Coordination Chemistry Reviews, 132 (1994) 15–22

The Design and Preparation of Transition Metal Triad Systems for Excited-State Charge Separation

J. D. Petersen*, S. L. Gahan, S. C. Rasmussen and S. E. Ronco[1]

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

ABSTRACT

A series of multimetal complexes have been prepared with the intent of mimicking the charge separation process that occurs in photosynthesis. The systems have three component parts: antenna or absorbing fragment, electron donor, and electron acceptor. Synthetic modification of these components and the spacers which covalently couple these components will be discussed in terms of the thermodynamics and kinetics leading to the formation and lifetime of the charge-separated state. Systems with polyazine ruthenium(II) antenna, cyanoferrate(II) electron donors and a viologen electron acceptors will be described which have a lifetime of 37 - 86 ns.

A. INTRODUCTION

There have been numerous studies involving the use of transition metal inorganic systems to mimic the charge separation used in photosynthesis.[2] Many studies have been centered around the tris(2,2'-bipyridine)ruthenium(II) cation or related systems as an antenna fragment in both intermolecular and intramolecular electron-transfer processes.[3] The ruthenium(II) azine complexes have been used extensively because they have intense absorption bands in the visible region of the spectrum, they typically have a long-lived electronic excited-state, this excited-state (metal-to-

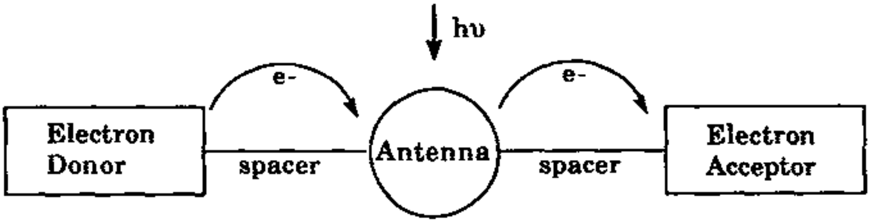
0010-8545/94/$26.00
SSDI 0010-8545 (94) 02001-Y

ligand charge transfer, MLCT) is easily oxidized and reduced, and the products of oxidation and reduction are kinetically stable.

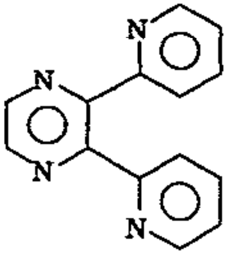
Previously,[4] we prepared the monometallic complex, $Ru(dpp)_3^{2+}$ (where dpp = 2,3-bis(2-pyridyl)pyrazine). The dpp ligand has the ability to chelate to metal centers simultaneously in a bidentate fashion. This enabled us to expand this system to a tetrametallic complex with $Ru(dpp)_3^{2+}$ as the core and three metal centers on the periphery.[5] An interesting aspect of these tetrametallic systems was that one remote metal center does not feel the presence of the other remote centers electrostatically or through electronic coupling. This fact indicated that replacement of the remote centers with electron donor and electron acceptor fragments may generate a small molecular system where an electron/hole pair may be generated without rapid back-electron transfer. The properties of the first generation of these systems will be discussed here.

B. SYSTEM DESCRIPTION

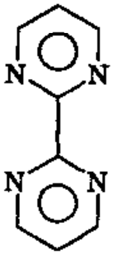
The molecular assembly used is schematically represented below:



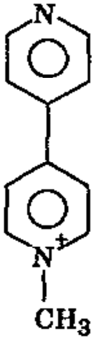
The ligands used to bridge the various metal centers were either dpp or 2,2'-bipyrimidine, bpm. The electron donor in the system was a tetracyanoferrate(II) fragment bound to the ruthenium center through either the dpp or bpm bridging ligands. The electron acceptor, N-methyl-4,4'-bipyridinium (MQ^+) was either directly bound to the ruthenium(II) antenna center or bound to a rhodium(III) 2,2':6',2"-



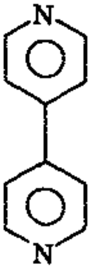
dpp



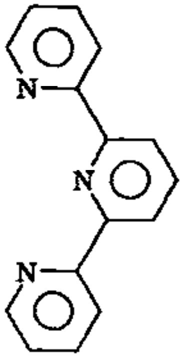
bpm



MQ$^+$



4,4'-bpy



tpy

terpyridine (tpy) center which was coupled to the Ru(II) through bpm or dpp. Synthetic preparation of these compounds is described elsewhere.[6]

Excitation of the MLCT transitions on Ru(II) leads to the generation of an excited state which is approximately 2.0eV above ground state in energy. This excited state has just sufficient energy to reduce the MQ$^+$ ligand to the neutral radical, MQ$^\bullet$. The resulting ruthenium(III) species can be readily reduced by the cyanoferrate(II) center with a driving force of ~0.7V.[7]

C. RESULTS AND DISCUSSION

The absorption spectra of the triad complexes, $(NC)_4Fe^{II}(BL_1)Ru^{II}(bpy)(BL_2)Rh^{III}(tpy)(MQ^+)^{4+}$, BL_1 and BL_2 = bpm or dpp, display a broad, multicomponent MLCT transition which ranges from 400 - 700 nm. Flash photolysis (Nd - YAG laser at 355 nm) on the series of complexes $(NC)_4Fe^{II}(BL_1)Ru^{II}(bpy)(BL_2)Rh^{III}(tpy)(MQ^+)^{4+}$ gave rise to a broad transient absorption spectrum from ~420 - 700 nm. Although there were no specific spectral features, the largest absorbance change occurred in the 650 - 700 nm region. This absorption region corresponds to the region where $MQ^{\bullet}$ absorbs.[8]

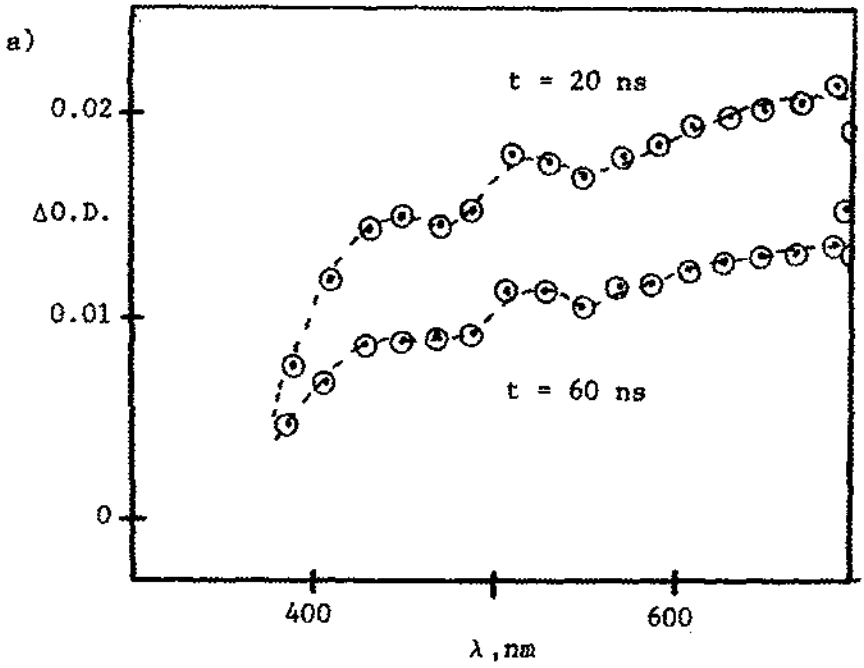
Figure 1 displays the transient absorption spectrum for $(NC)_4Fe^{II}(bpm)Ru^{II}(dpp)Rh^{III}(MQ^+)$ irradiated at 355 nm. In a), the transient absorption spectrum is displayed between 300 and 700 nm at 20 and 60 ns after excitation. In Figure 1b), the decay of the absorbance at 640 nm is illustrated *vs.* time. The lifetime of the transient is 46 ns.

The summary of the transient absorbance data all four trimetallic complexes is shown in Table I. The transient absorbance is similar to the entry shown in Figure 1a) for the rest of the complexes. The lifetimes vary from 37 ns to 70 ns and seem to be shorter when BL_2 is dpp.

TABLE 1
Lifetime of $(NC)_4Fe^{II}(BL_1)Ru^{II}(bpy)(BL_2)(tpy)(MQ^+)^{4+}$ [a]

BL_1	BL_2	τ, ns
bpm	dpm	70
bpm	dpp	46
dpp	bpm	61
dpp	dpp	37

[a] Room temperature, acetonitrile solution, λ_{ex} = 355 nm



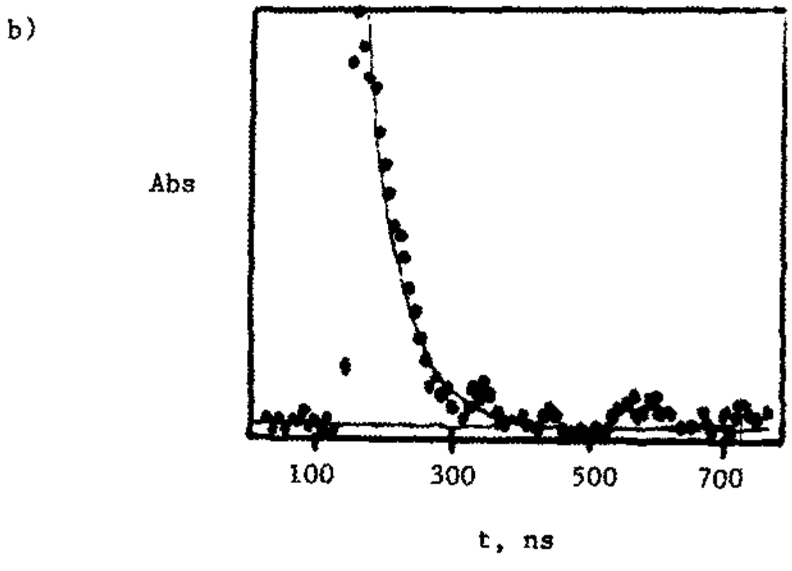


Figure 1. Transient Absorption Spectra (a) and Decay at 640 nm (b) for $(NC)_4Fe(bpm)Ru(bpy)(dpp)Rh(tpy)(MQ^+)^{4+}$.

Previous work on bimetallic[9] and tetrametallic[5,10] complexes have shown that there is better communication between metal centers joined by a bpm bridge than by a dpp bridge. This is shown both through electrochemical and emission lifetime studies. The fact that the most rapid decay occurs when BL_2 = dpp is not consistent with previous observations although less than a factor of two separates the lifetime of the four complexes.

Control experiments were run without the electron donor and with the spacer between antenna and the electron acceptor removed and with the electron acceptor modified. In the former, complexes of the type $Cl_2Ru^{II}(bpy)(BL)Rh^{III}(tpy)(MQ^+)^{4+}$ were excited as above. The missing component was the cyanoferrate electron donor. The lifetime of the two species, BL = bpm or dpp, was less than 8 ns.

Two complexes were studied where the spacer was removed from between the antenna and the electron acceptor by direct binding of MQ^+ to the Ru(II) metal center. In the first experiment, excitation of $(NC)_4Fe^{II}(dpp)Ru^{II}(tpy)(MQ^+)^+$ resulted in a transient with the characteristic absorption between 650 and 700 nm and a lifetime of 86 ns. Removal of the methyl group from the electron acceptor to give $(NC)_4Fe^{II}(dpp)Ru^{II}(tpy)(4,4'\text{-bpy})$ led to a transient absorption peaks at 400 and 550 nm, characteristic of the radical anion of tpy or 4,4'-bpy, and a lifetime of 52 ns.

D. CONCLUSIONS AND FUTURE STUDIES

The triad systems involving Ru(II) azine antenna complexes, cyanoferrate(II) electron donors and MQ^+ as an electron acceptor display charge separation lifetimes ranging from 30 - 90 ns. No estimation has been made concerning the efficiency of the formation of the charge-separated state; however, calculations involving the excited state energy of the antenna and the reduction potential of MQ^+ place the electron-transfer process very close to an isoenergetic conversion. Without a driving force thermodynamically to assist with the electron transfer to MQ^+, efficiency may be a problem. We are currently preparing electron acceptors that are 0.1 - 0.3V easier to reduce to aid in the charge separation process. Unfortunately, any increase in the amount of driving force to generate a charge-separated species reduces the amount of energy stored by the corresponding amount.

An additional area under study in order to lengthen the lifetime of the charge-separated species is the use of a longer, semi-conducting or conducting bridge. We have previously reported[11] a polymetallic complex where Cu(II) units have been alternately bridged by bpm and $(OH)_2$. The magnetic interaction between Cu(II) centers across both bridges is substantial and this material functions as a semiconductor. Efforts are currently underway to bind the bpm and of this polymer to a $Ru(bpy)_2^{2+}$ unit and an electron acceptor, such as a quinone to the $(OH)_2$ end of the polymer chain.

E. ACKNOWLEDGMENT

The authors thank the U. S. Department of Energy, Office of Basic Energy Sciences (DE-FG09-87ER13768) for support of this research.

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