PHOTOINDUCED CHARGE SEPARATION IN LINKED
DONOR - CHROMOPHORE - ACCEPTOR SYSTEMS

Progress Report

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Introduction. The focuses of our efforts during this funding period have been almost exclusively in two areas: The first area is the preparation and characterization of triply bridged dinuclear complexes containing a tris-2,2'-bipyridineruthenium chromophore and a second tris-bipyridine metal complex which is to serve as an electron donor or acceptor. The second area is the preparation and characterization of linked RuL_3 -containing D-C-A complexes where D is a phenothiazine donor and A is a diquat type acceptor.

Rigid, Triply-Bridged Dinuclear Complexes. We have developed a synthetic route to the preparation of heterodinuclear metal complexes based on bisbipyridyl alkane ligands. In these ligands the bipyridines are attached in the 4-position to the termini of methylene chains of virtually any length greater than one methylene. The complexes formed therefrom consist of two different trisbipyridine metal complexes linked by three alkane chains. The shorter-length-chain members of this series (namely, two and three methylenes) are quite rigid and hold the two metal centers at a fixed distance and orientation. Furthermore, molecular modeling and crystal structures of the analogous homodinuclear iron complexes indicate that, despite the different numbers of carbons in the linkages, the two and three carbon complexes have the two metal centers located at the same distance and with the same relative ligand orientations. Therefore these complexes appear to be potentially ideal systems for probing the importance of through-sigma-bonding superexchange in intramolecular electron transfer reactions.

Much of the time since the beginning of this grant has been spent on perfecting the synthesis, purification and characterization of several Ru(II)/M complexes. We have focused primarily of Co and Fe. The advantages of cobalt are several. First, within the potential range where the Ru center remains as Ru(II) , cobalt can exist as Co(I) , Co(II) , and Co(III) . Thus a single Ru(II)/Co complex can, in theory, provide three different electron acceptor/donor species. Second, previous studies suggest that, at least for Co(II) and Co(III) the quenching mechanism of Ru(II) is electron transfer (rather than energy transfer). The disadvantages are, first, that Co(II) and Co(I) are fairly labile in solution. Second, the potential of the Co(II)/Co(III) couple is such that, during work-up of the Ru(II)/Co dinuclear complex we have been unable to maintain either complex in a pure cobalt oxidation state (i.e., either Co(II) or Co(III)). We continue to work on these problems.

The Ru(II)/Fe(II) complexes, in contrast, are relatively easily prepared and purified; and once prepared, are quite stable. The major disadvantage with iron is that Fe(II)L_3 efficiently quenches the MLCT excited state of the Ru(II)L_3 by energy transfer. Consequently, photoinduced electron transfers cannot be studied in this system. However, it should be possible to measure the rates of electron transfer in these complexes by pulse radiolysis. At least three oxidation state isomers should be amenable to study: Ru(II)/Fe(II) , Ru(II)/Fe(III) , and Ru(III)/Fe(III) . We have arranged with John Miller to collaborate on these experiments with his group at Argonne. We plan, in the near future, to conduct the first of these time-resolved pulse radiolysis experiments on the Ru(II)/Fe(II) complexes having two- and three-methylene chain linkages.

In addition to the ligand systems having simple alkane chain linkages we have recently succeeded in preparing a bis-bipyridine ligand having a $-\text{CH}_2-\text{O}-\text{CH}_2-$ linkage. Additionally, while it has not been characterized fully, we believe we have prepared the $-\text{CH}_2-[\text{Si}(\text{CH}_3)_2]-\text{CH}_2-$ linked bisbipyridine. Both of these new ligands are analogs of the three-carbon alkane-

linked ligand, but with the central carbon replaced with a heteroatom. Both ligands should form Ru(II)/M complexes which are nearly isostructural to the all-carbon case. We are presently characterizing these ligands further and preparing metal complexes from them.

Linked Donor/Chromophore/Acceptor Complexes. Previously, we had studied the effects of driving force on electron transfer quenching in D-C-A complexes where D is a phenothiazine-type donor, A is a diquat-type acceptor and C is a trisbipyridineruthenium chromophore. In each case the donor and acceptor have been linked to the RuL₃ complex by methylene chains. We observed, and reported previously, that it is important to take into consideration exactly where the excited-state electron is localized prior to the quenching event in order to rationalize the electron transfer rates in terms of Marcus theory.

In only one published study, so far, have we dealt with the implications of the linkage between the chromophore and the acceptor or donor. In this study the number of methylenes in the linkage between the acceptor and the chromophore was varied in a series of C-A complexes (i.e., no donor present). We are presently preparing and characterizing the complexes necessary to investigate how the length of the chain between the chromophore and the donor influences (1) the quantum efficiency for formation of the D⁺-C-A⁻ charge separated state and, (2) once formed, how the recombination rate from this state is effected. In all of our previous work, the length of the chain linking the phenothiazine to the chromophore has contained either one or four carbons. The one-carbon complex is a special case. Since the carbon attached to the phenothiazine is nominally a benzylic carbon, the redox potential of the donor is different in the one-carbon case from those ligands containing two or more methylenes.

We have now prepared phenothiazine linked bipyridine ligands which contain methylene chains having from three to eight carbons. Furthermore, we have prepared D-C and D-C-A complexes from each of these ligands. We anticipate, as with the four-methylene linked D-C complexes, that the reductive quenching rate of the RuL₃ MLCT state will be slow relative to the oxidative quenching rates with the diquat acceptors; thus, we also expect the initial electron transfer event in each of the complexes to be reduction of the diquat. The main point of interest, as mentioned above, will be to determine how the chain length effects the quantum efficiency for forming the charge separated state. The quantum efficiency will be determined by the rate of back-electron transfer from the diquat to the Ru(III) relative to the rate of electron transfer from the phenothiazine to the Ru(III). Given that there is no electrostatic work term involved in the latter process, the length of the chain linking the donor and the chromophore will almost certainly influence this rate (especially for the shorter chains). The lifetime of the fully charge-separated state will depend upon two things: the average distance of separation between the reduced diquat and the oxidized phenothiazine and the ease with which they can approach each other. Again, both of these will be effected by the chain length.

Time resolved emission and transient absorption experiments are planned in the near future on all of these systems in collaboration with Professor D. F. Kelley of this department. Emission studies are expected to confirm that the initial electron transfer is independent of the donor ligand. Transient absorption will allow us to determine the recombination rates of the charge separated states.

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