Inorg. Chem. **1996,** *35,* 6299−6307 **6299**

Synthesis and Characterization of Amide-Derivatized, Polypyridyl-Based Metallopolymers

Laurence M. Dupray and Thomas J. Meyer*

Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27590-3290

Received December 19, 1995⊗

A new series of soluble metallopolymers based on amide-derivatized, styrene−*p*-(aminomethyl)styrene, containing on the average 16 repeat units, has been synthesized. The amino copolymer was prepared by treating styrene−*p*-(chloromethyl)styrene with potassium phthalimide 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 the acid-functionalized metal complexes, $[\mathrm{M^{II}b_2b{-}COOH}](\mathrm{PF_6})_2]$ ($\mathrm{M^{II}} = \mathrm{Ru^{II}}$, $\mathrm{Os^{II}}$; 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, $[co\text{-}\mathrm{PS{-}CH_2NHCO{-}(Ru^{II}{}_x Me_{16-x})}](\mathrm{PF_6})_{2x}$ (x = 4, 7, 9, 12, 16) and $[co\text{-}\mathrm{PS{-}CH_2NHCO{-}(Os^{II}{}_x Me_{16-x})}](\mathrm{PF_6})_{2x}$ (x = 4, 8, 16) have been prepared where $\mathrm{M^{II}}$ is an abbreviation for $[\mathrm{M^{II}b_2b{-}CONH{-}}]^{2+}$ (M = Ru, Os) and Me for the methyl of the acetamide group. 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 absorptions and emissions which are only slightly solvent dependent. In some cases, luminescence decays are nonexponential but could be fit to a sum of two exponentials. Quantum yields and kinetic decay parameters are dependent on solvent, extent of loading, and incident excitation intensity.

Introduction

New approaches to the design of molecular assemblies for the study of photochemical conversion and storage of light energy continue to evolve. An ultimate goal is a molecular architecture which is able to mimic the photosynthetic process and achieve energy conversion based on multielectron redox reactions such as oxidation of water or reduction of carbon dioxide. Metal complex assemblies have been prepared by using covalently linked organic connectors,[1] ligand bridges,[2] and peptide links[3] to hold combinations of redox sites in defined geometries.

There is also an extensive literature on polymer-based assemblies.[4] Our investigations in this area began with the synthesis of styrene-*p*-(chloromethyl)styrene copolymers which were derivatized *via* nucleophilic displacement of chloride under basic conditions forming ether links.[5] Polypyridyl complexes of ruthenium and osmium as well as phenothiazine and methyl viologen were attached, and the photophysical properties of the resulting derivatized polymers were investigated. Efficient long-range electron and energy transfers were observed,[6] as well as the ability to store multiple redox equivalents on a single polymer strand.[7] The ether-linked polymers provided a benchmark against which the redox and excited state properties of related metallopolymers could be compared. In this manuscript we describe a new approach to the synthesis of a family of derivatized polymers based on amide coupling to a preformed styrene−*p*-(aminomethyl)styrene copolymer. The repeat units of the ether and amide polymers derivatized by metal complex addition are illustrated in Chart 1.

There are several advantages to the amide link. The coupling chemistry is quantitative and the derivatized polymers that result easily characterized by ^{1}H-NMR. Carboxylic acid derivatives of a variety of chromophores and quenchers are available; they have been used in previous work on modified peptides.[8] A more subtle point is that the amide link to the pyridyl ligand shown in Chart 1 is electron withdrawing relative to hydrogen. In contrast to the ether link, the excited state should lie dominantly on the derivatized ligand linked to the polymeric backbone rather than on a peripheral bipyridine. In this manuscript we describe the synthesis of a series of ruthenium- and osmium-containing

---

* To whom correspondence should be addressed.

⊗ Abstract published in *Advance ACS Abstracts,* July 15, 1996.

(1) (a) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991. (b) Sauvage, J. P.; Balzani, V.; et al. *Chem. Rev.* **1994**, *94*, 993. (c) Gust, D.; Moore, T. A. *Top. Curr. Chem.* **1991**, *159*, 103.

(2) (a) Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. *Top. Curr. Chem.* **1990**, *158*, 73. (b) Duesing, R.; Tapolski, G.;Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5378. (c) Powers, M. J.; Callahan, R. W.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1976**, *15*, 894. (d) Katz, N. E.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1988**, *27*, 1687. (e) Scandola, F. In *Photochemical Energy Conversion;* Norris, J. R., Jr., Meisel, D., Eds; Elsevier: Amsterdam, 1989.

(3) (a) Peek, B. M.; Ross, G. T.; Edwards, S. E.; Meyer, G. J.; Meyer, T. J.; Erickson, B. W. *Int. J. Peptide Protein Res.* **1991**, *38*, 114. (b) Mecklenburg, S. L.; Peek, B. M.; Schoonover, J. R.; McCafferty, D. G.; Wall, C. G.; Erickson, B. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 5479. (c) Mecklenburg, S. L.; McCafferty, D. G.; Schoonover, J. R.; Peek, B. M.; Erickson, B. W.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 2974.

(4) (a) Jones, W. E.; Watkins, D. M.; Fox, M. A. *Chem. Eng. News* **1993**, *71(11)*, 38. (b) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, U.K., 1985. (c) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469. (d) Stoessel, S. J.; Stille, J. K. *Macromolecules* **1992**, *25*, 1832. (e) Baxter, S. M.; Jones, W. E.; Danielson, E.; Worl, L. A.; Younathan, J.; Strouse, G. F.; Meyer, T. J. *Coord. Chem. Rev.* **1991**, *111*, 47.

(5) (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*, 2696.

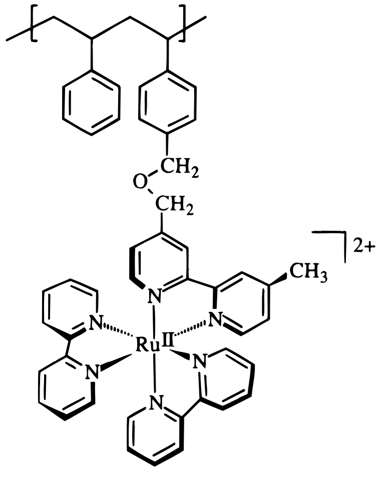
(6) (a) Younathan, J. N.; Jones, W. E.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 488. (b) Olmstead, J., III; McClanahan, S. F.; Danielson, E.; Younathan, J. N.; Meyer, J. *J. Am. Chem. Soc.* **1987**, *109*, 3297. (c) Jones, W. J., Jr.; Baxter, S. M.; Strouse, G. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 7363. (d) Strouse, G. F.; Worl, L. A.; Younathan, J. N.; Meyer, J. *J. Am. Chem. Soc.* **1989**, *111*, 9101.

(7) (a) Worl, L. A.; Strouse, G. F.; Younathan, J. N.; Baxter, S. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7571. (b) Jones, W. J. Ph.D. Dissertation, The University of North Carolina, Chapel Hill, 1991.

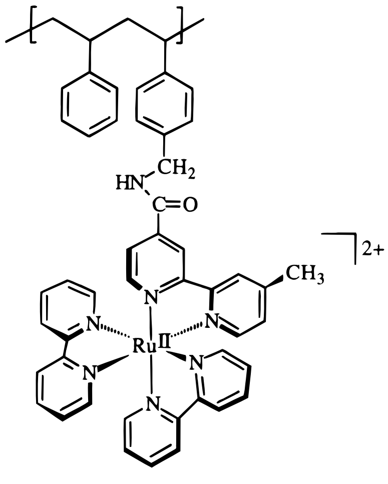
(8) McCafferty, D. G.; Bishop, B. M.; Wall, C. G.; Hughes, S. G.; Mecklenburg, S. L.; Meyer, T. J.; Erickson, B. W. *Tetrahedron* **1994**, *51*, 1093.

S0020-1669(95)01622-3 CCC: $12.00

Chart 1



[*co*-PS-CH_2OCH_2-(Ru^{II})]$^{2+}$



[*co*-PS-CH_2NHCO-(Ru^{II})]$^{2+}$

metallopolymers in which the degree of loading is varied. We also report their redox, spectral, and excited state properties.

Experimental Section

Materials. Spectroscopic grade acetonitrile (Burdick and Jackson) was used as received. Dimethyl formamide (DMF) was distilled from calcium hydride under reduced pressure and stored under nitrogen. Styrene (Aldrich) and *p*-(chloromethyl)styrene (Kodak) were passed through an alumina column prior to use in order to remove the inhibitor. BOP and HOBT were purchased from Novabiochem. All other materials were purchased from Aldrich and used as received. The following abbreviations are used throughout this paper. b = bpy = 2,2′-bipyridine; b−COOH = 4′-methyl-2,2′-bipyridine-4-carboxylic acid; BOP = (benzotriazoyloxy)tris(dimethylamino)phosphonium hexafluorophosphate; HOBT = 1-hydroxybenzotriazole hydrate; NMM = *N*-methylmorpholine; DMAP = (dimethylamino)pyridine; AIBN = azobisisobutyronitrile. $Os^{II}b_2Cl_2.2H_2O$[9] and b−COOH[3a] were prepared as described previously. $[Ru^{II}b_2b{-}COOH](PF_6)_2$[3a] was prepared as described previously, but was further purified by cation exchange chromatography. Cation exchange chromatography was conducted by using Sephadex CM C-25 as the column support. Sparingly water-soluble salts were dissolved in 9:1 water−acetonitrile mixtures to assist in loading. The eluent consisted of aqueous NH_4Cl solutions buffered to pH 7.0 with sodium phosphates. Pure products were precipitated by addition of NH_4PF_6 to the eluent. Stirring was maintained for 45 min at 0 °C before collection. The solids were washed with ice-cold water followed by anhydrous diethyl ether.

Bis(2,2′-bipyridine)(4′-methyl-2,2′-bipyridine-4-carboxylic acid)osmium(II) Bis(Hexafluorophosphate), $[Os^{II}b_2b{-}COOH](PF_6)_2$. $Os^{II}b_2Cl_2{\cdot}2H_2O$ (0.94 g, 1.64 mmol) and b−COOH (1.0 g, 4.67 mmol) were dissolved in 25 mL of ethylene glycol. This mixture was held at reflux for 1.5 h under nitrogen. The crude product was obtained by filtration following addition of aqueous NH_4PF_6. The green solid was redissolved in a small amount of acetonitrile and precipitated into diethyl ether. After filtration on a medium porosity frit, the product was dried under vacuum. ^{1}H-NMR (CD_3CN): δ 2.65 (s, 3H, CH_3), 3.82 (t, 2H, CH_2), 4.41 (t, CH_2, 2H), 7.18−7.38 (m, 5H), 7.45 (d, 1H), 7.56−7.65 (m, 5H), 7.78−7.93 (m, 5H), 8.47 (d, 4H), 8.62 (s, 1H) and 8.86 ppm (s, 1H). *This spectrum is consistent with the ester derivative of the desired carboxylic acid,* $[Os^{II}b_2b\text{-}COCH_2CH_2OH](PF_6)_2$. 0.76 g of the ester ($1.6 \times 10^{-4}$ mol) was dissolved in 10 mL of CH_3CN with 146 μL of NaOH solution (50%). The solution was kept at room temperature under stirring for 5 h. It was acidified to pH = 1 with HCl, and the organic solvent was removed by rotary evaporation. Subsequently, aqueous NH_4PF_6 was added until no further precipitation was observed. After isolation by filtration, the product was purified by ion-exchange chromatography. The monoacid was collected first (μ = 0.1); the unhydrolyzed ester eluted next (μ = 0.2). The aqueous solution was acidified with HCl, and NH_4PF_6 was added. Stirring was maintained for 30 min at 0 °C before collection of the green solid by filtration. The product was washed with ice-cold water followed by anhydrous diethyl ether. ^{1}H-NMR (CD_3CN): δ 2.65 (s, 3H, CH_3), 7.18−7.38(m, 5H), 7.43 (d, J = 5.9 Hz, 1H), 7.59−7.75 (m, 5H), 7.78−7.93 (m, 5H), 8.45−8.49 (m, 5H), and 8.86 ppm (s, 1H). IR: ν(C═O) = 1734 cm^{-1}. UV−vis (CH_3CN) λ (ϵ): 248 (23 126), 292 (45 909), 376 (8893), 486 (12 455), and 614 nm (3200 M^{-1} cm^{-1}). Anal. Calcd for $OsC_{32}H_{30}N_6O_4P_2F_{12}$: C, 37.43; H, 2.95; N, 8.19. Found: C, 37.33; H, 2.48; N, 8.14.

Bis(2,2′-bipyridine)(4′-methyl-2,2′-bipyridinyl-4-benzylamide)-metal(II) Hexafluorophosphate, $[M^{II}b_2b{-}CONHBz](PF_6)_2$ (M^{II} = Ru^{II} or Os^{II}). A 0.338 mmol sample of $[M^{II}b_2b{-}COOH](PF_6)_2$, 0.676 mmol of BOP, 0.507 mmol of HOBT, 0.338 mmol of NMM, and 0.338 mmol of benzylamine were dissolved in 50 mL of DMF. Then 0.338 mmol DMAP was added, and the reaction mixture was stirred under nitrogen for 2 h at room temperature. It was precipitated by addition to an excess of cold diethyl ether. The crude product was purified by cation exchange chromatography. The unreacted carboxylic acid eluted first (μ = 0.1) and the product second (μ = 0.2). The product was isolated by addition of NH_4PF_6 and collection of the precipitate that formed by filtration.

For M^{II} = Ru^{II}. ^{1}H-NMR (CD_3CN) δ 2.53 (s, 3H, CH_3), 4.59 (d, J = 6.03 Hz, CH_2), 7.2−7.45 (m, 9H), 7.55 (d, J = 5.82 Hz, 1H), 7.62−7.72 (m, 5H), 7.84 (d, J = 6.0 Hz, 1H), 7.91 (m, 1H), 7.99−8.09 (m, 4H), 8.48 (2 s, 5H), and 8.78 ppm (s, J = 1.4 Hz, 1H). IR(KBr) ν(C═O) = 1668 cm^{-1}. UV−vis (CH_3CN) λ (ϵ): 248 (27 310), 290 (50 115), and 456 nm (14 605 M^{-1} cm^{-1}); Anal. Calcd for $RuC_{39}H_{34}N_7O_{32}P_2F_{12}$: C, 46.11; H, 3.38; N, 9.65. Found: C, 46.09; H, 3.04; N, 9.53.

For M^{II} = Os^{II}. ^{1}H-NMR (CD_3CN) δ 2.62 (s, 3H, CH_3), 4.8 (d, J = 6.03 Hz, CH_2), 7.16−7.44 (m, 9H), 7.45 (d, J = 5.86 Hz, 1H), 7.50−7.77 (m, 5 H), 7.78−7.91 (m, 6H), 8.49 (2 s, 5H), and 8.78 ppm (d, J = 1.4 Hz, 1H). IR(KBr) ν(C═O) = 1668 cm^{-1}. UV−vis (CH_3CN) λ (ϵ): 246 (30 250), 292 (79 340), 374 (11 910), 486 (16 026), and 614 nm (5015 M^{-1} cm^{-1}). Anal. Calcd for $OsC_{39}H_{35}N_7O_2P_2F_{12}$: C, 42.05; H, 3.17; N, 8.80. Found: C, 42.11; H, 2.78; N, 8.77.

Poly(styrene−*p*-(chloromethyl)styrene), *co*-PS−CH_2Cl. This material was prepared by the method of Arshady *et al.*[10] AIBN (4 g, 24.4 mmol) was added to a solution of styrene (24.56 g, 0.236 mol), *p*-(chloromethyl)styrene (35.7 g, 0.234 mol), and 200 mL of chlorobenzene. The reaction mixture was heated at 75 °C for 20 h under a nitrogen atmosphere. After the mixture was cooled to room temperature, the polymer was precipitated by adding the solution into an excess of methanol by using a blender. The white solid was collected by

---

(9) Kober, E. M.; Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4587.

(10) Arshady, R.; Reddy, S. F.; George, M. H. *Polymer* **1984**, *25*, 716.

filtration, washed with methanol to remove unreacted monomer, and finally dried *in vacuo*. ^{1}H-NMR ($CDCl_3$): δ 1.2−2.0 (m, CH_2-CH), 4.5 (broad s, CH_2), and 6.1−7.2 ppm (m, aromatic protons). GPC: $DP_n = 4173$, $DP_w = 6371$, and MWD = 1.53.

Poly(styrene−*p*-(aminomethyl)styrene), *co*-PS−CH_2NH_2. In a typical experiment, a solution of *co*-PS−CH_2Cl (1 g, 0.238 mmol), potassium phthalimide (1.76 g, 9.5 mmol) and DMF (10 mL) were heated at 100 °C for 8 h. A pink precipitate formed as the reaction proceeded. The cooled solution was filtered through a fine-porosity frit in order to remove KCl. The filtrate was precipitated into a large volume of methanol, and the white solid was collected by filtration and washed with methanol. The ^{1}H-NMR of this product indicates quantitative conversion of the chloromethylstyrene into its phthalimide derivative. ^{1}H-NMR ($CDCl_3$): δ 0.6−2.2 (m, CH_2-CH, 6H), 4.70 (s, CH_2, 2H), 5.8−7.24 (m, aromatic protons, 9H) and 7.4−7.9 ppm (d, phthalimide protons, 4H).

The phthalimide derivative (1.2 g, 0.201 mmol) was mixed with 1200 μL of hydrazine monohydrate (1 mL/g) in 20 mL of ethanol. The solution was held at reflux for 20 h, during which time a white solid formed. The reaction mixture was filtered; the filtrates were concentrated by rotary evaporation and precipitated into water. The mixture was kept at 0 °C overnight. Filtration the following day yielded the amino polymer. It responded positively to the ninhydrin test (intense blue color) confirming the formation of the primary amine. ^{1}H-NMR ($CDCl_3$): δ 0.7−2.2 (m, CH_2-CH backbone, 6H), 3.3 (broad s, NH_2), 3.7 (broad s, CH_2), and 6.5−7.3 ppm (m, aromatic protons, 9H). Upon addition of D_2O to the NMR tube, the peak at 3.3 ppm disappeared.

[*co*-PS−CH_2NHCO−(M^{II}_n)](PF_6)$_{2n}$ (M = Ru, Os; $0 < n < 16$). A 0.17 mmol sample of [$M^{II}b_2b$−COOH](PF_6)$_2$, 0.343 mmol of BOP, 0.255 mmol of HOBT and 0.17 mmol of NMM were dissolved in 4 mL of DMF and added dropwise to a solution containing 39 μmol *co*-PS−CH_2NH_2 dissolved in 2 mL of dichloromethane. Then 0.17 mmol DMAP was added to the reaction flask. After 2 h of stirring under nitrogen, the mixture was precipitated into diethyl ether. The crude product was dissolved in a small amount of acetonitrile and precipitated into aqueous sodium bicarbonate (0.5 M). After filtration, the product was washed with H_2O and diethyl ether. This last step was repeated three times and the product was dried under vacuum.

For $M^{II} = Ru^{II}$ and $n = 4$. ^{1}H-NMR (CD_3CN): δ 0.2−2.8 (m, CH_2−CH backbone, CH_3, 118 H), 3.62 (s, NH_2), 3.62−5.1 (m, br, CH_2, 32 H), and 5.8−9.1 ppm (m, styrenic and bipyridyl protons, 232 H). IR (KBr): ν(C═O) = 1668 cm^{-1}.

[*co*-PS−CH_2NHCO−($M^{II}_nMe_{16-n}$)](PF_6)$_{2n}$. A 19.1 μmol sample of [*co*-PS−CH_2NHCO−(M^{II}_n)](PF_6)$_{2n}$ and 191 × (16-*n*) μmol of Ac_2O were mixed with 4 mL of acetonitrile and stirred at 40 °C for 2 h. The product was collected by filtration following precipitation by addition to diethyl ether. The solid obtained was dissolved in acetonitrile, precipitated again in diethyl ether, and dried under vacuum.

For $M^{II} = Ru^{II}$ and $n = 4$. ^{1}H-NMR (CD_3CN): δ 0.21−2.7 (m, CH_2−CH backbone, CH_3, 154 H), 4.2 (s, br, CH_2, 24 H), 4.45 (s, br, CH_2, 8 H) and 6.17−8.72 ppm (m, styrenic and bipyridyl protons, 232 H). IR (KBr) ν(C═O) = 1668 cm^{-1}. UV−vis (CH_3CN) λ (ϵ): 250 (34 260), 290 (81 860), and 456 nm (18 400 M^{-1} cm^{-1}). ^{1}H-NMR was used as the principal method of determining the loading and, in combination with IR, was used to establish purity. The results of combustion analysis were generally not reproducible even for multiple analyses of the same sample.

[*co*-PS−CH_2NHCO−(M^{II}_{16})](PF_6)$_{32}$. A 7.89 μmol sample of *co*-PS−CH_2NH_2 was dissolved in 2 mL of CH_2Cl_2. In another flask, 0.19 mmol of [$M^{II}b_2b$−COOH](PF_6)$_2$, 0.378 mmol of BOP, 0.283 mmol of HOBT, and 0.189 of mmol NMM were dissolved in 4 mL of DMF and added to the polymer-containing solution. Subsequently, 1.89 mmol of DMAP was added and the reaction mixture was held at room temperature for 2 h under nitrogen. The product was precipitated by addition to diethyl ether after removal of dichloromethane and collected by filtration on a medium porosity frit. The crude product was redissolved in a small amount of acetonitrile and added to 0.5 M $NaHCO_3$. The product was collected by filtration and rinsed with water and ether. This last step was repeated three times until the IR indicated the absence of unreacted metal complex.

For M = Ru^{II}. ^{1}H-NMR (CD_3CN): δ 0.21−2.64 (m, 154 H), 4.45 (s, br, 32 H), and 6.17−8.92 ppm (m, styrenic and bipyridyl protons, 496 H); IR (KBr): ν(C═O) = 1668 cm^{-1}. UV−vis (CH_3CN) λ (ϵ): 250 (25 778), 290 (56 650), and 458 nm (13 150 M^{-1} cm^{-1}).

Measurements. General Methods. UV−visible spectra were recorded on a Hewlett-Packard 8452A photodiode spectrophotometer. Infrared spectra were recorded on a Nicolet 20DX Fourier-transform IR spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker AC200 spectrometer. A Waters 150-CV gel permeation chromatograph with Ultrastyragel columns of 100, 500, 10^3, 10^4, and 10^5 Å porosities in tetrahydrofuran was used for the determination of molar mass and molar mass distribution.

Electrochemistry. Tetra-n-butylammonium hexafluorophosphate (TBAH) was recrystallized three times from absolute ethanol and dried *in vacuo*. Acetonitrile (Burdick and Jackson) was distilled over calcium hydride prior to use. Cyclic voltamograms were recorded in 0.1 M TBAH/CH_3CN solutions with a Princeton Applied Research Model 273 potentiostat/galvanostat. Two compartment cells were used for voltammetry with the working and reference electrodes occupying the upper compartment, a platinum coil counter electrode occupying the lower, and a glass frit separating the two. A Ag/$AgNO_3$/CH_3CN reference which is + 0.31 V *vs* SSCE and a platinum coil were employed as the reference and working electrodes, respectively.

Photophysical Measurements. Methanol, acetonitrile, and 1,2-dichloroethane for use as solvents in photophysical measurements were obtained as high purity solvents (Burdick & Jackson) and used as received. Steady state emission spectra were recorded on a Spex Fluorolog-212A photon counting spectrofluorimeter and were corrected for the instrument response. Optically dilute samples ($A_{\lambda(\mathrm{excitation})} < 0.12$) were freeze−pump−thaw degassed to 10^{-6} Torr prior to use. Emission quantum yields were calculated by relative actinometry by using eq 1.[11] In this equation, ϕ is the emission quantum yield of either

$$\phi_2 = \phi_1(I_2/I_1)(n_2/n_1)^2(A_1/A_2) \qquad (1)$$

the known or unknown species (subscript 1 or 2 respectively), *I* is the integrated sum of the emission profile, *n* is the refractive index of the solvent, and *A* is the absorbance in a 1 cm quartz cuvette cell. The reference was either [Ru^{II}(bpy)$_3$](PF_6)$_2$ for which $\phi_{em} = 0.062$[12] or [Os^{II}(bpy)$_3$](PF_6)$_2$ for which $\phi_{em} = 0.005$[13] in acetonitrile at 298 K.

Time-resolved emission measurements were conducted on a PRA LN1000/LN102 nitrogen laser/dye laser combination for excitation (λ = 457 nm, Coumarin 460). Emission was recorded at right angles by using a PRA B204-3 monochromator and a cooled, 10 stage, Hamamatsu R928 photomultiplier. The output from the PMT was terminated through a 50 Ω resistor to a Lecroy 7200 transient digitizer interfaced to an IBM PC. Samples were prepared with $A \sim 0.1$ at 460 nm and deoxygenated by either bubbling with Ar (30 min) or by freeze−pump−thaw degassing through a minimum of three cycles (10^{-6} Torr). The irradiance was varied by placing neutral density filters in the excitation path. It was monitored by using a joulemeter (Molectron Model J3-09).

Fitting of NMR and emission spectra to Gaussian−Lorentzian functions to assist in quantitative analysis based on spectral profiles was accomplished with the aid of GRAMS/386 application software (Galactic Industries). Fitting of luminescence decay traces to exponential and multiexponential functions was accomplished by using an ASYST implementation of the Levenberg−Marquart algorithm.

Results

Synthesis. Reaction of styrene−*p*-(chloromethyl)styrene copolymer, containing on the average 16 repeat units, with potassium phthalimide in DMF for 8 h led to the total displacement of chloride by phthalimide groups. Treatment of the resulting white solid with hydrazine monohydrate in ethanol solution afforded the fully aminated polymer (Scheme 1).

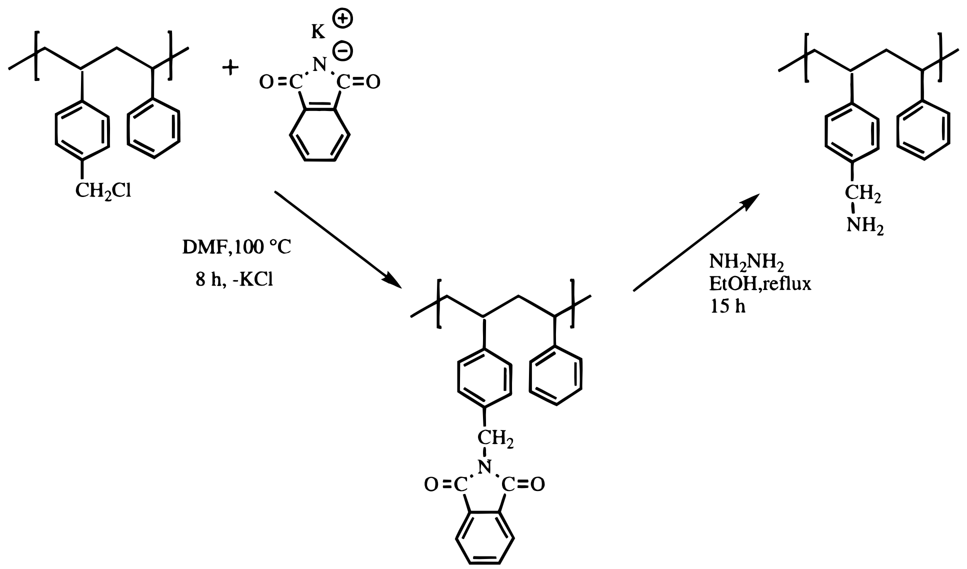
---

[11] (a) Parker, C. A.; Rees, W. T. *Analyst (London)* **1960**, *85*, 587. (b) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613.

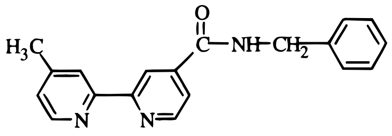
[12] Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583.

[13] Caspar, J. V. Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630.

Scheme 1



Attachment of various ruthenium- or osmium-based chromophores *via* the formation of an amide link was achieved by coupling the amino polymer to the carboxylic acid derivative of the polypyridyl complex by using Castro's reagent.[14] Prior to our attempts to derivatize the polymer, we prepared the model complexes [Ru^{II}b$_2$(b−CONHBz)](PF$_6$)$_2$ and [Os^{II}b$_2$(b−CONHBz)](PF$_6$)$_2$ by allowing the carboxylic acid derivative of the metal complexes to react with benzyl amine in the presence of the coupling reagents.



b-CONH-Bz

Separation of unreacted complex salts from the derivatized polymer was achieved by repeatedly dissolving the crude product in a small amount of acetonitrile and precipitating by addition to aqueous sodium bicarbonate solution (0.5 M). Metallopolymeric samples containing different proportions of the metal complex were attached to the polymer simply by varying the reactant ratio of polymer to complex. The remaining free amino groups were subsequently capped by reaction with acetic anhydride, thus forming an acetamide group (Scheme 2).

Characterization. ^{1}H-NMR, IR. After displacement of chloride by phthalimide groups, there was no significant change in the chemical shift of the methylene protons, but the degree of substitution could be verified by comparing the peak areas of the aromatic protons (styrenic and phthalimide) relative to that for the methylene protons. ^{1}H-NMR was used also to verify that hydrazinolysis led to complete displacement of phthalimide by amine. An upfield shift of 0.77 ppm in the resonance of the methylene protons was observed, along with a broad peak corresponding to the mobile protons of the amino groups. Derivatization of the polymer by treatment with the carboxylic acid-containing polypyridyl complexes caused a downfield shift of the methylene protons, signaling formation of the amide bond ($\delta_{CH_2NH_2}$ = 4.22 ppm, δ_{CH_2NHCO} = 4.45 ppm). The average percentage of metal complex on each strand was calculated from the ratio of the peak areas of the two sets of methylene protons. However, the amino protons also underwent a downfield shift from 3.5 to 4.43 ppm, bringing them into a region where they overlapped with the methylene protons. This would not have interfered with determination of loading were the amino protons inert to exchange. Unfortunately, due to exchange with water in the NMR solvent, the peak areas did not correspond to the actual number of protons. The problematic nature of the NMR spectra of such samples, and the reactivity of free amines, required us to cap the unreacted primary amines with the acetyl group. ^{1}H-NMR spectra in acetonitrile showed that the methylene protons linked to the acetamide group appear at 4.31 ppm. These overlap also with the methylene protons bearing the metal complex but only partially (Figure 1). The resolution of these two peaks enabled estimation of the extent of loading. This was double-checked by integrating the total peak areas of the methylene protons relative to those of the aromatic protons (bipyridyl and styrenic).

IR spectroscopy was also used to monitor amide formation. The infrared spectrum of the free ruthenium or osmium complex bearing a carboxylic acid is characterized by an intense band at 1734 cm^{-1} corresponding to the ν(C═O) of the acid group. After derivatization, ν(C═O) shifts to 1668 cm^{-1}. Thus, a simple IR measurement verifies separation from the monomer.

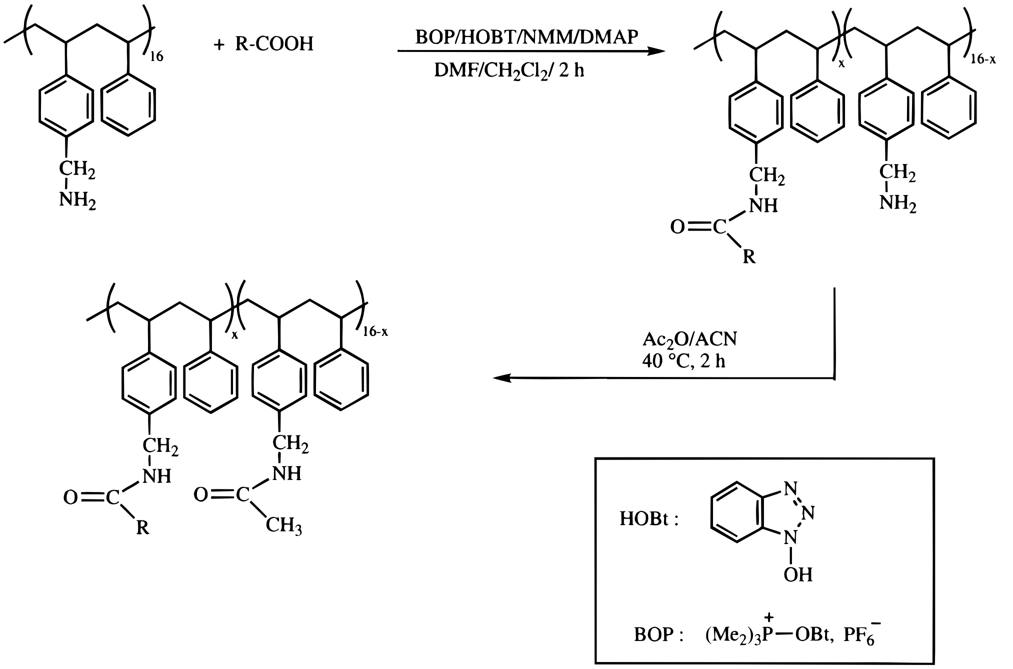
Cyclic Voltammetry. Cyclic voltamograms of the metallopolymers and model compounds were measured in acetonitrile solutions; half-wave potentials ($E_{1/2}$) are reported in Table 1. For all samples, a reversible oxidation and two reversible reductions were observed. Within each series, these processes occurred at nearly the same potentials. Half-wave potentials were also very close to those observed for the corresponding processes in the model compounds. The peak splitting ($E_{pa} - E_{pc}$) for the polymeric samples was typically 90 mV, which is greater than the 66 mV observed for the model compounds. Reduction of the polymeric samples past the second bipyridine reduction led to adsorption. Desorption peaks at −1.65 V for the ruthenium-based and at −1.45 V for the osmium-based polymers were observed on reversal of the reductive scan.

UV−Visible Spectra. Absorption spectra of the metallopolymeric samples in acetonitrile exhibit $\pi \rightarrow \pi^*$ bands in the UV and dπ(M^{II}) → π^*(bpy) metal-to-ligand charge transfer (MLCT) bands in the visible. The most intense MLCT feature has a maximum at 458 nm for ruthenium and at 486 nm for osmium. Extinction coefficients per repeat unit for ruthenium and osmium samples in CH$_3$CN were also calculated. The

---

[14] Castro, B.; Dormoy, J. R. *Tetrahedron Lett.* **1975**, 1219.

Scheme 2



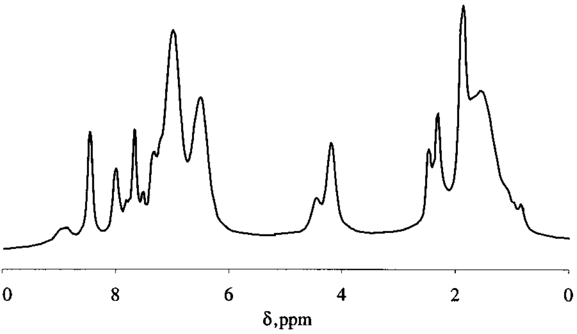


Figure 1. ^{1}H-NMR at 200 MHz in CD_3CN for [*co*-PS−CH_2NHCO−($Ru^{II}{}_4Me_{12}$)]$(PF_6)_8$.

concentration of the metallopolymeric samples was calculated from the average molecular weight. (We used MW = 1136 g/mol for the repeat units containing pendant ruthenium polypyridine complexes and MW = 279 g/mol for the acetyl capped units.) Each metallopolymeric sample obeys the Beer−Lambert law. However, from the variation of molar extinction coefficient per repeat unit with loading in Figure 2, the molar absorptivities of the attached chromophores are not additive. They decrease as loading is increased (Figure 2). MLCT band shapes in the metallopolymeric samples are slightly broadened compared to the model. As the metal content is increased per chain, the band shape is not changed.

Emission Quantum Yields. Emission quantum yields for the polymeric samples are reported in Tables 2 and 3. For ruthenium samples, emission measurements were conducted in acetonitrile, methanol, and 1,2-dichloroethane (DCE). It was found that for the same sample, the quantum yields increased with decreasing solvent polarity (Table 2). Emission quantum yields for lightly loaded polymeric samples were higher than those for the highly loaded polymers, and those for the model compounds were higher still. Variations in emission quantum yields and lifetimes as a function of the degree of derivatization are less pronounced for the osmium series than for the ruthenium series.

In the polar solvents methanol and acetonitrile, the emission maximum is not sensitive to the degree of loading. In 1,2-dichloroethane, the emission is red-shifted with increased loading from [*co*-PS−CH_2NHCO−($Ru^{II}{}_4Me_{12}$)]$(PF_6)_8$ at 634 nm to [*co*-PS−CH_2NHCO−($Ru^{II}{}_{16}$)]$(PF_6)_{32}$ at 642 nm. In all cases, the emission is shifted to the blue with decreasing solvent polarity as shown in Figure 3. The emission quantum yield for [*co*-PS−CH_2NHCO−($Ru^{II}{}_{16}$)]$(PF_6)_{32}$ in acetonitrile was invariant to concentration from 1×10^{-5} to 2×10^{-6} M.

Rate constants for radiative (k_r) and nonradiative (k_{nr}) decay were calculated from lifetimes (τ or τ_M, eq 4) and emission quantum yields by using eq 2 which assumes that the crossing efficiency to the emitting state is unity.[15]

$$\tau = (k_r + k_{nr})^{-1} \tag{2a}$$

$$\phi_{em} = k_r\tau \tag{2b}$$

Laser Flash Photolysis. Luminescence decay in the model complexes was exponential. Decay in the polymeric samples could be fit by using a sum of two exponentials. In eq 3, $I(t)$

$$I(t) = ae^{-k_1t} + (1 - a)e^{-k_2t} \tag{3}$$

is the emitted intensity at time t, k_1 and k_2 are the decay rate constants, and a is the fraction of the emitted intensity associated with k_1. A mean, weighted lifetime was also computed according to eq 4.[16]

$$\tau_M = ak_1^{-1} + (1 - a)k_2^{-1} \tag{4}$$

Emission decay from [*co*-PS−CH_2NHCO−($Ru^{II}{}_{16}$)]$(PF_6)_{32}$ following excitation at 460 nm is shown in Figure 4 as well as the best fit to the biexponential function. Lifetimes from

---

(15) (a) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 2841. (b) Demas, J. N.; Taylor, D. G. *Inorg. Chem.* **1979**, *18*, 3177. (c) Boletta, F.; Juris, A.; Maestri, M.; Sandrini, D. *Inorg. Chim. Acta* **1980**, *44*, L175.

(16) (a) Carraway, E. R.; Demas, J. N.; DeGraff, B. A. *Anal. Chem.* **1991**, *63*, 332. (b) Carraway, E. R.; Demas, J. N.; DeGraff, B. A.; Bacon, J. R. *Anal. Chem.* **1991**, *63*, 337.

Table 1. Spectral and Electrochemical Data (*vs* SSCE) at Room Temperature in Acetonitrile

salt	$\lambda_{\mathrm{max\ abs}}$, nm[a] ($\epsilon$, 10^{-4}, M^{-1} cm^{-1})	$E_{1/2}^{\mathrm{ox}}$, V[b]	$E_{1/2}^{\mathrm{red1}}$, V[b]	$E_{1/2}^{\mathrm{red2}}$, V[b]
[Rub$_2$b−CH$_2$OBz](PF$_6$)$_2$	454 (1.48)	1.26	−1.33	−1.53
[Rub$_2$b−COOBz](PF$_6$)$_2$	458 (1.48)	1.32	−1.12	−1.47
[Rub$_2$b−CONHBz](PF$_6$)$_2$	458 (1.46)	1.31	−1.24	−1.48
[*co*-PS−CH$_2$NHCO−(Ru$_4$Me$_{12}$)](PF$_6$)$_8$	458 (0.46)	1.31	−1.20	−1.41
[*co*-PS−CH$_2$NHCO−(Ru$_7$Me$_9$)](PF$_6$)$_{14}$	458 (0.75)	1.31	−1.20	−1.41
[*co*-PS−CH$_2$NHCO−(Ru$_9$Me$_7$)](PF$_6$)$_{18}$	458 (0.91)	1.31	−1.21	−1.40
[*co*-PS−CH$_2$NHCO−(Ru$_{12}$Me$_4$)](PF$_6$)$_{24}$	458 (1.15)	1.30	−1.21	−1.40
[*co*-PS−CH$_2$NHCO−(Ru$_{16}$)](PF$_6$)$_{32}$	458 (1.31)	1.30	−1.20	−1.40
[Osb$_2$b−CONHBz](PF$_6$)$_2$	468 (1.60)	0.85	−1.19	
[*co*-PS−CH$_2$NHCO−(Os$_4$Me$_{12}$)](PF$_6$)$_8$	468 (0.41)	0.86	−1.16	
[*co*-PS−CH$_2$NHCO−(Os$_8$Me$_8$)](PF$_6$)$_{16}$	468 (0.79)	0.87	−1.18	
[*co*-PS−CH$_2$NHCO−(Os$_{16}$)](PF$_6$)$_{32}$	468 (1.46)	0.87	−1.18	

[a] Absorption maximum (±3 nm) and molar extinction coefficients per repeat unit, for the most intense metal-to-ligand charge transfer (MLCT) feature. [b] Half-wave potentials for Ru^{II} oxidation and the first two ligand reductions obtained in CH$_3$CN solution with 0.1 M TBAH as supporting electrolyte.

Table 2. Excited State Properties of Ruthenium-Derivatized Polymers in Various Solvents at 295 K

solvent	compound	E_{em} (nm)[a]	ϕ_{em}[b]	τ_1 (μs)[c]	a_1[c]	τ_2 (ns)[c]	τ_M (μs)[d]	10^4 k_r (s^{-1})	10^5 k_{nr} (s^{-1})
DCE	[Rub$_2$b−CONHBz](PF$_6$)$_2$	630	0.11	1.48				7.4	6.0
	[*co*-PS−CH$_2$NHCO−(Ru$_4$Me$_{12}$)](PF$_6$)$_8$	634	0.10	1.35	0.88	119	1.07	8.5	7.4
	[*co*-PS−CH$_2$NHCO−(Ru$_7$Me$_9$)](PF$_6$)$_{14}$	634	0.09	1.30	0.75	157	1.01	8.9	9.0
	[*co*-PS−CH$_2$NHCO−(Ru$_9$Me$_7$)](PF$_6$)$_{18}$	638	0.09	1.35	0.67	121	0.94	9.6	9.7
	[*co*-PS−CH$_2$NHCO−(Ru$_{12}$Me$_4$)](PF$_6$)$_{24}$	642	0.09	1.34	0.71	160	1.00	9.0	9.1
	[*co*-PS−CH$_2$NHCO−(Ru$_{16}$)](PF$_6$)$_{32}$	642	0.08	1.26	0.70	187	0.94	8.5	9.8
CH$_3$CN	[Rub$_2$b−CONHBz](PF$_6$)$_2$	648	0.09	1.40				6.3	6.5
	[*co*-PS−CH$_2$NHCO−(Ru$_4$Me$_{12}$)](PF$_6$)$_8$	646	0.09	1.33	0.95	135	1.27	7.5	7.1
	[*co*-PS−CH$_2$NHCO−(Ru$_7$Me$_9$)](PF$_6$)$_{14}$	644	0.09	1.33	0.78	188	1.08	8.0	8.4
	[*co*-PS−CH$_2$NHCO−(Ru$_9$Me$_7$)](PF$_6$)$_{18}$	646	0.08	1.35	0.73	223	1.05	7.2	8.8
	[*co*-PS−CH$_2$NHCO−(Ru$_{12}$Me$_4$)](PF$_6$)$_{24}$	646	0.06	1.15	0.78	126	0.92	6.6	10.2
	[*co*-PS−CH$_2$NHCO−(Ru$_{16}$)](PF$_6$)$_{32}$	646	0.05	1.21	0.72	126	0.91	5.6	10.4
MeOH	[Rub$_2$b−CONHBz](PF$_6$)$_2$	652	0.08	1.06				7.3	8.7
	[*co*-PS−CH$_2$NHCO−(Ru$_4$Me$_{12}$)](PF$_6$)$_8$	654	0.06	0.96	0.84	104	0.82	7.6	11.4
	[*co*-PS−CH$_2$NHCO−(Ru$_7$Me$_9$)](PF$_6$)$_{14}$	654	0.06	0.92	0.80	108	0.75	7.9	12.4
	[*co*-PS−CH$_2$NHCO−(Ru$_9$Me$_7$)](PF$_6$)$_{18}$	654	0.06	0.93	0.84	100	0.80	7.8	11.7
	[*co*-PS−CH$_2$NHCO−(Ru$_{12}$Me$_4$)](PF$_6$)$_{24}$	654	0.05	0.90	0.77	135	0.73	6.9	13.0
	[*co*-PS−CH$_2$NHCO−(Ru$_{16}$)](PF$_6$)$_{32}$	656	0.04	0.92	0.69	124	0.67	5.6	14.3

[a] Emission band maximum (±2). [b] Emisson quantum yield (±15%) determined by actinometry with [Ru(bpy)$_3$](PF$_6$)$_2$ as the standard. [c] Lifetime (±2−4 ns) obtained by analyzing emission decay curves at the emission maxima following laser flash excitation at 460 nm, by using eq 3. The incident pulse energy was 95−100 μJ/pulse. Note Tables 4 and 5. [d] Calculated from eq 4.

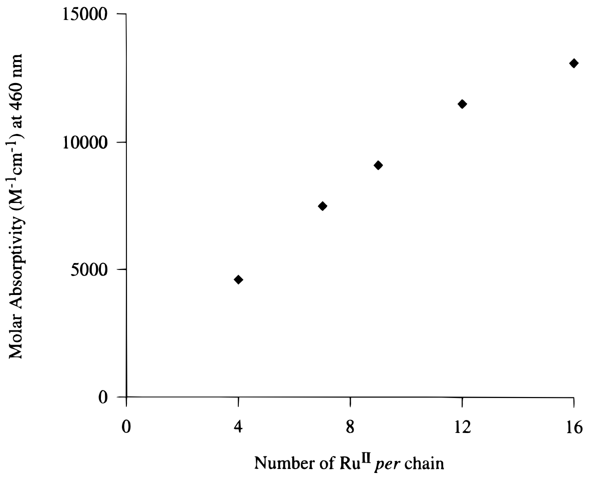


Figure 2. Variation of the molar extinction coefficient (M^{-1} cm^{-1}) at 460 nm as a function of loading for [*co*-PS−CH$_2$NHCO−(Ru^{II}$_n$Me$_{16-n}$)]-(PF$_6$)$_{2n}$ in acetonitrile.

exponential fits and mean, weighted lifetimes (τ_M) calculated from eq 4, for the metallopolymeric samples with integrated input pulse energies in the range 95−100 μJ/pulse are reported in Tables 2 and 3. In acetonitrile, lifetimes decrease by 20% from the most lightly to the most highly loaded samples for M^{II} = Ru^{II}. The same trend is observed in methanol and 1,2-dichloroethane. Lifetimes increase as the polarity of the solvent is decreased and the emission energy increases.

A series of experiments was conducted to establish the effect of incident laser energy on lifetime. Results for [*co*-PS−CH$_2$NHCO−(Ru^{II}$_4$Me$_{12}$)](PF$_6$)$_8$ and [*co*-PS−CH$_2$NHCO−(Ru^{II}$_{16}$)](PF$_6$)$_{32}$, are given in Tables 4 and 5. The lifetime of the model complex was independent of the irradiation intensity regardless of solvent. Excited state decay in the metallopolymers was dependent on laser power in the range 10−100 μJ/pulse. With the exception of the fully loaded metallopolymer in methanol, the lifetime increases as the energy of the laser pulse decreases. Under the same conditions, excited state decay from the model, [Ru^{II}b$_2$(b−CONHBz)](PF$_6$)$_2$, was exponential.

Discussion

Synthesis. Our study started with the synthesis of a 1:1 styrene−*m*,*p*-(chloromethyl)styrene copolymer by free radical polymerization. Gel permeation chromatography indicated that it contains, on average, 16 repeat units. The conversion of chloromethylated, cross-linked polystyrene beads to their amine derivatives has been previously reported.[17] The solubility of our polymer in DMF permitted us to carry out the reaction under homogeneous conditions, where it was found to be quantitative. The reaction was achieved in two steps. First, styrene−*p*-

---

(17) Weishenker, N. M.; Shen, C. M. *Tet. Letters* **1972**, *32*, 3281.

Table 3. Excited-State Properties of Osmium-Derivatized Polymers at 298 K in Acetonitrile

compound	E_{em} (nm)[a]	$10^3\ \phi_{em}$[b]	τ (ns)[c]	$10^4\ k_r$ (s^{-1})	$10^7\ k_{nr}$ (s^{-1})
[Osb$_2$b−CONHBz](PF$_6$)$_2$	782	3.5 10^{-3}	51	6.8	2.0
[*co*-PS−CH$_2$NHCO−(Os$_4$Me$_{12}$)](PF$_6$)$_8$	778	4.7 10^{-3}	49	9.6	2.0
[*co*-PS−CH$_2$NHCO−(Os$_8$Me$_8$)](PF$_6$)$_{16}$	778	4.4 10^{-3}	49	8.9	2.0
[*co*-PS−CH$_2$NHCO−(Os$_{16}$)](PF$_6$)$_{32}$	780	3.9 10^{-3}	47	8.4	2.1

[a] Emission band maximum (±2). [b] Emisson quantum yield (±15%) determined by actinometry with [Os(bpy)$_3$](PF$_6$)$_2$ as the standard. [c] Exponential lifetime (±2−4 ns) obtained by analyzing emission decay curves following laser flash excitation at 460 nm.

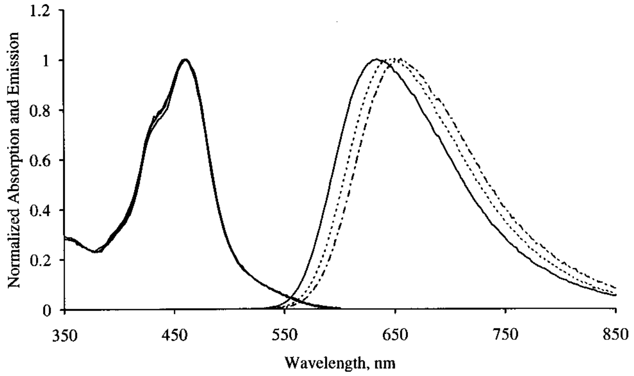


Figure 3. Normalized absorption and emission spectra for [*co*-PS−CH$_2$NHCO−(Ru$^{II}_4$Me$_{12}$)](PF$_6$)$_8$ in 1,2-dichloroethane (—), acetonitrile (···), and methanol (−•−).

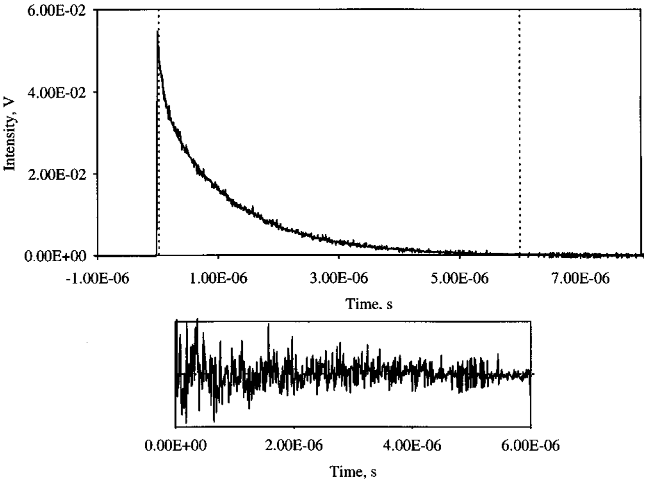


Figure 4. Luminescence decay from [*co*-PS−CH$_2$NHCO−(Ru$^{II}_{16}$)](PF$_6$)$_{32}$ in acetonitrile at 298 K. The overlaid trace is the fit, and the residual from the best fit to eq 4 with $k_1 = 8.8 \times 10^6$ s^{-1} ($a = 0.26$) and $k_2 = 8.3 \times 10^5$ s^{-1}.

(chloromethyl)styrene was treated with potassium phthalimide to yield the phthalimide-derivatized polymer, quantitatively. This material was isolated and characterized by ^{1}H-NMR and by analysis. Subsequent hydrazinolysis led to the fully aminated polymer. This material allowed us to take advantage of a variety of carboxylic acid derivatives of chromophores and quenchers which were commercially available or had been developed for use in related peptide chemistry. The osmium carboxylic acid derivative was prepared specifically for this study. The exceptional substitution-inertness of Os^{II} required that forcing conditions be used in the addition of the last bipyridyl ligand.[9] These were sufficient to esterify the carboxylic acid functional group by condensation with the glycol solvent. A subsequent saponification step was necessary before the desired complex could be isolated. For this and for the analogous ruthenium carboxylic acid complex, we found that total removal of "scrambled" products [M^{II}b(b−COOH)$_2$]$^{2+}$, [M^{II}(b−COOH)$_3$]$^{2+}$, and [M^{II}b$_3$]$^{2+}$ was best achieved by cation exchange chromatography.

Table 4. Excitation Energy Dependence of Excited State Decay for [*co*-PS−CH$_2$NHCO−(Ru$^{II}_4$Me$_{12}$)](PF$_6$)$_8$ in Various Solvents at 298 K with Excitation at 460 nm[a]

solvent	power (μJ/pulse)	τ_1 (μs)	τ_2 (ns)	a	τ_M (μs)
DCE	109	1.36	119	0.77	1.07
	69	1.44	171	0.83	1.23
	45	1.42	154	0.88	1.27
		1.42	160	0.89	1.27
	18	1.39	128	0.95	1.33
	12	1.46	269	0.94	1.39
CH$_3$CN	97	1.33	135	0.95	
	59	1.32	52	0.95	
	38	1.32[b]			
	23	1.30[b]			
	15	1.32[b]			
	11	1.28[b]			
MeOH	105	0.96	104	0.84	0.82
	66	0.96	69	0.86	0.84
	43	0.96	76	0.88	0.86
	26	0.99	104	0.90	0.90
	16	0.99	67	0.96	0.95
	11	0.98	60	0.96	0.95

[a] The data were fit to the biexponential expression in eq 3. The average lifetime, τ_M, was calculated according to eq 4. [b] Single exponential decays.

Table 5. Excitation Energy Dependence of Excited State Decay for [*co*-PS−CH$_2$NHCO−(Ru$^{II}_{16}$)](PF$_6$)$_{32}$ in Various Solvents at 298 K with Excitation at 460 nm[a]

solvent	power (μJ/pulse)	τ_1 (μs)	τ_2 (ns)	a	τ_M (μs)
DCE	94	1.26	187	0.70	0.94
	59	1.24	188	0.72	0.95
	39	1.22	203	0.78	0.99
	23	1.22	177	0.81	1.02
	15	1.21	190	0.83	1.03
	10	1.27	268	0.83	1.10
CH$_3$CN	99	1.21	126	0.72	0.91
	60	1.22	143	0.81	1.02
	39	1.23	127	0.85	1.06
	23	1.23	151	0.86	1.07
	14	1.17	74	0.88	1.04
	9	1.22	183	0.87	1.09
MeOH	113	0.92	124	0.69	0.67
	69	0.87	91	0.70	0.64
	45	0.95	112	0.67	0.68
	27	0.88	137	0.70	0.66
	17	0.80	91	0.64	0.54

[a] The data were fit to the biexponential expression in eq 3. The average lifetime, τ_M was calculated according to eq 4.

Peptide coupling reagents are abundant in the literature.[18] We used Castro's (benzotriazoyloxy)tris(dimethylamino)phosphonium hexafluorophosphate (BOP) in conjunction with 1-hydroxybenzotriazole and *N*-methylmorpholine and (dimethylamino)pyridine as bases, under mild conditions to prepare the model salts [Ru^{II}b$_2$b−CONHBz](PF$_6$)$_2$ and [Os^{II}b$_2$b−CONHBz](PF$_6$)$_2$

---

(18) Jones, J. In *Amino Acid and Peptide Synthesis*; Oxford University Press: New York, 1992; Chapter 5.

in quantitative yield. The same conditions employed to prepare the amide model compounds were used to attach various chromophores and quenchers to the polymer. Significantly, these conditions allowed the synthesis of polymeric samples containing a high content of metal complex on each polymer strand, including the fully derivatized [*co*-PS$-$CH$_2$NHCO$-$(Ru^{II}$_{16}$)](PF$_6$)$_{32}$. We have previously found this extent of loading to be unachievable with the analogous ester-linked complex. Since it was possible to prepare a fully loaded anthracene polymer by this approach, we concluded that the size of the derivatizing group and/or electrostatic repulsion between adjacent units play a significant role in determining the extent of loading.[19] It is an important advantage that amide bond formation allows complete derivatization.

Unreacted carboxylic acid derivatives and coupling reagents were efficiently removed from the polymer products by repeated washings with aqueous sodium bicarbonate. Infrared spectroscopy was used to verify the absence of unreacted carboxylic acids.[20] In contrast, purification of the ether-linked metallopolymer samples required lengthy chromatographic techniques and solvent extractions. We were able to prepare samples containing various proportions of ruthenium and osmium by simply varying the ratio of the complex to the polymer. In the case of partially loaded samples the remaining free amine groups were capped as acetamides. ^{1}H-NMR of the capped metallopolymeric samples allows straightforward determination of the degree of loading. This is due to the fact that the methylene protons attached to amide groups exhibit distinct resonances which depend on the nature of the distal substituent. The ratio of the integrated intensities of all aromatic protons to all methylene protons gives an additional estimate of the loading, and verification of purity. The latter is the only method suitable for determination of the loading of the ether-linked polymers, due to coincidence of the resonances of all methylene groups.

Electrochemistry. The electrochemical properties of the metallopolymers are comparable to those of the model complexes. Reduction potentials for metal oxidation and ligand reduction are reported in Table 1. Bipyridine ligands having electron-withdrawing groups such as the ester or amide model complexes are more easily reduced than those containing unsubstituted bipyridine. The first reduction of [Ru^{II}b$_2$b$-$CH$_2$OBz](PF$_6$)$_2$ occurs at -1.33 V as in [Ru^{II}(bpy)$_3$](PF$_6$)$_2$ since the unsubstituted bipyridine is reduced first in both cases. Half-wave potentials for the M(III/II) couples in metal-derivatized polymers are the same as for the models to within 10 mV, but as in other redox polymers,[21] the peak-to-peak splittings are larger. This is consistent with the multi-electron nature of the redox couples. For the fully loaded polymer, for example, 16 electrons are consumed in cycling through the M$^{III/II}$ wave at a series of closely spaced $E_{1/2}$ values with the spread caused by statistical effects and intrastrand interactions.[22] In all ruthenium-derivatized polymers, cycling through the second reduction leads to a desorption spike when the scan is reversed. Apparently, reduction gives rise to bpy-reduced neutral polymers which precipitate onto the electrode as reported for [Ru^{II}(bpy)$_3$]^0.[23] Similarly, a desorption peak is observed on a reverse scan following bipyridine reduction for the osmium-derivatized samples except for the most highly loaded sample.

Visible Absorption Spectra. Polypyridyl complexes of ruthenium and osmium exhibit intense metal-to-ligand charge transfer (MLCT) absorption in the visible.[24] In the polymers, bands arise from overlapping MLCT transitions to bpy and bpy$-$CONH$-$ as the acceptor ligands. The π^* acceptor level of bpy$-$CONH$-$ is slightly lower than π^* in bpy and is the ligand most easily reduced (-1.24 V). This may account for the slight red shift of the most intense MLCT feature for the ruthenium and osmium model complexes compared to [M^{II}(bpy)$_3$](PF$_6$)$_2$. bpy$-$CONH$-$ is the lowest acceptor ligand in [Ru^{II}b$_2$b$-$CONHBz](PF$_6$)$_2$ and in [*co*-PS$-$CH$_2$NHCO$-$(Ru^{II}$_{16}$)](PF$_6$)$_{32}$ in CH$_3$CN as verified by transient resonance Raman spectroscopy.[3b] This suggests that in the polymers the lowest MLCT excited state may also be bpy$-$CONH$-$ based with the excited electron and excited state dipole directed toward the polymeric backbone (structure shown in the Introduction). This is in contrast to the ether-linked polymers where, on the basis of substituent effects, the excited electron is expected to reside on bpy, directed away from the backbone. Further studies on these systems will be directed toward establishing the effects of these features on rates of intrastrand electron and energy transfer. The decreased distance between the excited state dipole and the adjacent chromophore may enhance energy transfer rates, for example.

MLCT absorption bands are known to be solvent dependent and to respond to changes in local environment.[24,25] In this context, it is significant that absorption band energies and band shapes for the metallopolymers are relatively unchanged in the visible, as the content of metal is varied. There are only slight increases in bandwidths compared to the model complex. There is no evidence in these data for significant interactions between neighboring units in the ground state. Similarly, absorption spectra display only slight solvent shifts as the solvent is varied from 1,2-dichloroethane to methanol. For the Ru^{II} $\rightarrow$ bpy$-$CONH$-$ MLCT absorptions, this could be a consequence of partial shielding of the excited state dipole from solvent by the polymeric backbone. The Ru^{II} $\rightarrow$ bpy absorption should retain a solvent dependence since the excited state dipole is directed away from the backbone, toward the solvent. There is a slight but noticeable solvent dependence on emission, Table 2.

Molar extinction coefficients for the ruthenium and osmium polymers in acetonitrile are reported in Table 1 and illustrated in Figure 2 as a function of the extent of loading. It is clear from these data that ϵ decreases as more metal complex ions are added onto each polymeric chain. This is true even though each separate polymeric sample was found to obey Beer's law from 1×10^{-5} to 2×10^{-6} M. This effect may be likened to deviations from the Beer$-$Lambert law which have been observed on surfaces[26] where there is association or aggregation of chromophores. This "hypochromic effect" has also been observed previously in solution with vinylic polymers having large pendant π-electron groups such as poly-*N*-vinylphenanthrene, poly-*N*-vinylcarbazole, poly-3-vinylpyrene and even

---

(19) Dupray L. M. Unpublished results.

(20) The stretching frequency of the carbonyl function upon conversion from carboxylic acid to amide is shifted by -66 cm^{-1} ($\pm$ 4 cm^{-1}).

(21) Crumbliss, A. L.; Cooke, D.; Castillo, J.; Wisian-Neilson, P. *Inorg. Chem.* **1993**, *32*, 6088.

(22) (a) Brown, G. M.; Meyer, T. J.; Cowan, D. O.; La Vanda, C.; Kaufman, F.; Roling, P. V.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 506. (b) Flanagan, J. B.; Margel, S.; Bard, A. C.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248. (c) Brown, G. M.; Callahan, R. W.; Johnson, E. C.; Meyer, T. J.; Weaver, T. R. *Am. Chem. Soc. Symp. Ser.* **1975**, *No. 5*, 66.

(23) Abruna, H. D.; Teng, A. Y.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 6745.

(24) (a) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193. (b) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (c) Krausz, E.; Fergusson, J. *Prog. Inorg. Chem.* **1989**, *37*, 293. (d) Crosby, G. A.; Highland, K. A.; Truesdall, K. A. *Coord. Chem. Rev.* **1985**, *64*, 41. (e) Watts, R. J. *J. Chem. Ed.* **1983**, *60*, 834. (f) Juris, A.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

(25) Chen, P.; Meyer, T. J. Manuscript in preparation.

(26) (a) Kamat, P. V. *Chem. Rev.* **1993**, *93*, 267. (b) Abdo, S.; Canesson, M. C.; Fripiat, J. J.; Van Damme, H. *J. Phys. Chem.* **1981**, *85*, 797. (c) Shi, W.; Wolfgang, S.; Gafney, H. D. *J. Phys. Chem.* **1985**, *89*, 974. (d) Ghosh, P.; Bard, A. J. *J. Phys. Chem.* **1984**, *88*, 5519.

isotactic polystyrene.[27] It has been postulated that hypochromicity originates from electronic interactions between neighboring groups. This is not the case for the Ru^{II} and Os^{II} polymers since there is no evidence for significant electronic coupling in the ground state.

Excited-State Lifetimes. The MLCT excited states of these polypyridyl complexes decay largely by nonradiative processes with $k_{nr} > k_r$ and $\tau^{-1} \sim k_{nr}$. The effects of the energy gap, coupled vibrations and interactions with solvent on k_{nr} from the lowest lying MLCT state are well understood.[28] There is a contribution to k_{nr} from thermal activation and decay through upper MLCT states[29] and for Ru^{II}, dd states as well.[30]

Emission decay from the model was exponential with lifetimes slightly longer than for $[M^{II}(bpy)_3](PF_6)_2$. Emission decays for the metallopolymeric samples in all three solvents were fit by the biexponential function in eq 3. This approach has been used widely to model processes occurring in disordered and heterogeneous media where relaxation is a superposition of exponential processes.[31] Other nonexponential functions that have been applied to the fitting of MLCT-based luminescence decays include the William−Watts function[32] and its first derivative.[33] The data were fit satisfactorily to the biexponential function in eq 3.

There are many potential sources of nonexponentiality in macromolecules. Our polymer is a random copolymer of styrene and aminomethylstyrene units, with a statistical distribution in chain length and a random loading of luminophores on each strand. Microscopically equivalent excited states are immobilized in slightly different environments leading to a distribution of natural lifetimes. The observed decay curve is a superposition of exponential decays from each of these discrete environments.

The environmental effects are not dynamic. Emission spectra are time independent with emission maxima unchanged during the course of the decays. This shows that solvent relaxation or relaxation of local segmented motions in the backbone are rapid on the time scale for excited state decay. Lifetimes and emission quantum yields decrease as the extent of loading increases. These effects are largely due to an increase in k_{nr}. The loading effect is a relatively small one, only important in the two highly polar solvents. It is not simply an energy gap effect since emission maxima are relatively unaffected, Table 2. The decreased lifetimes in MeOH, compared to CH_3CN are a result of the differences in dielectric properties and, in part to the abilities of ν(O−H) to act as an energy acceptor.[34]

An additional contribution to nonexponential decay is the existence of a dependence of lifetime on the energy of the incident excitation pulse. This effect is not profound but does lead to a decrease in τ_M of up to 30% as the excitation intensity is increased by a factor of 10, Table 4. It appears for both lightly and heavily loaded polymers, except for [*co*-PS−CH_2NHCO−(Ru$^{II}_{16}$)]$(PF_6)_{32}$ in MeOH. The power dependence provides evidence for multiphoton excitation effects in the polymers followed by intrastrand deactivation of the excited states that result. Possible multiphotonic quenching mechanisms include triplet−triplet annihilation either by energy transfer giving a ground state and singlet excited state or by electron transfer to give reduced and oxidized [Rub$_2$b-CONH-]$^{2+}$.[35]

In order for either of these mechanisms to play an important role, it would be necessary to have rapid intrastrand energy transfer hopping, Ru^{II}*,Ru^{II} → Ru^{II},Ru^{II}*. Intrastrand energy transfer in the ether-linked polymers is known to be slow but is greatly enhanced in these amide-linked polymers.[19] Another possibility is that the interaction between excited states is largely a polarization effect. Excitation at one site on a polymeric strand creates an excited state dipole, polarizing the surrounding solvent and the local polymeric backbone. The energy gap of a second excited state formed within the polarization field of the first would be affected as would its nonradiative decay rate constant.

Acknowledgments are made to the Department of Energy under Grant DE-FG05-86ER13633 for support of this research. We wish to thank George Coia for helpful suggestions during the preparation of this paper and Michael Hunt for GPC analysis.

IC9516222

---

(27) (a) Kowal, J. *Macromol. Chem. Phys.* **1995**, *196*, 1195. (b) Klöpffer, W.; Rippen, G.; Kowal, J. *Makromol. Chem., Macromol. Symp.* **1986**, *5*, 187. (c) Pielichowski, J.; Obzrut, J. *Makromol. Chem.* **1980**, *181*, 1209. (d) Okamoto, K.; Itaya, A.; Kusabayashi, S. *Chem. Letters* **1974**, 1167.

(28) (a) Caspar, J. V.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *Chem. Phys. Lett.* **1982**, *91*, 91. (b) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722. (c) Freed, K. F. *Top. Curr. Chem.* **1972**, *31*, 105. (d) Treadway, J. A.; Loeb, B.; Lopez, R.; Anderson, P. A.; Keene, R.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 2242.

(29) (a) Lumpkin, R. S.; Kober, E. M.; Worl, L. A.; Murtaza, Z.; Meyer, T. J. *J. Phys. Chem.* **1990**, *94*, 239. (b) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3967.

(30) (a) Van Houtten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1978**, *17*, 3381. (b) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4803. (c) Wacholtz, W. M.; Auerbach, R. A.; Schmel, R. H.; Ollino, M.; Chery, W. R. *Inorg. Chem.* **1985**, *24*, 1758.

(31) (a) Ghosh, P. K.; Bard, A. J. *J. Phys. Chem.* **1984**, *88*, 5519. (b) Castellano, F. N.; Heimer, T. A.; Tandhasetti, M. T.; Meyer, G. J. *Chem. Mater.* **1994**, *6*, 1041.

(32) (a) Kolrausch, R. *Ann.* **1847**, *5*, 430. (b) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1971**, *66*, 80.

(33) Danielson, E. unpublished results.

(34) Caspar, J. V.; Sullivan, B. P. Kober, E. M.; Meyer, T. J. *Chem. Phys. Lett.* **1982**, *91(2)*, 91.

(35) Balzani V.; Boleta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.