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Communications to the Editor

Long-Range Energy Transfer in a Soluble Polymer by an Energy-Transfer Cascade

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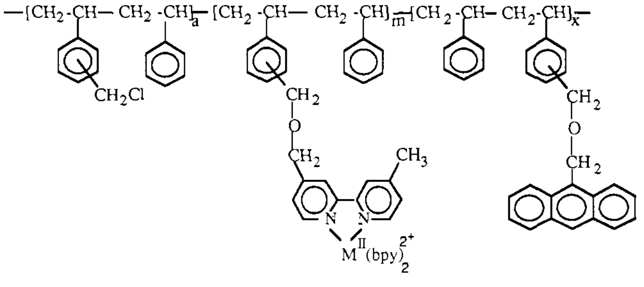
In the study of intramolecular energy or electron transfer, soluble polymers offer the advantage of having multiple sites which can be used to concentrate combinations of chromophores and quenchers within the same molecular framework.[1-4] We have prepared a functionalized 1:1 copolymer of styrene:*m*,*p*-(chloromethyl)styrene that contains (1) a polypyridyl complex of Ru^{II} which upon excitation gives a high-energy metal to ligand charge transfer (MLCT) excited state, (2) a polypyridyl complex of Os^{II} which has a lower energy excited state, and (3) an anthryl derivative based on 9-anthracenemethanol which has a triplet state of intermediate energy. By using this polymer we have been able to demonstrate that, following excitation of the Ru^{II} chromophore, rapid, efficient long-range energy transfer occurs to Os^{II} via an energy transfer cascade mechanism in which the intervening anthryl groups act as energy relays.

The composition of the final polymer and the structures of the Ru^{II}, Os^{II}, and anthryl groups are illustrated below (bpy is 2,2′-bipyridine). Given the method of preparation, the Ru^{II}, Os^{II}, and anthryl groups are located randomly along the backbone of the polymer.

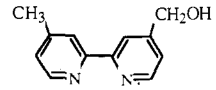


$[PS\text{-}Ru^{II}_3An_{12}Os^{II}_3](PF_6)_{12}$

[a = 12, m = 3 (M = Ru), m = 3 (M = Os), x = 12; a + m + x = 30]

The polymers will be abbreviated by the use of formulas such as $[PS\text{-}Ru^{II}_3An_{12}Os^{II}_3]^{12+}$. In these formulas, the subscript indicates the number of the ~30 available *m*,*p*-chloromethylated sites that are occupied by Ru^{II}, Os^{II}, or OCH_2An.

The anthryl derivative and the complexes $[M(bpy)_2(bpyCH_2OH)]^{2+}$ (M = Ru, Os) were added to the styrene–(chloromethyl)styrene copolymer[5-8] by nucleophilic displacement of Cl^- under basic conditions,[8,9] by using procedures that were described previously.[8b] A polymer in which 10% (3/30) of the available *m*,*p*-chloromethylated sites were used to bind $[Ru(bpy)(bpyCH_2O)]^+$ and 10% to bind $[Os(bpy)(bpyCH_2O)]^+$ was prepared by sequential nucleophilic displacements of chloride by using the complexes as limiting reagents. In the preparation of the mixed Ru^{II},Os^{II} polymer, $[PS\text{-}Ru^{II}_3](PF_6)_6$ (0.41 g, 1.39 mmol),[8b,10c] $[Os(bpy)_2(bpyCH_2OH)](PF_6)_2$ (0.138 g, 0.139 mmol), and $CsOH{\cdot}2H_2O$ (~0.04 g) in 4 mL of DMSO were allowed to react under argon at room temperature for 20 h and purified as described elsewhere.[8b,10a,c] The polymer salt $[PS\text{-}Ru^{II}_3An_{12}Os^{II}_3](PF_6)_{12}$[10b] was prepared by the reaction between $[PS\text{-}Ru^{II}_3Os^{II}_3](PF_6)_{12}$ (0.25 g, 0.71 mmol), 9-anthracenemethanol (0.15 g, 0.71 mmol), and $CsOH{\cdot}2H_2O$ (~0.04 g) under the same conditions.



$(bpyCH_2OH)$

Lifetime and emission spectral studies on $[PS\text{-}Ru^{II}_3Os^{II}_3](PF_6)_{12}$ in 2-methyltetrahydrofuran (2-MeTHF) at 295 ± 2 K show that the separate emissions from the Ru^{II}- and Os^{II}-based MLCT excited states are essentially unperturbed by the presence of the other chromophore. Excitation at 460 nm, where both chromophores absorb appreciably, leads to emission decay profiles that can be satisfactorily fit to two contributors. One has a lifetime of $\tau = 753$ ns, and the second has $\tau = 32$ ns. These lifetimes are consistent with the lifetimes of Ru^{II*} in $[PS\text{-}Ru^{II}_3](PF_6)_6$ (753 ns) and of Os^{II*} in $[PS\text{-}Os^{II}_3](PF_6)_6$ (31 ns) under the same conditions. Emission decays for $[PS\text{-}Ru^{II}_3Os^{II}_3](PF_6)_{12}$ in 1,2-dichloroethane are more complex, suggesting that there may be a minor contribution by energy transfer from Ru^{II*} to Os^{II}. However, emission from Ru^{II*} remains essentially unquenched. From these results, there is no evidence for significant energy transfer from Ru^{II*} to Os^{II} in 2-MeTHF or 1,2-dichloroethane

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(5) Polymer samples were prepared by AIBN (azobisisobutyronitrile) free radical polymerization.[6,7] They were fractionated by gel permeation chromatography in THF by using an IBM LC/9560 solvent delivery system equipped with a LC/9525 differential refractometer detector and styrene–divinylbenzene column types A, C, and E (IBM) connected in order to decreasing pore size. Molecular weights were established by using polystyrene standards. The 1:1 copolymer has a molecular weight distribution of $\bar{M}_W/\bar{M}_n = 2.38$ with $\bar{M}_W = 16\,420$ g mol^{-1} and $\bar{M}_n = 6899$ g mol^{-1}. From the molecular weight, the polymer consists of 30 subunits. Elemental anal. Calcd for 46% chloromethylation of the copolymer ($C_{510}H_{510}Cl_{30}$): C, 80.35; H, 6.76; Cl, 12.90. Found: C, 80.23; H, 6.74; Cl, 12.75.

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(10) (a) Elemental anal. Calcd for ($[PS\text{-}Ru^{II}_3Os^{II}_3](PF_6)_{12}$)($C_{702}H_{672}N_{36}O_6P_{12}F_{72}Cl_{24}Ru_3Os_3$): C, 63.94; H, 5.11; N, 3.83; Cl, 6.42. Found: C, 63.97; H, 5.07; N, 4.72; Cl, 6.58. (b) Elemental anal. Calcd for ($[PS\text{-}Ru^{II}_3An_{12}Os^{II}_3](PF_6)_{12}$) ($C_{882}H_{804}N_{36}O_{18}P_{12}F_{72}Cl_{12}Ru_3Os_3$): C, 60.00; H, 5.30; N, 3.31; Cl, 2.81. Found: C, 59.65; H, 5.54; N, 3.92; Cl, 3.09. (c) Strouse, G. F.; Worl, L. A.; Younathan, J. F.; Meyer, T. J. Manuscript in preparation.

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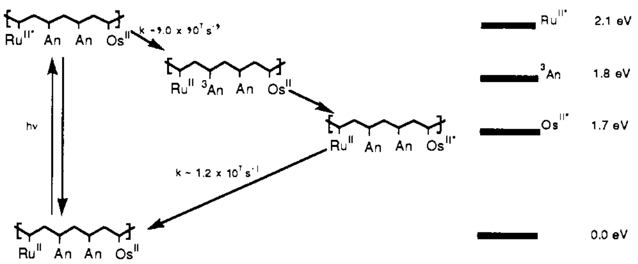
Scheme I



(DCE, 295 ± 2K)

(DCE) in the mixed polymer, reaction 1, even though energy transfer is favored by 0.4 eV. The excited-state energies are 2.1 eV for Ru^{II*} and 1.7 eV for Os^{II*}.[11]

$$\xrightarrow{h\nu} [\text{PS-Ru}^{II}{}_2\text{Ru}^{II*}\text{Os}^{II}{}_3](\text{PF}_6)_{12} \rightarrow [\text{PS-Ru}^{II}{}_3\text{Os}^{II*}{}_1\text{Os}^{II}{}_2](\text{PF}_6)_{12} \quad (1)$$

In the absorption spectrum of [PS-Ru$^{II}_3$An$_{12}$Os$^{II}_3$](PF$_6$)$_{12}$ in polar organic solvents, $d\pi(\text{Os}) \rightarrow \pi^*(\text{bpy})$ transitions appear in the region 410–700 nm, $d\pi(\text{Ru,Os}) \rightarrow \pi^*(\text{bpy})$ transitions from 410 to 550 nm, and vibronically resolved $\pi \rightarrow \pi^*(\text{An})$ transitions from 325 to 400 nm. Excitation of [PS-Ru$^{II}_3$An$_{12}$Os$^{II}_3$](PF$_6$)$_{12}$ in DCE at 460 nm results in a significant (90%) loss in the Ru^{II} emission at 620 nm compared to [PS-Ru$^{II}_2$Ru^{II*}](PF$_6$)$_6$, while the lower energy, Os^{II*}-based emission at 740 nm is enhanced compared to [PS-Os$^{II}_2$Os^{II*}](PF$_6$)$_6$. The lifetime of the Ru^{II*} emission is shortened to ~100 ns compared to the 753-ns lifetime for Ru^{II*} in [PS-Ru$^{II}_3$](PF$_6$)$_2$. Independent experiments on a polymer of composition [PS-Ru$^{II}_3$An$_{12}$](PF$_6$)$_6$ show the same shortened lifetime compared to [PS-Ru$^{II}_2$Ru^{II*}](PF$_6$)$_{12}$ and, from transient absorbance measurements, the appearance of the anthryl triplet at $\lambda_{max} = 430$ nm ($\tau > 5$ μs) following laser flash excitation at 460 nm. From these results, the loss in emission intensity and the decreased lifetimes in [PS-Ru$^{II}_2$Ru^{II*}An$_{12}$Os$^{II}_3$](PF$_6$)$_{12}$ and [PS-Ru$^{II}_2$Ru^{II*}An$_{12}$](PF$_6$)$_6$ can be attributed to intrapolymeric energy transfer from Ru^{II*} to An to give the anthryl triplet, ^{3}An, of energy 1.8 eV.[13]

$$\xrightarrow{h\nu} [\text{PS-Ru}^{II}{}_2\text{Ru}^{II*}\text{An}_{12}](\text{PF}_6)_6 \rightarrow [\text{PS-Ru}^{II}{}_3{}^3\text{AnAn}_{11}](\text{PF}_6)_6 \quad (2)$$

The origin of the quenching of Ru^{II*} in [PS-Ru$^{II}_3$An$_{12}$Os$^{II}_3$](PF$_6$)$_{12}$ is by Ru^{II*} → An energy transfer, but the excited-state energy ultimately reaches Os^{II}. From emission quantum yield studies as a function of excitation wavelength over the range 420–530 nm, Os^{II*} is reached with near unit efficiency even in regions (420–500 nm) where Ru^{II} is a significant light absorber.

The combination of anthryl quenching of Ru^{II*} and the appearance of Os^{II*} leads to the suggested quenching mechanism in Scheme I. Excitation at Ru^{II} is followed by energy transfer, first to An ($\tau \sim 100$ ns) and then to Os^{II}. From the composition of the polymer, on the average there are two intervening anthryl groups between the Ru^{II} and Os^{II} sites. The net effect of adding the anthryl groups to the polymer is to create an energy transfer "cascade" pathway, which allows long-range energy transfer to occur from Ru^{II*} to Os^{II}. The anthryl groups act as intervening energy-transfer relays and act as a "molecular light pipe" in providing a spatial link between the two emissive MLCT chromophores.

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(11) Excited-state energies were calculated from the results of a two-mode Franck–Condon analysis of the emission band shapes that is described in detail elsewhere.[12] These values are in good agreement with excited-state energies estimated as the energy on the low-energy side of the spectral profile where the emission intensity had fallen by 1/4 compared to the maximum.

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Selective Monoacylation of 1,*n*-Diols Catalyzed by Metallic Sulfates Supported on Silica Gel

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It is important for organic synthesis to establish general methods for selective and differential functionalization of the same kind of plural functional groups having similar stereoelectronic and steric factors. Monoprotection or monofunctionalization of polyols is achieved in some cases by carefully controlled reaction conditions,[1] by continuous extraction,[2] by the use of alumina[3] and insoluble polymer supports,[4] or via cyclic compound formation.[5] In the course of studying the dehydration of alcohols catalyzed by metallic sulfates supported on chromatographic silica gel (abbreviation: M$_m$(SO$_4$)$_n$–SiO$_2$),[6] we found that alcohols were acylated in high yields when esters were used as solvents. Here, we report highly selective monoacylation of 1,*n*-diols by transesterification catalyzed by M$_m$(SO$_4$)$_n$–SiO$_2$.

The acylation was quite easy to perform, and the results are summarized in Table I.[7] For the catalysts, several supported sulfates and hydrogen sulfates were examined and were found to show nearly the same order of activity as in the dehydration of alcohols.[6] This result suggests that the characteristics of these catalysts are alike in the acylation and in the dehydration of alcohols.[8] Table I shows that the larger the acyl group of the solvent, the slower the reaction rate of acylation and the higher the selectivity. Figure 1 shows the time dependence of the yields of the products in the acylation of 1,4-butanediol by methyl propionate. The diester appeared when the yield of the monoester reached 90% and most of the diol had been consumed. The maximum value of the slope showing the maximum rate of the monoester formation is roughly twice as large as the value showing the maximum rate of the diester formation. These results may

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(7) For example, M$_m$(SO$_4$)$_n$–SiO$_2$ function as acid catalysts in the dehydration of alcohols.

(8) Changing the solid support from silica gel to neutral alumina, Celite-535, and powdered 3A molecular sieves lowered the catalytic activity and the selectivity in the acetylation of 1,4-butanediol catalyzed by Fe$_2$(SO$_4$)$_3$. Addition of methanol or ethanol lowered reaction rates and the selectivity. For example, 4% of the diester was detected at the 80% yield of the monoester when 2 mmol of methanol was added under the conditions shown in Figure 1.

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