An Antenna Polymer for Visible Energy Transfer

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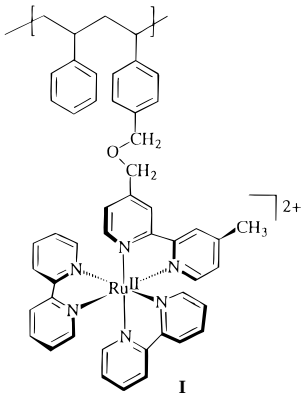
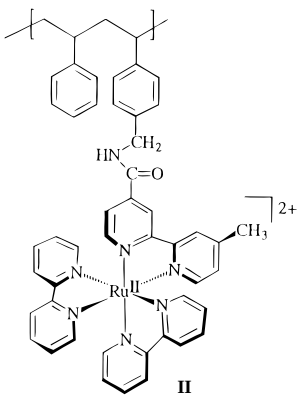
Derivatized polymers provide a versatile platform for creating multifunctional assemblies.[1] This includes polypyridyl complexes of Ru^{II} and Os^{II} which have high absorptivities in the visible based on metal-to-ligand charge transfer (MLCT) transitions.[2,3] An early synthetic strategy for these involved attachment to polystyrene by an ether linkage (**I**). We have developed a new strategy based on amide linkage (**II**)[3] and find that there is a dramatic difference between the two in their ability to promote intrastrand energy transfer.



I



II

The amide polymer was prepared from a 1:1 styrene-*p*-aminomethylstyrene copolymer of polydispersity 1.5 and an average of 16 repeat units.[3] The amide link was formed by reaction with the acid-derivatized complexes, $[M^{II}b_2b\text{-}COOH](PF_6)_2$ (M = Ru, Os; b = 2,2′-bipyridine (bpy), b-COOH = 4′-methyl-2,2′-bipyridine-4-carboxylic acid) by using standard amide coupling conditions (see the Supporting Information).[3] The resulting homopolymer samples are distributions, on the average, containing 16 complexes and abbreviated as [*co*-PS-CH_2NHCO-$(M^{II}{}_{16})](PF_6)_{32}$ (M = Ru, Os). A mixed polymer was prepared by sequential coupling, first to the Os^{II} complex in limited amount (in a ratio of 3:16 relative to available anine sites on the polymer) with isolation and purification and then with the Ru^{II} complex in excess. This gave a polymer of average composition [*co*-PS-CH_2NHCO-$(Ru^{II}{}_{13}Os^{II}{}_3)](PF_6)_{32}$ (**1**). The derivatized polymers were purified and characterized by ^{1}H NMR, IR, UV−vis, and electrochemical measurements, as described previously.[3,4] For example, for mixed polymer **1**, waves for the $Ru^{III/II}$ and $Os^{III/II}$ couples appear at 1.30 and 0.87 V vs SCE in CH_3CN 0.1 M in $[N(n\text{-}C_4H_9)_4](PF_6)$ having the expected relative peak currents of 13:3.

Transient resonance Raman measurements on an ether-linked model complex, $[Ru^{II}b_2b\text{-}CH_2OBz](PF_6)_2$ (b-CH_2OBz is 4-CH_2-OBz-4′-CH_3bpy, Bz is benzyl) in acetonitrile, show that bpy is the acceptor ligand in the lowest MLCT excited state.[5] Transient resonance Raman measurements (Supporting Information) on model complexes for the amide, $[Ru^{II}b_2b\text{-}CONHBz](PF_6)_2$ (b-CONHBz is 4-CONHBZ-4′-CH_3bpy), $[Ru^{II}(b\text{-}CONHBz)_3](PF_6)_2$, $[Ru^{II}b_3](PF_6)_2$, and the polymer [*co*-PS-CH_2NHCO-$(Ru^{II}{}_{16})](PF_6)_{32}$ in acetonitrile reveal that the acceptor ligand is the bpy-amide. This is shown by the appearance of resonantly enhanced bands for b-CONH- radical anion in the region 1000−1700 cm^{-1} at 1594, 1550[a], 1492[a], 1442, 1428, 1332[a], 1286, 1208, 1195, 1127, and 1040 cm^{-1} with 368.9 nm excitation and scattering (the superscript "a" denotes bands which overlap with neutral ligand bands). On the basis of structure **II** and the results of molecular modeling,[4] this means that the excited-state dipole is aligned along the amide ligand oriented toward the polymer backbone and nearest neighbor complexes.

In the ether-linked polymer, [*co*-PS-CH_2OCH_2-$(Ru^{II}{}_{22}Os^{II}{}_5)](PF_6)_{54}$ (**2**), *energy transfer* from Ru^{II}* to Os^{II} is favored by 0.36 eV and occurs rapidly with $k > 2 \times 10^8$ s^{-1} ($\tau < 5$ ns) in acetonitrile solution at room temperature. However, *energy migration* by Ru^{II}* to Ru^{II} self-exchange is slow ($\tau > 1$ μs, $k < 1 \times 10^6$ s^{-1}).[4]

In mixed polymer **1**, there is evidence for both facile energy transfer *and* migration in deaerated acetonitrile at room temperature. This is shown in the emission spectra in Figure 1. These spectra demonstrate that excitation at 460 nm, where Ru^{II} is the dominant light absorber (Figure 2), results in nearly complete Ru^{II}* quenching compared to [*co*-PS-CH_2NHCO-$(Ru^{II}{}_{16})](PF_6)_{32}$ (**3**). There is clear evidence for emission from Os^{II}* as shown by comparison with [*co*-PS-CH_2NHCO-$(Os_{16})](PF_6)_{32}$ (**4**). Emission quantum yields for **3** and **4** are $\phi_{Ru^{II}*} = 5.0 \times 10^{-2}$ and $\phi_{Os^{II}*} = 4.6 \times 10^{-3}$.[3] The efficiency of Ru^{II}* to Os^{II} energy transfer is $\eta_{en} = 0.94 \pm 0.08$ in acetonitrile solution at room temperature with 420 nm excitation, 0.98 with 460 nm excitation, and 0.92 with 500 nm excitation. These values were calculated by using eq 1. A_{Os} and A_{Ru} are the absorbances of Os^{II} and Ru^{II} at the excitation wavelength and I_{RuOs} and I_{Ru} the integrated emission intensities for **1** and **3**.[6,7] In solutions containing comparable concentrations of homopolymers **3** and **4**, there is no evidence for Ru^{II}* quenching.

$$\eta_{en} = \frac{A_{Os}}{A_{Ru}}\left[1 - \frac{I_{RuOs}}{I_{Ru}}\right] \qquad (1)$$

Time-dependent emission and absorption measurements reveal that net energy transfer is rapid with Os^{II}* completely formed during the laser pulse of the apparatus used (5 ns). Emission decay at 800 nm, where Os^{II}* is the sole emitter, occurs with $\tau = 65$ ns ($k = 1.54 \times 10^7$ s^{-1}), the lifetime obtained for Os^{II}* in homopolymer **4**.[3] The decay of the small amount of residual Ru^{II}* emission (<2%), monitored at 600 nm where only Ru^{II}* emits, is nonexponential.[9]

On the basis of the results of molecular modeling calculations, these polymers have extended spatial structures dominated by the large (∼14 Å diameter) metal complex dications.[4] For the ether-linked polymers, the average spacing between the peripheries of nearest neighbor complexes is ∼7 Å and that between

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(2) (a) Younathan, J. N.; McClanahan, S. F.; Meyer, T. J. *Macromolecules* **1989**, *22*, 1048. (b) Margerum, L. D.; Meyer, T. J.; Murray, R. W. *J. Phys. Chem.* **1986**, *90* (12), 2696.

(3) Dupray, L. M.; Meyer, T. J. *Inorg. Chem.* **1996**, *35* (21), 6299.

(4) Jones, W. E.; Baxter, S. M.; Strouse, G. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 7573.

(5) The excited-state resonance Raman spectrum in CH_3CN with 368.9 nm excitation and scattering is essentially identical with $[Ru(bpy)_3]^{2+}$*.

(6) (a) Holden, D. A.; Guillet, J. *Macromolecules* **1980**, *13*, 289. (b) Schiller, P. W. In *Biochemical Fluorescence*, Chen, R. F., Edelhoch, H., Eds.; Marcel Dekker: New York, 1975; Vol. 1, pp 285−303.

(7) The separate Ru^{II}* and Os^{II}* emissions in [*co*-PS-CH_2NHCO-$(Ru^{II}{}_{13}Os^{II}{}_3)](PF_6)_{32}$ were deconvoluted by application of a Frank−Condon-based spectral fitting procedure to each component[8] and constructing the combined emission profile from 500 to 1200 nm.

(8) Claude, J. P. Ph.D. Dissertation, University of North Carolina, Chapel Hill, NC, 1995.

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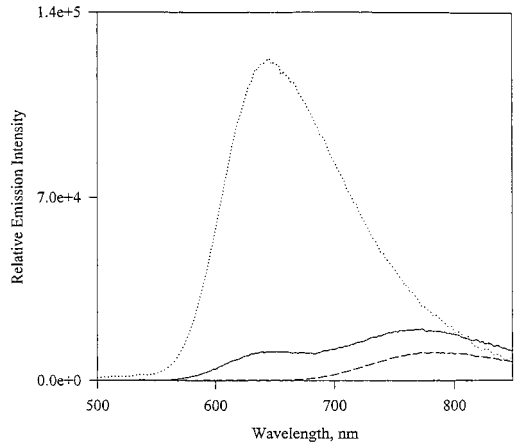


Figure 1. Emission spectra of [*co*-PS-CH_2NHCO-($Ru^{II}_{13}Os^{II}_3$)]$(PF_6)_{32}$ (—), [*co*-PS-CH_2NHCO-(Ru^{II}_{16})]$(PF_6)_{32}$ (•••), and [*co*-PS-CH_2NHCO-(Os^{II}_{16})]$(PF_6)_{32}$ (- - -) (460 nm excitation) in deaerated acetonitrile at room temperature. Emission profiles for the Ru^{II} and Os^{II} homopolymers have been scaled to their relative emission quantum yields.

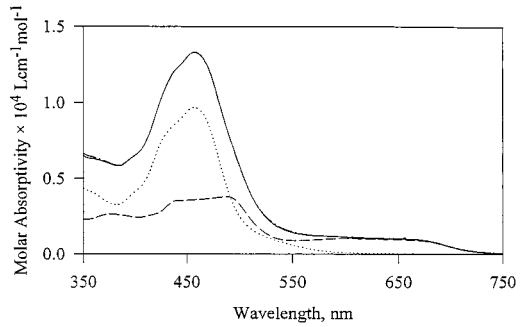
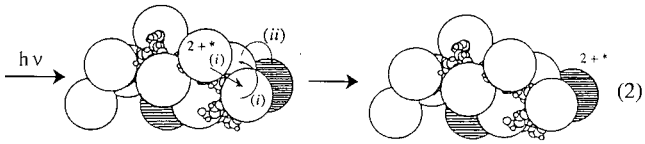


Figure 2. Absorption spectra of [*co*-PS-CH_2NHCO-($Ru^{II}_{13}Os^{II}_3$)]$(PF_6)_{32}$ (—), and a mixture of [*co*-PS-CH_2NHCO-(Ru^{II}_{16})]$(PF_6)_{32}$ and [*co*-PS-CH_2NHCO-(Os^{II}_{16})]$(PF_6)_{32}$ in molar ratio 13:3 (-•-), in CH_3CN at room temperature. The two spectra are nearly completely overlapped. The spectra of the separate Ru^{II} (•••) and Os^{II} (- - -) homopolymers at a 13:3 ratio are also shown.

non-nearest neighbors is ∼21 Å. On the basis of the loading statistics, $\sim^1/_2$ of the Ru^{II} sites on the backbone are not adjacent to Os^{II}. As illustrated in eq 2, with the open spheres representing Ru^{II} and the cross-hatched spheres representing Os^{II}, net energy transfer from Ru^{II}* to Os^{II} requires two processes: Ru^{II}* to Ru^{II} energy migration (k_i in eq 2), for which $\Delta G° =$ eV, and the actual energy transfer step (k_{ii} in eq 2) for which $\Delta G° = -0.36$ eV. On the basis of our results, $k > 2 \times 10^8$ s^{-1} for both migration and transfer.



(2)

For ether-linked polymer **2**, $k_{ii} > 2 \times 10^8$ s^{-1} but energy migration is slow with $k_i < 1 \times 10^6$ s^{-1}.[4] This is a dramatic difference apparently caused by the difference in orientation of the excited-state dipole. The excited-state resonance Raman results show that the dipole is oriented away from the backbone in **2** and toward the backbone in amide-linked polymer **1**. The mechanism of energy transfer may be through space (Förster) or through bond (Dexter), or a combination of the two. In either case, orientation toward the backbone decreases the distance to adjacent chromophones enhancing the rate of energy transfer. The resulting enhancement in k_i of >200 provides a dramatic example of the use of substituent effects to control supramolecular dynamics.

The amide-linked polymers are polychromophoric arrays and intense visible light absorbers with $\epsilon = 214\,000$ L cm^{-1} mol^{-1} per average strand at the absorption maximum of 458 nm for **1**. Intrastrand energy transfer is highly efficient with energy migration ($\tau < 5$ ns) occurring >200 times faster than excited-state decay ($\tau_M = 910$ ns).[3] This opens the possibility of using suitably derivatized polymers as visible light collectors and antenna for sensitizing photoinduced electron transfer, as occurs in the photosynthetic apparatus of green plants.[10]

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Supporting Information Available: Descriptions of the syntheses of the mixed metallopolymer and transient resonance Raman measurements (2 pages). See any current masthead page for ordering and Internet access instructions.

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(9) These emission decays could be fit to the biexponential decay function, $I(t) = a \exp(-k_1 t) + (1 - a)\exp(-k_2 t)$, with $I(t)$ the emission intensity at time t, $k_1 = 4.4 \times 10^7$ s^{-1} ($a = 0.78$), and $k_2 = 6.9 \times 10^6$ s^{-1} in CH_3CN at room temperature. We assume that this emission is from a small fraction of partially quenched Ru^{II}* sites. The average lifetime, τ_M, calculated from, $\tau_M = ak_1 + (1 - a)k_2$ was 50 ns compared to $\tau_M = 910$ ns for pure homopolymer **3** under the same conditions.[3]

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