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PHOTOINDUCED ELECTRON AND ENERGY TRANSFER IN SOLUBLE POLYMERS

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Abstract

In soluble polystyrene polymers that contain polypyridyl complexes of Ru^{II} or Os^{II} it has been possible to demonstrate the existence of intrastrand photochemical electron and energy transfer.

1. Introduction

We are approaching a time when chemical systems may provide a basis for new families of devices. An example is artificial photosynthesis where the goal is to use solar energy to make high energy chemicals. In the application of chemical systems to this problem it is necessary to combine a number of molecular features in the same structure.[1] They include light absorption, spatially directed electron transfer by the utilization of free energy gradients, and the delivery of the photochemically produced oxidative and reductive equivalents to catalytic sites. As in natural photosynthesis, it seems inevitable that in order for these several features to be combined in a single molecular system will require a high level of molecular complexity.

A number of approaches are being explored at the molecular level for creating for artificial photosynthesis molecular assemblies. They

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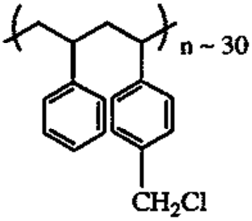
include: 1) "Giant" molecules, in which the desired components are assembled by linear synthesis. 2) Peptide assemblies where the idea is the same but advantage is taken of the Merrifield synthesis in which amino acids are linked to form peptides with controlled spatial compositions. 3) Microstructures in polymeric films. 4) Molecular assemblies on surfaces and interfaces. 5) Membranes where there is a basis for assembling multiple components.

Another approach is based on soluble polymers. Soluble polymers have been prepared which contain organic or transition metal chromophores or combinations of chromophores and electron transfer groups.[2-4] Collective phenomena have been observed in these molecules such as fast, site-to-site energy transfer hopping and photochemically induced electron transfer.

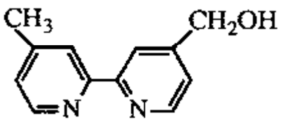
In our use of soluble polymers we have chosen to use preformed polymeric backbones which are capable of being derivatized. The thought was to take advantage of what was already known about a particular polymeric system and modify it chemically by attaching appropriate groups whose photochemical, electron transfer, or energy transfer properties had already been established in solution.

The particular polymeric system that was chosen for study was a ~1:1 copolymer of styrene and chloromethyl styrene. The copolymer was chosen because of its desirable solubility properties.

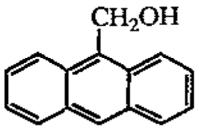


It was prepared by free radical (AIBN) polymerization[5] to give samples with n~30.[5] Samples prepared in this way are atactic and polydisperse with M_n/M_w ~2.4 where M_n and M_w are the number and weight average molecular weights.

The desirable feature of this polymer was the availability of the chloromethyl group. It provided a basis for chemically modifying the polymer at will based on straightforward, organic nucleophilic substitution reactions.[6] We have utilized a number of different procedures for the displacement chemistry. For example, under strongly basic conditions, with a stoichiometric amount of added base, alcohol derivatives are converted into alkoxides which displace chloride quantitatively to form ether links. These reactions occur under mild conditions at room temperature and take several hours to reach completion. Examples of alcohol derivatives that have been attached in this way include, $[Ru(bpy)_2(bpyCH_2OH)](PF_6)_2$ and $AnCH_2OH$. Characterization of the samples with regard to composition has been based on ^{1}H-nmr, IR, elemental analyses, and routine electrochemical and spectroscopic measurements.



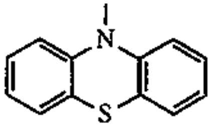
($\mathrm{bpyCH_2OH}$)



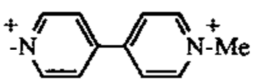
($\mathrm{AnCH_2OH}$)

Since the displacment reactions are essentially quantitative, it is possible to prepare samples containing more than one added group simply by recycling already modified polymers through the displacment procedure in the presence of a second component. This synthetic chemistry and its flexibility offer the promise of preparing complex molecules having properties that can be varied systematically. However, it is important to realize that these procedures only allow the compositions of the resulting materials to be varied. There is no control over the spatial distribution of sites along a single polymeric strand.

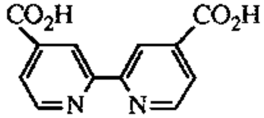
The nucleophilic displacement chemistry has been extended to other bases. These reactions have resulted in samples that contain controlled loadings of phenothiazene (PTZ), a pyridinium derivative ($\mathrm{PQ^{2+}}$) ,and the carboxyalato substituted complex $[\mathrm{Ru(bpy)_2(4,4'\text{-}(CO_2H)_2bpy)}]^{2+}$.



(-PTZ)



($\mathrm{-PQ^{2+}}$)



($\mathrm{4,4'\text{-}(CO_2H)_2\text{-}bpy}$)

As examples, samples were prepared of compositions $[\mathrm{PS\text{-}PTZ_3}]$, $[\mathrm{PS\text{-}PQ^{2+}{}_9}](\mathrm{PF_6})_{18}$, and $[\mathrm{PS\text{-}Ru^{II}{}_3}](\mathrm{PF_6})_6$. In these formula the attached groups are shown by the abbreviations, PTZ, etc. with $\mathrm{Ru^{II'}}$ used as an abbreviation for $[Ru(bpy)_2(4,4'\text{-}CO_2H)_2bpy)]^{2+}$ with one of the carboxylato groups bound to the polymer by an ester link. The subscripts indicate the number of sites substituted out of the ~30 available on an average polymeric strand. The added sites retain their electron transfer characteristics as shown by electrochemical measurements.

With these derivatized polymers in hand, it was possible to carry out the polymer-based analog of the sequence of reactions in Scheme 1 as demonstrated by laser flash photolysis.[8]

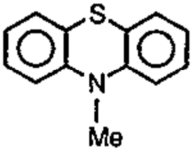
SCHEME 1

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} Ru(bpy)_3^{2+*}$$

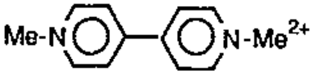
$$Ru(bpy)_3^{2+*} + \text{10-MePTZ} \longrightarrow Ru(bpy)_3^{+} + \text{10-MePTZ}^{+}$$

$$Ru(bpy)_3^{+} + PQ^{2+} \longrightarrow Ru(bpy)_3^{2+} + PQ^{+}$$

$$\overline{\text{10-MePTZ} + PQ^{2+} \xrightarrow{h\nu} \text{10-MePTZ}^{+} + PQ^{+}}$$



(10-MePTZ)

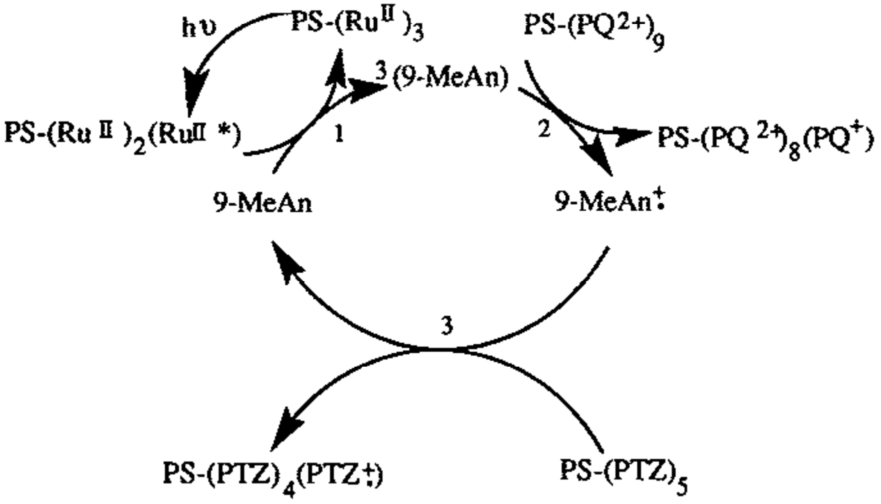


(PQ^{2+})

This was an important sequence when it was first reported since it demonstrated the feasibility of utilizing excited state quenching and sequential electron transfer to obtain separated redox equivalents in solution. When the same experiment was conducted, but with solutions dilute in the three polymers, $[PS\text{-}PTZ_3]$, $[PS\text{-}PQ^{2+}{}_9](PF_6)_{18}$, and [PS-

$Ru^{II}{}_3](PF_6)_6$, no excited state quenching occurred and there was no evidence for electron transfer products. However, in the presence of sufficient anthracene to quench polymer bound Ru^{II*}, the series of events shown in Scheme II occurs.[9]

SCHEME 2

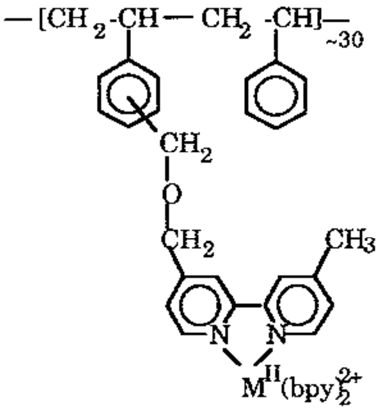


In the series of reactions anthracene acts as a shuttle amongst the three separate polymeric strands. In the first step it quenches the metal-to-ligand charge transfer (MLCT) excited state of the complex. The resulting triplet excited state of anthracene is relatively long-lived and diffuses to a second strand containing $-PQ^{2+}$ where oxidative electron transfer occurs. The anthracene cation which is produced in this step makes a third shuttle to a polymeric strand containing -PTZ where it is reduced and -PTZ oxidized.

This is an important experiment for two reasons. One is that back electron transfer between $-PQ^+$ and $-PTZ^+$ is slowed by factor of ~100 compared to the case in Schema I because of the diffusional characteristics of the redox sites on the polymeric strands. More importantly, the experiment demonstrates that is possible to carry out photochemically induced redox splitting with the resuctive and oxidative equivalents isolated on separate polymeric strands which opens some interesting possibilities for the future in such areas as artificial photosynthesis.

Heavily Loaded Polymers

Polymeric samples have been prepared in which each of the available chloromethyl groups on the separate polymeric strands is substituted by $[M(bpy)_2(bpyCH_2OH)](PF_6)$ (M = Ru, Os).[10,11] The generic structure of the repeating units in the resulting polymers is illustrated below.



$M = \mathrm{Ru}$: $[\mathrm{PS\text{-}Ru}^{II}_{30}](\mathrm{PF}_6)_{60}$

Os: $[\mathrm{PS\text{-}Os}^{II}_{30}](\mathrm{PF}_6)_{60}$

In these materials the diameter of the individual complexes (~14 Å) is significantly greater than the unit repeat distance along the polymeric backbone (5-6 Å). As shown below, these relative dimensions have important implications for intratrand transport properties. A molecular modeling study has been conducted by treating the complexes as dicationic spheres of diameter 14 Å.[12] These calculations show that interstrand rotations that would lead to coiled structures are excluded because of the relatively large fraction of the total molecular volume occupied by the complexes. This calculation also gives an average distance of separation between the peripheries of adjacent complexes of ~7 Å in structures that are minimized in energy. Local segmental motions exist which allow for closer contact between sites, but they represent high energy structures.

As might have been expected for samples like these which contain a high local concentration density of Ru-bpy chromophores, the highly loaded samples have some unusual photophysical properties.[11] There are shifts in the emission spectrum compared to the model $[Ru(bpy)_2(bpyCH_2OH)^{2+}$. Under some conditions, MLCT excited state decay can be decidedly non-exponential on the highly loaded polymers. The degree of non-exponentiality depends on solvent and light intensity with the effect increasing as the light intensity increases. In 1,2-dichloroethane the effect is magnified and in acetronitrile it is minimized. The decay data can be satisfactorily fit to the function shown in eq 1 for all light intensities and

$$I(t) = \gamma\ t^{\alpha-1}e^{-(\beta)^{\alpha}} \tag{1}$$

all solvents.[12] In eq 1, I(t) is the intensity of the incident light at time, t, and γ, α, and β are empirical constants. Equation **1** is the first derivative, with respect to time, of the Kohlrausch/Williams-Watts function[13] which has been derived and applied to described relaxation in disordered media.[14]

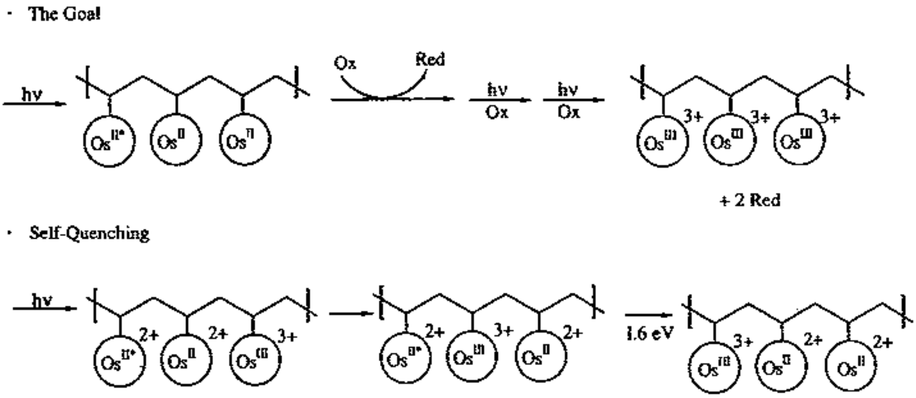
In polymeric samples that are dilute in complex, for example $[PS\text{-}Ru^{II}{}_3](PF_6)_6$, the excited state behavior is essentially superimposable with that of the model $[Ru(bpy)_2(bpyCH_2OH)]^{2+}$. The nonexponential behavior in the highly loaded polymers is clearly a consequence of the high effective local density of metal complex sites. From the available results, it is an excited state and not a ground state phenomenon.

There may be short timescale processes (such as self-quenching by adjacent excited states) that occur on timescales that are short compared to the resolution of our instrument (~5 ns). However, the nonexponential behavior observed at $\tau > 5$ ns has a different origin. For example, energy transfer hopping amongst sites is relatively slow, see below. Microscopically, the nonexponentiality may arise from polarization effects in the surrounding solvent and the local polymeric backbone created when an excited state is formed.. When a second excited state is created near the first, it senses these effects and decays in a different environment which leads to a distribution of decay times.

It is also possible to carry out photochemistry with the highly loaded polymers. One of our interests in polymeric systems was the possibility of utilizing their implied capability of behaving as multiple electron oxidants or reductants. In principle, this could be important in creating a basis for energy transduction between single photon, single electron events and the multi-electron demands of small molecule reactions such as the reduction of CO_2 or the oxidation of H_2O.[10] In either of these cases, any mechanism involving one electron steps is energetically untenable since intermediates such as $CO_2^{\cdot-}$ or HO· are of high energy content.

The ability to create and store multiple redox equivalents on a single polymeric strand would appear to be self-defeating, at least at first glance. The problem is illustrated in Scheme III for a highly loaded sample of the Os^{II} polymer based on $[Os(bpy)_2(bpyCH_2OH)]^{2+}$. Once excitation and electron transfer quenching have occured, oxidative equivalents, as Os^{III}, appear on the individual polymeric strands. If the next excitation act were to occur at a site adjacent to Os^{III}, electron transfer from Os^{II*} to Os^{III} is favored by -1.6 eV and this would lead to unproductive quenching of the excited state. Even if excitation occurs at a nonadjacent site, mechanisms exist for bringing the oxidized site to the excited state or vice-versa. In the first case, the oxidized site would be transported by electron transfer hopping and in the second the excited state would be transported by energy transfer hopping.

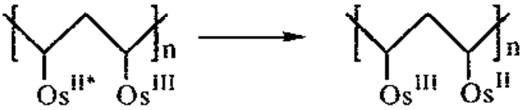
SCHEME 3



In fact, both CW photolysis and time-resolved, laser-flash experiments reveal that it <u>is</u> possible to build up multiple oxidative equivalents on single strands of the highly loaded Ru and Os polymers.[10] There is some variation in rate constants and quantum yields for quenching of the remaining Os^{II*} sites as oxidation proceeds, but complete oxidation of Os^{II} to Os^{III} can be achieved when $[(PS\text{-}Os^{II}{}_{30}](PF_6)_{60}$ is photolyzed with an excess of the irreversible oxidative quencher [p-

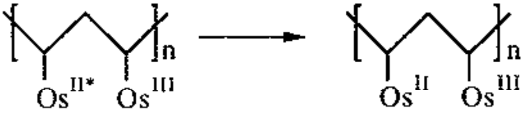
$CH_3OC_6H_4N_2](BF_4)$. Lifetime measurements as a function of mole fraction of Os^{III} on the individual strands reveal that τ for Os^{II*} is unaffected as $\chi_{Os^{III}}$ increaseS from 0 to 0.9. These experiments reveal that quenching of Os^{II*} by an adjacent Os^{III} is slow compared to normal excited state decay. The two processes are compared in Scheme 4.

SCHEME 4



$\Delta G^\circ = 1.6$ eV

k (CH_3CN, 295 K) < 1×10^7 s^{-1}



$\Delta G^\circ = 1.6$ eV

k (CH_3CN, 295 K) = 2.2×10^7 s^{-1}

As shown in the scheme, oxidative quenching gives the same net result as excited state decay except that the site of oxidation is shifted. This reaction is relatively slow because it is highly favored and occurs in the inverted region where $-\Delta G^\circ > \lambda$; ΔG° is the free energy change and λ the reorganizational energy.[15] It is the effect of the inverted region on the rate of oxidative quenching that allows for multiple redox equivalents to accumulate on single polymeric strands.

We have also investigated the ability of the highly loaded polymers to undergo multiple photon, multiple electron transfer by carrying out photolyses in intense transient laser beams in the presence of an excess of quencher. The experiment that was conducted involved the photolysis of $[PS\text{-}Ru^{II}{}_{30}](PF_6)_{60}$ in the presence of a large excesss of PTZ. Laser excitation of $[Ru(bpy)_3]^{2+}$ in the presence of PTZ is followed by reductive quenching to give PTZ^+ and $[Ru(bpy)_3]^+$, Scheme 1.

The same experiment was conducted, but as a function of incident laser irradiance with $[PS\text{-}Ru^{II}{}_{30}](PF_6)_{60}$ and an excess of PTZ in acetonitrile. It was possible to show with these results that at high laser irradiances up to ~1/3 of the available sites on the individual polymeric strands could be photoreduced.[16]

Intrastrand Electron and Energy Transfer

In constructing even more complex polymeric systems that contain more than one functional group, it was important to establish the properties of the polymers toward intrastrand electron and energy transport. For example, is electron transfer quenching at one site on a polymeric strand followed by intramolecular electron transfer down the polymeric chain? This is an important property if redox equivalents are to be delivered to a catalytic site, for example.

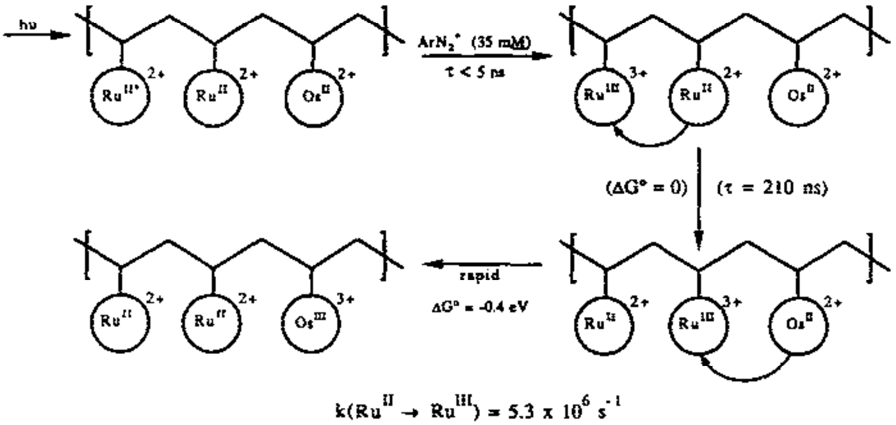
We have explored the question of transport by turning to mixed-chromophore polymers. The first set of experiments were conducted on on the polymer $[PS\text{-}Ru_{25}{}^{II}Os_5{}^{II}](PF_6)_{60}$. The exchange of Os^{II} for Ru^{II} in

$[PS\text{-}Ru^{II}{}_{30}](PF_6)_{60}$ is appealing since in terms of charge and molecular size, it is an isomorphous replacement. From studies on $[PS\text{-}Ru^{II}{}_{30}](PF_6)_{60}$ and $[PS\text{-}Os^{II}{}_{30}](PF_6)_{60}$ average lifetimes for Ru^{II*} and Os^{II*} are ~ 1.13 (±0.05) μs and ~46 (±5) ns at irradiances of 4.3×10^{-2} einstein/cm^2-s. The difference in excited stae energies is ~0.4 eV. From electrochemical measurements the Os^{II} sites are easier to oxidize than the Ru^{II} sites by 0.4 V.

The light absorption characteristics of $[PS\text{-}Ru^{II}{}_{25}Os^{II}{}_{5}](PF_6)_{60}$ are dominated by Ru^{II}, and given the difference in lifetimes between Ru^{II*} and Os^{II*}, it is possible to carry out essentially selective excitation and quenching at Ru^{II}. We have taken advantage of this fact to study intramolecular electron transfer in the mixed sample. In these experiments we once again utilized the irreversible oxidative quencher $[p\text{-}MeOC_6H_4N_2](BF_4)$ in this case at sufficiently high concentrations that complete quenching of Ru^{II*} occurred in < 5 ns. Following oxidative quenching, intramolecular electron transfer between Ru^{III} and Os^{II} can be monitored by spectroscopic measurements following laser flash photolysis. The overall series of reactions that occur are shown in scheme 5.[17]

SCHEME 5

• CH_3CN, 298°, $[PS\text{-}Os_5^{II}Ru_{25}^{II}](PF_6)_{60}$ + 35 m$\underline{M}$ $(p\text{-}MeOC_6H_4N_2)(BF_4)$



In these samples, each Os^{II} on the average is separated from the next by five Ru^{II} sites. Electron transfer from Os^{II} to a nearest neighbor Ru^{III} would be too rapid to be observed on the timescale of measurement (~5 ns) since it is favored by -0.4 eV. These reactions are expected to have small reorganizational energies. The self-exchange rate constant for the $[Ru(bpy)_3]^{3+/2+}$ couple in CH_3CN is $k(\mu = 0.05) = 8$ x 106 $\underline{M}^{-1}s^{-1}$.[18] The actual kinetic event observed in the laser flash photolysis experiments is net $Os^{II} \rightarrow Ru^{III}$ electron transfer but rate limited by site to site $Ru^{II} \rightarrow Ru^{III}$ electron transfer hopping as indicated in Scheme 5. From our experimental measurements, we estimate a lower limit for the rate constant of intramolecular site to site hopping of $\geq 5.3 \times 10^6$ s^{-1} in CH_3CN at 298 K. This value is lower, within an order of magnitude of the rate constant for electron transfer within an association complex between

$[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{3+}$ k ~ 3 x $10^7 s^{-1}$, as estimated from the $[Ru(bpy)_3]^{3+/2+}$ self-exhange rate constant.

Intramolecular energy transfer from Ru^{II*} to Os^{II} in $[PS\text{-}Ru^{II}{}_{25}Os^{II}{}_5](PF_6)_{60}$ must be slower with k(22°, CH_3CN) < 2 x 10^5 s^{-1}. This conclusion follows from our experimental observations. If energy transfer hopping from Ru^{II*} to Ru^{II} were rapid, complete quenching of the Ru^{II*} emission would have been observed along with the appearance of Os^{II*} based emission. In fact, no evidence for significant experimentally quenching was observed by either lifetime or quantum yield measurements even though energy transfer is spontaneous by -0.4 eV.

Given the electron transfer result, this is somewhat perplexing. Further, in a recent set of experiments, M. Furue and co-workers have demonstrated that relatively facile energy transfer occurs from $Ru^{II*} \rightarrow Os^{II}$ in a series of covalently-linked complexes $[(bpy)_2Ru(L)Os(bpy)_2]^{4+}$ where the L are bpy ligands linked by $-(CH_2)n-$.[19] For example, for the complex $[(bpy)_2Ru(L)Os(bpy)_2]^{4+}$ with n = 2, k(CH_3CN, 298) = 8.3 x 10^8 s^{-1} as determined by time-correlated single photon counting.

At this early stage we can only conclude that there is a surprising inhibition to $Ru^{II*} \rightarrow Os^{II}$ energy transfer in $[PS\text{-}Ru^{II}{}_{25}Os^{II}{}_5](PF_6)_{60}$. The explanation for the effect may lie in the results of the molecular modeling study which suggested that in energetically favorable conformations, a separation distance of ~7 Å exists between the metal complex sites on the polymeric strands. A requirement for relatively close contact between the donor and acceptor for exchange energy transfer is expected and that may be inhibited in the polymers.

We have been able to demonstrate that facile, intrastrand energy transfer can occur in a different polymer. These experiments were conducted on polymers containing both bound $[Ru(bpy)_2(bpyCH_2OH)]^{2+}$ and the alcohol-substituted anthracene derivative $AnCH_2OH$ shown above. The photophysical properties of a series of samples in which the -An/Ru^{II} ratio was varied, e.g. $[PS\text{-}Ru^{II}_3An_6](PF_6)_6$, $[PS\text{-}Ru^{II}_3An_{21}](PF_6)_6$ was studied by laser flash photolysis. From the results of these experiments we were able to conclude that intrastrand energy transfer can occur and by two different types of mechanism.[20] For example, for the sample, $[PS\text{-}Ru^{II}_3An_6](PF_6)_6$, it was possible to time resolve the appearance of the anthryl triplet following laser flash excitation of Ru^{II} by monitoring the growth in absorbance at 430 nm. In $ClCH_2CH_2Cl$ (DCE) at room temperature, $k(DCE, 298) = 7.6 \times 10^6\ s^{-1}$ for energy transfer from Ru^{II*} to -An. It appears that in relatively lightly loaded samples the mechanism for intrastrand quenching is by local segmental rotation and intrastrand coiling which brings the donor and acceptor sites into close proximity. The evidence for this conclusion comes from the results of two different types of experiment. In one, the rate constant for energy transfer was found to decrease with increasing viscosity as expected for a process limited by rotational diffusion.[21] In the second, there was no evidence of intrastrand energy transfer for the polymer in a rigid polymethylmethacrylate (PMMA) plastic film where changes in intrastrand conformations can not occur..

An additional energy transfer quenching mechanism appears for the highly loaded polymer $[PS\text{-}Ru^{II}_3An_{21}](PF_6)_6$. In this polymer, on the average, a Ru^{II} chromophore finds an anthryl group as a nearest neighbor. In this case, $Ru^{II*} \rightarrow An$ energy transfer is rapid (< 5 ns in

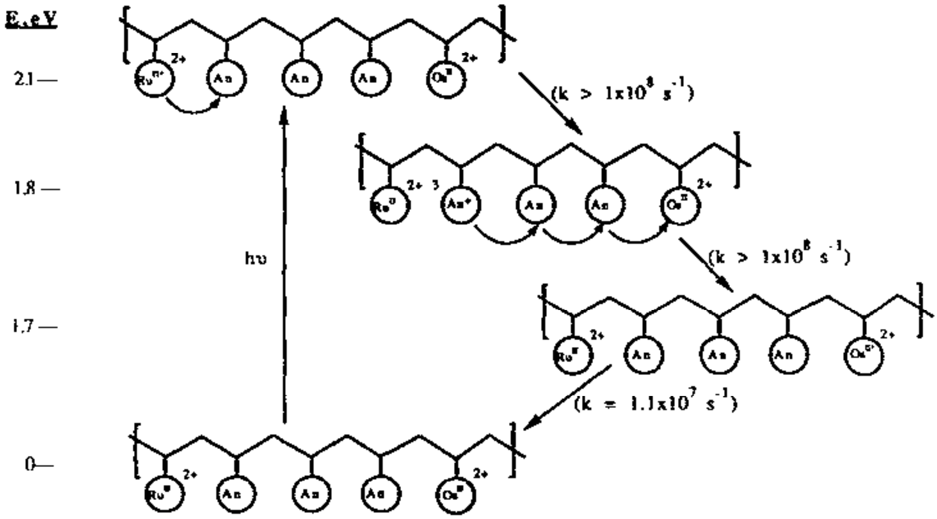
DCE at 25°) based on the quenching of the emission from the MLCT excited state and the prompt appearance of the anthracene triplet as shown by transient absorption measurements.

Although direct energy transfer between Ru^{II*} and Os^{II} was not observed in $[Ps\text{-}Ru^{II}_{25}Os^{II}_{5}](PF_6)_{60}$, it is possible to use the observations of rapid quenching of Ru^{II*} by the anthryl sites to achieve energy transfer between Ru^{II*} and Os^{II} via an indirect, intrastrand shuttle mechanism. In this experiment a polymer was prepared that was lightly loaded in Ru^{II} and Os^{II} with the remaining $-CH_2Cl$ sites heavily substituted by $-AnCH_2OH$. The anthryl triplet is intermediate in energy between Ru^{II*} and Os^{II*} and thus, in principle, could provide an intermediate energy transfer "bridge" between Ru^{II*} and Os^{II}. It has been shown that degenerate energy exchange processes between organic groups on polymeric backbones can be very facile.[2,3a,3d,22]

Laser flash photolysis and emission quantum yield measurments on the polymer $[Ps\text{-}Ru^{II}_{3}An_{17}Os^{II}](PF_6)_{12}$ have been used to demonstrate that energy transfer to Os^{II} does occur following excitation at Ru^{II}.[23] In these experiments nearly complete quenching of Ru^{II*} occurs with Os^{II*} appearing by energy transfer on the timescale of the laser pulse (~5 ns). The sequence of events that appears to occur is illustrated in Scheme 6.

SCHEME 6

• 1,2-DCE, 298°, $[\text{PS-Ru}_3{}^{II}\text{Os}_3{}^{II}\text{An}_{17}](\text{PF}_6)_{12}$



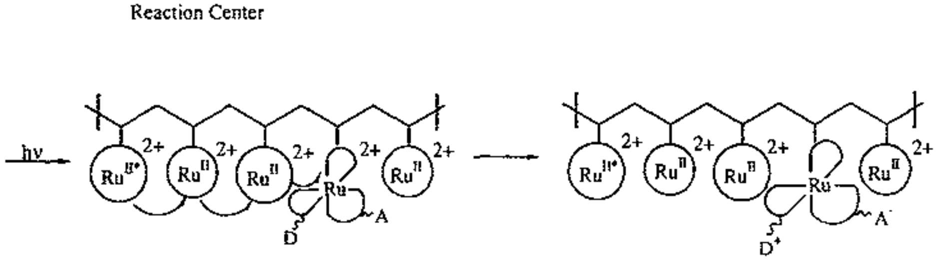
Given the average spacings between Ru^{II} and Os^{II} sites of 3-4 anthryl groups, these experiments demonstrate that long-range energy transfer can occur on individual polymeric strands. Energy transfer occurs with high efficiency with the anthryl chain acting as a "molecular lightpipe" in conducting energy in a spatially controlled way along the polymeric backbone.

Future Experiments

The experimental results that have been described here are encouraging in suggesting the use of the polymers to prepare novel, multifunctional materials. The intrastrand transport properties of these materials are also beginning to emerge. Much remains to be known about the fundamentals of excited state properties and reactivities on the polymers. Nonethelesss, it is possible to look ahead and anticipate new ways that polymers can be utilized in the future.

In our own work we have a series of short-term goals that are currently under investigation. One is illustrated in Scheme 7.

SCHEME 7



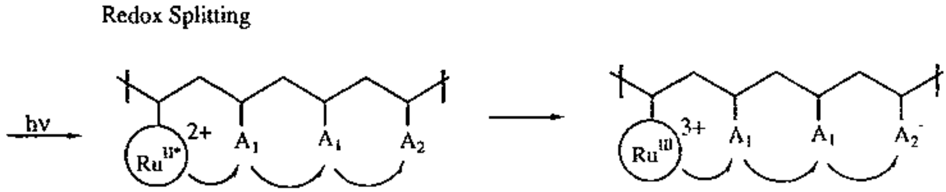
It is an attempt to mimic the various functionalities that appear in the light-harvesting, excited state, electron transfer apparatus in the reaction center of photosynthesis. The idea is to utilize the multiple chromophoric capabilities of modified single polymeric strands: 1) to mimic the antennae effect in the chloroplast, and 2) to bring the excitation energy to a donor-acceptor site where electron transfer occurs to give spatially separated oxidative and reductive equivalents following sensitization of a local MLCT excited state. For the example shown, model systems have already been prepared for the donor-acceptor site[24] and the chemistry required to prepare unsymmetrical, *tris*-chelated complexes that would allow polymer binding is currently under investigation.[25]

In order to overcome slow site to site energy transfer hopping we are exploring two approaches. The first is to use substituent effects on the bpy ligands to ensure that following MLCT excitation, the lowest MLCT excited state will have the electron on the bpy ligand which is attached to the polymeric backbone. Based on the electronic substituent effects of the alkyl groups on $bpyCH_2OH$, the excited electron in $[PS\text{-}M^{II}_{29}M^{II*}](PF_6)_{60}$ (M = Ru,Os) is expected to be on one of the two peripheral bpys away from the polymeric backbone. If the electron can be directed toward the polymeric backbone, it should be obvious in the changes that occur in photophysical properties. For example, solvent effects on lifetimes and emission energies should be strongly affected compared to $[PS\text{-}M^{II}_{29}M^{II*}]^{60+}$. In terms of energy transfer, directing the excited state toward the polymeric backbone will decrease the average separation distance for energy transfer and, hopefully, accelerate intramolecular energy transfer hopping along the polymeric strands.

In a second approach we are attaching to the peripheral bpys organic substituents that are mixed electronically with their π^* systems. This will extend the MLCT excited state radically and "fill in" the space between complexes. This should enhance outer-sphere electronic coupling and intrastrand energy transfer.

A second target that is currently being explored is illustrated in Scheme 8. The goal there is to achieve long-lived redox separation following

SCHEME 8



$$E^{o'}(A_2^{0/-}) > E^{o'}(A_1^{0/-})$$

photoexcitation. This should be achievable on polymeric strands that contain low concentrations of chromophore and two different electron acceptors. One of the acceptors (A_1) is highly loaded and the second (A_2) is highly loaded. The reduction potentials for the two must be poised so that ($E^o(A_2^{0/-}) > E^o(A_1^{0/-})$. Excitation followed by stepwise electron transfer should lead to separated redox equivalents as Ru^{III} and A_2^-. Back electron transfer will be inhibited given the redox potentials of the acceptors since the first step will be an uphill by
$\Delta E_{1/2} = E_{1/2}(A_1^{0/-}) - E_{1/2}(A_2^{0/-})$.

An additional challenge that must be met in this area is to exploit to a greater degree the high level of sophistication that has been achieved in polymer sythesis. Possibilities exist for preparing materials where such features as stereochemistry or tacticity are better controlled or to achieve spatial control by using block copolymers to isolate redox units. We are collaborating in this and related areas with the research group of Professor DeSimone at the University of North Carolina and with their help hope to add a new dimension to the photoinduced electron and energy transfer properties of soluble polymers.

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References

1. Mclendon, G. et al. In Photochemical Energy Conversion, Proc. Int. Conf. Photochem. Convers. Solar Energy Storage, Elsevier: New York, 1989. b) Meyer, T. J. Acc. Chem. Res. 1989, 22, 163. c) Gratzel, M. Ed. Energy Resources through Photochemistry and Photocatalysis, Academic Press: New York, 1983. d) Gust, D.; Moore, T. A. Science, 1989, 35-41.

2. a) Rabani, J. in Photoinduced Electron Transfer, Part B: Fox, M. A.; Chanon, M.; Eds.; Elsevier: New York, 1988. b) Guillet, J., Polymer Photophysics and Photochemistry; Cambridge University Press:Cambridge, 1985. c) Phillips, D. ed. Polymer Photophysics, Chapman and Hall: New York, 1985. d) Winnik, M. A., ed. Photophysical and Photochemical Tools in Polymer Science: NATO-ASI Series; Reidel: Dordrecht, 1986.

3. a) Webber, S. E. Chem. Rev. 1990, 90, 1469. b) Chatterjee, P. K.; Kamioka, K.; Batteas, J. D.; Webber, S. E. J. Phys. Chem., 1991, 95, 960. c) Morsihima, Y.; Kobayashi, T.; Furui, T.; Nozakurg, S. I. Macromolecules 1987, 20, 1707. d) Sienicki, K. Macromolecules 1990, 23, 5025.

4. a) Forster, R. J.; Vos, J. G. Macromolecules 1990, 23, 4372. b) Kaneko, M.; Yamada, A.; Tsuchida, E.; Kurimura, Y. J. Phys. Chem. 1984, 88, 1061. c) Furue, M.; Sumi, K.; Nozakura, S.-I. Chem. Lett., Jpn. 1981, 1349. d) Ennis, P. M.; Kelly, J. M. J. Phys. Chem. 1989, 93, 5735.

5. Arshady, R.; Reddy, B.S.R., George, M.H. Polymer, 1984, 25, 716.

6. Younathan, J. N.; McClanahan, S. F.; Meyer, T. J. Synthesis and Characterization of Soluble Polymers Containing Electron- and energy- Transfer Reagents. Macromolecules, 1989, 22, 1048.

7. a) Schaap, A. P.; Thayer, A. L.;Blossey, E. C.; Neckers, D. C.; J. Am. Chem. Soc., 1975, 97, 3241. b) Cochet, X.; Morteux, A.; Petit, F. C.R. Seances Acad. Sci., Ser. C., 1979,105.

8. Young, R. C.; Meyer, T. J.; Whitten, D. G. J. Am. Chem. Soc. 1975, 97, 4781.

9. Olmsted III, J.; McClanahan, S. F.; Danielson, E.; Younathan, J. N.; Meyer, T. J. J. Am. Chem. Soc. 1987, 109, 3297.

10. Worl, L. A.; Strouse, G. F.; Younathan, J. N.; Baxter, S. M.; Meyer, T. J. J. Am. Chem. Soc. 1990, 112, 7571.

11. Danielson, E.; Worl, L. A.; Murtaza, Z.; Meyer, T. J., in preparation.

12. Danielson, E., personal communication.

13. a) Kohlrausch, R. Ann. 5, 1847, 430. b) Williams, G.; Watts, D. C. Trans. Faraday Soc. 1971,66,80.

14. a) Scher, H.; Lax, M. Phys. Rev., 1973, B7,4491. b) Blumen, A.; Klafter, J.; Silbey, R. Jour. Chem. Phys. 1980,72,5320. c) Schlesinger, M.F.; Fractal Time Defect Diffusion and the Williams-Watss Model of Dielectric Relaxation in Relaxations in Complex Systems, edited by K.L. Ngai and G.B. Wright (NTIS, Springfield, 1984, pp 261-73. d) Dissado, L.A.; Hill, R.M. Proc. Royal Soc. London, 1983, A390, 131. e) Palmer, R.G.; Stein, D.L.; Abrahams, E.; Anderson, P.W. Phys. Rev. Letts. 1984, 53, 958.

15. a) Marcus, R.A.; Discuss Faraday Soc. 1960, 29,21. b) Marcus, R.A., J. Chem. Phys., 1965,45,1261.

16. Jones, Jr., W. E., unpublished results.

17. Jones, Jr., W. E.; Baxter, S. M.; Meyer, T. J., in preparation.

18. Charr, N.S.; Whal, A.C. J. Phys. Chem., 1978, 82,2542.

19. Furue, M.; Yoshidzumi, T.; Kinoshita, S.; Kushida, T.; Nozakura, S.; Kamachi, M. Bull. Chem. Soc. Jpn. 1991, 64, 1632.

20. Baxter, S. M.; Jones, Jr., W. E.; Strouse, G. F.; Meyer, T. J. in preparation.

21. a) Horie, K.; Schanabel, W.; Mita, I.; Ushiki, H. Macromolecules 1981,14, 1422. b) Martinbo, J. M. G.; Sienicki, K.; Blue, D.; Winnick, M. A. J. Am. Chem. Soc. 1988, 110, 773. c) Liu, G.; Guillet, J. E. Macromolecules 1990, 23, 1388.

22. a) Itoh, Y.; Webber, S. E.; Rodjers, M. A. Macromolecules, 1989, 22, 2766. b) Janesevan Rensburg, E. J.; Whittington, S. G.; Macromolecules, 1991, 24, 1969.

23. Strouse, G.F.; Worl, L.A.; Younathan, T.N.; Meyer, T.J. J. Am. Chem. Soc., 1989, 111, 9101.

24. Danielson, E.; Elliott, C. M.; Merkert, J. W.; Meyer, T. J. . Am. Chem. Soc. 1987, 109, 2519.

25. Strouse, G.F. work in progress.