical to the energy transfer process.[3] For the series of complexes, $(bpy)Ru^{II}(BL)Rh^{III}(PEt_2Ph)_2H_2^{3+}$, where BL = bpm, dpp and dpq, irradiation of the Ru(II) $\longrightarrow$ bpy or BL metal-to-ligand charge-transfer (MLCT) transitions leads to reductive elimination of H_2 from the Rh(III) center. The threshold energy necessary to sensitize the Rh(III) reaction is greater than that necessary for Ru(II)-based emission. In a

0010-8545/91/$03.50

subsequent study with the anionic, bridging ligand, bpt$^-$, the energy of the bridging ligand π^* orbitals has now been raised well above the π^* orbitals of bpy.[4] In this case, not only is the energy of the donor level important, but also the results indicate that the π^* orbitals of the bridging ligand must be involved in the donor excited state in order for energy transfer to occur.

Figure 1



bpy bpm 4,4'-bpy MQ$^+$ dpq

tpp tpy dpp

In past studies, the excited-state energy of the rhodium hydride reactive fragment has precluded the photoinduced formation of H_2 at irradiation wavelengths longer than 436 nm. In order the lower the energy of the reactive fragment excited states responsible for H_2 production, the use of analogous hydrides is being explored.

In preparing Ru(II)-Co(III) and Fe(II)-Co(III) complexes, both bidentate and tridentate bridging ligands were used. The antenna fragments for the cobalt(III) hydrides were either cyanoferrate(II) or polypyridylruthenium(II) species. The photochemical results are listed in Table I. The only complexes that demonstrated measurable H_2 photoproduction in the visible region of the spectrum were the cyanoferrate systems. The tpp bridged system, $(NC)_3Fe(tpp)Co(PEt_2Ph)H_2$, displays a quantum yield of 1.3×10^{-3} mol/ein at 577 nm irradiation but suffers from thermal degradation as well. This is presumably due to the presence of

Table I
Quantum Yield for Formation of H_2.[a]

Complex	λ_{irr}, nm	Φ_{H_2}, mol/ein[b]
$(NC)_3Fe(tpp)Co(PPh_3)H_2$	365	1.4×10^{-2}
$(NC)_3Fe(tpp)Co(PEt_2Ph)H_2$	365	1.9×10^{-3}
	577	1.3×10^{-3}
$(tpy)Ru(tpp)Co(PPh_3)H_2^{3+}$	365	8.4×10^{-2}
$(NC)_4Fe(dpp)Co(PEt_2Ph)_2H_2^-$	577	$\sim 8 \times 10^{-2}$

[a] Measured in aqueous solution at 25°C.
[b] Measured directly by GC, corrected for thermal reaction (± 10%)

only one phosphine ligand on cobalt to stabilize the hydride. The dpp bridged complex, $(NC_4)Fe(dpp)Co(PEt_2Ph)_2H_2^-$, is a preliminary measurement, but shows promise in that the quantum yield is higher than the other species ($\sim 8 \times 10^{-2}$ mol/ein) and there is less thermal degradation.

Previous researchers have avoided the use of tridentate bridging and terminal ligands because of the relatively short room-temperature lifetime of $Ru(tpy)_2^{2+}$ (<5 ns) compared to the much longer lifetime of $Ru(bpy)_3^{2+}$ (~800 ns). However, we have found that the lifetime of metal centers containing one tpy or other tridentate ligands are much longer than anticipated. The emission quantum yield and lifetimes of a number of tpy complexes are listed in Table II. The lifetime for all hexaazine complexes in Table II are longer than that of $Ru(bpy)_3^{2+}$. In addition, there is not much difference in either the emission maximum or the lifetime as the sixth ligand site is changed. Electrochemistry and detailed spectroscopic studies show that the lowest excited state is a Ru(II) ⟶ tpy MLCT state. In comparing the 4,4'-bpy entry to that of MQ^+, remote metallation does not affect the excited state properties substantially although electrochemical studies show that the remote methylated pyridine on MQ^+ is the first site of reduction on the complex.

The conclusions that we have reached concerning energy transfer processes in multi systems are that 1) the energy of the donor state must be higher than the energy of the acceptor state; 2) the participation of bridging ligand orbitals in the excited states involved in energy transfer are essential; and 3) the efficiency of energy transfer is attenuated by distance to a greater degree than what is observed for excited-state, electron-transfer reactions.

Table II
Luminescence Properties of [Ru(tpy)(bpy)L]$^{n+}$ Complexes.[a]

Complex Ion[b]	λ_{max}^{ex} [c]	λ_{max}^{em} [d]	τ, μs[e]
Ru(tpy)(bpy)Cl$^+$	466	734	0.78
Ru(tpy)(bpy)(CH$_3$CN)$^{2+}$	457	615	1.38
Ru(tpy)(bpy)(py)$^{2+}$	457	617	1.08
Ru(tpy)(bpy)(pz)$^{2+}$	462	618 (654 sh)	1.08
Ru(tpy)(bpy)(4,4'-bpy)$^{2+}$	465	618	1.65
Ru(tpy)(bpy)(MQ)$^{3+}$	463	618 (654 sh)	1.35

[a] In acetonitrile at room temperature
[b] Ligand abbreviations illustrated in Figure 1
[c] Excitation spectrum maximum in nm (± 3 nm)
[d] Emission maximux in nm (± 3 nm)
[e] Measured lifetime in μs (± 8%)

3. ELECTRON TRANSFER

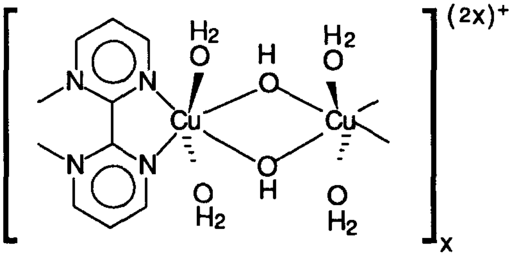
In parallel experiments, we have been developing multimetal centers whose goal is to generate sustained charge separation. These studies were originally designed using the premise that electronic communication in the ground state attenuates with distance[5] while excited state electron transfer is reasonably efficient over relatively long distances.[6]

The multimetal system has four component parts; light absorber, electron donor, electron acceptor, and spacers. The light absorber is a polyazine ruthenium(II) system related to the complexes in Table II. The electron donor system is a cyanoferrate(II) system. The electron acceptor is a methylated aromatic azine such as N-methyl-4,4'-bipyridinium (MQ$^+$), and the spacer can be either a single, non-electrochemically active metal center or a metallopolymer.

The extent and variation of the interaction between the light absorber and the acceptor is demonstrated by the photophysics of (bpy)$_2$Ru^{II}(dpp)Fe^{II}(CN)$_4$ and (bpy)$_2$Ru^{II}(bpm)Fe^{II}(CN)$_4$.[7] Irradiation of MLCT bands associated with the Ru(II) center in the dpp-bridged complex gives rise to the typical Ru-based emission from the lowest MLCT state on Ru(II). However, in the bpm-bridged complex, the presence of the Fe(II) center quenches the emission. The fact that the emission is quenched by the lower-energy iron-based MLCT state in the latter case is not surprising. The surprising point is that the dpp-bridged system displays no emission quenching, even though bimolecular quenching studies with the separated monometallic complex show this to be an energetically favorable process.

Coupling of a donor/absorber system to an acceptor such as MQ^+ can either occur directly or through a spacer. The spacer needs to maintain communication between the absorber and acceptor system without interfering in the redox process. Initially[8], we have looked at the Rh(III) metal center as a spacer. Coordination of MQ^+ to Rh(III) leads to very positive oxidation potentials and a first reduction associated with MQ^+. Preparation of the precursor molecule, $[(NC)_4Fe(bpm)Ru(bpy)(bpm)Rh(bpy)_2(PF_6)_3$, results in a polymetallic complex with an absorption spectrum containing Fe-based MLCT, Ru-based MLCT, and a π-π* region similar to $Cl(bpm)Ru(bpy)(bpm)Rh(bpy)_2](PF_6)_4$. The trimetallic complex doesn't emit in fluid solution at room temperature which is consistent with the "Fe bpm Ru" portion of the molecule (vide infra). Inclusion of a methylated ligand, such as MQ^+, into the trimetallic complex is currently under study.

A more recent spacer under study is the metallopolymer illustrated below:



The alternating μ-$(OH)_2$/μ-bpm Cu(II) polymer is a semiconductor[9] and has extensive magnetic interactions across both bridges.[10] This type of system will allow the light absorber to be bound to the bpm end of the polymer and an electron acceptor, such as tetrahydroxyquinone, to be bound to the μ-$(OH)_2$ side. The model complex, $(bpy)_2Ru(bpm)Cu(OH)_2(OH_2)_2^{2+}$, has been prepared and characterized by x-ray crystallography.[11]

The opportunity for photoinduced charge separation created by building multifunctional, polymetallic complexes are limitless. The major difficulty in generating a successful system is the synthesis of the materials. Each of the functions present in the molecule can be tuned independently by synthetic variations. Optimal charge separation will depend upon our ability to generate synthetically systems which under rapid forward electron transfer in the excited state and slow, back electron transfer in the ground state of the charge separated species.

4. ACKNOWLEDGMENT

The authors would like to acknowledge the Office of Basic Energy Sciences, U. S. Department of Energy for support of this research. JDP also acknowledges an Alexander von Humboldt Research Fellowship at the University of Reginsburg during some of the preliminary studies.

5. REFERENCES

1. V. Balzani (ed.), Supramolecular Photochemistry, NATO ASI Series No. 214 D. Reidel, Dordrecht, 1987.
2. V. Balzani, F. Barigelletti and L. De Cola, Chapter 2 in Topics in Current Chemistry, 158. Photoinduced Electron Transfer II, J. Mattay (ed.), Springer-Verlag, Berlin, 1990.
3. D. B. MacQueen and J. D. Petersen, Inorg. Chem. 29 (1990) 2313.
4. D. B. MacQueen and J. D. Petersen, Coord. Chem. Revs. 97 (1990) 249.
5. W. R. Murphy, Jr., K. J. Brewer, G. Gettliffe and J. D. Petersen, Inorg. Chem. 28 (1989) 81.
6. J. R. Miller, pp. 241-254 in reference 1.
7. J. D. Petersen in Photochemistry and Photophysics of Coordination Compounds, H. Yersin and A. Vogler (eds.), Springer-Verlag, Berlin, 1987, p. 147.
8. M. A. Billadeau, Ph.D. Dissertation, Clemson University, 1991.
9. Measurements made in collaboration with Professor Marye Anne Fox, University of Texas, Austin.
10. M. L. Kirk, W. E. Hatfield, M. S. Lah, D. Kessissoglou, V. L. Pecoraro, L. W. Morgan and J. D. Petersen, Phys. Rev. Lett., in press.
11. L. W. Morgan, W. T. Pennington and J. D. Petersen, work in progress.