PROGRESS REPORT

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Excited State Processes in Transition Metal Complexes. Redox Splitting in Soluble Polymers

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INTRODUCTION

In our DOE funded research in the last grant period, there were two major themes. The first was the continued development of MLCT excited states as sensitizers. In one sequence of experiments the synthetic aspects of this area were developed in further detail both by extending the chemistry of the polypyridyl-accepting ligands associated with the excited state and by developing a new procedure for the preparation of unsymmetrical tris-chelate complexes. The second important aspect of this work was the continued investigation of the molecular and electronic structure characteristics of this class of excited states and how those factors determine such properties as photostability and excited state decay. This effort was extended to complexes of Re(I) and an examination of their excited state characteristics, the role of the hydride ligand in determining the properties of MLCT excited states, the calculation of relative nonradiative decay rate constants for a series of complexes of Ru(II), the participation of higher lying MLCT excited states in MLCT decay in complexes of Ru(II) and Os(II), and the application of the transient infrared (TRIR) technique to the elucidation of a photochemical intermediate following laser flash excitation.

The second area of study involved MLCT excited states in soluble polymers to investigate photoinduced electron and energy transfer in multi-component assemblies. This work was based on chemically derivatized polystyrene polymers which contain combinations of MLCT chromophores and electron or energy transfer quenchers. In these experiments it was possible to demonstrate: 1) the effect of electron and energy transfer shuttling following laser flash excitation of solutions containing chromophores and electron and energy transfer acceptors on separate polymeric strands, 2) the possibility of producing and storing multiple oxidative equivalents on single polymeric strands, 3) the measurement of rate constants for intrastrand electron and energy transfer following laser flash excitation, and 4) to demonstrate the existence of long-range intrastrand energy transfer by the exploitation of an energy transfer cascade.

In addition to the advances made in these areas, our DOE supported effort was featured in three review articles. In one, a general approach to artificial photosynthesis was developed based on MLCT excited states. In another, the emphasis was on energy conversion processes at the molecular level and in the third, on long-range electron and energy transfer in soluble polymers.

MLCT EXCITED STATES

In our work on synthesis an important advance was made in developing general procedures for the synthesis of side-chain derivatives of 2,2'-bipyridine. In this work we were able to develop general and versatile synthetic methods for the preparation of a variety of derivatized 2,2'-bipyridine compounds bearing a single functionalized side-chain at the 4-position.[1] More recently the synthetic work was extended to the preparation of unsymmetrically substituted complexes of Ru(II). In this work a step-wise sequential procedure was developed for the incorporation of three different bipyridine ligands based on the polymeric precursor $[Ru(CO_2)Cl_2]_n$. This is an important synthetic advance since it provides a general procedure for the preparation of sensitizers in complex molecular assemblies.[2]

Our systematic studies on the characterization of MLCT excited states have been extended to the series $[Re(4,4'\text{-}(X)_2bpy)(CO)_3(4\text{-}Etpy)]^+$ (X = NH_2, OCH_3, CH_3, $CONEt_2$, CO_2Et; 4-Etpy is 4-ethylpyridine). By a combination of ground and excited state measurements and emission spectral fitting, we were able to conclude that these excited states have shortened lifetimes compared to related complexes of Ru(II) and Os(II) having similar energy gaps because of a higher contribution to nonradiative decay from low frequency modes and the solvent as well as from a contribution from a high frequency CO stretching mode.[3] The observation was also made of large solvatochromic shifts for the metal-to-ligand charge transfer absorption bands in these complexes and rationalized by applying dielectric continuum theory.[4] In a more recent application, in collaboration with the group of Brian Dyer at Los Alamos and Carlo Bignozzi at Ferrara, we were able to utilize transient infrared spectroscopy to demonstrate that energy transfer occurs across the cyanide bridge in $[(bpy)(CO)_3Re(NC)Ru(CN)(bpy)_2]^+$ following Re → bpy excitation. The utilization of this technique relied on comparisons in CO and CN stretching modes for the transient observed following laser flash photolysis with those obtained for related ground and excited states.[5]

We were also able to extend our knowledge of photophysical properties of complexes of Ru^{II} by a series of studies involving a combination of lifetime and emission measurements. In an extension of an earlier study on polypyridyl complexes of Os(II), we were able to use the results of low temperature emission fitting to obtain the required parameters (energy gap, quantum spacing, electron-vibrational coupling constants, solvent reorganizational energy) to calculate the vibrational overlap factors for nonradiative decay. We were able to use these factors to calculate relative rate constants for nonradiative decay.[6] In a second study, by acquiring temperature dependent lifetime data on a series of polypyridyl complexes of Os(II), we were able to demonstrate the contribution of a fourth MLCT state to excited state decay. Based on the results of this analysis, it is now possible to account for the nonradiative decay characteristics of this family of complexes over an extended temperature range.[7]

The excited state studies were extended to complexes of Ru^{II} and Os^{II} containing a hydride ligand, e.g., *cis*-$[M(bpy)_2(CO)H]^+$ (M = Ru, Os). The initial intent of the study was to explore the possibility of MLCT excitation and activation of the metal hydride bond. In fact, these molecules are stable photochemically. We did discover, however, that for M = Ru there was a significant participation by υ(Ru-H) in nonradiative decay.[8]

PHOTOINDUCED ELECTRON AND ENERGY TRANSFER ON SOLUBLE POLYMERS

Our work on soluble polymers has been based on chemical derivatization of a 1:1 copolymerof styrene and 4-chloromethylstyrene. In earlier work we had developed synthetic techniques for chemical modification based on nucleophilic displacement of chloride. The synthetic chemistry is sufficiently flexible that it allows for polymers of mixed content to be prepared where first one component is added with an additional component or components added in subsequent steps. In one series of experiments, the synthetic chemistry was exploited to demonstrate the existence of intermolecular energy and electron transfer shuttling between polymers of different compositions. In these experiments it was demonstrated that excitation of $[Ru(bpy)_3]^{2+}$ in the presence of separate polymeric strands, one containing an anthracene derivative and a phenothiazine derivative and the second a derivative of paraquot led to a series of diffusional events. Energy transfer quenching by anthracene was followed by electron transfer from phenothiazine to the anthracene triplet to paraquat followed by intrastrand electron transfer from the anthracene cation. This experiment was designed to demonstrated new approach to energy conversion based on interstrand dynamics.[9]

In more recent work our attention was turned to intrastrand electron and energy transfer dynamics. One series of experiments was based on polymeric samples in which, of the average 30 available chloromethystyrene sites, 25 were occupied by a $[Ru(bpy)_3]^{2+}$ derivative and 5 by a corresponding osmium derivative. Following $Ru^{II} \rightarrow$ bpy excitation of this sample, rapid energy transfer occurred but only from Ru^{II*} excited states that were formed next to Os^{II}. Energy transfer from Ru^{II*} to Os^{II} was favored by 0.4 eV. The same study demonstrated that energy transfer hopping from Ru^{II*} to Ru^{II} along the polymeric backbone was relatively slow, $k < 1 \times 10^6 s^{-1}$.[10,11]

By using the same polymer it was also possible to explore intrastrand electron transfer. In these experiments initial $Ru^{II} \rightarrow$ bpy excitation in the presence of the irreversible diazonium quencher p-$CH_3OC_6H_4N_2^+$ led to the formation of Ru^{III}. This was followed by intra-strand oxidation of Os^{II} by Ru^{III}, which is favored by 0.5 eV. As for energy transfer, electron transfer from Ru^{III} to an adjacent Os^{II} was too rapid ($>2 \times 10^8 s^{-1}$) to be time-resolved experimentally using our current capabilities. However, it was possible to time-resolve intrastrand $Ru^{II} \rightarrow Ru^{III}$ electron transfer hopping by observing the bleach in a characteristic $Os^{II} \rightarrow$ bpy MLCT and following laser excitation. From these experiments a rate constant for $Ru^{II} \rightarrow Ru^{III}$, self-exchange electron transfer of $5 \times 10^6 s^{-1}$ was established.[10,11]

In another series of experiments, based on fully loaded polymers containing, on the average, thirty $[Ru(bpy)_3]^{2+}$ or $[Os(bpy)_2]^{2+}$ derivatives, we were able to demonstrate that photoexcitation in the presence of p-$O_2NC_6H_6N_2^+$ led to the build-up and storage of multiple oxidative equivalents. The importance of these experiments was that they demonstrated the feasibility of utilizing polymers as sources of multiple redox equivalents perhaps to drive catalytic systems for energy conversion.[12]

The experiments on the mixed ruthenium-osmium polymers demonstated that intrastrand energy transfer between metal complex sites in not necessarily facile. In order to find ways to achieve facile energy transfer, the photophysical properties of polymers lightly loaded in Ru^{II} and Os^{II} and highly loaded in an anthracene derivative were investigated. The triplet excited state energy of the anthracene derivative (1.8 eV) was between the MLCT excited state energies for Ru^{II} and Os^{II}. We are able to demonstrate that following laser flash excitation at Ru^{II}, energy transfer occurred from Ru^{II*} to anthracene. This was followed by energy transfer hopping amongst anthracenes with the final step being energy transfer from triplet anthracene to Os^{II} to give the Os^{II}-based MLCT excited state.[13]

REVIEWS

The DOE funded portion of our work on photochemistry provided the basis for three articles which summarized the current status of energy conversion based on MLCT excited states in molecular assemblies. One dealt with the theme of the photochemical reduction of CO_2 and was presented at a Nobel Symposium on "CO_2-fixation and CO_2-reduction in Biological and Model Systems" in Stockholm in December, 1991. The second dealt with long-range electron and energy trnsfer in molecular assemblies.[15] The third summarized our results to date on soluble polymers.[16]

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