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Step-Scan FTIR Time-Resolved Spectroscopy Study of Excited-State Dipole Orientation in Soluble Metallopolymers

Gregory D. Smith,[†] **Kimberly A. Maxwell,**[‡] **Joseph M. DeSimone,**[‡] **Thomas J. Meyer,***[,‡] **and Richard A. Palmer***[,†]

Departments of Chemistry, Duke University, Durham, North Carolina 27708, and University of North Carolina, Chapel Hill, North Carolina 27599

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Step-scan FTIR time-resolved spectroscopy (S^{2}FTIR TRS) in acetonitrile-d_3 has been used to probe the acceptor ligand in metal-to-ligand charge transfer (MLCT) excited states of amide-substituted polypyridyl complexes of Ru^{II} and in analogues appended to polystyrene. On the basis of ground-to-excited state shifts in ν(C=O) of -31 cm^{-1} for the amide group in [Ru^{II}(bpy)$_2$(bpyCONHEt′)]$^{2+}$ (bpyCONHEt′ = 4′-methyl-2,2′-bipyridine-4-carboxamide-Et′; Et′ = $-$CH$_2$CH$_2$BzCH$_2$CH$_3$) (**1**) and in the derivatized polystyrene abbreviated {PS$-$[CH$_2$CH$_2$NHCObpy$-$Ru^{II}(bpy)$_2$]$_{20}$}$^{40+}$ (**3**), the excited-state dipole is directed toward the amide-containing pyridyl group in the polymer side chain. Smaller shifts in ν(C=O) of -17 cm^{-1} in [Ru^{II}(4,4′-(CONEt$_2$)$_2$bpy)$_2$(bpyCONHEt′)]$^{2+}$ (**2**) and in the derivatized polystyrene abbreviated {PS$-$[CH$_2$CH$_2$NHCObpy$-$Ru^{II}(4,4′-(CONEt$_2$)$_2$bpy)$_2$]$_{20}$}$^{40+}$ (**4**) indicate that the excited-state dipole is directed toward one of the diamide bpy ligands. The nearly identical results for **1** and **3** and for **2** and **4** show that the molecular and electronic structures of the monomer excited states are largely retained in the polymer samples. These conclusions about dipole orientation in the polymers are potentially of importance in understanding intrastrand energy transfer dynamics. The excited-state dipole in **3** is oriented in the direction of the covalent link to the polymer backbone, and toward nearest neighbors. In **4**, it is oriented away from the backbone.

Introduction

Step-scan FTIR time-resolved spectroscopy (S^{2}FTIR TRS) has been used extensively to study the excited-state properties of transition metal complexes.[1−4] This specific time-resolved IR (TRIR) technique offers the advantages of molecular structure specificity, broad spectral range, spectral multiplexing, the ability to access time scales from milliseconds to nanoseconds, and relatively short data acquisition times. Although TRIR in general has found widespread use in examining the excited-state electronic structures of isolated metal complexes, there have been few applications to molecular assemblies containing multiple metal centers.[2] Such studies are warranted considering that synthetic efforts in designing molecular antennas for artificial photosynthesis are leading toward complex multichromophore arrays.[5]

We report here the application of S^{2}FTIR TRS to the determination of excited-state dipole orientation in two 20-mer polystyrene samples derivatized with Ru^{II} polypyridyl complexes. The repeat units of these polymers are illustrated below along with the structures of models, [Ru^{II}bpy$_2$(bpyCONHEt′)]$^{2+}$ (bpyCONHEt′ = 4′-methyl-2,2′-bipyridine-4-carboxamide-Et′; Et′ = $-$CH$_2$CH$_2$BzCH$_2$CH$_3$) (**1**) and [Ru^{II}(4,4′-(CONEt$_2$)$_2$bpy)$_2$(bpyCONHEt′)]$^{2+}$ (**2**). The abbreviations used for the derivatized polystyrenes are {PS$-$[CH$_2$CH$_2$NHCObpy$-$Ru^{II}(bpy)$_2$]$_{20}$}$^{40+}$ (**3**) and {PS$-$[CH$_2$CH$_2$NHCObpy$-$Ru^{II}(4,4′-(CONEt$_2$)$_2$bpy)$_2$]$_{20}$}$^{40+}$ (**4**).

In previous work, intrastrand energy migration was studied in the heteropolymers [*co*-PS$-$CH$_2$NHCO$-$(Ru^{II})$_{13}$(Os^{II})$_3$]$^{32+}$ (**5**) and [*co*-PS$-$CH$_2$OCH$_2-$(Ru^{II})$_{25}$(Os^{II})$_5$]$^{60+}$ (**6**).[6,7] These molecules differ from **3** in that they contain random styrene spacers, and the metal complex linkages to the polystyrene backbone are based on a single $-$CH$_2-$ spacer in **5** and an ether linkage in **6**. Furthermore, these molecules are heteropolymers with a random loading of the Ru^{II} or Os^{II} complex in the ratios indicated. Following Ru^{II} → bpy metal-to-ligand charge transfer (MLCT) excitation of the majority Ru^{II} sites in **5** to give the MLCT excited state, Ru^{II*} (2.13 eV),[8] rapid intrastrand Ru^{II*} → Ru^{II} energy migration occurs with $k > 2 \times 10^8$ s^{-1} in CH$_3$-

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* Corresponding authors.

[†] Duke University.

[‡] University of North Carolina.

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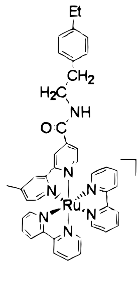

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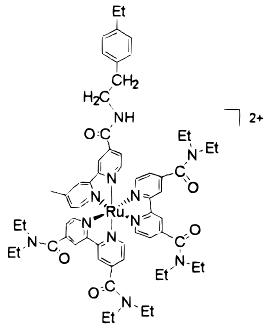

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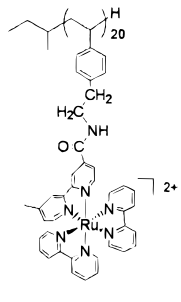

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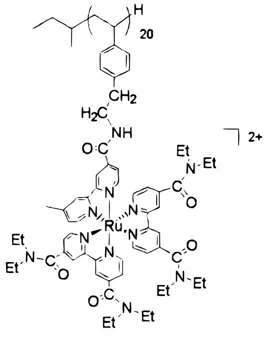

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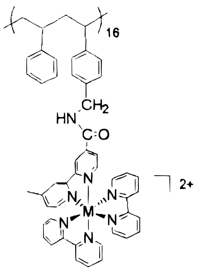
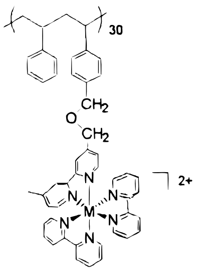


M = Ru^{II}:Os^{II} (13:3)

5



M = Ru^{II}:Os^{II} (25:5)

6

CN at 298 K.[6] By contrast, energy migration following MLCT excitation of Ru^{II} in **6** is slow, with $k < 1 \times 10^6$ s^{-1}.[7]

A possible explanation for the dramatic difference in energy migration rates, based on a difference between the expected excited-state dipole orientations, has been proposed. In **5**, the excited-state dipole is predicted to be oriented toward the amide-containing ligand because of the electron-withdrawing effect of the amide substituent. This would orient the excited-state dipole toward the polymer backbone, and therefore toward nearest neighbors. In **6**, bpy should be the acceptor ligand because of the electron-donating effect of the ether substituent. In this case, the excited-state dipole would be oriented away from the backbone.

We report here the use of S^{2}FTIR TRS to unequivocally determine the orientation of excited-state dipoles in the derivatized polymers **3** and **4**. The application is based on the use of ν(C=O) of amide substituents to confirm the acceptor ligand, and thus the orientation of the excited-state dipole. These results provide convincing evidence that this technique can identify the acceptor ligand even in complex multi-chromophore arrays, and that substituent effects can be used to change the orientation of the excited-state dipole in a predictable manner. Our work also appears to be the first application of this technique to such large metal complex assemblies and provides direct evidence that excited-state molecular and electronic structure are largely retained in the polymeric arrays.

Experimental Section

IR Measurements. The spectra reported here were measured on a step-scan modified Bruker IFS88 spectrometer at 6 cm^{-1} spectral resolution. The samples were dissolved in acetonitrile-d_3 at sufficient concentrations to give an IR absorbance of 0.15−0.5 in a 250 μm path length cell for the amide band analyzed. This gave an approximate concentration of 6 mM for Ru^{II} chromophores in each sample. The solutions were sparged with argon for 50 min before being loaded by syringe into a CaF$_2$-windowed cell. Ground-state spectra were recorded by using the standard rapid-scan mode and corrected for absorption due to trace amounts of water picked up during sample handling. As noted in other similar work,[3] no adverse effects from these trace amounts of water were detected in the transient spectra.

For time-resolved measurements, the samples were excited with the third harmonic (355 nm, 10 ns, 10 Hz) from a Q-switched Quanta-Ray DCR-1A Nd:YAG laser. The lifetime dependence on excitation power dictated that lower irradiance (3 mJ/(pulse cm^2)) be used for polymer samples **3** and **4** compared to that used for samples **1** and **2** (5 mJ/(pulse cm^2)) in order to achieve a sufficient signal-to-noise ratio (SNR). By reducing the laser irradiance, the longer lifetimes for the polymer samples allowed more postexcitation time slices to be averaged. The remaining experimental details for collecting time-resolved data have been fully described elsewhere.[1d]

The interferogram response before and after each laser flash was digitized at 10 ns intervals. In a typical experiment, data from 240 to 2400 laser flashes were averaged at each of the 369 interferogram points. The (ΔA) spectra were calculated from the single beam ΔI transforms by the relation $\Delta A(\bar{\nu},t) = -\log[1 + \Delta I(\bar{\nu},t)/I(\bar{\nu})]$, where $I(\bar{\nu})$ is the intensity before the laser flash and $\Delta I(\bar{\nu},t)$ is the change in intensity at time t. For the ΔA "snapshots," 5−10 time slices immediately following laser excitation were averaged to improve the SNR.

Lifetime Measurements. All CH$_3$CN solutions were sparged with argon for 50 min before emission measurements were performed. Emission lifetimes as a function of incident laser irradiance were measured by using a series of neutral density filters to reduce the power of a 10 Hz Surelite II-10 (Continuum) Nd:YAG−OPO laser system with a pulse width of 6 ns (fwhm) as an excitation source. The excitation wavelength was 460 nm, and the irradiance of the beam (defocused to ∼7 mm in diameter) at the sample was varied randomly from 0.9 to 8.7 mJ/(pulse cm^2) with a pulse width of 5−7 ns (fwhm). The excitation beam from the laser was used to irradiate the sample perpendicular to the optical axis of an f3.4 monochromator and Hammamatsu R446 PMT. The output from the PMT was coupled to a LeCroy 7200A oscilloscope interfaced with an IBM-PC. The solution absorbance was 0.25 at 460 nm for **1** and **3**. Kinetic traces for **3** (average of 500) with decay to >5 lifetimes of the excited state were fit to the triexponential decay function in eq 1. Average lifetimes for **3**, $\langle\tau\rangle$, were calculated by using eq 2. A single-exponential decay function was used to fit the lifetimes for **1** at all incident laser irradiances.

$$I(t) = a_1 e^{-(k_1 t)} + a_1 e^{-(k_2 t)} + a_1 e^{-(k_3 t)} \tag{1}$$

$$\langle\tau\rangle = \frac{a_1 k_1^{-1} + a_2 k_2^{-1} + a_3 k_3^{-1}}{a_1 + a_2 + a_3} \tag{2}$$

Molecular Modeling. Energy-minimized structures of 18-mer analogues of **3** and **4** were calculated by using modified MM2 parameters and CAChe software. In these calculations, the pendant complexes were modeled as open spheres of diameter 14 Å and net 2+ charge with carbon skeletons of the polymer backbone between them.[9a] A schematic representation of the resulting models with the tethered complexes projected onto the spheres is available as Supporting Information.

Table 1. Ground-State (gs) and Excited-State (es) Band Energies and Shifts in ν(C═O) for the ΔA Spectra in Figure 1

	ν(C═O), cm^{-1}		
sample[a]	$\bar{\nu}_{gs}$	$\bar{\nu}_{es}$	$\Delta\bar{\nu} = \bar{\nu}_{es} - \bar{\nu}_{gs}$
$[Ru^{II}bpy_2(bpyCONHEt')]^{2+}$ (**1**)	1672	1641	−31
$[Ru^{II}((CONEt_2)_2bpy)_2(bpyCONHEt')]^{2+}$ (**2**)	1672	1682	~+10[b]
	1637	1620	−17
$\{PS-[CH_2CH_2NHCObpy-Ru^{II}(bpy)_2]_{20}\}^{40+}$ (**3**)	1672	1641	−31
$\{PS-[CH_2CH_2NHCObpy-Ru^{II}(4,4'-(CONEt_2)_2bpy)_2]_{20}\}^{40+}$ (**4**)	1672		
	1637	1620	−17

[a] As PF_6^- salts in acetonitrile-d_3. [b] Uncertain due to poor SNR.

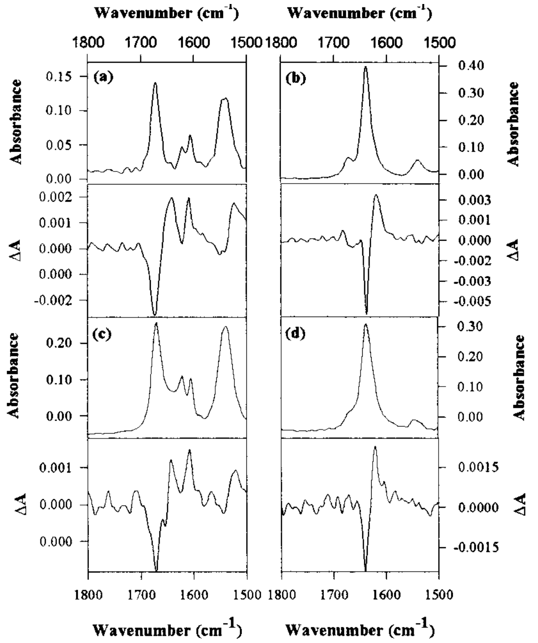


Figure 1. Ground-state IR and S^{2}FTIR ΔA spectra for monomers (a) **1** and (b) **2** and polymers (c) **3** and (d) **4** in acetonitrile-d_3 at 298 K.

Results

Ground-state IR and ΔA snapshot spectra for monomers **1** and **2** and polymers **3** and **4** in the mid-infrared region from 1500 to 1800 cm^{-1} are shown in Figure 1a−d, respectively. Table 1 lists ν(C═O) ground- and excited-state band energies and excited-state shifts for each sample.

For **1** and **3**, with a single amide substituent, ν(C═O) in the ground-state spectra appears at 1672 cm^{-1}, and bpy ring modes occur at 1622, 1605, and 1541 (split) cm^{-1}. For the diamide substituents in **2** and **4**, an additional ground-state ν(C═O) band appears at 1637 cm^{-1}. This mode is the asymmetric ν(C═O) for the diethylamide substituents on the nontethered bpy ligands. At the lower concentrations necessary to obtain reasonable SNR for the strong 1637 cm^{-1} band, only the most intense bpy band at 1541 cm^{-1} was observed.

The ΔA spectra for **1** and **3** are identical within experimental error. A bleach of the ground-state band at 1672 cm^{-1} is observed, and ν(C═O) shifts −31 cm^{-1} to 1641 cm^{-1} in the excited state. Changes in the bpy ring modes are also observed at lower energy. Analogous bands have been noted previously in the analysis of the ΔA spectrum of $Ru(bpy)_3^{2+}$.[3]

The ΔA spectra for **2** and **4** are also similar. A bleach of the ground-state diamide ν(C═O) is observed at 1637 cm^{-1} with a shift of −17 cm^{-1} to 1620 cm^{-1} for ν(C═O) in the excited state in both spectra. Because of the dilute solutions used, the changes in the bpy bands were not generally observable. However, a bleach of the ground-state monoamide ν(C═O) at 1672 cm^{-1} with a positive feature appearing at 1682 cm^{-1} can be distinguished above the noise for **2** in the ΔA spectrum.

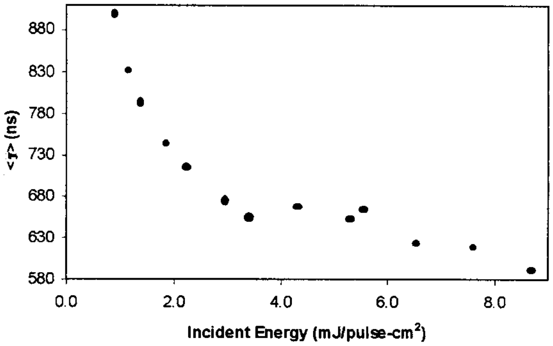


Figure 2. Average lifetime of the MLCT excited state of **3** in CH_3CN at 298 K as a function of irradiance following 460 nm laser flash excitation.

The SNRs of the ΔA spectra for the model **1** and polymer **3** are 7.9 and 2.8, respectively, as calculated by taking the absolute values of the signal strengths of the bleach at 1672 cm^{-1} and dividing by the peak-to-peak average noise of the baseline from 1800 to 1700 cm^{-1}. The spectra were obtained by using a similar number of coadditions on solutions having comparable concentrations of chromophore. The lower SNR for the polymeric sample **3** is a consequence of a shorter average excited-state lifetime. Furthermore, as illustrated by the data in Figure 2, the average lifetime for **3** decreases as the laser irradiance is increased. The average lifetime of the MLCT excited state in **3** was found to decrease from 900 to 590 ns as the excitation irradiance was increased from 0.9 to 8.7 mJ/(pulse-cm^2). There was no laser power dependence for the single-exponential lifetime (1.5 μs) for model complex **1**.

Discussion

The ΔA spectra of model complexes **1** and **2** in Figure 1 illustrate the power of this transient IR technique in identifying the acceptor ligand in asymmetrical polypyridyl complexes, in this case based on shifts in ν(C═O) of the amide substituents. The shift in ν(C═O) for the monoamide ligands in **1** and **3** of −31 cm^{-1} is comparable to the value of −26 cm^{-1} reported earlier for $[Ru^{II}(bpy)_2(4\text{-}CONEt_2\text{-}4'\text{-}CH_3bpy)]^{2+}$.[4a,b] These shifts are consistent with π^* acceptor levels of the amide-containing ligands that have considerable CO character.

Similarly, in the bis(diamide) complexes **2** and **4**, the bleach of the ground-state ν(C═O) at 1672 cm^{-1} and its shift of −17 cm^{-1}, approximately half that found for **1** and **3**, are indicative of a diamide-bpy ligand as the acceptor.[4a] Given the small energy difference between the reduction potentials for the

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monoamide-bpy ligand and diamide-bpy ligand in these complexes,[4b] there might exist some possibility for interligand electron transfer on a fast time scale in **2** and **4**.[10] However, even if this is the case, the diamide-bpy ligand is shown by these experiments to be the dominant MLCT acceptor.

The larger shift in ν(C═O) for the monoamide complexes relative to the diamide complexes points to extensive localization of the excited electron on the pyridine ring bearing the amide substituent. The smaller shift for the diamides and the presence of a single excited-state diamide band in the ΔA spectrum are consistent with delocalization of the excited electron over both of the amide-substituted pyridine rings, at least on the time scale of this experiment (>10 ns). These same conclusions have been reached previously for $[Ru^{II}(bpy)_2(4\text{-}CONEt_2\text{-}4'\text{-}CH_3bpy)]^{2+}$ and $[Ru^{II}(bpy)_2(4,4'\text{-}(CONEt_2)_2bpy)]^{2+}$, where $\Delta\bar{\nu}$ (C═O) was found to be -26 and -15 cm^{-1}, respectively.[4]

The apparent shift in ν(C═O) of $\sim+10$ cm^{-1} for the monoamide in **2** is consistent with the previous statements concerning electron distribution in the excited state. The monoamide-bpy ligand changes from the acceptor ligand in **1** to a spectator ligand in **2**. In the conversion from ground state $[Ru^{II}(4,4'\text{-}(CONEt_2)_2bpy)_2(4\text{-}CONEt_2\text{-}4'\text{-}CH_3bpy)]^{2+}$ to excited-state $[Ru^{III}(4,4'\text{-}(CONEt_2)_2bpy)(4,4'\text{-}(CONEt_2)_2bpy)(4\text{-}CONEt_2\text{-}4'\text{-}CH_3bpy)]^{2+}$, partial oxidation at the metal center results in a frequency shift in ν(C═O) for the spectator ligand because of the loss in $d\pi \rightarrow p\pi^*$(bpy) back-bonding. As shown earlier, oxidative quenching of the MLCT excited state of $[Ru^{II}(bpy)_2(4\text{-}CONEt_2\text{-}4'\text{-}CH_3bpy)]^{2+}$ by methyl viologen results in a comparable shift in ν(C═O) of $\sim+10$ cm^{-1}.[4]

The average excited-state lifetime for polymer **3** diminishes with increasing excitation irradiance, as shown by the data in Figure 2. This effect has been observed previously for polymers **5** and **6** and attributed to a multiphoton effect arising from local polarization and excited-state−excited-state quenching.[6b,7]

Aside from the variation in substitution on the nontethered bpy ligands, there is another, more complex, structural dimension in the polymers arising from the orientation of the excited-state dipoles relative to the polymer backbone that appears to play an important role in intrastrand dynamics. The monoamide tether defines the covalent linkage to the backbone and the relative spatial projection of the complex toward the acceptor ligands on adjacent complexes. The transient IR results clearly show that the MLCT excited-state dipole is oriented toward the tether in **3** and away from it (toward one of the diamide-bpy ligands) in **4**.

Molecular modeling of these polymer-bound complexes has been used to examine the orientation of the excited-state dipole relative to other complexes along an 18-mer chain (illustration available in Supporting Information). In the 18-mer analogue of **3**, the orientation of the dipole along the chemical link directs it toward the polymer backbone and toward nearest neighbors. In the analogue of **4**, the dipole is oriented away from the backbone and away from nearest neighbors. Orientation of the excited-state dipole toward the backbone in **3** greatly decreases the through-bond distance to nearest neighbors relative to the dipole orientation in polymer **4**. With the diamide acceptor ligands in **4**, the through-space distance to nearest neighbors is decreased.

The earlier results comparing amide-linked copolymer **5** with ether-linked copolymer **6** point to the importance of the relative orientation of the excited-state dipole to intrastrand energy transfer, at least in these 1:1 random styrene copolymers. The results of a study currently in progress show that there are differences in energy migration rates between **3** and **4**, but that they are less dramatic than between **5** and **6**, indicating that there may be significant contributions to energy migrations from both through-space and through-bond mechanisms in metallopolymers **3** and **4**. These results will be reported in a subsequent paper.

The transient IR spectra of **1** and **3** are similar, as are the transient spectra of **2** and **4**. This similarity is important in that it demonstrates that the excited states of bound pendant groups in the polymeric samples have the same electronic and molecular structures as the model complexes. These results also demonstrate that the acceptor ligands and local orientation of excited-state dipoles are retained in the metallopolymers and can potentially affect their intrastrand energy transfer dynamics.

Syntheses

Materials. Diethyl ether (Mallinckrodt), CH_3CN (Burdick & Jackson), chloroform-*d* (Cambridge Isotope Laboratories, 99.8 atom % D), acetonitrile-d_3 (Cambridge Isotope Laboratories, 99.96 atom % D), *N*,*N*-bis(trimethylsilyl)lithium amide (1.00 M in hexane), chloromethyl methyl ether, and all other materials were used without further purification unless otherwise stated. Amine−acid coupling reagents, benzotriazol-1-yloxy tris(dimethylamino)phosphonium hexafluorophosphate (BOP, Nova Biochem), 4-(dimethylamino)pyridine (DMAP, Aldrich), 4-methylmorpholine (NMM, Aldrich), and 1-hydroxybenzotriazole hydrate (HOBT, Aldrich) were also used as received. Acetonitrile-d_3 (99.6 atom % D), NH_4PF_6, and *sec*-BuLi (2.5 M in THF) were obtained from Aldrich. Styrene and 4-(chloromethyl)styrene (Aldrich) were passed through short alumina columns to remove *tert*-butylcatechol inhibitor. The styrene was then passed through three freeze−pump−thaw cycles and distilled from dibutylmagnesium (Aldrich, 1.0 M in heptane) before polymerization. Titration of *sec*-BuLi used as initiator in the living anionic polymerizations was performed (three times) using *N*-pivaloyl-*o*-benzylaniline[11] as an indicator in dry THF distilled from Na/benzophenone. Dimethylformamide (DMF, Fisher), CH_2Cl_2 (Mallinckrodt), cyclohexane (Fisher Scientific, stirred over concentrated H_2SO_4 for at least 1 week), and diethylamine (Aldrich) were freshly distilled from CaH_2 before use. Hydrated $RuCl_3$ was obtained from Janssen Chimica. SP-Sephadex C25 resin was purchased from Pharmacia Biotech. 4-Methyl-2,2′-bipyridine-4′-carbaldehyde (bpyCHO),[12] 4-carboxylic acid-4′-methyl-2,2′-bipyridine (bpyCOOH),[12] 4,4′-dicarboxylic acid-2,2′-bipyridine (bpy(COOH)$_2$),[13] and $[Ru^{II}(bpy)_2(bpyCOOH)](PF_6)_2$[6b,12] were synthesized according to published procedures.

4,4′-Diethylamide-2,2′-bipyridine (4,4′-(CONEt$_2$)$_2$bpy) was prepared according to a related published procedure.[14] Bpy(COOH)$_2$ (3.55 g, 14.6 mmol) was added to a flame-dried 500 mL round bottom flask. To the flask was added $SOCl_2$ (200 mL), and the reaction mixture was refluxed and stirred for 22 h. The solvent was removed by vacuum distillation, and the residue was dried under vacuum. The reaction flask was purged with argon, and dry, distilled CH_2Cl_2 was cannulated onto the yellow-brown solid. The mixture was refluxed to enhance the solubility of the acid chloride in CH_2Cl_2 and then cooled to room temperature. Freshly distilled diethylamine was slowly added to the mixture. The reaction mixture was stirred at room temperature for 30 min and then refluxed for 30 min. The solvent was removed by rotary evaporation, and the brown oil was purified by column chromatography (alumina; 2% MeOH in CH_2Cl_2). Solvent was again removed by rotary evaporation, and hexanes were added to precipitate a yellow solid. The pure product was afforded by recrystallization with diethyl ether/

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hexanes. Yield: 2.74 g, 53%. ^{1}H NMR, δ (chloroform-*d*): 1.09−1.14 (3H, t, CH_3), 1.25−1.28 (3H, t, CH_3), 3.19−3.27 (4H, q, CH_2), 3.51−3.59 (4H, q, CH_2), 7.27−7.30 (2H, dd, 5,5′-bpy), 8.39 (2H, s, 3,3′-bpy), 8.69−8.71 ppm (2H, d, 6,6′-bpy). Anal. Calcd for $C_{20}H_{26}N_4O_2$: C, 67.77; H, 7.39; N, 15.81. Found: C, 69.06; H, 7.62; N, 16.21.

$Ru^{II}(4,4'\text{-}(CONEt_2)_2bpy)_2Cl_2\cdot 2H_2O$ was synthesized according to a procedure for $Ru(bpy)_2Cl_2\cdot 2H_2O$ with the following modifications.[15] The reaction was monitored by UV/visible spectroscopy (4.5 h, Abs(395 nm):Abs(568 nm) = 1.05). DMF was removed by vacuum distillation, and the remaining oil was dissolved in water and extracted with CH_2Cl_2 (500 mL, six times). The CH_2Cl_2 was removed by rotary evaporation, and the remaining DMF was removed under vacuum (100 °C, 4 h). The residue was dissolved in a minimum amount of CH_2Cl_2 and triturated with hexanes overnight. Violet crystals resulted and were used without further purification. Yield: 1.42 g, 92%.

$[Ru^{II}(4,4'\text{-}(CONEt_2)_2bpy)_2(bpyCOOH)](PF_6)_2$ was synthesized according to the procedure for $[Ru^{II}(bpy)_2(bpyCOOH)](PF_6)_2$.[6b,12] $Ru^{II}(4,4'\text{-}(CONEt_2)_2bpy)_2Cl_2\cdot 2H_2O$ (1.356 g, 1.479 mmol) and bpyCOOH (0.380 g, 1.78 mmol) were refluxed in 75% EtOH/water for 17 h. A portion of the product (∼250 mg) was dissolved in ∼50 mL of CH_3CN and added slowly to ∼500 mL of deionized water containing a 0.01 M NaH_2PO_4/0.01 M Na_2HPO_4 buffer. The solution was filtered and product separated 2−3 times by cation exchange chromatography (SP-Sephadex C25, 0.0−0.2 M aqueous NaCl gradient; containing buffer). The desired product was eluted with a 0.1 M solution of NaCl. The complex was precipitated by addition of excess NH_4PF_6 in water, acidified with dilute HCl, and cooled to 0 °C for 2 h. The product was filtered on a fine porosity frit and rinsed with dilute aqueous NH_4PF_6 (acidic) and diethyl ether. Crude yield: 90%. ^{1}H NMR, δ (acetonitrile-d_3): 1.03−1.24 (24H, dt, ligand $-CON(CH_2CH_3)_2$), 2.57 (3H, s, bpy-CH_3), 3.21−3.54 (16H, dq, ligand $-CON(CH_2CH_3)_2$), 7.32−7.38 (5H, m), 7.60−7.62 (1H, d), 7.69−7.72 (2H, dd), 7.80−7.83 (3H, m), 7.94 (1H, d), 8.46 (4H, s), 8.56 (1H, s), 8.90 ppm (1H, s). IR: $\nu(C{=}O) = 1636$ (diethylamide) and 1731 cm^{-1} (acid). Anal. Calcd for $RuC_{52}H_{62}N_{10}O_5P_2F_{12}$: C, 47.53; H, 4.76; N, 10.66. Found: C, 45.87; H, 4.67; N, 10.05.

[p-$CH_3CH_2C_6H_5CH_2CH_2NH_4Cl$] was synthesized by the hydrogenation of 4-{2-[*N*,*N*-bis(trimethylsilyl)amino]ethyl}styrene in ethanol with Pd/C as catalyst at 30 psig for 12 h to yield the mostly deprotected amine, which was allowed to react with HCl in THF for 20 min to ensure complete deprotection and quaternization of the amine. The hydrochloric salt was stored under nitrogen for further use. ^{1}H NMR, δ (D_2O): 1.01−1.08 (3H, td, CH_3), 2.44−2.54 (2H, qd, CH_3CH_2Ar), 2.79−2.86 (2H, td, $-ArCH_2CH_2-$), 3.08−3.15 (2H, td, $-CH_2-N-$), 6.99−7.24 ppm (4H, m, Ar).

$[Ru^{II}bpy_2(bpyCONHEt')](PF_6)_2$ (1) was synthesized by reaction of [p-$CH_3CH_2C_6H_5CH_2CH_2NH_4Cl$] (167 mg, 0.899 mmol) with $[Ru^{II}(bpy)_2(bpyCOOH)](PF_6)_2$[13] (150 mg, 0.164 mmol), BOP (145 mg, 0.327 mmol), HOBT (33 mg, 0.25 mmol), NMM (100 μL, 1.4 mmol), and DMAP (25 mg) in dry DMF (∼3 mL) at room temperature for 2 h, followed by precipitation in aqueous NH_4PF_6, rinsing with water and ether, and purification by cation exchange chromatography (same method as described for $[Ru^{II}(4,4'\text{-}(CONEt_2)_2bpy)_2(bpyCOOH)](PF_6)_2$ above, elution with 0.2 M NaCl). ^{1}H NMR, δ (acetonitrile-d_3): 1.09−1.20 (3H, m, CH_3CH_2Ar-), 2.52−2.65 (5H, m, bpy-CH_3 and CH_3CH_2Ar-), 2.85−2.91 (2H, t, $-ArCH_2CH_2N-$), 3.58−3.66 (2H, q, $-CH_2CH_2-N$), 7.05−7.09 (2H, m, Ar), 7.14−7.20 (2H, m, Ar), 7.25−7.27 (1H, d, bpy), 7.35−7.41 (4H, m, bpy), 7.46 (1H, br t, NH), 7.53−7.58 (2H, t, bpy), 7.67−7.71 (4H, m, bpy), 7.81−7.83 (1H, d, bpy), 8.01−8.07 (4H, t, bpy), 8.47−8.50 (5H, m, bpy), 8.72 ppm (1H, s, bpy). IR: $\nu(C{=}O) = 1670$ cm^{-1}. UV−vis (CH_3CN) λ (ε): 248 (26 660), 290 (69 800), 456 nm (15 040 M^{-1} cm^{-1}). Anal. Calcd for $RuC_{42}H_{39}N_7OP_2F_{12}$: C, 48.10; H, 3.75; N, 9.35. Found: C, 47.30; H, 3.67; N, 9.15.

$[Ru^{II}(4,4'\text{-}(CONEt_2)_2bpy)_2(bpyCONHEt')](PF_6)_2$ (2) was synthesized by reaction of [p-$CH_3CH_2C_6H_5CH_2CH_2NH_4Cl$] (167 mg, 0.899 mmol) with $[Ru^{II}(4,4'\text{-}(CONEt_2)_2bpy)_2(bpyCOOH)](PF_6)_2$ (215 mg, 0.164 mmol), BOP (145 mg, 0.327 mmol), HOBT (33 mg, 0.25 mmol), NMM (100 μL, 1.4 mmol), and DMAP (25 mg) in dry DMF (∼3 mL) at room temperature, followed by precipitation in aqueous NH_4PF_6, rinsing with water and ether, and purification by cation exchange chromatography (same method as described for $[Ru^{II}(4,4'\text{-}(CONEt_2)_2bpy)_2(bpyCOOH)](PF_6)_2$ above, elution with 0.2 M NaCl). ^{1}H NMR, δ (acetonitrile-d_3): 1.03−1.21 (27H, m, CH_3CH_2Ar- and ligand $-CON(CH_2CH_3)_2$), 2.56 (5H, m, bpy-CH_3 and CH_3CH_2Ar-), 2.86−2.91 (2H, t, $-ArCH_2-$), 3.12−3.29 (8H, m, ligand $-CON(CH_2CH_3)_2$), 3.42−3.68 (10H, m, $-CH_2CH_2-NH-$ and ligand $-CON(CH_2CH_3)_2$), 7.03−7.23 (4H, m, Ar), 7.59−7.36 (5H, m, bpy), 7.50 (1H, br t, NH), 7.59−7.72 (4H, m, bpy), 7.78−7.88 (3H, m, bpy), 8.45−8.49 (5H, m, bpy), 8.74 ppm (1H, s, bpy). IR: $\nu(C{=}O) = 1636$ (diethylamide) and 1669 cm^{-1} (monoamide). UV−vis (CH_3CN) λ (ε): 250 (38 700), 298 (75 540), 464 nm (18 620 M^{-1} cm^{-1}). Anal. Calcd for $RuC_{62}H_{76}N_{11}O_5P_2F_{12}$: C, 51.52; H, 5.23; N, 10.66. Found: C, 50.85; H, 5.17; N, 10.48.

Poly(4-{2-[*N*,*N*-bis(trimethylsilyl)amino]ethyl}styrene) parent polymer was synthesized similarly to published procedures.[9] The glassware and stir bars were washed with HF solution (10%), thoroughly rinsed with distilled water, dried overnight, and flame-dried with a strong argon purge. All solvents were purged with argon for ∼20 min before use and left under ∼10 psi of argon. Dry THF (∼200 mL) was cannulated into a 500 mL round bottom flask. Monomer, 4-{2-[*N*,*N*-bis(trimethylsilyl)amino]ethyl}styrene (10.0 g, 34.3 mmol), was added to the reaction flask via glass syringe. The stirred solution was cooled to −78 °C in a dry ice/acetone bath. In a separate flask, a titration of styrene in THF was performed (0.06 mL of *sec*-BuLi was added before the characteristic yellow color persisted) to determine the additional amount of *sec*-BuLi initiator needed. The polymerization was initiated by the rapid addition of *sec*- BuLi (1.45 mL, 1.79 mmol, 1.23 M solution in cyclohexane, 0.762 mmol) via a 1 mL glass syringe, and the solution was stirred for 2 h at −78 °C. The polymerization was terminated by the addition of argon-purged MeOH (2 mL). The polymer was precipitated by dropwise addition to excess methanol, filtered on a medium-porosity frit, and rinsed with MeOH. The polymer was precipitated two more times. Yield: ∼9.7 g. The product was stored in a desiccator. ^{1}H NMR, δ (chloroform-*d*): 0.2 (18H, s, $SiMe_3$), 1.1−2.0 (3H, br, backbone $-CH_2-CH-$), 2.58 (2H, br, $-Ar-CH_2-$), 2.92 (2H, br, $-N-CH_2-$), 6.0−7.1 ppm (4H, br, aromatic). GPC: $\bar{M}_n$ (calcd) = 5.8×10^3, $\bar{M}_w = 6.4 \times 10^3$, $\bar{M}_n = 5.9 \times 10^3$ (DP = 20), $\bar{M}_w/\bar{M}_n = 1.08$. DSC: $T_g = 43.8$ °C.

Poly[4-(2-aminoethyl)styrene] deprotected parent polymer was prepared similarly to previous methods.[9] The parent polymer, poly(4-{2-[*N*,*N*-bis(trimethylsilyl)amino]ethyl}styrene) (1 g), was dissolved in THF (30 mL). Concentrated HCl (∼4 mL) was added, and the resulting white suspension was stirred for ∼15 min. THF (∼50 mL) was added, and the hydrochloric salt of the amine was filtered and rinsed with THF. The white powder was dissolved in water and added dropwise to a solution of Na_2CO_3 (200 mL, 1 M), and a cloudy white mixture resulted. The pH was adjusted to ∼7 (very important), and the mixture was cooled for 20 min and poured into ∼300 mL of cold water. A white precipitate resulted and was filtered off on a 600 mL medium porosity frit. The solid was rinsed with water and ether.

$\{PS-[CH_2CH_2NHCObpy-Ru^{II}(bpy)_2]_{20}\}(PF_6)_{40}$ (3) was synthesized similarly to a published method[9a] by reaction of poly[4-(2-aminoethyl)styrene] (65 mg, 2.18×10^{-5} mol) with $[Ru^{II}(bpy)_2(bpyCOOH)](PF_6)_2$ (600 mg, 6.54×10^{-4} mol), BOP (579 mg, 1.31×10^{-3} mol), HOBT (133 mg, 9.81×10^{-4} mol), NMM (92 μL, 1.3×10^{-3} mol), and DMAP (80 mg) in dry DMF (∼3 mL) at room temperature for 2 h, followed by precipitation in diethyl ether. The solid was filtered, dissolved in a minimum amount of CH_3CN, and precipitated by addition to a solution of $NaHCO_3$ (∼0.5 M). The product was filtered and washed with water and diethyl ether. The polymer was further reacted with acetic anhydride (420 μL, 4.45 mmol) in CH_3CN at 40 °C for 2 h to ensure complete conversion of the amines to amide functionalities. The polymer was purified either by passing a CH_3CN solution through a pipet filled with silica gel or by metathesis to the chloride salt with LiCl, followed by gel filtration chromatography on a Sephadex LH-20 resin using a 30 cm × 5 cm^2 column with MeOH as eluent. ^{1}H NMR, δ (acetonitrile-d_3 with 2 drops of D_2O added):

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1.0−1.6 (2H, backbone −C*H*$_2$CHAr−), 2.2−2.8 (6H, bpy-CH$_3$, backbone −CH$_2$*CH*Ar−, and −ArC*H*$_2$CH$_2$N−), 3.15−3.55 (2H, −CH$_2$C*H*$_2$N−), 6.0−7.1 (4H, −CH$_2$CH*Ar*−), 7.1−7.4 (5H, bpy), 7.4−7.75 (6H, bpy), 7.75−8.1 (5H, bpy), 8.2−8.5 (5H, bpy), 8.6−8.9 ppm (1H, bpy). IR: ν(C=O) = 1667 cm^{-1}. UV−vis (CH$_3$CN) λ (ϵ): 248 (27 020), 290 (66 540), 456 (15 280 M^{-1} cm^{-1}). Anal. Calcd for Ru$_{20}$C$_{844}$H$_{790}$N$_{140}$O$_{20}$P$_{40}$F$_{240}$: C, 48.24; H, 3.69; N, 9.33. Found: C, 48.36; H, 3.66; N, 9.20.

{**PS−[CH$_2$CH$_2$NHCObpy−Ru^{II}(4,4′-(CONEt$_2$)$_2$bpy)$_2$]$_{20}$**}**(PF$_6$)$_{40}$ (4)** was synthesized as described for **3** by reaction of poly[4-(2-aminoethyl)-styrene] (30 mg, 1.01 × 10^{-5} mol) with [Ru^{II}(4,4′-(CONEt$_2$)$_2$bpy)$_2$-(bpy-COOH)](PF$_6$)$_2$ (400 mg, 3.04 × 10^{-4} mol), BOP (269 mg, 6.08 × 10^{-4} mol), HOBT (62 mg, 4.6 × 10^{-4} mol), NMM (43 μL, 6.1 × 10^{-4} mol), and DMAP (40 mg) in dry DMF (~3 mL) at room temperature for 2 h. The polymer was further reacted with acetic anhydride (193 μL, 2.05 mmol) in CH$_3$CN at 40 °C for 2 h. ^{1}H NMR, δ (acetonitrile-d_3 with 2 drops of D$_2$O added): 0.9−1.3 (26H, backbone −C*H*$_2$CHAr− and ligand −CON(CH$_2$C*H*$_3$)$_2$), 2.3−2.9 (6H, bpy-CH$_3$, backbone −CH$_2$C*H*Ar−, and −ArC*H*$_2$CH$_2$N−), 3.0−3.7 (ligand −CON-(C*H*$_2$CH$_3$)$_2$), 3.7−3.65 (ligand −CON(C*H*$_2$CH$_3$)$_2$ and −CH$_2$C*H*$_2$NH−), 6.1−7.15 (4H, Ar), 7.2−7.5 (5H, bpy), 7.5−8.0 (7H, bpy), 8.35−8.95 ppm (6h, bpy). IR: ν(C=O) = 1635 (diethylamide) and 1667 cm^{-1} (monoamide). UV−vis (CH$_3$CN) λ (ϵ): 250 (26 670), 298 (50 970), 464 (13 010 M^{-1} cm^{-1}). Anal. Calcd for RuC$_{62}$H$_{76}$N$_{11}$O$_5$P$_2$F$_{12}$: C, 51.66; H, 5.12; N, 10.65.

Measurements. The molecular weights and molecular weight distribution for the trimethylsilyl-protected parent polymer were obtained by gel permeation chromatography (GPC) on a Waters 150-CV GPC with THF eluent and Ultrastyragel columns of 100, 500, 10^3, and 10^4 Å porosities. Polystyrene standards (Showa Denko) were used to determine the molar mass and molar mass distribution. Differential scanning calorimetry analysis was performed on a Perkin-Elmer DSC-7 with a heating rate of 5 °C/min. A Bruker AX500 NMR spectrometer with a 30° pulse, a relaxation delay of 1 s, and 256 scans was used to generate high resolution ^{1}H NMR spectra of **3** and **4** in acetonitrile-d_3 (99.95 atom % D) with 2 drops of D$_2$O (99.96 atom % D) at 323 K. The extent of loading of the Ru^{II} complexes on the polymers was determined to be complete.[16] All other ^{1}H NMR spectra were obtained on a Bruker Aspect 3000 (WM 250 MHz) spectrometer (acetonitrile-d_3, 99.6 atom % D). UV−visible spectra (CH$_3$CN solutions) were recorded on a Hewlett-Packard HP-8452A diode array spectrophotometer with quartz cells. The IR spectrum of **1** was obtained by using a Mattson Galaxy 5000 series FT-IR spectrometer at 2 cm^{-1} resolution and averaging 25 scans. Elemental analyses were performed by Oneida Research Services, Inc. (Whitesboro, NY).

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Supporting Information Available: Schematic drawing of energy-minimized structures of analogues of **3** and **4** (see text). This material is available free of charge via the Internet at http://pubs.acs.org.

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