DOE/ER/13633--T1

ENERGY CONVERSION BASED ON MOLECULAR EXCITED STATES. REDOX SPLITTING IN SOLUBLE POLYMERS.

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Project Final Report, Award Number DE-FG05-86ER13633

In the past grant period, our DOE sponsored work has focused on six related topics. First, we have developed an entirely general method for the preparation of complexes of Ru(II) incorporating three different bidentate ligands. This method is presently being extend to allow for monodentate ligands as well thus achieving unprecedented synthetic versatility. Second, we have utilized this method to prepare a series of complexes with pre-designed absorption properties, the ultimate goal being the synthesis of "black absorbers" for use as antenna chromophores in a light to chemical energy conversion array. Third, we have further extended our work with the energy gap law for nonradiative decay to allow us to prepare a series of near-IR luminophores with long excited state lifetimes. Fourth, we have focused on the omnipresent problem of destructive dd excited states in Ru(II) polypyridyl complexes and have been successful at determining the factors that lead to photo-inert complexes. This work has led to the preparation of an extremely photo-inert complex incorporating monodentate pyridine ligands. Fifth, we have extended our studies of time-resolved resonance Raman spectroscopy and time-resolved infrared spectroscopy and have applied these useful techniques to the elucidation of subtle excited state properties of complexes of Ru(II), Os(II), and Re(I). Finally, we have had a great deal of success with the controlled immobilization of d^6 chromophores and quenchers on styrenic polymers. Having perfected our technique for the synthesis of these systems, we have begun the process of optimizing the ground and excited state properties such as chromophore density, dipole orientation, and lifetime. These studies have led to the publication or submission of 22 manuscripts during the grant period.

Tris-heteroleptic compounds. Prior to the beginning of the last grant period, we identified what is a very important factor limiting the use of the ubiquitous Ru(II) polypyridine complexes as valuable components in the study of excited state electron and energy transfer. Only one method for the preparation of heteroleptic complexes had thus far been developed. The procedure involves the preparation of $[Ru(LL)_2Cl_2]$ (LL = derivatized bipyridine) from $RuCl_3$ followed by the replacement of the two chloride ligands with a different bipyridyl ligand.

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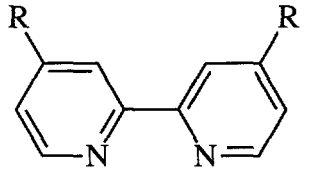
Though a simple high yield pathway, this scheme severely limits the utility of resultant complexes since a maximum of two different types of ligands can be incorporated. In an effort to overcome this limitation, we have devoted considerable effort to the preparation of complexes of Ru(II) which contain three different diimine ligands. In collaboration with the group of Dr. F. R. Keene at James Cooke University of North Queensland, Australia, we have developed an entirely general synthetic methodology that has afforded us a large degree of synthetic control in the preparation of these complexes.

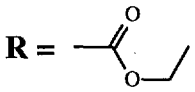
In a refinement of a pre-existing method, we have been able to prepare an array of complexes of the type *cis*(CO), *trans*(Cl)-[Ru(bpy$_a$)(CO)$_2$Cl$_2$] (where bpy$_a$ is derivatized bipyridine) from the oligomeric μ-bis(chloride) bridged intermediate [Ru(CO)$_2$Cl$_2$]$_n$. Substitution of the chloride ligands with trifluoromethanesulfonate forms *cis, cis*-[Ru(bpy$_a$)(CO)$_2$(triflate)$_2$]. A second, different, polypyridyl ligand can be added to the triflato complex to produce [Ru(bpy$_a$)(bpy$_b$)(CO)$_2$]$^{2+}$ which is isolated as the hexafluorophosphate salt. Trimethylamine N-oxide (a common decarbonylating reagent) can be used in the presence of a third polypyridyl ligand to prepare [Ru(bpy$_a$)(bpy$_b$)(bpy$_c$)](PF$_6$)$_2$. Last year we reported this synthetic strategy along with the characterization of over fifty tris-heteroleptic complexes. Since then, we have extended this method to the production of complexes of the type [Ru(bpy$_a$)(bpy$_b$)XY]$^{n+}$ in which X, Y = Cl$^-$, SCN$^-$, py, H$_2$O, or acac (bidentate). More exciting has been our observation that careful control of stoichiometry, temperature, and solvent allows us to prepare such complexes in which X and Y are different. For instance, we have prepared [Ru(bpy)(dmb)(4-Etpy)(CO)](PF6)2, and [Ru(bpy)(dmb)(4-Etpy)(4-^{t}butyl-py)]2+ in which dmb is 4,4'-dimethylbipyridine, 4-Etpy is 4-ethylpyridine, and 4-^{t}butyl-py is 4-(*tert*-butyl)pyridine. This refinement of the method promises a heretofore unprecedented versatility in the preparation of Ru(II) polypyridyl compounds.

Black MLCT Absorbers. Our first utilization this new synthetic strategy is an attempt to optimize the ground state properties of Ru(II) polypyridines for use in light to chemical energy conversion, and photocatalytic systems. All of these systems share the requirement that the initial chromophore in the multicomponent array absorb broadly throughout the UV and visible regions of the spectrum. Ideally, the chromophore would absorb most of the solar spectrum so as to maximize photon conversion efficiency.

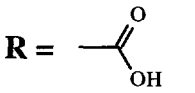
UV absorption in Ru(II) polypyridyl complexes is dominated by intense ligand centered $\pi \rightarrow \pi^*$ transitions. So long as the chromophore contains bipyridine derivatives, absorbance in this region is assured. Most of the absorptivity in the visible spectrum is due to metal to ligand charge transfer (MLCT) transitions in which an electron is promoted from a mostly metal-based $d\pi$ orbital to a π^* orbital localized on one of the ligands. In mixed chelate complexes, separate transitions occur to the π^* orbitals on each of the different ligands. For complexes incorporating



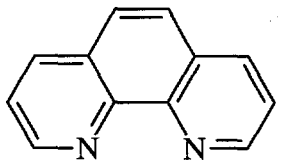
R = H **bpy**
R = -CH_3 **dmb**



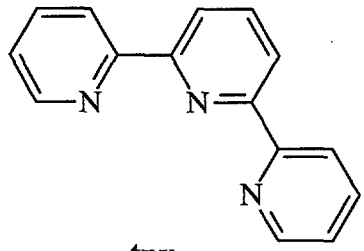
bpy(COOEt)$_2$



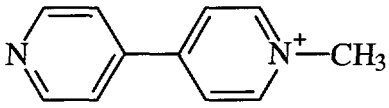
bpy(COOH)$_2$



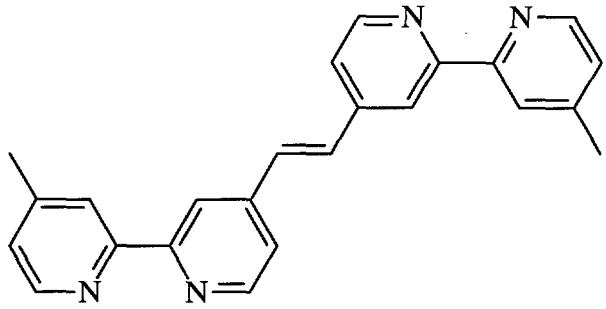
phen



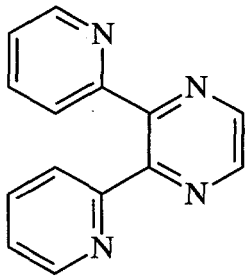
tpy



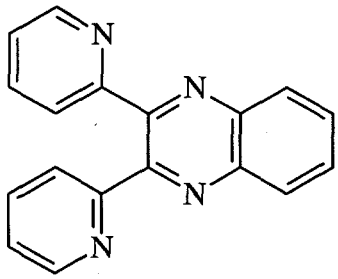
MQ^+



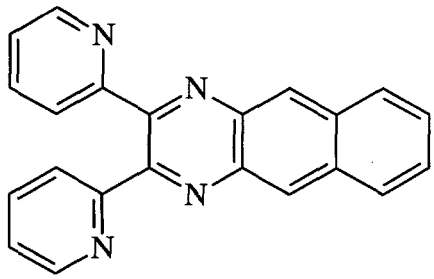
bbpe



dpp



dpq



dpb

extremely low energy acceptors, additional MLCT transitions to higher-lying π_2* orbitals are also observed in the visible. By controlling the energy of these transitions through judicious choice of ligands we hoped to utilize these overlapping transitions to form a continuous absorption plateau.

Delocalized ligands with low-lying acceptor orbitals such as dipyridobenzoquinoxaline (dpb) provide absorption in the red while bipyridine and alkyl-bipyridines "fill in" the higher energy region of the spectrum. Anionic ligands such as diethyldithiocarbamate (Et_2dtc^-) stabilize the excited state hole at Ru(III) shifting the composite spectrum uniformly to the red. We have

had some success in utilizing these two concepts and a knowledge of electrochemical parameters to prepare complexes such as $[Ru(bpy(COOEt)_2(dpb)(Et_2dtc)]^+$ ($bpy(COOEt)_2$ is 4,4'-dicarboxybipyridine diethyl ester) in which continuous significant absorption ($\varepsilon > 3000$) is extended from the UV through the visible well past 700 nm. Given our recent success (above) with the preparation of even more asymmetric complexes, we hope to extend this limit in two ways. The use of two monodentate thiocyanate ligands should stabilize the hole at Ru(III) even more than the mono-anionic Et_2dtc^- chelate. This should push the low energy edge of the absorbance even farther to the red. Similarly, an even better acceptor, dipyridophenazine (dpop), promises to allow us to extend absorbance to possibly 1000 nm.

Near-IR Emitters with Long Lifetimes. Our work with tris-heteroleptic complexes in the last grant period has allowed us to prepare rare examples of complexes exhibiting near-IR region emission. It is well known that, following MLCT excitation, intersystem crossing and internal conversion lead with near unit efficiency to the triplet MLCT state in which the excited electron is localized on the bipyridine ligand having the most positive reduction potential. Since black chromophores necessarily have at least one low energy excited state (for red region absorbance), emission from these complexes is generally found far into the red. Sufficiently low energy absorptions lead to near-IR emission.

In general, the usefulness of near-IR emitters is limited by the extremely short excited state lifetimes that arise as a consequence of the energy gap law for nonradiative decay. Since luminescence quantum yields are generally small for Ru(II) polypyridyl complexes, the excited state lifetime in fluid solution at room temperature is dominated by nonradiative decay. In the absence of competing deactivating pathways such as metal-centered dd states (below) the nonradiative decay rate constant, k_{nr} reflects the degradation of electronic excitation energy vibrationally *via* skeletal stretching modes centered on the acceptor ligand. In such a case, the rate of decay can be calculated using the energy gap law, eq. 1, in which β is the electronic coupling, and FC is Franck-Condon overlap term. FC can be expanded as in eqs. 2 in which E_o is the ground-excited state energy gap, γ is a dimensionless collection of terms, $\hbar\omega$ is the average vibrational spacing of the ground and excited state, and $\Delta\bar{\nu}$ is the full width at half maximum intensity for the vibronic components in the emission band.

$$\ln k_{nr} = \ln(\beta) + \ln[FC] \qquad \textbf{(1)}$$

$$\ln[FC] = -\frac{1}{2}\ln\left[\frac{\hbar\omega E_0}{\left(1000\ cm^{-1}\right)}\right] - S_m - \frac{\gamma E_0}{\hbar\omega} + \frac{(\gamma+1)^2\left(\frac{\Delta\bar{\nu}_{0,1/2}}{\hbar\omega}\right)^2}{16\cdot\ln(2)} \qquad \textbf{(2a)}$$

$$\gamma = \ln\left(\frac{E_0}{S_m \hbar\omega}\right) - 1 \qquad \textbf{(2b)}$$

The Huang-Rhys factor, S_m, is related to the degree of distortion in the excited state as in eq. 3 where M is reduced mass and ΔQ_e is the change in equilibrium displacement for the average acceptor vibration. As can be seen from eqs. 1-3, a smaller excited state energy gap tends to produce a shorter excited state lifetime (larger k_{nr}).

$$S_m = \frac{1}{2}\frac{M\omega}{\hbar}(\Delta Q_e)^2 \qquad \textbf{(3)}$$

In order to overcome this problem, we have focused on S_m. As can be seen from the above equations, decreasing S_m should also decrease k_{nr} and therefore lead to a longer lifetime. Anything that decreases the degree of excited state distortion relative to the ground state would be expected to lengthen the lifetime. To this end, we have utilized ligands in the series dpp, dpq, and dpb as acceptors. Through this series, the ligand becomes both more rigid and more delocalized. Since the excited state involves the promotion of an electron from a nonbonding metal-centered $d\pi$ orbital to an antibonding π^* orbital on the acceptor ligand, the major contribution to a large S_m value is the decrease in the π bond order for the acceptor ligand. Obviously, increasing the rigidity of the acceptor through the σ framework would be expected to decrease the degree of excited state distortion (and therefore S_m). Additionally, delocalizing the electron over a larger π system would be expected to lessen its effect on the average C-C and C-N distances.

Indeed, this is exactly what we found. In the series $[Ru(dmb)(bpy(COOEt)_2)(LL)]^{2+}$ in which LL = dpp, dpq, and dpb, λ_{max} for the emission shifts from 678 nm, to 790 nm, to >850 nm. The excited state lifetimes are 788 ns, 29 ns, and 98 ns respectively. In accordance with previous observations the lifetime decreases with energy gap on going from LL = dpp to LL = dpq, however the lifetime increases with energy gap on going from LL = dpq to LL = dpb. In the past grant period, we have identified several examples from our own work, and from that of other workers, in which the effect is very important. For instance, $[Os(tpy)_2]^{2+}$ has a lifetime of 296 ns with λ_{max} for emission of 736 nm. The less rigid, less delocalized $[Os(bpy)_3]^{2+}$ exhibits a lifetime of only 60 ns at an even higher energy gap (λ_{max} = 709 nm). We have designed the new ligand bbpe to take advantage of this effect. The dimer $[(bpy)_2Os\ (bbpe)Os(bpy)_2]^{4+}$ exhibits a lifetime (52 ns) comparable to $[Os(bpy)_3]^{2+}$ even though λ_{max} > 850 nm. Clearly, this work has set the stage for designing useful complexes with lifetimes sufficient to undergo intermolecular electron and energy transfer, independent of other excited state properties such as energy gap.

Metal-centered dd states. The above discussion of excited state lifetime does not include the impact of competing excited states. These states can be a large and pervasive problem with the use of Ru(II) polypyridyl complexes. For instance, at room temperature in fluid solution ~25% of excited state deactivation of the lowest manifold of MLCT excited states of $[Ru(bpy)_3]^{2+}$ can be attributed to population of low-lying dd excited states which rapidly decay back to ground state. These states become ever more important in complexes which do not incorporate three bidentate ligands. In the absence of the chelate effect, $[Ru(bpy)_2(py)_2]^{2+}$ exhibits a quantum yield for photo-decomposition of 0.2, rendering the complex all but useless for spectroscopic studies.

We have applied our tris-heteroleptic strategy to this problem in a unique way. Since the disposition of the dd state above ground state is a factor of the overall ligand field that the metal experiences, incorporation of a weaker field ligand into a complex could be compensated for by the concomitant incorporation of a very strong field ligand. The energy above ground of the lowest MLCT is primarily an effect of the ease of reduction of the best acceptor ligand in the coordination sphere. The heteroleptic approach gives us for the first time the ability to control these factor independently so that complexes can be designed with very large MLCT-dd state energy gaps. Large energy gaps should retard population of the dd state and photo-decomposition. To this end, we prepared a series of heteroleptic pyridine-containing complexes and measured the photo-decomposition quantum yields. The yields were found to vary according to predictions so that, in the best case, $[Ru(dmb)(bpy(COOEt)_2)(py)_2]^{2+}$ exhibits a quantum yield that could only be placed at $< 1 \times 10^{-4}$. For the first time, then, we are no poised to prepare complexes in this class with confidence that they will be sufficiently stable not only for spectroscopic investigation, but possibly for practical application to a light to chemical energy conversion device.

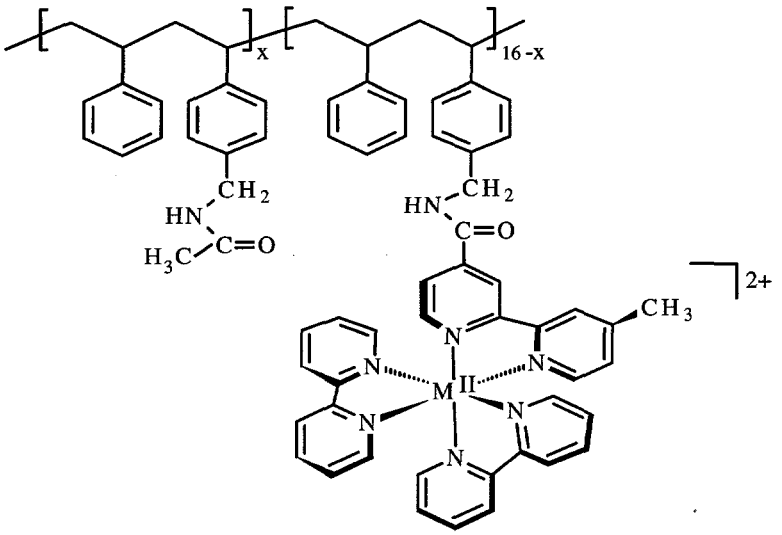
Vibrational spectroscopy. We have put to use both time resolved resonance Raman (TR^3) and time resolved infrared (TRIR) spectroscopy throughout the last grant period. For example, in our work with the polymetallic complexes $[(NC)(bpy)_2Ru^{II}(CN)Ru^{II}(bpy)_2(CN)]^+$, $[(NC)(bpy)_2Ru^{II}(CN)Ru^{II}(phen)_2(CN)]^+$, $[(NC)(phen)_2Ru^{II}(CN)Ru^{II}(bpy)_2(CN)]^+$, $[(NC)(bpy)_2Ru^{II}(CN)Ru^{II}(bpy)_2(NC)Ru^{II}(bpy)_2(CN)]^{2+}$, $[(NC)(bpy)_2Ru^{II}(CN)Ru^{II}$-$(bpy(COOH)_2)_2(NC)Ru^{II}(bpy)_2(CN)]^{2+}$, and model monomeric complexes, we observed TR^3 spectra including vibrations from only a single reduced ligand. This experiment has allowed us to unequivocally prove that the excited electron is localized on the polypyridine ligand of the N-bound (to bridging CN^-) chromophore. These results, coupled with visible transient absorbance data have also allowed us to refute former assumptions of delocalization across the bridging ligands. Recent TRIR studies confirm these results.

We have been able to probe intramolecular electron transfer utilizing this technique applied to complexes incorporating the monoquat cation (MQ^+ or N-methyl-4,4'-bipyridinium). In both $[Ru(CO)_3(bpy)(MQ)]^{2+}$ and $[(bpy)_2Os(CO)(MQ)]^{3+}$ the transient spectra verify that $bpy^- \rightarrow MQ^+$ electron transfer proceeds in < 7 ns. Interestingly, spectral comparison with model ligands such as 4,4'-bipyridine have allowed us to determine that the two pyridyl rings assume a coplanar arrangement in the excited state so that the excited electron can be delocalized over the entire ligand. Presently, we are applying these techniques to the newly available tris-heteroleptic compounds in order to verify the nature of the lowest-lying excited state (e.g. the ultimate acceptor ligand).

Long Range Electron and Energy Transfer in Soluble Polymers. In earlier work, we derivatized a styrene-*p*-chloromethylstyrene copolymer with polypyridine complexes of ruthenium(II) and osmium(II), and with organic donors and acceptors, by nucleophilic displacement of the chloride atoms in basic conditions. A series of polymers containing mostly ruthenium, and some osmium traps was prepared to study long-range energy transfer. Analysis of time-resolved and steady-state data revealed that rapid energy transfer $Ru^{II*} \rightarrow Os^{II}$ ($\tau < 5$ ns) was occurring only from Ru(II) sites directly adjacent to Os(II).

During this grant period, we successfully prepared a new series of soluble metallopolymers based on amide-derivatized styrene-*p*-aminomethylstyrene, containing, on the average, 16 repeat units. The amino-copolymer was prepared by treating styrene-*p*-chloromethylstyrene with potassium phtalimide and then with hydrazine monohydrate. The derivatization chemistry is based on amide coupling to the amino polymer. The aminated polymer was derivatized by reaction with a stoichiometric amount of acid-functionalized metal complexes, $[M^{II}b_2b\text{-}COOH](PF_6)_2]$ ($M^{II} = Ru^{II}$, Os^{II}; b = 2,2'-bipyridine, b-COOH = 4'-methyl-2,2'-bipyridine-4-carboxylic acid), in the presence of a coupling reagent. The remaining amino sites were capped by the acetyl group by treatment with acetic anhydride. Samples of varying composition PS-NHCO-$[Ru^{II}_xMe_{16-x}](PF_6)_{2x}$ (x = 4, 7, 9, 12, 16) and PS-NHCO-$[Os^{II}_xMe_{16-x}](PF_6)_{2x}$ (x = 4, 8, 16) have been prepared where M^{II} is an abbreviation for $[M^{II}b_2b\text{-}CONH\text{-}]$ (M = Ru, Os) and Me for the methyl of the acetamide group. The repeat unit of the amide polymer derivatized by metal complex addition is illustrated below. Compositions were determined by ^{1}H-NMR and infrared spectroscopy.

Photophysical properties of the samples have been studied as a function of loading and of solvent. All exhibit characteristic metal-to-ligand charge transfer absorption and emission which are only slightly solvent dependent. In some cases, luminescence decays are non-exponential but could be fit to a sum of two exponentials. We have shown also that quantum yields and kinetic decay parameters are dependent on solvent, extent of loading, and incident excitation intensity.



Following this preliminary work, we prepared some mixed metallopolymers containing ruthenium, osmium and anthracene in order to determine the influence of the anchoring group on energy transfer rates. The emission of PS-NHCO-$[Ru^{II}_4Os^{II}_4\ Me_8](PF_6)_{16}$ and PS-NHCO-$[Ru^{II}_{13}Os^{II}_3](PF_6)_{32}$ in acetonitrile, following excitation wavelengths between 380 and 540 nm showed almost complete quenching of the $^3MLCT(Ru^{II})$ and sensitization of $^3MLCT(Os^{II})$. Analysis of the decay traces confirm fast, energy transfer from Ru^{II}* to Os^{II} ($\tau < 5$ ns), as well as efficient intramolecular energy migration between Ru^{II}*and Ru^{II} ($k = 5.4 \times 10^7\ s^{-1}$). We were able to show also that the efficiency of energy transfer, which is about 95% in the mixed ruthenium, osmium samples in acetonitrile can be tuned in two different ways. First, in a more polar solvent such as MeOH/EtOH, the polymer adopts a more extended structure leading to a decrease in the efficiency of energy transfer. On the other hand, when the acetyl groups are replaced by anthracene, less residual ruthenium emission is detected, indicating more efficient energy transfer. We are now investigating the mechanism of this energy transport, whether it occurs *via* a Dexter-type or Förster-type mechanism.

In more recent work, we turned our attention toward the study of photoinduced electron transfer using mixed metallopolymeric samples containing polypyridine complexes of ruthenium and PTZ (phenothiazine) as the reductive quencher or $MV(PF_6)_2$ (methyl viologen dication) as oxidative quenchers. We started by investigating intermolecular electron transfer using 10-methylphenothiazine and paraquat as quenchers. Intermolecular quenching rate constants were determined by studying the variation of quantum yields and lifetimes of excited ruthenium-based polymers and model compounds as the concentration of quencher was varied and by using the Stern-Volmer relationship. We are continuing our efforts now on the study of intramolecular electron transfer. So far, we prepared and spectroscopically characterized samples containing

various proportions of ruthenium and phenothiazine. Emission data revealed significant quenching of ruthenium excited states.

Finally, we synthesized a new polymeric matrix, poly(*p*-aminoethyl)styrene, having controlled molecular weight and narrow molecular weight distribution. Its derivatization with metal complexes is now routinely done in our laboratory. Photophysical properties of this new class of materials is currently under investigation.

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