DOE/ER/14309--T2

Report for DE-FG05-92ER14309

Photoinduced Energy Transfer in Transition Metal Complex Oligomers

Contents:

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DISCLAIMER

I. Introduction

The work we have done over the past three years has been directed toward the preparation, characterization and photophysical examination of mono- and bimetallic diimine complexes. The work is part of a broader project directed toward the development of stable, efficient, light harvesting arrays of transition metal complex chromophores. One focus has been the synthesis of rigid bis-bidentate and bis-tridentate bridging ligands. We have managed to make the ligand **bphb** (figure 1) in multigram quantities from inexpensive starting materials. The synthetic approach used has allowed us prepare a variety of other ligands which may have unique applications (*vide infra*). We have prepared, characterized and examined the photophysical behavior of Ru(II) and Re(I) complexes of the ligands. Energy donor/acceptor complexes of **bphb** have been prepared which exhibit nearly activationless energy transfer. Complexes of Ru(II) and Re(I) have also been prepared with other polyunsaturated ligands (see p.10) in which two different long lived (> 50 ns) excited states exist; results of luminescence and transient absorbance measurements suggest the two states are metal-to-ligand charge transfer and ligand localized $\pi \rightarrow \pi^*$ triplets. Finally, we have developed methods to prepare polymetallic complexes which are covalently bound to various surfaces. The long term objective of this work is to make light harvesting arrays for the sensitization of large band gap semiconductors. Details of this work are provided in the body of the report.

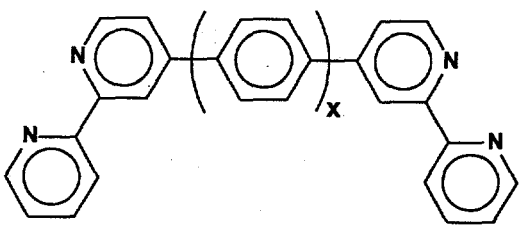
II. Ligand Syntheses

A. Phenyl and polyphenylene bridged bis-bipyridines and bis-terpyridines .

A focus of the initial work was to examine intramolecular electronic energy transfer between transition metal complex chromophores bridged by rigid spacers. Detailed studies of energy transfer rate constants as a function of donor-acceptor distance and the relative orientation of donor and acceptor dipoles are possible with ligands such as **bphb** (figure 1). The initial procedure devised for the preparation of **bphb** required five steps, three of which had very low yields.[1] An early objective of our synthetic work was to devise an improved approach to the synthesis of **bphb** and develop methods to prepare polyphenylene analogs. We managed to employ an extension of work initially reported by Krohnke for polypyridine synthesis to prepare **bphb** (figure 2A) and other derivatives discussed below.[2,3] The method of Krohnke for bipyridine synthesis is simple, employs inexpensive reagents and can be generalized to a large number of systems. In the preparation of **bphb** the first step involves reaction of terephthalaldehyde with pyruvic acid in base to yield 1,4-bis(3-carboxy-3-oxo-prop-1-enyl)benzene. This product is refluxed with 2-acetylpyridine pyridinium iodide

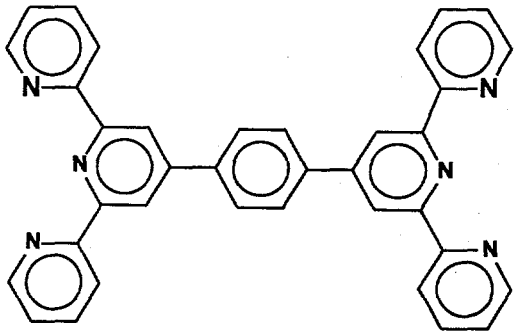
Figure 1. Ligands Prepared in Reported Work

1. Rigidly bridged bis-bipyridines and bis-terpyridines



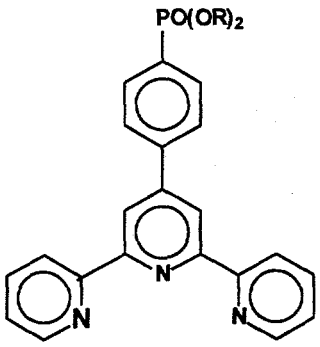
bph_xb

x = 1- 4

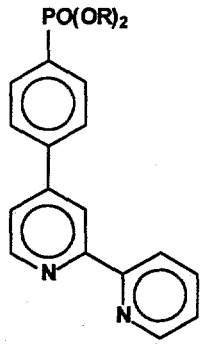


tpht

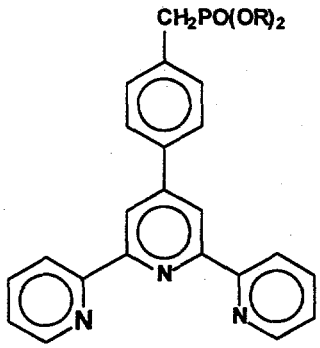
2. Bipyridine and Terpyridine phenylphosphonates and phosphonic acids



$H_2O_3PPhtpy$



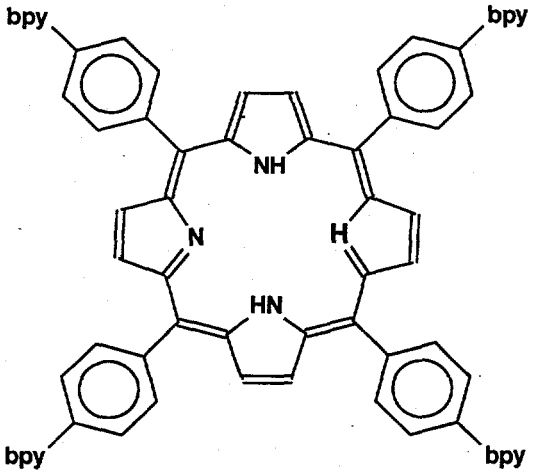
$H_2O_3PPhbpy$



$H_2O_3PCH_2Phtpy$

R = Et, H

3. Tetrakis - 4-(2,2'-bipyrid-4-yl)phenyl porphyrin



$H_2TbpyPP$

and ammonium acetate in methanol to yield 1,4-bis(6-carboxy-2,2'-bipyrid-4-yl)-benzene as the ammonium salt. Decarboxylation leads to **bphb** in 25 % overall yield from terephthalaldehyde. Preparation of **bph_2b** made use of the same procedure used in the synthesis of **bphb** except that biphenyl-4,4'-dicarboxaldehyde was used in place of terepthalaldehyde.

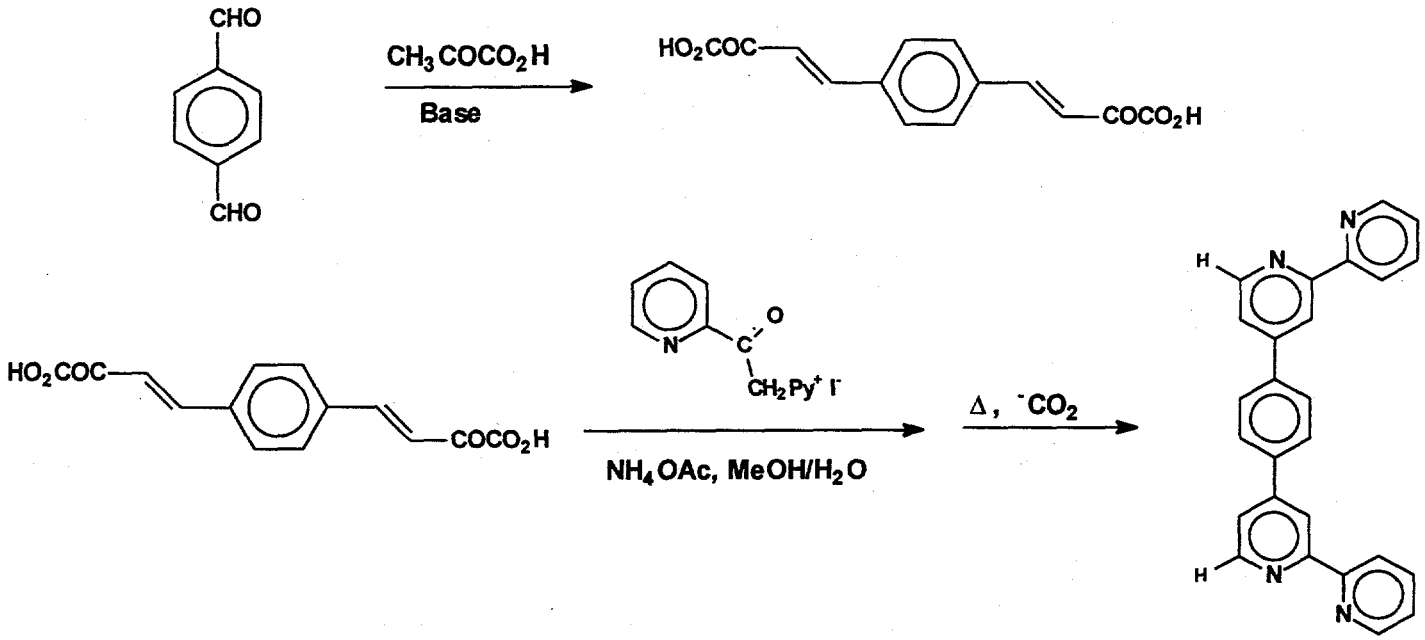
The derivatives having three or four phenyl spacers, **bph_3b** and **bh_4b,** were made by Suzuki coupling of 4-(4-bromophenyl)-2,2'-bipyridine with either benzene-1,4-diboronic acid or biphenyl-4,4'-diboronic acid (figure 2B). The 4-(4-bromophenyl)-2,2'-bipyridine is made via the Krohnke procedure using 4-bromobenzaldehyde as the starting aldehyde. The Suzuki procedure affords an efficient approach to aromatic cross coupling reactions employing $Pd(PPh_3)_3$ as catalyst.[4]

B. Bipyridyl and Terpyridyl Phosphonates and Phosphonic Acids. Very recent work of Gratzel has shown that Ru(II) complex sensitizers having coordinated terpyridine phosphonic acids serve as efficient sensitizers for TiO_2 in photoelectrochemical cells (*vide infra*).[5] In addition, several research groups (in particular Mallouk and Thompson) have shown that α,ω- bisphosphonic acids can be used in the step by step growth of films on various solid supports by alternate reaction of particular metal ions and the bisphosphonic acid with surfaces modified with an anchoring phosphonic acid.[6,7] We were interested in extending the Krohnke methodology to develop simple synthetic methods for bipyridine and terpyridine phosphonic acids in an effort to broaden the range of ligands available for TiO_2 sensitization and to prepare films of redox and photoactive transition metal complexes using the methods developed by Mallouk and others. The ligands prepared in this way are shown in figure 1 and the syntheses are outlined in figure 2C. The ligands $H_2O_3PPhbpy$ and $H_2O_3PPhtpy$ were prepared by reacting 4-(p-bromophenyl)-2,2'-bipyridine and 4'-(p-bromophenyl)-2,2',6',2"-terpyridine, respectively, with triethylphosphite using $[Pd(PPh_3)_4]$ as catalyst. Following flash chromatography of the product the isolated phosphonate was first coordinated to a metal center (i.e. Ru(II) or Os(II)) and was then hydrolyzed using $(CH_3)_3SiBr$ in dry acetonitrile. The ligand $H_2O_3PCH_2Phtpy$ was prepared by initial NBS bromonation of 4'-(p-methylphenyl)-2,2',6',2"-terpyridine, followed by Michaelis-Arbuzov reaction with triethylphosphite to yield the triethylphosphonate. The product was coordinated and then hydrolyzed with $(CH_3)_3SiBr$ as above.

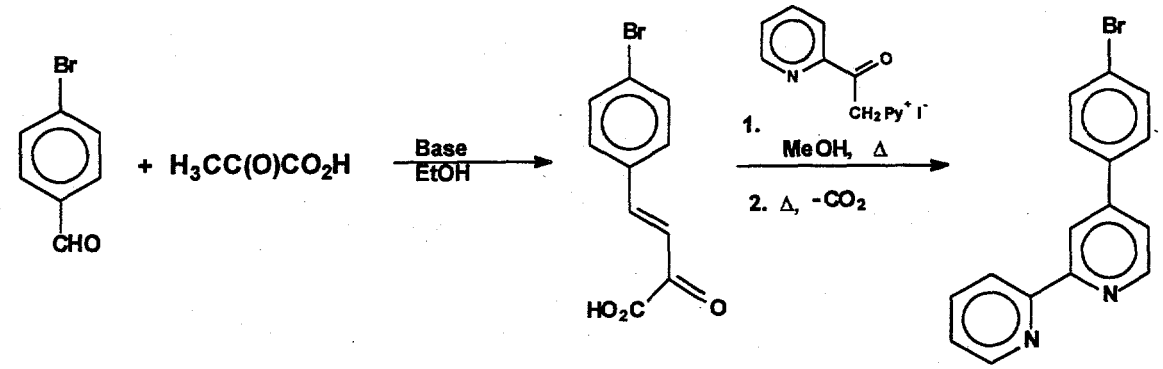
C. 5,10,15,20-Tetra(2,2'bipyrid-4-yl)-phenyl porphyrin. Recently we have used the Krohnke procedure to prepare 4-(2,2'-bipyrid-4-yl)benzaldehyde which we have used further to make 5,10,15,20-tetra[4-(2,2'-bipyrid-4-yl)phenyl]porphyrin (figure 2 D). The synthesis illustrates an example of extending the Krohnke procedure to make ligands which can be used to prepare unique multichromophoric complexes. We have used this tetra-bipyridine ligand in a reaction with

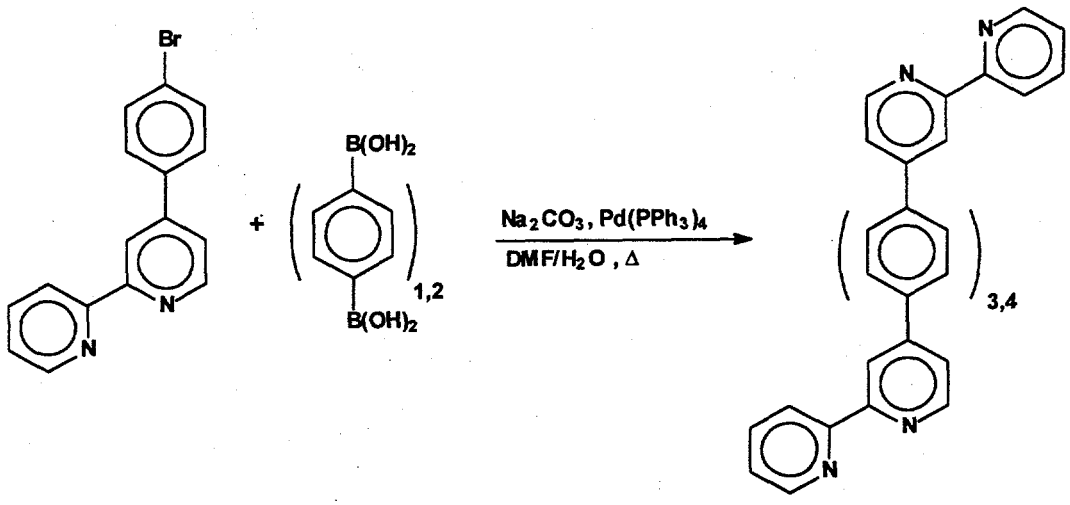
Figure II.

A. Synthesis of bphb

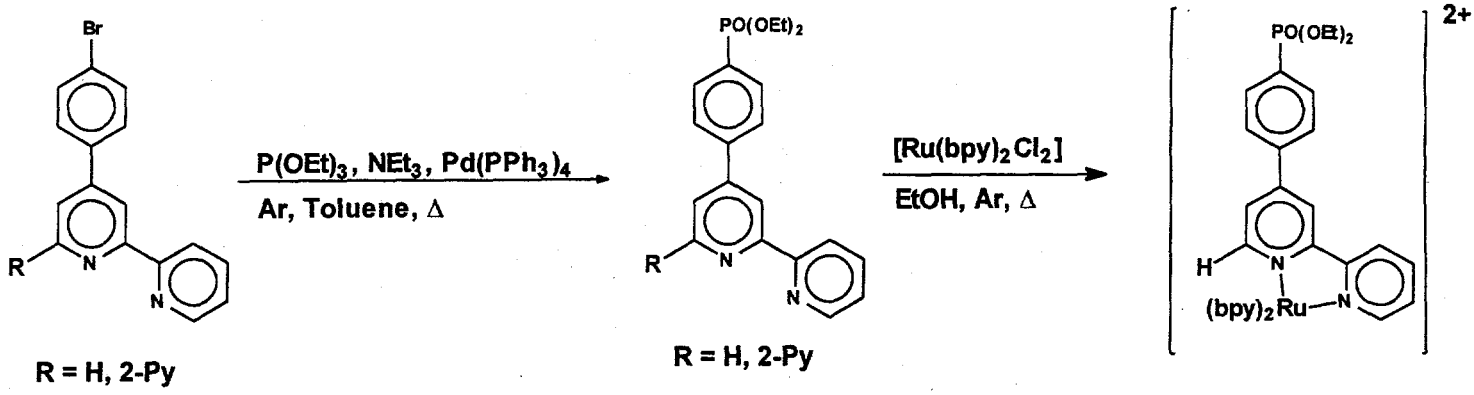


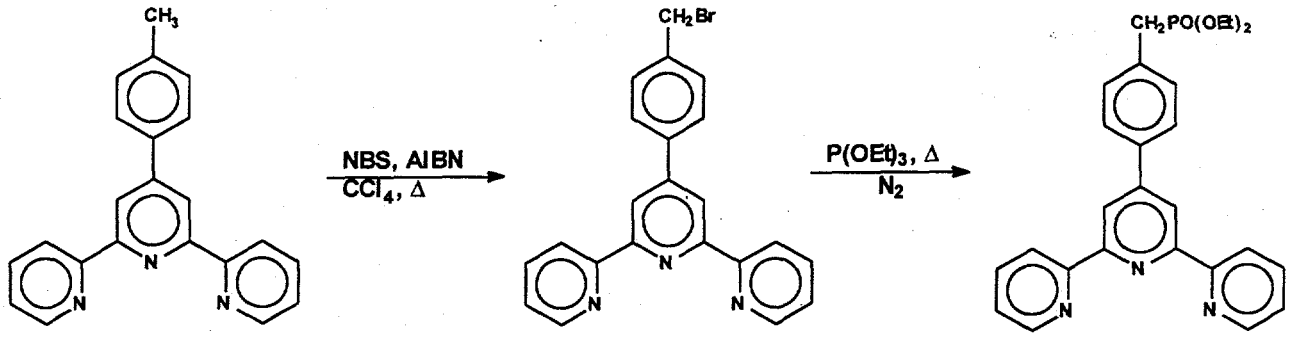
B. Synthesis of bph_3b and bph_4b

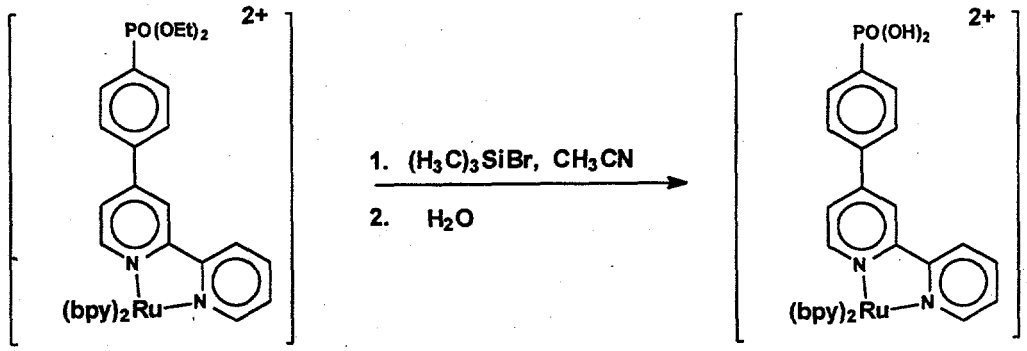




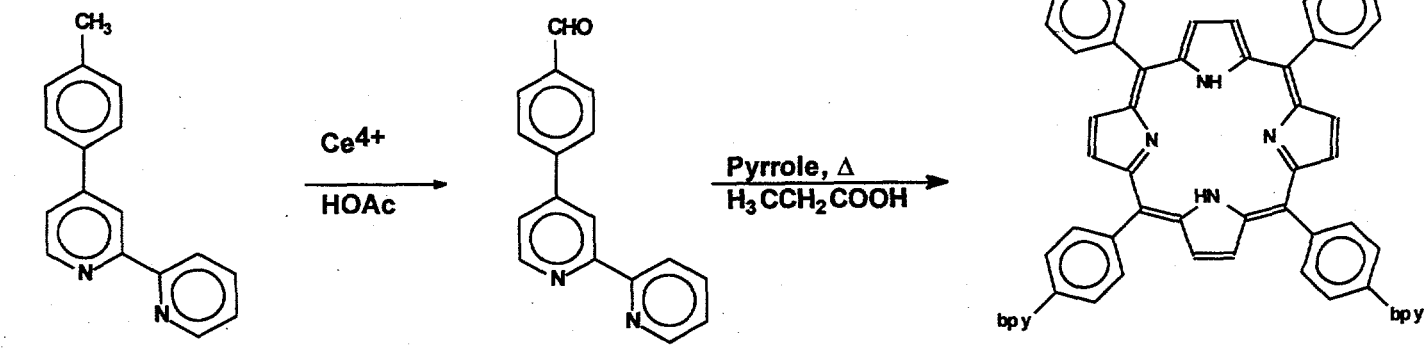
C1. Synthesis of Ru(II) Complexes of Bipyridine and Terpyridine Phosphonic Acids







D1. Synthesis of tetra-(2,2'-bipyrid-4-yl)phenyl porphyrin



$[(bpy)_2RuCl_2]$ and we are currently working on the purification of the complexes produced in the reaction.

III. Spectroscopy of Ru(II) and Re(I) Complexes of Bridging Ligands

A. *Intramolecular Electronic Energy Transfer in $[(bpy)_2Ru(BL)Ru(tpy)(CN)](PF_6)_3$ and related complexes.*

One objective of the proposed research was to directly measure rate constants close to self-exchange energy transfer rate constants in ligand bridged trimetallic complexes having two nearly identical donors (spectroscopically) and an acceptor : D_1-D_2-A. A part of this work involved preparation of rigid bridging ligands and investigation of intramolecular electronic energy transfer in bimetallic complexes linked by the bridging ligand. Using the ligand **bphb** we prepared a series of bimetallic complexes having either $[(bpy)_2Ru(\mathbf{bphb})]^{2+}$ or $[(CO)_3(py)Re(\mathbf{bphb})]^{+}$ donor chromophores and $[[(tpy)(L)Ru(\mathbf{bphb})]^{+}$ (L = CN^-, py) as the acceptor chromophores. Table I lists room temperature absorption and luminescence characteristics for acetonitrile solutions of complexes in this series. In each complex the lowest energy allowed electronic transition is metal-to-ligand charge transfer (MLCT) to the bridging **bphb**. Thus energy transfer in the complex $[(bpy)_2Ru(\mathbf{bphb})Ru(tpy)(CN)]^{3+}$ is as shown below :

$$[(bpy)_2Ru(III)(\mathbf{b^-phb})Ru(II)(tpy)(CN)]^{3+*} \rightarrow [(bpy)_2Ru(II)(\mathbf{bphb^-})Ru(III)(tpy)(CN)]^{3+*} \quad (1)$$

The symmetric donor-donor complex $[(bpy)_2Ru(\mathbf{bphb})Ru(bpy)_2]^{4+}$ has a high quantum yield and a lifetime which is long relative to other ruthenium bipyridine complexes. The symmetric acceptor-acceptor complexes, $[(tpy)(CN)Ru(\mathbf{bphb})Ru(tpy)(CN)]^{2+}$ and $[(tpy)(py)Ru(\mathbf{bphb})Ru(tpy)(py)]^{4+}$ emit at energies only slightly lower than the donor-donor complex but have much lower lifetimes and quantum yields. From table I it is evident that the donor luminescence both in $[(bpy)_2Ru(\mathbf{bphb})Ru(tpy)(CN)]^{3+}$ and $[(bpy)_2Ru(\mathbf{bphb})Ru(tpy)(py)]^{4+}$ is nearly completely quenched in room temperature solution.

The trimetallic complex $[(bpy)_2Ru(\mathbf{bphb})Ru(bpy)(\mathbf{bphb})Ru(tpy)(CN)]^{5+}$ exhibits a higher overall luminescence yield but the luminescence lifetime is very short. Small amounts of a strongly luminescent impurity have complicated detailed analysis of the photophysical behavior of this complex.

Table I. Spectroscopic Properties of Complexes examined

Complex	λ_{max},nm (log ε)	λ_{em}, nm (298K)	λ_{em}, nm (77k)	Φ_{em} (298K)	τ_{em},ns (298K)	τ_{em},ns (77K)
$[(bpy)_2Ru(\mathbf{bphb})Ru(bpy)_2]^{4+}$	460(4.68)	624	598	0.158	2008	5600
$[(tpy)CNRu(\mathbf{bphb})Ru(tpy)CN]^{2+}$	494(4.52)	668	642	0.00042	6.0	4135
$[(bpy)_2Ru(\mathbf{bphb})Ru(tpy)CN]^{3+}$	468(4.54)	656	640	0.00084	6.1	3913
$[(bpy)_2Ru(\mathbf{bphb})Ru(bpy)(\mathbf{bphb})Ru(tpy)CN]^{5+}$	468(4.55)	629	617	0.013	---	>4990
$[(py)(tpy)Ru(\mathbf{bphb})Ru(py)(tpy)]^{4+}$	484(4.48)	632	634	0.001	<6.1	---
$[(bpy)_2Ru(\mathbf{bphb})Ru(py)(tpy)]^{4+}$	470(4.29)	628	630 602(sh)	0.0048	<10	5163
$[(py)(CO)_3Re(\mathbf{bphb})Ru(py)(tpy)]^{3+}$	472(--)	630	628	0.0033	<6.1	---

The luminescence quenching mechanism in $[(bpy)_2Ru(\mathbf{bphb})Ru\ (tpy)(CN)]^{3+}$ in acetonitrile solutions may involve either reductive electron transfer (eq . 2) or energy transfer (eq. 1). The free energy for the electron transfer quenching process can be estimated from the

$$[(b)_2Ru(III)(\mathbf{b^-phb})Ru(II)(t)(CN)]^{3+*} \rightarrow [(b)_2Ru(II)(\mathbf{b^-phb})Ru(III)\ (t)(CN)]^{3+} \qquad (2)$$

zero-zero emission energy of the excited donor , E_{oo} { $[(bpy)_2Ru\ (\mathbf{bphb})]^{2+}$}, the one electron reduction potential of the donor complex (3a, $E(Ru_D(II/I))$ and the one electron potential for oxidation of the acceptor complex (3b, $E(Ru_A(III/II))$. For the above bimetallic complex

$$[(b)_2Ru(II)(\mathbf{bphb})Ru(II)(t)(CN)]^{3+} + e^- \rightarrow [(b)_2Ru(II)(\mathbf{b^-phb})Ru(II)(t)(CN)]^{2+} \qquad (3a)$$

$$[(b)_2Ru(II)(\mathbf{bphb})Ru(III)(t)(CN)]^{4+} + e^- \rightarrow [(b)_2Ru(II)(\mathbf{bphb})Ru(II)(t)(CN)]^{3+} \qquad (3b)$$

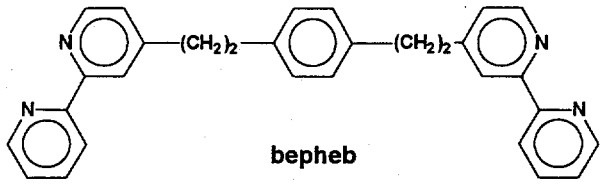
the free energy for reductive electron transfer is slightly endoergic even in the absence of any work term associated with the charge redistribution in the process. The free energy for the energy transfer process is exoergonic by approximately 950 cm^{-1}. Excitation spectra for the bimetallic complex are independent of the emission wavelength observed and clearly show that MLCT excitation of the $[(bpy)_2Ru(\mathbf{bphb})]^{2+}$ chromophore results in luminescence from the $[(tpy)(CN)Ru(\mathbf{bphb})]^{+}$ MLCT state. Thus, while electron transfer in this system cannot be excluded definitively, evidence for energy transfer quenching of the donor luminescence is clear.

Determination of room temperature energy transfer rate constants in these systems is hampered by the fact that the luminescence of the donors in the donor-acceptor complexes overlaps extensively with that of the acceptors. All that can be said is that the donor decay rate constant in the donor-acceptor complex is at least as large as that of the acceptor complex. Using the assumption that the difference in the decay rate constants for the donor complex luminescence of the donor-acceptor

$$k_{en} = \frac{1}{\tau_{DA}} - \frac{1}{\tau_{DD}} \qquad (4)$$

and donor-donor complexes equals the quenching rate constant (eq 4), the minimum rate constant was found to be $1.7 \times 10^8\ s^{-1}$. The related complex $[(bpy)_2Ru(\mathbf{bepheb})\ Ru(tpy)CN]^{3+}$, exhibits measureable luminescence from the $[(bpy)_2Ru(\mathbf{bepheb})]^{2+}$ donor chromophore and the energy transfer rate constant is $2 \times 10^7\ s^{-1}$.

In an attempt to obtain rate constant data for $[(bpy)_2Ru(\mathbf{bphb})\ Ru(tpy)CN]^{3+}$, the luminescence was examined at temperatures between 20 K and 110 K in EtOH/MeOH glasses. Steady state emission spectra of the complex are nearly identical to spectra of the acceptor chromophore over the entire temperature range. Time resolved emisson spectra of the complex clearly show that no donor luminescence can be observed in the first 200 ns of decay at temperatures as low as 20 K. We were able to obtain a very weak decay with a lifetime of 19 $\pm$ 2 ns using time correlated single photon counting at temperatures between 90 and 110 K; luminescence from the complex was collected with a narrow band pass filter selected for the donor luminescence maximum (585 nm). Using this lifetime, data from Franck-Condon fits to steady state spectra of $[(bpy)_2Ru(\mathbf{bphb})Ru(bpy)_2]^{4+}$ and $[(tpy)(CN)Ru(\mathbf{bphb})Ru(tpy)CN]^{2+}$ and a semi-classical expression for an exchange energy transfer process, an estimate of 0.6 cm^{-1} for the electronic coupling matrix element for donor-acceptor interaction through the **bphb** bridging ligand is obtained (see attached preprint).[8] The estimate is consistent with data obtained for bimetallic Ru(II)-Os(II) donor-acceptor complexes linked through the ligand **tpht**.[9] A preprint of this work, containing more detail, is attached to the report. Very recently we have examined the luminescence behavior of $[(bpy)_2Ru(\mathbf{bph_3b})Ru(tpy)CN]^{3+}$; preliminary studies indicate that this complex exhibits behavior identical to that of the complex having a single phenyl bridge. That is, even at temperatures as low as 20 K no detectible luminescence is observed from the donor chromophore in time resolved luminescence spectra.

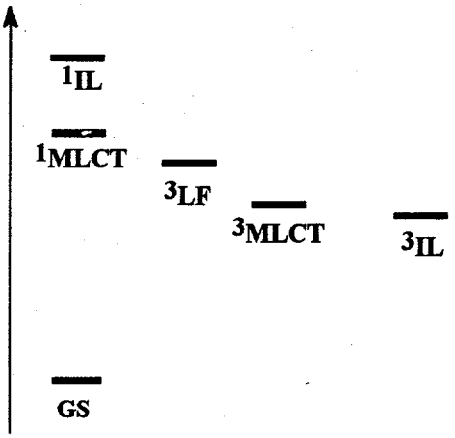


bepheb

We have initiated a collaboration with Dr. Steven Atherton, a staff scientist at the Center for Photoinduced Charge Transport at the University of Rochester, to use ps transient absorption spectroscopy in an effort to obtain room temperature rate constant data on these complexes . Initial results indicate that, for $[(bpy)_2Ru(\mathbf{bphb})Ru(tpy)(CN)]^{3+}$, sensitization of the acceptor chromophore is complete within 20 ps when photolysis is carried out in acetonitrile solution. The proposed research focuses on examining the free energy dependence and excited state dipole orientation effects for energy transfer in bimetallic complexes linked by $\mathbf{bph_xb}$.

B. *Intraligand and MLCT Excited States in Ru(II) and Re(I) Complexes*

A growing number of inorganic complexes exist that have spectroscopically observable ^{3}MLCT and ligand localized (^{3}IL) excited states. For example, luminescence from Re(I) complexes of the type [(NN)Re(I)(CO)$_3$L] (NN= bpy, phen , etc; L = Cl , CH_3CN, py, etc.) has been observed to occur from both purely ^{3}MLCT states and purely ligand localized (IL) states. [10-12] But examples also exist where the luminescence spectra, lifetimes, quantum yields and radiative decay rate constants cannot be clearly linked to either MLCT or IL states. Recent work of Rillema, Crosby and Demas has provided examples of complexes for which the excited state assignment is unclear and spin-orbit coupling interactions are significant. [13,14] Our interest has been in defining the relationship between the relative energies of the excited states involved and the photophysical behavior observed in complexes of this type. The spectroscopically active states are the singlet and triplet MLCT states, the triplet $\pi\rightarrow\pi^*$ state(s) (IL) of the diimine ligand(s), and metal centered ligand field (LF) states. A typical energy level diagram for complexes having both spectroscopically observable MLCT and $\pi\rightarrow\pi^*$ states is shown below. Excitation into either the ^{1}IL state or the ^{1}MLCT state can lead to population of both the ^{3}MLCT and ^{3}IL states. In room temperature solutions, luminescence is most often observed only from the ^{3}MLCT state. Evidence for population of the ^{3}IL state is obtained from transient absorption experiments and indirectly from luminescence quantum yield information. In general, dissociative photochemistry associated with population of ^{3}LF states is not observed in complexes having relatively low energy ^{3}IL states.



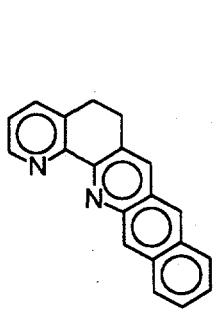
The general approach we have used in examining diimine ligands which are likely to have photoactive ^{3}IL states in complexes is to prepare both the $[(bpy)_2Ru(NN)]^{2+}$ complex and the [(NN)Re(I)(CO)$_3$L] complex (NN = diimine ligand, L = Cl, CH_3CN, py) and examine their photophysical behavior. Characterization of the complexes includes obtaining absorption and emission spectra in solution at room temperature and in low temperature glasses, room temperature luminescence quantum yields and lifetimes, low temperature luminescence lifetimes and room temperature excited state absorption spectral data. The combination of luminescence quantum yield

and lifetime data for emission from the ^{3}MLCT state provides indirect evidence for population of states other than the ^{3}MLCT state following excitation into the ^{1}MLCT state. The ^{3}MLCT state emission quantum yield represents the product of the intersystem crossing efficiency to populate the state, the radiative decay rate constant and the luminescence lifetime (eq. 5). Values of $\eta_{isc}k_r$ have been determined for ^{3}MLCT emission from numerous Ru(II) and Re(I) diimine

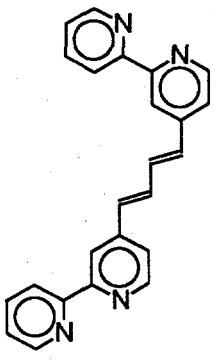
$$\theta_{em,CT} = \eta_{isc}\, k_{r,CT}\, \tau_{em,CT} \qquad (5)$$

complexes and usually are in the range of 5×10^4 s^{-1} to 10^5 s^{-1}. Measured values of $\eta_{isc}k_r$ substantially lower than this range can result from low intersystem crossing efficiencies to the ^{3}MLCT state and, in complexes having diimine ligands with low energy $^3\pi\rightarrow\pi^*$ states, population of the $^3\pi\rightarrow\pi^*$ state represents one possible explanation. More direct evidence for involvement of a $^3\pi\rightarrow\pi^*$ state can be obtained from transient absorption spectroscopy and low temperature luminescence spectra. Often Re(I) diimine complexes exhibit structured luminescence in low temperature glasses (77 K) which can be assigned as ligand localized phosphorescence. Transient absorption data can sometimes be associated with the presence of ^{3}IL states if (1) the transient spectrum has features that strongly resemble the spectrum of the ligand $^3\pi\rightarrow\pi^*$ state, (2) the decay rate constant of the transient absorption differs significantly from that of the ^{3}MLCT state luminescence decay or (3) a large difference exists between rate constants for quenching ^{3}MLCT state luminescence and rate constants for reaction of the excited state exhibiting transient absorbance with triplet energy quenchers.

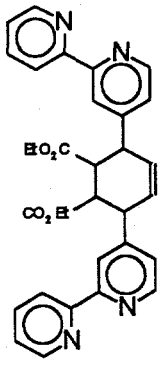
The ligands we have investigated in detail during the past three years are shown below. The ligand **dmpbq** and its corresponding Ru(II) complex were prepared by Randy Thummel's group at the University of Houston. Appended to the report is a reprint of the work on Ru(II) complexes of **bbdb**,



dmpbq



bbdb



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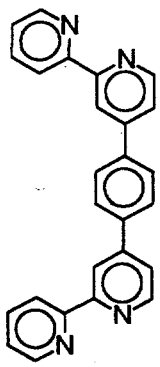


bphb

bchb and **bphb** and a preprint of the photophysical characterization of the Ru(II) complex of **dmpbq**. For all the ligands other than **dmpbq**, both the monometallic, $[(bpy)_2Ru(NN)]^{2+}$, and bimetallic, $[(bpy)_2Ru(NN)Ru(bpy)_2]^{4+}$ complexes were prepared and characterized. The complexes of **bphb** and **bchb** exhibit redox and photophysical properties that are characteristic of complexes having no involvement of ^{3}IL excited states. The complexes of **bbdb** and **dmpbq** exhibit very weak luminescence and have transient absorbance spectra which are indicative of the presence of another excited state. For $[(bpy)_2Ru(\mathbf{bbdb})]^{2+}$ the room temperature lifetime of the ^{3}MLCT state differs from the lifetime of the transient absorbance and the luminescence and transient absorbance are quenched with different rate constants by a series of triplet quenchers. The excited species giving rise to the unique transient absorbance could be due to solvent exciplex formation, but the lack of a pronounced dependence of the photophysical behavior on solvent suggests that this is not the explanation. The transient absorption has features that resemble those of triplet states of N-alkyl-4-styrylquinolinium salts, suggesting the excited state is ^{3}IL ($\pi \rightarrow \pi^*$). In addition, the approximate energy of the state exhibiting the transient absorbance (as determined by the free energy dependence of quenching with triplet energy quenchers) is nearly the same as that of 1,4-diphenylbutadiene, an aromatic hydrocarbon having a framework similar to that of **bbdb**. Work of Göerner and coworkers has shown that little energy difference exists between many polyunsaturated hydrocarbons and various aza-derivatives.[15] Others have shown that only small differences exist in the triplet energies of coordinated and free nitrogen heterocycles (such as phenanthrolines).[16,17] For the ligands **bphb** and **dmpbq** the corresponding aromatic hydrocarbon analogs are p-terphenyl and anthracene, respectively. The p-terphenyl triplet energy lies well above the energy of the ^{3}MLCT state in $[(bpy)_2Ru(\mathbf{bphb})]^{2+}$, while the anthracene triplet is much closer to the energy of the ^{3}MLCT state of $[(bpy)_2Ru(\mathbf{dmpbq})]^{2+}$. In fact, the **dmpbq** complex has a transient absorption which is much longer lived than the ^{3}MLCT luminescence and the excited state spectrum is very similar to the spectrum obtained by subtracting the ground state absorption spectrum of $[(bpy)_2Ru(\mathbf{dmpbq})]^{2+}$ from the spectrum of the **dmpbq** triplet state. We are presently examining other complexes which have ligands with relatively low triplet energies.

Several Re(I) complexes of **bphb** and **bbdb** have been prepared and characterized. Spectroscopic data for $\{[(CO)_3Re(L)]_2(\mathbf{bphb})\}^{2+}$ (L = py, CH_3CN and N-methylimidazole) and $\{[(CO)_3Re(CH_3CN)]_2(\mathbf{bbdb})\}^{2+}$ have been obtained and are reported in Table II. The principal observations from the data are (1) the complexes of **bphb** exhibit clearly defined double exponentaial decays in solution and in ethanol/methanol glasses and (2) the bbdb complex emits only very weakly

in room temperature acetonitrile.

The behavior of the **bphb** complex is similar to that observed for $[(CO)_3Re(CH_3CN)(\mathbf{styb})]PF_6$ (**styb** = β-(2,2'-bipyrid-4-yl)styrene) where luminescence from both ^{3}IL and ^{3}MLCT states is clearly observed in time resolved spectra in low temperature glasses. Given the large difference in lifetimes of the two decays of $\{[(CO)_3(CH_3CN)Re]_2\mathbf{bphb}\}^{2+}$ at 77 K we obtained time resolved emission spectra at different delays. With no delay (2 μs gate), broad, structureless emission was observed with a maximum of 530 nm. By changing the delay to 30 μs (gate = 20 μs), the spectrum sharpened to include maxima at 520 and 545 nm. A simple interpretation of this is that the luminescence at early times following pulsed excitation is predominantly from the ^{3}MLCT state while the longer lived emission arises from the a nearly equienergetic ^{3}IL state. The zero-zero energy of the ^{3}IL luminescence is approximately 2.53 eV. The triplet energy of the simplest aromatic hydrocarbon having a structural framework similar to **bphb**, p-terphenyl, is 2.53 eV. This preliminary evidence indicates that (1) both the MLCT and IL states are populated and (2) internal conversion between the states is slow relative to other radiative and nonradiative processes.

The **bbdb** complex exhibits behavior which is not readily interpretable. The luminescence spectrum of $\{[(CO)_3(CH_3CN)Re]_2\mathbf{bbdb}\}^{2+}$ in ethanol/methanol glasses at 77 K has a maximum at 490 nm and shows some structure. In addition, the weak room temperature luminescence has nearly the same maximum, but is much broader. The lack of a blue shift in the emission maximum between room temperature and 77 K suggests the emission does not arise from a ^{3}MLCT state. The transient absorption spectrum of the complex in acetonitrile solutions has a maximum of approximately 600 nm and a lifetime of nearly 2 μs; no bimolecular excited state quenching experiments have been conducted on this system. Results from transient absorption spectra and triplet quenching of $\{[(bpy)_2Ru]_2\mathbf{bbdb}\}^{4+}$ suggest the triplet state energy for **bbdb** is approximately 1.75 eV, much lower than the 2.3 eV energy of the observed luminescence. It is possible that the luminescence observed in the Re(I) **bbdb** complex originates from a ^{3}IL state of a different geometric isomer of the bridging ligand; for stilbene, the Z isomer triplet excited state energy is approximately 0.25 eV higher than that of the E isomer.[18] We are currently investigating this complex in greater detail; since the luminescence is very weak, emission from an impurity cannot be dismissed.

Table II. Spectroscopic Properties of Re(I) Complexes Examined

Complex	λ_{max},nm (log ε)	λ_{em}, nm (298K)	λ_{em}, nm (77k)	Φ_{em} (298K)	τ_{em},ns (298K)	τ_{em},μs (77K)	η_{isc} k_r, s^{-1} (298 K)
$[(CO)_3Re(CH_3CN)(dmb)]^+$	330	532	478	0.04	660	4.3	6×10^4
$\{[(CO)_3Re(CH_3CN)]_2$(**bphb**)$\}^{2+}$	354(4.46)	556	514	0.27	1550 3980	3.9 17.4	2×10^4
$\{[(CO)_3Re(py)]_2$(**bphb**)$\}^{2+}$	354(4.59)	554	514	0.08	800	6.5 24.7	1×10^4
$\{[(CO)_3Re(NMI)]_2$(**bphb**)$\}^{2+}$	354(4.30)	592	548	0.01	99	4.9 16.2	1×10^4
$\{[(CO)_3Re(CH_3CN)]_2$(**bbdb**)$\}^{2+}$	388(4.65)	540	540	$<10^{-3}$	41	3.6 18.9	---

NMI = N-methyl-imidazole

IV. Excited State Acid Dissociation of $[(bpy)_2Ru(H_2O_3PPhbpy)](PF_6)_2$

A resurgence has occurred over the past several years in the development of dye sensitized photoelectrochemical cells. This research has been fueled by the observation that high photon to current efficiencies are obtained for cells having 5 - 10 μm thick films of nanocrystalline semiconductors deposited on the photoelectrode with the dye adsorbed to the surface of the nanocrystalline particles.[5,19] Ru(II) diimine complexes have been found to be very effective sensitizers in these systems and initial work was done with complexes of 4,4'-dicarboxy-2,2'-bipyridine; the carboxy substituents were found to be necessary for adsorption of the complex on the semiconductor particles. Very recently it was found that complexes of bipyridine phosphonic acids also adsorb on nanocrystalline semiconductor particles.[20] In fact the phosphonic acid complexes are adventageous because they remain adsorbed over a wide pH range, unlike the carboxylate complexes. In an effort to contribute to this particular development, we devised simple procedures for preparing bipyridine and terpyridine ligands having phosphonic acid substituents (figure 1). In addition, we have prepared Ru(II) complexes containing the ligands and have characterized the complex $[(bpy)_2Ru(H_2O_3PPhbpy)](PF_6)_2$ in some detail. A manuscript describing the synthesis, redox and luminescence behavior of the complexes is in preparation. Samples of $[(bpy)_2Ru(H_2O_3PPhbpy)](PF_6)_2$ have been given to research groups at Caltech, Penn State and the Radiation Lab at Notre Dame for investigation of photoelectrochemical behavior. A brief description of the redox and luminescence behavior of the bipyridine phosphonic acid complex is given below.

The redox and photophysical behavior of $[(bpy)_2Ru(H_2O_3PPhbpy)](PF_6)_2$ is similar to that of $[(bpy)_3Ru](PF_6)_2$. The absorption maximum in acetonitrile solutions is 456 nm and the luminescence maximum is 616 nm (θ_{em} = 0.065; τ_{em} = 700 ns). The Ru(III/II) potential is at 1.25 V vs SSCE and the Ru(II/I) potential is -1.37 V. All of these properties are very similar to $[(bpy)_3Ru](PF_6)_2$. The PF_6 salt of the complex is soluble in water (unlike $[(bpy)_3Ru](PF_6)_2$) and the luminescence intensity and lifetime are dependent on the pH. The ground state pK_a values of $[(bpy)_2Ru(H_2O_3PPhbpy)](PF_6)_2$ are 3.2 and 6.3 for pK_1 and pK_2 of eq. 6. The emission intensity of the complex rises and the lifetime increases from pH 1.8 to pH

$$[(bpy)_2Ru(bpyPhPO_3H_2)]^{2+} \rightleftharpoons [(bpy)_2Ru(bpyPhPO_3H)]^{+} + H^{+} \quad pK_1 \quad (6a)$$

$$[(bpy)_2Ru(bpyPhPO_3H)]^{+} \rightleftharpoons [(bpy)_2Ru(bpyPhPO_3)]^{0} + H^{+} \quad pK_2 \quad (6b)$$

3.5. The luminescence decays appear to be single exponential over the entire pH range suggesting the acid-base equlibrium in the excited state is rapid relative to relaxation of either state (the lifetime increases from 490 ns at pH 1.8 to 550 ns at pH 3.0). The excited state pK_1 value obtained from the combined intensity and lifetime measurements is 2.3. Above pH 3.5 the luminescence intensity and lifetime decrease. In this case

also the luminescence decays appear to be single exponential and the pK_2 value is approximately 4.9. The implication is that the MLCT excited state is localized on the bpy ligands in the excited complex since the ground state pK values are higher than the excited state values. We plan to investigate the photophysical behavior of other complexes for which the MLCT excited state is more likely to be localized on the bipyridine phosphonic acid ligand (i.e. where bpy is replaced with bipyridines alkylated in the 3,3' and 4,4' positions); the excited state pK values in such complexes should be higher than those of the ground state since charge is transfered to the bipyridine phosphonic acid upon excitation.

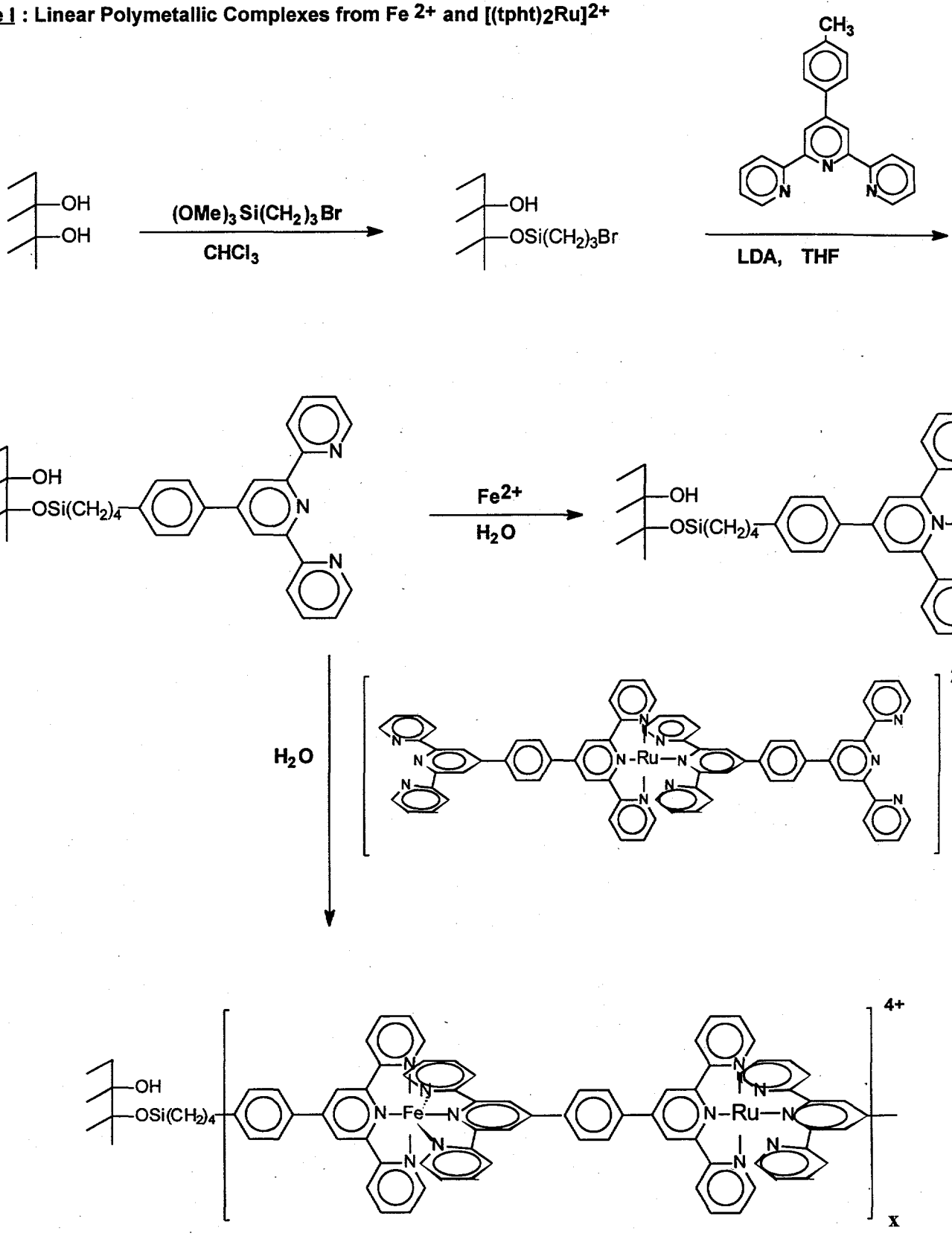
V. Synthesis of Metal Complex Oligomers at Surfaces one Metal at a Time.

Among the complexes used as sensitizers for photoelectrochemical cells are trimetallic complexes having two antenna chromophores covalently linked to the surface bound sensitizer chromophore.[21] Recently we have begun to explore ways to synthesize polymetallic light harvesting arrays at surfaces by beginning with a surface bound anchor and building up the array by covalent attachment of one metal center at a time. Our initial efforts have focused on developing different approaches to make multimetallic complexes on surfaces without regard for the applicability of particular assemblies as light harvesting arrays. One approach we have demonstrated is shown in Scheme 1. Clean quartz surfaces are initially treated with an ω-bromo- alkoxysilane in dry chloroform. This is followed by nucleophilic substitution of the bromide with the anion formed by reaction of 4-(2,2',6',2"-terpyrid-4'-yl)toluene with LDA in THF. The terpyridine modified surface is then exposed sequentially to aqueous solutions containing Fe^{2+} and solutions of $[(\mathbf{tpht})_2Ru]^{2+}$ to yield surfaces modified with alternating $(tpy)_2Fe^{2+}$ and $(tpy)_2Ru^{2+}$ centers. The growth of the polymetallic complex on quartz was followed spectrophotometrically and the initial surface modification to make the tethered terpyridine was observed spectrophotometrically and by contact angle measurements. A communication of this work has been published.[22]

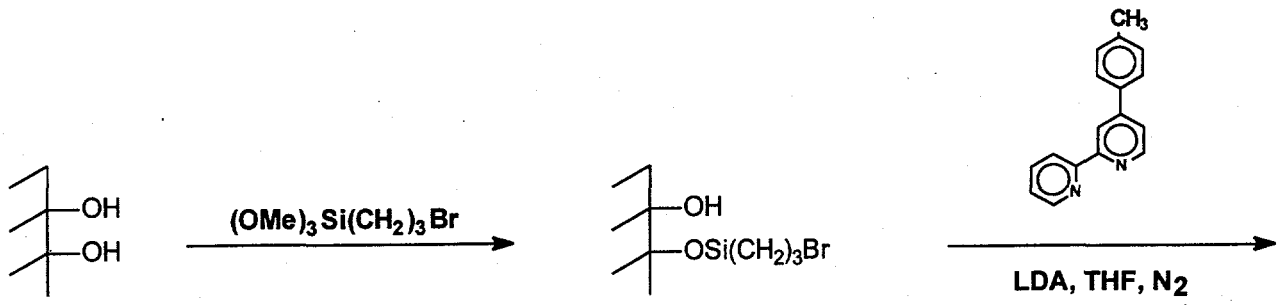
A variation of this approach leads to the formation of branched polymetallic complexes (Scheme II). In this case a bipyridine derivative is anchored to the surface of quartz using a procedure analogous to that used in making the terpyridine modified surfaces. This is then followed by sequential reaction with $RuCl_3$ and **bphb** to yield the initial metal complex layer; this layer has two non-coordinated bipyridine ligands. Reaction of this surface with $RuCl_3$ followed by **bphb** will produce an array of three metal centers; subsequent reaction cycles will, in principle, produce arrays of 7, 15, 31, etc. metal centers. Spectrophotometric studies of growth in these systems reveals that, while the absorbance increases more than expected for linear growth, the 2^n increase is not observed.

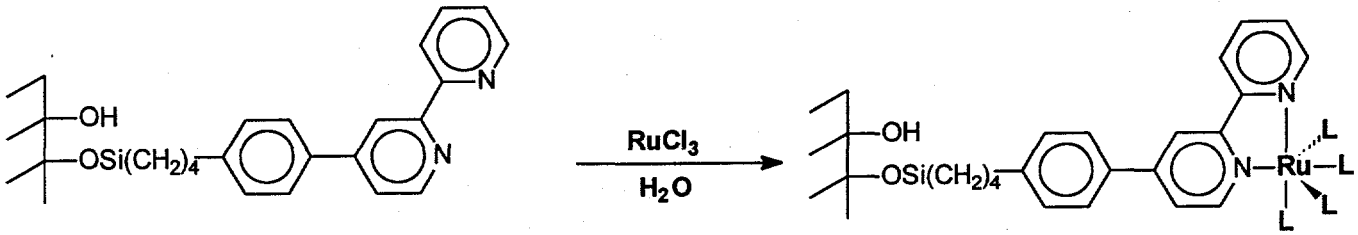
The final approach we have employed involves the preparation of multilayer metal phosphonate thin

Scheme I : Linear Polymetallic Complexes from Fe^{2+} and $[(tpht)_2Ru]^{2+}$

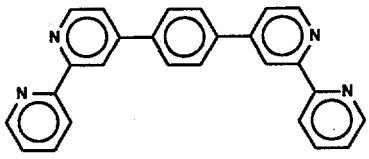


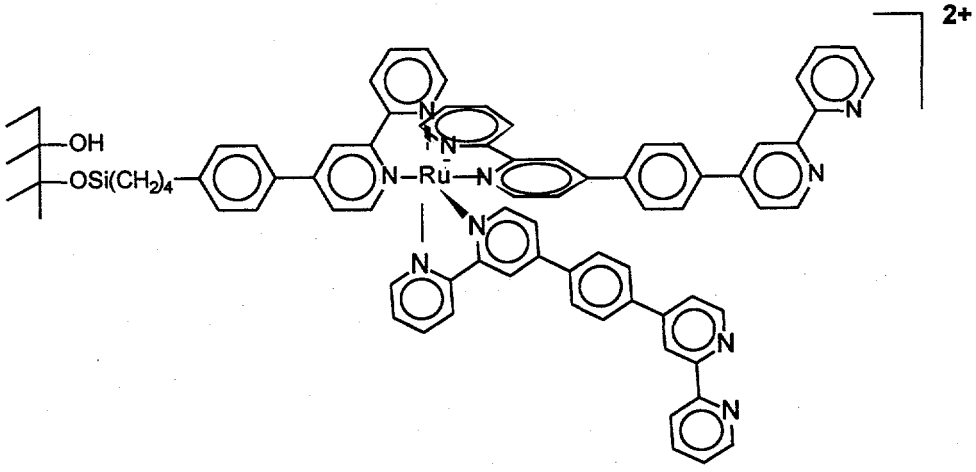
Scheme II : **Branched Polymers with bphb and $RuCl_3$**





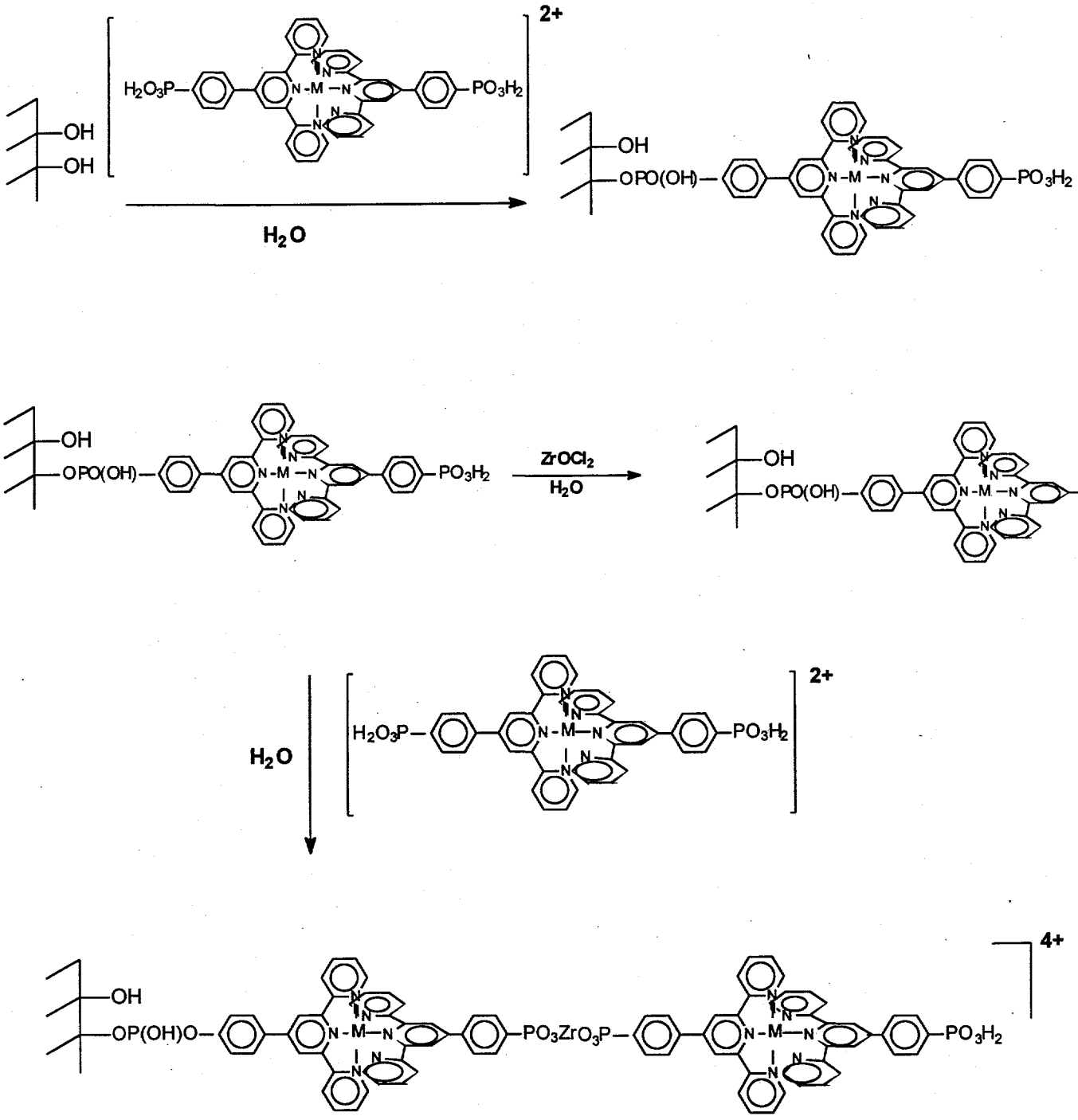
L = solvent, Cl^-





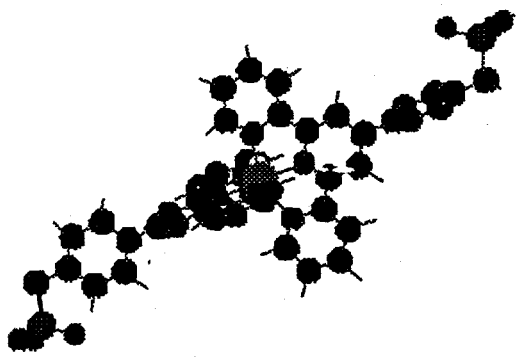
Scheme III : Linear Polymers on ITO with $[(H_2O_3Ptpy)_2M]^{2+}$ and $ZrOCl_2$

M = Fe(II), Ru(II), Os(II)



Presently no information available on the zirconyl phosphonate surface structure

films using techniques developed by Mallouk and exploited by others.[6, 7, 23] In this case the bis-phosphonate used is a Ru(II) complex which can span two layers : $[(H_2O_3PCH_2Phtpy)_2Ru](PF_6)_2$. A ball and stick representation of the complex is shown below. The complex directly adsorbs onto surfaces such as mica and indium tin oxide (ITO). Atomic Force Microscopy of a monolayer of the complex on mica indicates the thickness is about 8 Å; this suggests the CH_2-Ru-CH_2 axis of the molecule is at an angle of approximately 20^0 relative to the surface. Multilayers of the complex are prepared as shown in Scheme III. Following adsorption of the initial layer of complex onto ITO, the surface is exposed alternately to aqueous $ZrOCl_2$ and the complex. Multilayers were also prepared on quartz surfaces by initial covalent attachment of an alkyl phosphonic acid to the surface using literature procedures[24] followed by alternate treatment of the surface with $ZrOCl_2$ and $[(H_2O_3PCH_2Phtpy)_2Ru](PF_6)_2$. Films prepared in this way are reasonably robust and can withstand sonication in aqueous solutions for periods of at least one hour. Figure 3 shows uv-vis spectra obtained following each deposition cycle on quartz surfaces. From the average absorbance per layer, a surface coverage of approximately 2×10^{-10} mol cm^{-2} is obtained (average of 83 $Å^2$ $molecule^{-1}$). This is somewhat smaller than the area per molecule estimated assuming a molecular diameter of 11 Å , but is not unreasonable given the fact that the substrate is amorphous and surface roughness has not been accounted for.



$[(H_2O_3PCH_2Phtpy)_2Ru]^{2+}$

Films of $[(H_2O_3PCH_2Phtpy)_2Ru](PF_6)_2$ deposited on ITO can be examined using electroanalytical methods. In particular cyclic voltammetry can be used to provide a measure of film permeability and interlayer penetration. Cyclic voltammograms of ITO surfaces having the initial adsorbed monolayer and one or more additional layers of the complex linked through Zr(IV) exhibit a linear increase in peak current for the Ru(III/II) wave with increasing sweep rate indicative of an adsorbed redox active species. Repeated cycling through the Ru(III/II) wave results in gradual loss of $[(H_2O_3PCH_2Phtpy)_2Ru](PF_6)_2$ from the surface when the electrode is immersed in acetonitrile solutions. We are currently examining the factors that influence film stability in more detail.

A qualitative measure of film permeability can be obtained from cyclic voltammograms of modified electrodes in solutions containing a redox active species. Figure 4 shows a cyclic voltammogram of an ITO electrode having three layers of $[(H_2O_3PCH_2Phtpy)_2Ru](PF_6)_2$ in solutions containing $[Os(bpy)_3]^{2+}$. No

Figure 3. Absorption spectra obtained for deposition of $[(H_2O_3PCH_2Phtpy)_2Ru]^{2+}$ / Zr(IV) on a quartz surface modified with $(OCH_3)_3Si(CH_2)_3PO_3H_2$. The inset shows the absorbance due to adsorbed complex as a function of the number of layers deposited.

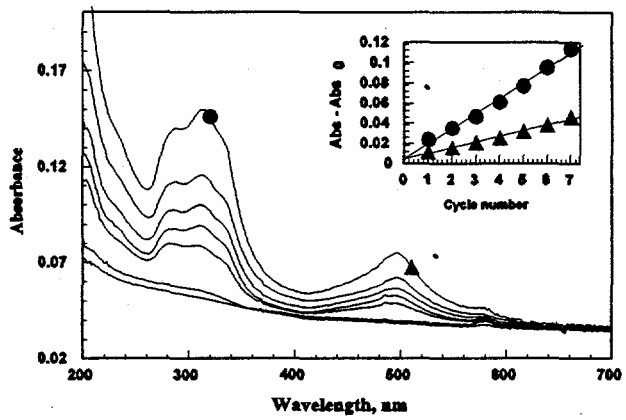
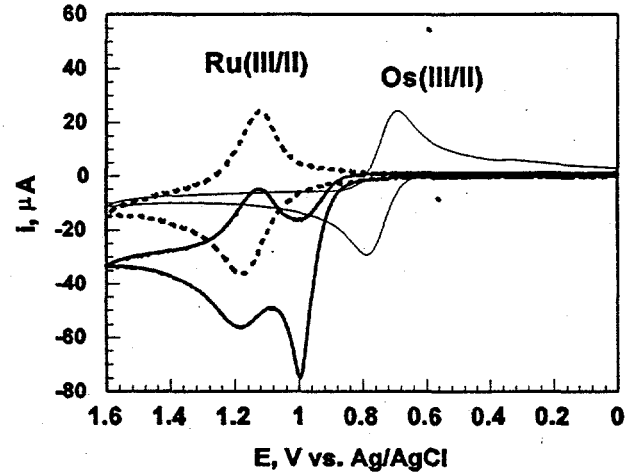


Figure 4. Cyclic voltammograms of (—) $[Os(bpy)_3](PF_6)_2$ in acetonitrile, (----) $[(H_2O_3PCH_2Phtpy)_2Ru]$ $(PF_6)_2$ in clean acetonitrile and (▬) $[(H_2O_3PCH_2Phtpy)_2Ru](PF_6)_2$ in acetonitrile containing $[Os(bpy)_3](PF_6)_2$.



current for Os(II) oxidation is observed until the electrode is at potentials where Ru(II) in the film can be oxidized; at that point a prewave on the Ru(III/II) wave is observed which corresponds to catalytic oxidation of the Os(II) in solution near the electrode surface. The voltammogram also illustrates unidirectional electron transfer since the Os(III) in solution is not reduced by the Ru(II) in the film and direct reduction of the Os(III) at the electrode surface is inhibited because the Os(III) complex cannot penetrate the film. The experiment illustrates that no large exposed areas of the bare electrode exist in the modified electrodes.

We have also made films which contain both $[(H_2O_3PCH_2Phtpy)_2Ru](PF_6)_2$ and the corresponding Fe(II) complex. Films containing three layers of the Fe(II) complex deposited over three layers of the Ru(II) complex on ITO have cyclic voltammograms for which both the Fe(III/II) and the Ru(III/II) waves are resolved at very slow sweep rates (10 mV /s). As the sweep rate is increased iron oxidation begins to appear as a prewave on the Ru(III/II) wave. Qualitatively the system is evolving from one in which charge migration through the Ru inner layers is rapid enough to effect Fe(II) oxidation at any given applied potential to one where charge migration through the film on the edge of the Ru(III/II) wave is rate determining. Mixed multilayer films of this type provide the opportunity to make rectifying interfaces; we have recently prepared the Os(II) terpyridine phosphonic acid complex and are currently examining the redox behavior of mixed multilayer films containing this complex.

All of the research on the phosphonic acid complexes has been conducted during the last four months of funding prior to this report. Our aim is to expand studies of these complexes to include investigation of electronic energy transfer within and between layers deposited on atomically flat surfaces.

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VI. Personnel Overview

Below is a list of persons involved in the research associated with this project over the past three years; not all of the persons have received financial support from the grant. Two graduate students earned degrees during this period and both are presently employed. Aaron Baba is working as an Assistant Professor at Tuskeegee University and Yinquin Li is working for Nutrilite Co. Liang Yongwu is presently employed as a synthetic chemist at Tulane University Medical Center. The present group consists of 2 Undergraduate Summer Research Assistants (both Tulane students), 3 Graduate students (two have independent fellowships) and 1 Postdoctoral Associate. One former undergraduate summer research assistant, Laura Strong, is now in Graduate school at another university.

Name	Position	Dates	Degree (Year)
Aaron Baba	Research Assistant	9/89 - 5/94	Ph.D. (1994)
Yinquin Li	Research Assistant	1/92 - 7/94	M.S. (1994)
Wei Wang, Ph.D.	Postdoctoral Associate	1/93 - 6/93	
Won Kim	Research Assistant	9/92 - Present	Ph.D. (in progress)
Liang Yongwu, Ph.D.	Postdoctoral Associate	7/93 - 6/95	
Laura Strong	Summer Research Asst.	6/93-8/93	
Mike Kelly*	Research Assistant	9/93 - Present	Ph.D. (in progress)
Rachael Kipp*	Summer Research Asst.	6/94 - 8/94	
	Research Assistant	9/94- Present	Ph.D. (in progress)
Nancy D. Miller	Summer Research Asst.	6/94 - 8/94	
Jerry Simon, Ph.D.	Postdoctoral Associate	6/95 - Present	
Steve Curry	Summer Research Asst.	6/95 - 8/95	
Tekeda Freeman	Summer Research Asst.	6/95 - 8/95	

* = Louisiana Board of Regents Fellowship Awardee (4 year Fellowship)

VII. Publications (DOE related, 1992 - 1995)

** Publication resulting from sabbatical work in the lab of Tom Mallouk on DOE related research.

A. I. Baba, W. Wang, W. Y. Kim, L. A. Strong, R. H. Schmehl *"Convenient Synthesis of Bis-Bipyridines and Bis-terpyridines Bridging by Phenyl and Biphenyl Tethers"*, Synthetic Communications, **1994**, 24, 1029.

** E. H. Yonemoto, R. H. Schmehl, S. M. Hubig, R. L. Riley, B. L. Iverson, T. E. Mallouk *"Electron Transfer Reactions of Ruthenium Tris(bipyridyl)-Viologen Diads: Comparison of the Distance Dependence of Electron Transfer Rates in the Normal and Marcus Inverted Regions"*, J. Am. Chem. Soc., **1994**, 116, 4786.

R. Wang, Y. Liang, R. H. Schmehl *"Light Induced Exchange Energy Transfer Reactions of Micelle Forming Ru(II) Diimine Complexes"*, Inorg. Chim. Acta, **1994**, 225, 275.

** Edward H. Yonemoto, Yeong Il Kim, Russell H. Schmehl, Jim O. Wallin, Ben A. Shoulders, Benny R. Richardson, James F. Haw and Thomas E. Mallouk *"Photoinduced Electron Transfer REactions in Zeolite Based Donor-Acceptor and Donor-Donor-Acceptor Diads and Triads"*, J. Am. Chem. Soc., **1994**, 116, 10557.

Y. Liang,, R. H. Schmehl *"Coordination Chemistry at a Surface: Polymetallic Complexes Prepared on Quartz by Alternate Deposition of Fe(II) and Ru(II) Centres"* , J. Chem. Soc. Chem. Commun., **1995**, 1007.

A. I. Baba, H. E. Ensley and R. H. Schmehl *"Influences of Bridging Ligand Unsaturation on Excited State Behavior in Mono and Bimetallic Ru(II) Diimine Complexes"*, Inorg. Chem, **1995**, 34, 1198.

E. Taffarel, S. Chirayil, W. Y. Kim, R. Thummel , R. H. Schmehl *"Coexistence of Ligand Localized and MLCT Excited States in a 2-(Pyridyl)Benzoquinoline Complex of Ru(II)"*, Inorg. Chem., in press.

Y. Liang, A. I. Baba, R. H. Schmehl *"Nearly Activationless Energy Transfer in a Bimetallic Ru(II) Diimine Complex"* , J. Phys. Chem., submitted.

W. Wang, A. Baba, R. H. Schmehl, J. T. Mague *"A Rigid Bis-Bidentate Bridging Ligand : 1,4-Bis-(2,2'-bipyrid-4-yl) benzene*, Acta Cryst., submitted

R. H. Schmehl *"Intramolecular Electronic Energy Transfer in Multimetallic Transition Metal Complexes"*, in preparation for Prog. Rxn. Kinetics