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Multiphoton, Multielectron Transfer Photochemistry in a Soluble Polymer

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The effects of laser irradiance and quencher concentration on photochemical electron transfer in a Ru^{II}-bpy derivatized, polystyrene polymer have been studied. The polymer was a 1:1 copolymer of styrene:*p*-chloromethylstyrene with, on the average, ∼30 repeat units in which each of the chloro groups was replaced by a $[Ru^{II}(bpy)_2(4\text{-}CH_2O\text{-}4'\text{-}CH_3bpy)]^{2+}$ chromophore by nucleophilic substitution. The abbreviation for the resulting polymer salt is $[co\text{-}PS\text{-}CH_2OCH_2\text{-}(Ru^{II}{}_{30})](PF_6)_{60}$. Upon visible excitation by laser flash photolysis at high irradiances, multiphoton excitation in the presence of high concentrations of the reductive quencher phenothiazine leads to individual polymeric strands that are reduced, on the average, by up to seven electrons to give $PS\text{-}CH_2\text{-}OCH_2\text{-}(Ru^{2+}{}_{23}Ru^{+}{}_{7})]^{53+}$.

Introduction

The metal-to-ligand charge transfer (MLCT) excited states of polypyridyl complexes of Ru^{II} and Os^{II} undergo facile electron transfer as either oxidants or reductants, eqs 1 and 2 (bpy is 2,2′-bipyridine, MV^{2+} is 1,1′-dimethyl-4,4′-bipyridinium ion, DMA is dimethylaniline).[2−5]

$$Ru(bpy)_3{}^{2+*} + MV^{2+} \rightarrow Ru(bpy)_3{}^{3+} + MV^{+} \qquad (1)$$

$$Ru(bpy)_3{}^{2+*} + DMA \rightarrow Ru(bpy)_3{}^{+} + DMA^{+} \qquad (2)$$

Synthetic procedures have been devised for adding or incorporating derivatives of these complexes into soluble polymers, including vinylic derivatives of bpy,[6−9] pyridine,[10,11] or polystyrene.[12−14] For a 1:1 copolymer of styrene:*p*-chloromethylstyrene, a procedure has been devised in which the chloro groups are replaced by polypyridyl complexes of Ru^{II} or Os^{II} with controlled stoichiometries by nucleophilic substitution.[13] An extensive excited-state chemistry has been shown to exist for these polymers including inter- and intrastrand electron and energy transfer.[14a,13d−g]

A special feature of the polymers is that they provide a chemical scaffold for the concentration of multiple chromophores in a single assembly. This raises the possibility of observing multiphoton effects arising from simultaneous, multiple excitations in an array of chemically linked chromophores. Light-intensity-dependent lifetimes have been reported.[14b,c] We

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(2) (a) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759. (b) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: London, 1992. (c) Scandola, F.; Bignozzi, C. A.; Indelli, M. T. *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*; Kluwer Academic: Dordrecht, The Netherlands, 1993. (d) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163. (e) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991. (f) Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. *Top. Curr. Chem.* **1990**, *158*, 73.

(3) (a) Gafney, H. D.; Adamson, A. W. *J. Am. Chem. Soc.* **1972**, *94*, 8238. (b) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 2909. (c) Young, R. C.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 4781. (d) Jones, W. E.; Bignozzi, C. A.; Chen, P.; Meyer, T. J. *Inorg. Chem.* **1993**, *32*, 1167. (e) Treadway, J. A.; Chen, P.; Rutherford, T. J.; Keene, F. R.; Meyer, T. J. *J. Phys. Chem. A* **1997**, *101*, 6824.

(4) Fox, M. A.; Jones, W. E.; Watkins, D. M. *Chem. Eng. News* **1993**, *71*, 1 (11), 38.

(5) (a) Hoffman, M. Z. *J. Phys. Chem.* **1988**, *92*, 3458. (b) Hoffman, M. Z. *J. Phys. Chem.* **1991**, *95*, 2606. (c) Chiorboli, C.; Indelli, M. T.; Scandola, M. A. R.; Scandola, F. *J. Phys. Chem.* **1988**, *92*, 156. (d) Kim, H.-B.; Kitamura, N.; Kawanishi, Y.; Tazuke, S. *J. Am. Chem. Soc.* **1987**, *109*, 2506.

(6) (a) Sumi, K.; Furue, M.; Nozakura, S.-I. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 3059. (b) Sumi, K.; Furue, M.; Nozakura, S.-I. *Photochem. Photobiol.* **1985**, *42*, 485. (c) Furue M.; Sumi, K.; Nozakura, S.-I. *Chem. Lett.* **1981**, 1349.

(7) (a) Barrié, M. S.; Delaire, J. A.; Kaneko, M. *New J. Chem.* **1991**, *15*, 65. (b) Kaneko, M.; Nakamura, H. *Macromolecules* **1987**, *20*, 2265. (c) Hou, X.-H.; Kaneko, M.; Yamada, A. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 2749. (d) Kaneko, M.; Yamada, A.; Tsuchida, E.; Kurimura, Y. *J. Phys. Chem.* **1984**, *88*, 1061.

(8) Leasure, R. M.; Kajita, T.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 5962.

(9) (a) Ennis, P. M.; Kelly, J. M. *J. Phys. Chem.* **1989**, *93*, 5735. (b) Ennis, P. M.; Kelly, J. M.; O'Connell, C. M. *J. Chem. Soc., Dalton Trans.* **1986**, 2485.

(10) (a) Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 27. (b) Calvert, J. M.; Casper, J. V.; Binstead, R. A.; Westmoreland, T. D.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 6620.

(11) Rajagopalan, R.; Aoki, A.; Heller, A. *J. Phys. Chem.* **1996**, *100*, 3719.

(12) (a) Kurimura, Y.; Shinozaki, N.; Ito, F.; Uratani, Y.; Shigehara, K.; Tsuchida, E.; Kaneko, M.; Yamada, A. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 380. (b) Card, R. J.; Neckers, D. C. *J. Am. Chem. Soc.* **1977**, *99*, 7733. (c) Kelly, J. M.; Long, C.; O'Connell, C. M.; Vos, J. G.; Tinnemans, A. H. A. *Inorg. Chem.* **1983**, *22*, 2818.

(13) (a) Baxter, S. M.; Jones, W. E.; Danielson, E.; Worl, L.; Strouse, G.; Younathan, J.; Meyer, T. J. *Coord. Chem. Rev.* **1991**, *111*, 47. (b) Worl, L. A.; Strouse, G. F.; Younathan, J. N.; Baxter, S. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7571. (c) Younathan, J. N.; McClanahan, S. F.; Meyer, T. J. *Macromolecules* **1989**, *22*, 1048. (d) Jones, W. E.; Baxter, S. M.; Strouse, G. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 7363. (e) Olmsted, J., III; McClanahan, S. F.; Danielson, E.; Younathan, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 3297. (f) Margerum, L. D.; Murray, R. W.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 2696. (g) Margerum, L. D.; Murray, R. W.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 728.

(14) (a) Dupray, L. M.; Devenney, M.; Striplin, D. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 10243. (b) Dupray, L. M.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 6299. (c) Friesen, D. A.; Kajita, T.; Danielson, E.; Meyer, T. J. *Inorg. Chem.* **1998**, *37*, 2756.

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report here that with intense laser irradiation it is possible to achieve multiphoton, multielectron transfers to a multichromphoric polymer in acetonitrile solutions containing high concentrations of the electron transfer donor phenothiazine.

Experimental Section

Materials. Spectroscopic grade acetonitrile (CH_3CN) was used as received from Burdick and Jackson. Phenothiazine (PTZ, Alpha) was recrystallized twice from toluene and was stored in the dark. Tetra-*n*-butylammonium hexafluorophosphate (TBAH, Aldrich) was recrystallized twice from hot ethanol−water three times and stored in a desiccator.

Syntheses. The preparation and characterization of the Ru^{II}-containing polymers have been described elsewhere.[13b] The sample used here was characterized as the PF_6- salt, [*co*-PS-CH_2OCH_2-(Ru^{II}_{30})]-(PF_6)$_{60}$ by ^1H NMR, elemental analysis (<0.06% Cl), and UV−vis (λ_{max} = 462 nm in CH_3CN; $\varepsilon = 13\,400$ cm^{-1} M^{-1}) and emission spectra ($\lambda_{max,em}$ = 640 nm in CH_3CN). The starting styrene:*p*-chloromethylstyrene copolymer was atactic and had a polydispersity of ~2.4 as determined by GPC. From the number-average molecular weight of the polymeric backbone before nucleophilic substitution, M_n was 7700 g/mol, showing that an average polymeric chain contained ~30 repeating units.

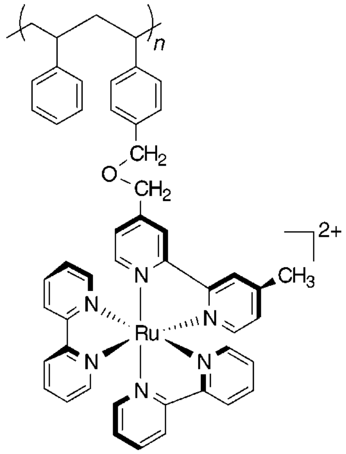
Instrumentation. Laser flash photolysis experiments were performed on an apparatus which incorporated a Nd:YAG, q-switched laser/dye laser combination (Spectra Physics) coupled to an Applied Photophysics laser kinetic spectrometer. A dichroic beam splitter (CVI East) with >99% reflectance at 532 nm (30 nm bandwidth) at 45° was utilized in the optical path to align the excitation to be coaxial to the probe. In these experiments, the high-energy excitation pulse of the Nd:YAG laser was kept constant for all experiments, and neutral density filters, Newport set (FS-3), were used to reduce the irradiation intensity in the power dependence experiments. The pulse energies were varied from ~1 mJ/pulse to ~5 mJ/pulse. The pulse width was 6 ns. The interrogation path length of the system was determined by the path length of the cell (1 cm). ΔOD values were taken as the maximum change in absorbance at 510 nm produced following the laser pulse after electron transfer quenching was complete (<400 ns).

Quenching Experiments. Excited-state quenching rate constants were determined by steady-state emission and lifetime measurements by the Stern−Volmer technique. Samples were dissolved at 6×10^{-5} M in [-Ru^{II}](PF_6)$_2$ sites in 0.05 M [N(n-C_4H_9)$_4$](PF_6)-CH_3CN and degassed for 30 min with PTZ added in the concentration range of 1×10^{-4} to 3.5×10^{-2} M. The extent of quenching of the sample was determined by the decrease in the relative integrated emission intensities. From plots of I_o/I vs the quencher concentration, [Q], the slope is equal to the Stern−Volmer constant, $K_{SV} = k_q\tau_o$. The quantities I_o and τ_o are the integrated emission intensity and the lifetime, respectively, without added quencher. I is the integrated emission intensity with quencher added, and k_q is the bimolecular quenching rate constant.

Results and Discussion

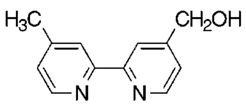
The Ru^{II}-bpy-containing polymers were prepared by nucleophilic displacement of Cl^- from poly(*p*-chloromethylstyrene-*co*-styrene) under basic conditions as described previously.[13c] In this procedure, the complex [Ru(bpy)$_2$(4-CH_2OH-4′-CH_3bpy)](PF_6)$_2$ was attached to the polymer by ether linkages to give the repeat unit illustrated below. From the number-average molecular weight of the starting polymer, an average polymeric strand contained ~30 repeat units and is abbreviated as [*co*-PS-CH_2OCH_2-(Ru^{II}_{30})](PF_6)$_{60}$. A second metal-complex-derivatized sample was prepared from the same polymer by using [Ru(bpy)$_2$(4-CH_2OH-4′-CH_3bpy)](PF_6)$_2$ in a controlled amount to give [*co*-PS-CH_2OCH_2-(Ru^{II}_3)](PF_6)$_6$.

Laser flash excitation of solutions containing [Ru(bpy)$_2$(4-CH_2OH-4′-CH_3bpy)](PF_6)$_2$ or [*co*-PS-CH_2OCH_2-(Ru^{II}_{30})](PF_6)$_{60}$ at 532 nm results in formation of MLCT excited states, which subsequently undergo reductive electron-transfer quenching, eq 3. Following the laser flash, characteristic absorbance features appeared for the reduced complex (λ_{max} = 480 nm) and PTZ^+ (λ_{max} = 517 nm). In the reduced complexes, the electron resides on a π^* orbital on a bpy ligand.[15]

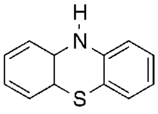


$$\xrightarrow{h\nu} \mathrm{PTZ} + [\mathrm{Ru(bpy)_2(4\text{-}CH_2OH\text{-}4'\text{-}CH_3bpy)}]^{2+*} \longrightarrow \mathrm{PTZ^+} + [\mathrm{Ru(bpy)_2(4\text{-}CH_2OH\text{-}4'\text{-}CH_3bpy)}]^{+} \quad \text{(3a)}$$

$$\xrightarrow{h\nu} \mathrm{PTZ} + [co\text{-}\mathrm{PS\text{-}CH_2OCH_2\text{-}(Ru^{II}{}_{29}Ru^{II*})}]^{60+} \longrightarrow \mathrm{PTZ^+} + [co\text{-}\mathrm{PS\text{-}CH_2OCH_2\text{-}(Ru^{II}{}_{29}Ru^{+})}]^{59+} \quad \text{(3b)}$$



(4-CH_2OH-4′-CH_3bpy)



(PTZ)

Stern−Volmer analysis of emission quenching (as plots of I_o/I vs [PTZ] with I_o and I the integrated emission intensities in the absence and presence of quencher) at low excitation intensities gave $k_q = 4.8 \times 10^9$ M^{-1} s^{-1} for the quenching of [Ru(bpy)$_2$(4-CH_2OH-4′-CH_3bpy)]$^{2+*}$ by PTZ in CH_3CN 0.05 M in [N(n-C_4H_9)$_4$](PF_6). For [*co*-PS-CH_2OCH_2-(Ru^{II}_{30})](PF_6)$_{60}$, I_o/I vs [PTZ] plots were nonlinear at [PTZ] > 1 mM, with a downward curvature occurring as [PTZ] was increased past 1 mM. Stern−Volmer analysis at low excitation intensities gave $k_q = 5.1 \times 10^9$ M^{-1} s^{-1} from the linear region of the fit.[16]

Emission decay from [Ru(bpy)$_2$(4-CH_2OH-4′-CH_3bpy)]$^{2+*}$ was exponential and independent of irradiance with $k = 9.7 \times 10^5$ s^{-1}. Emission decay from the polymers in CH_3CN was nonexponential and somewhat dependent on excitation irradiance, as described earlier for a series of amide linked polymers.[14b−d] The dependence on irradiance arises from multiphoton absorption and local polarization effects. The decays could be satisfactorily fit to the first derivative of the Williams−Watts function, eq 4. In a typical experiment at low incident excitation irradiance, $k = 1.1 \times 10^6$ s^{-1}, $\beta = 0.89$.[13a,d,14c]

$$I(t) = \alpha t^{\beta-1}\, e^{-(kt)\beta} \qquad (4)$$

With PTZ added at 35 mM for the fully loaded polymer, [*co*-PS-CH_2OCH_2-(Ru^{II}_{30})](PF_6)$_{60}$, quenching of the Ru^{II*} sites was

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[15] (a) DeArmond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* **1981**, *36*, 325. (b) Omberg, K. M.; Schoonover, J. R.; Treadway, J. A.; Leasure, R. M.; Dyer, R. B.; Meyer, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 7013.

[16] A figure showing the linear region of the Stern−Volmer quenching data for [*co*-PS-CH_2OCH_2-(Ru^{II}_{30})](PF_6)$_{60}$ at 6×10^{-5} M in [-Ru^{II}](PF_6)$_2$ sites in 0.05 M [N(n-C_4H_9)$_4$](PF_6)-CH_3CN is available as Supporting Information. PTZ was added in the concentration range 1×10^{-4} to 2.5×10^{-3} M.

~95% complete based on the Stern–Volmer results. This is an upper limit because the high irradiances used in the transient absorbance measurements decreased lifetimes by the multiphoton effects described above.[16b]

A series of experiments was conducted to establish how the amount of Ru^+ and PTZ^+ produced depends on the laser irradiance. Irradiance was varied by placing neutral density filters in the excitation path and monitored by using a joulemeter (Molectron model J3–09). The maximum change in absorbance at 510 nm was measured as a function of irradiance, and $[Ru^+] = [PTZ^+]$ was calculated by applying Beer's Law in the form

$$[\mathrm{Ru}^+] = [\mathrm{PTZ}^+] = \Delta\mathrm{OD}/l\Delta\varepsilon \qquad (5)$$

In eq 5, ΔOD is the absorbance change from after to before the laser flash, and *l* is the path length. $\Delta\varepsilon$ is the difference in the sum of molar extinction coefficients between the products and reactants ($\Delta\epsilon = \epsilon(\mathrm{Ru}^+) + \epsilon(\mathrm{PTZ}^+) - \epsilon(\mathrm{Ru}^{2+})$); the absorbance of PTZ at 510 nm is negligible. Application of eq 5 is appropriate if the quenching time scale is shorter than the time scale for back electron transfer, e.g., eq 6. In these calculations, the ϵ values used were $\mathrm{PTZ}^+ = 8100\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$;[17a] $\mathrm{Ru}^+ = 11\,000\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$;[17b] $\mathrm{Ru}^{\mathrm{II}} = 2500\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$.[17c] The absorbance change produced during and after the laser flash decreased after 400 ns as a result of back electron transfer:

$$[\mathrm{Ru(bpy)_2(4\text{-}CH_2OH\text{-}4'\text{-}CH_3bpy)}]^+ + \mathrm{PTZ}^+ \rightarrow [\mathrm{Ru(bpy)_2(4\text{-}CH_2OH\text{-}4'\text{-}CH_3bpy)}]^{2+} + \mathrm{PTZ} \qquad (6)$$

These experiments were conducted in CH_3CN, 35 mM in PTZ, 0.05 M in $[N(n\text{-}C_4H_9)_4](PF_6)$, and 2.0×10^{-6} M in polymer (6.0×10^{-5} M in $[\text{-}Ru^{II}](PF_6)_2$) sites. A parallel set of experiments was conducted on solutions that contained either the monomer $[Ru(bpy)_2(4\text{-}CH_2OH\text{-}4\text{-}CH_3bpy)](PF_6)_2$ or the lightly loaded polymer, $[co\text{-}PS\text{-}CH_2OCH_2\text{-}(Ru^{II}_3)](PF_6)_6$, having the same absorbance (OD = 0.10) at 532 nm and a sufficient amount of PTZ (15 and 20 mM, respectively) to achieve 95% quenching. It was necessary to add a higher concentration of PTZ to the polymer solutions to achieve 95% quenching.

In Figure 1 are shown plots of the fraction of Ru^+ ($=PTZ^+$) produced per repeat unit on individual polymeric strands as a function of incident irradiance. Data derived from reductive quenching of $[Ru(bpy)_2(4\text{-}CH_2OH\text{-}4'\text{-}CH_3bpy)]^{2+}$ are shown for comparison. These data show that the number of redox equivalents produced by laser flash photolysis increases nonlinearly as the irradiance is increased. At the highest irradiances used, ~25% of the available $[\text{-}Ru^{II}](PF_6)_2$ sites on the polymer had undergone excitation and electron-transfer quenching to give separated redox products. This corresponds to a seven-photon, seven-electron reduction per laser pulse on an average polymeric strand, eq 7. Variations in the concentration of polymer (0.8–3.0×10^{-6} M) or quencher (35–60 mM) yielded no significant change in this result. For the lightly loaded sample, $[co\text{-}PS\text{-}CH_2OCH_2\text{-}(Ru^{II}_3)](PF_6)_6$, a limiting efficiency of ~28% was reached under the same conditions.

$$[co\text{-}\mathrm{PS\text{-}CH_2OCH_2\text{-}(Ru^{II}_{30})}]^{60+} + 7h\nu + 7\mathrm{PTZ} \rightarrow [co\text{-}\mathrm{PS\text{-}CH_2OCH_2\text{-}(Ru^{II}_{23}Ru^{+}_{7})}]^{53+} + 7\mathrm{PTZ}^+ \qquad (7)$$

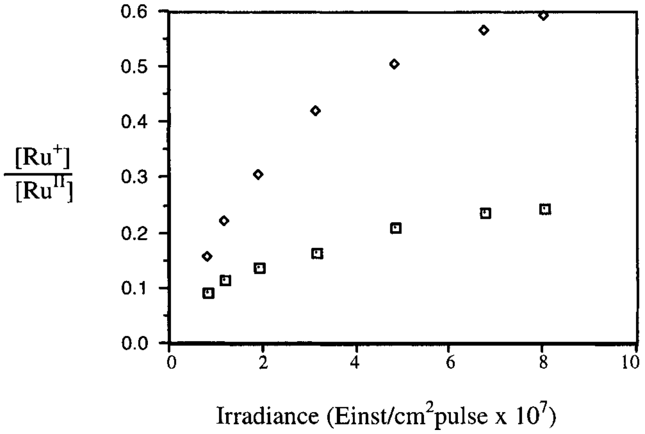

Figure 1. Plots of the fraction of Ru^+ ($=PTZ^+$) produced per monomeric $[Ru(bpy)_2(4\text{-}CH_2OH\text{-}4'\text{-}CH_3bpy)]^{2+}$ (◊) or per Ru^{II} repeat unit on an average polymer strand of $[co\text{-}PS\text{-}CH_2OCH_2\text{-}(Ru^{II}_{30})](PF_6)_{60}$ (□) as a function of laser irradiance at 532 nm in 0.05 M $[N(n\text{-}C_4H_9)_4]$-(PF_6)-CH_3CN, 15 and 35 mM in PTZ, respectively. Each data point is an average of five independent determinations with a standard deviation of ~10%.

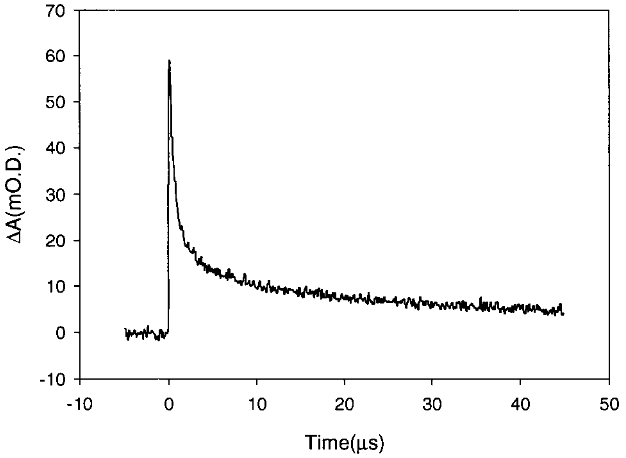

Figure 2. Transient absorbance spectral changes vs time at 510 nm following 532 nm laser flash excitation of the polymer containing solution in 1. The irradiance was 6×10^{-7} einstein/cm^2 pulse.

For $[Ru(bpy)_2(4\text{-}CH_2OH\text{-}4'\text{-}CH_3bpy)](PF_6)_2$ at the highest irradiance, ~60% of the available chromophores yielded separated redox equivalents under the same conditions. The independently measured cage escape yield for $[Ru(bpy)_3]^+ + PTZ^+$ following reductive quenching of $[Ru(bpy)_3]^{2+*}$ by PTZ in acetonitrile is 1.[3e]

Back electron transfer occurs following laser flash photolysis, eq 8. When monitored at 510 nm, back electron transfer between PTZ^+ and $[Ru(bpy)_2(4\text{-}CH_2OH\text{-}4'\text{-}CH_3bpy)]^+$ followed equal-concentration, second-order kinetics with $k = 8.1 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. Absorbance-time traces were more complex for the polymer, Figure 2. This is expected given the distribution of reduced polymers both in molecular weight and in the extent to which individual strands are reduced.

$$[co\text{-}\mathrm{PS\text{-}CH_2OCH_2\text{-}(Ru^{II}_{30-n}Ru^{+}_{n})}]^{(60-n)+} + n\mathrm{PTZ}^+ \rightarrow [co\text{-}\mathrm{PS\text{-}CH_2OCH_2\text{-}(Ru^{II}_{30})}]^{60+} + n\mathrm{PTZ} \qquad (8)$$

The results of these experiments show that it is possible to achieve multiphoton, multielectron transfer photochemistry on single strands of soluble polymers with up to seven reductive equivalents accumulating on an average strand. In principle, the multielectron transfer character of these polymers could play a

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(17) (a) Alkaitis, S. A.; Beck, G.; Grätzel, M. *J. Am. Chem. Soc.* **1975**, *97*, 5723. (b) Anderson, C. P.; Salmon, D. J.; Meyer, T. J.; Young, R. C. *J. Am. Chem. Soc.* **1977**, *99*, 1980. (c) This is the molar extinction coefficient per repeat unit on an average polymeric chain.

role in providing a basis for coupling single photonic excitation at individual sites with the multielectron transfer requirements of small molecule reactions such as the reduction of CO_2 or the oxidation of H_2O.

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Supporting Information Available: A figure showing the linear region of the Stern−Volmer quenching data. This material is available free of charge via the Internet at http://pubs.acs.org.

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