

## FINAL REPORT: DE-FG02-88ER13944

“Photoinduced Charge and Energy Transfer Processes in Molecular Aggregates”

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### A. Summary of research.

**1. Photoinduced electron transfer studies and charge transfer excited state characterization.** In the early years of the project we examined the electron transfer properties of donor/acceptor polypyridyl complexes substituted at the 1 and 2 positions of ethane. The electron transfer behavior was typical of weakly coupled (non-adiabatic) donor/acceptor systems with its nuclear transmission coefficient well described by Marcus theory. This line of research then turned to the examination of the electron transfer properties of systems in which the electron transfer coupling matrix element is very large (adiabatic electron transfer). This aspect of the work largely involved the spectroscopic implications of electronic-coupling in electron transfer systems. The systems examined ranged from the demonstration of vibronic constraints on the electronic coupling in cyanide-bridged trimetallic D/A complexes to the examination of the implications of strong electronic coupling on the properties of charge transfer excited states of polypyridyl complexes. The work on D/A complexes in which the donor and acceptor were bridged by a di-cyano metal complex demonstrated: (a) the interdependence of the D/A electronic coupling and the bridging ligand vibrational frequency; and (b) a well defined vibronic constraint on D/A electronic coupling. Further studies of these systems led to the first well documented observation of transition metal-to-transition metal electron transfer emission in some cyanide-bridged Cr(III)/Ru(II) complexes. Since the non-radiative relaxation of the MMCT excited states of these systems amounts to electron transfer in the Marcus Inverted region, and since the excited state distortions are mostly in low frequency vibrational modes, the excited state lifetimes tend to be much longer than those of Ru-polypyridyl complexes with similar energy gaps but distortions in higher frequency modes. Work with polypyridyl ligand-bridged bimetallic complexes has demonstrated that population of the LUMO of the bridging ligand reduces its effectiveness in mixing the bridged donor and acceptor orbitals. Much of this work and the issues it has raised are summarized in Endicott, J. F. In *Comprehensive Coordination Chemistry II*; McCleverty, J., Meyer, T. J., Eds.; Pergamon: Oxford, UK, 2003; Vol. 7; pp 657-730.

Photoacoustic and thermal lensing techniques were used to directly determine the enthalpy of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  triplet MLCT excited state in ambient solutions and to explore excited state energetics in a few other simple systems. Attempts to extend the methodology to more complicated systems of interest were frustrated by its sensitivity to light absorbed by photo-generated intermediates and products.

Various aspects of the structural implications of electronic excitation have been investigated, and overall these studies have shown that both the dynamics and distortions of transition metal excited states are greatly influenced by the large number of different

excited states which differ only a little in energy; thus: (a) Work with simple Cr(II) complexes demonstrated that a major excited state relaxation pathway of these complexes involved a trigonal twisting distortion and were summarized in Endicott, J. F.; Perkovic, M. W.; Heeg, M. J.; Ryu, C. K.; Thompson, D. In *Electron Transfer Reactions: Inorganic, Organometallic and Biological Applications*; Isied, S. S., Ed.; American Chemical Society: Washington, D. C., 1997; Vol. 253; pp 199-221. (b) Dual emissions, from ligand field and MMCT excited states, were characterized for some cyanide-bridged Cr(III)/Ru(II) complexes. Work still in progress has been exploring the use of the vibronic sidebands of emission spectra to characterize the lowest energy MLCT excited state structures of Ru(II) and Os(II) complexes. So far this work has demonstrated: (c) that configurational mixing and the small energy differences between CT and ligand field excited states result in larger distortions of the CT excited states in metal-ligand vibrational modes than expected based on ground state correlations; and (d) that the distortions of the triplet MLCT excited state are much less than those of the related singlet excited state, apparently due to different distortions of the spin-orbit components of the triplet state. This effect is over and above the effect of configurational mixing between the excited and ground states to reduce the excited state distortions; however, the effects of configurational mixing are very complicated and they are still being evaluated.

In the course of the studies of the emission spectra of transition metal excited states we have found CT emissions in the near infrared spectral region, implicating previously unobserved low energy excited states. The lowest so far are a Cr(II)-(CN)-Ru(III) MMCT excited state emission at ca. 7,500  $\text{cm}^{-1}$ , the  $[\text{Ru}(\text{acac})_2\text{bpy}]^{2+}$  MLCT excited state emission at ca. 9,000  $\text{cm}^{-1}$  and the  $[(\text{NH}_3)_4\text{Ru}]_2\text{dpp}^{4+}$  MLCT excited state emission at ca. 10,000  $\text{cm}^{-1}$ . This indicates that simple coordination complexes can be used to generate viable charge transfer excited states whose energies span the full range of the solar spectrum.

The MLCT excited states of  $[\text{M}(\text{L})_n(\text{bpy})_p]^{m+}$  complexes appear to be distorted in at least a dozen or so vibrational modes and this leads to a huge number of vibronic channels that can contribute to the degradative non-radiative relaxation of these states. As a consequence even low frequency vibrational modes can make some contributions to the complex vibronic relaxation pathways. Since the distortions of a CT excited state can be related to its reactivity as an electron transfer reagent, the inference that the lowest energy spin orbit components of MLCT excited states of heavy metal polypyridyl complexes can be relatively undistorted suggests that it may be possible to design systems in which electron transfer to an external acceptor (molecule or electrode) can be structurally favored over the degradative relaxation to the ground state, which requires appreciable vibronic distortion, thereby optimizing the utilization of the excited state energy.

**2. Synthesis and solution chemistry of model transition metal complexes.** A number of simple model compounds have been synthesized, some for the first time. These fall into the following categories: (a) Monometallic Ru(II)bipyridine complexes with tetraaza-macrocyclic ancillary ligands; (b) monometallic complexes with other polypyridine ligands; (c) bimetallic complexes with polypyridine bridging ligands; (d) bimetallic and trimetallic complexes with CN<sup>-</sup> bridging ligands; (e) bimetallic complexes with xylene linked tetraaza-macrocyclic ligands. These complexes have been characterized by means of standard spectroscopic, electrochemical and X-ray

crystallographic techniques (where possible). The synthesis and characterization of these complexes is described in the various attached publications.

3. **Other systems.** We have constructed several series of complexes in which two macrocyclic ligand complexes are ortho-substituted onto a phenyl linker. These provide nice models for energy and electron transfer processes in simple systems. When the macrocyclic ligands coordinate labile divalent metals the bimetallic complexes have very large affinities for halides, and the halides of the resulting ion pairs are more or less centered between nearly co-facial macrocyclic ligand complexes. The halide-bridged Ni(II) complexes are comprised of one high and one low spin center which are localized at low temperature (-100 C), but under ambient conditions the Ni(II) centers are equivalent with the triplet-singlet exchange apparently mediated by the vibrational excited states of the bridging halide. Work in progress will investigate the use of these phenyl-linked bimetallic complexes as simple models for probing excited state electron and energy transfer processes where one of the macrocyclic moieties is coordinated to Ru(II)bpy and the other to any of a variety of metals.