Synthesis and Study of the Absorption and Luminescence Properties of Polymers Containing $Ru(BpyMe_2)_3^{2+}$ Chromophores and Coumarin Laser Dyes

Jason Serin,[†] Xavier Schultze,[†] Alex Adronov,[‡] and Jean M. J. Fréchet*,[†]

Department of Chemistry, University of California, Berkeley, 718 Latimer Hall,
Berkeley, California 94720-1460; and Department of Chemistry, McMaster University,
Hamilton, Ontario, Canada L8S 4M1

Received February 19, 2002; Revised Manuscript Received May 2, 2002

ABSTRACT: Polymers containing coumarin and $Ru(BpyMe_2)_3^{2+}$ chromophores were synthesized using a grafting approach and also a copolymerization approach. It was found that the solubility of polymers made from Ru-containing monomers was higher than that observed for comparable polymers obtained by grafting of Ru complexes onto bpy-containing prepolymers. The resulting bichromophoric macromolecules exhibited enhanced absorption and luminescence properties compared to the single $Ru(BpyMe_2)_3^{2+}$ complexes due to a very efficient (>95%) energy transfer between the coumarin donor dyes and the ruthenium chromophores. In addition, a novel system in which two different donor dyes are present together with the Ru complex was synthesized and also found to deliver efficient energy transfer to the ruthenium complexes.

Introduction

Solar irradiation on the earth's surface provides several times the energy needed by its population.[1] Considering the rapid and widespread depletion of fossil fuels, the utilization of this abundant source of energy is clearly important. Among the artificial systems capable of harvesting and using solar energy, ruthenium complexes have been the center of extensive research due to their unique photophysical and electrochemical properties.[2−5] In particular, ruthenium polypyridine complexes have attracted much interest due to their ability to oxidize or reduce a wide range of substrates under visible light irradiation, leading to systems capable of photocatalytic decomposition of water[6−8] and applications such as the sensitization of wide band-gap semiconductors.[9−11] The quenching of excited-state ruthenium has also been used in pH, temperature and pressure sensors as well as for the production of singlet molecular oxygen.[12] However, ruthenium(II) complexes display relatively low extinction coefficients in the visible ($<14\,000$ $M^{-1}\cdot cm^{-1}$), as well as low quantum yields of luminescence.[13]

Our lab has recently developed several light-harvesting dendrimers exhibiting very efficient Förster-type energy transfer from laser dyes at the periphery of the molecule toward a single chromophore at the focal point.[14] The luminescence of the acceptor dye is thus greatly enhanced due to energy transfer from the numerous donor dyes that act as an efficient light-harvesting antenna. Although the energy transfer efficiencies within our dendrimers are extremely high, their widespread use as functional materials may be limited to high added value applications due to the relative complexity of their preparation. To explore the applicability of more readily addressed architectures, we have also explored certain dye-functionalized polymeric systems that bear some resemblance to the light-harvesting dendrimers.[15] Although these polymers did not achieve the level of performance of true dendrimers, they indeed functioned as light-harvesting antennae affording relatively high energy transfer efficiencies, depending on the incorporation ratios of the dye-labeled monomers.

Recently, the synthesis of metal-containing polymers has attracted considerable attention due to their numerous applications in the fields of catalysis, conducting and photoresponsive materials, as well as in supramolecular chemistry.[16] Particularly noteworthy are the works of Fraser[17] and Meyer[18] concerning the synthesis of linear and star-shaped polymeric ruthenium complexes from bipyridine-functionalized polymers. Along similar lines, we have shown that polymers containing ruthenium complexes in combination with a single type of coumarin chromophore also undergo energy transfer and function as light-harvesting antennae.[19] In an attempt to improve the light-harvesting and conversion efficiencies, and expand the spectral range of absorption within these structures, we now report an extensive study of the synthesis and characterization of polymeric complexes of ruthenium tris(dimethylbipyridine) ($Ru(BpyMe_2)_3^{2+}$) in combination with multiple laser dyes. These new polymer systems display very high energy transfer efficiencies and are therefore potentially interesting for applications in photovoltaics, luminescence-based sensors, and catalytic systems.

Initially, the grafting of $Ru(BpyMe_2)_2Cl_2$[20] onto copolymers with pendant bipyridine groups having various linkers was studied. In addition, polymerization of a ruthenium-functionalized monomer was attempted and found to be a better alternative. This strategy enabled us to synthesize a terpolymer containing the ($Ru(BpyMe_2)_3^{2+}$) complex and two different coumarin donor chromophores, effectively demonstrating an efficient energy transfer system in which excitation energy is passed from the two types of donors to the acceptor chromophore either in a stepwise cascade fashion or by direct energy transfer.

---

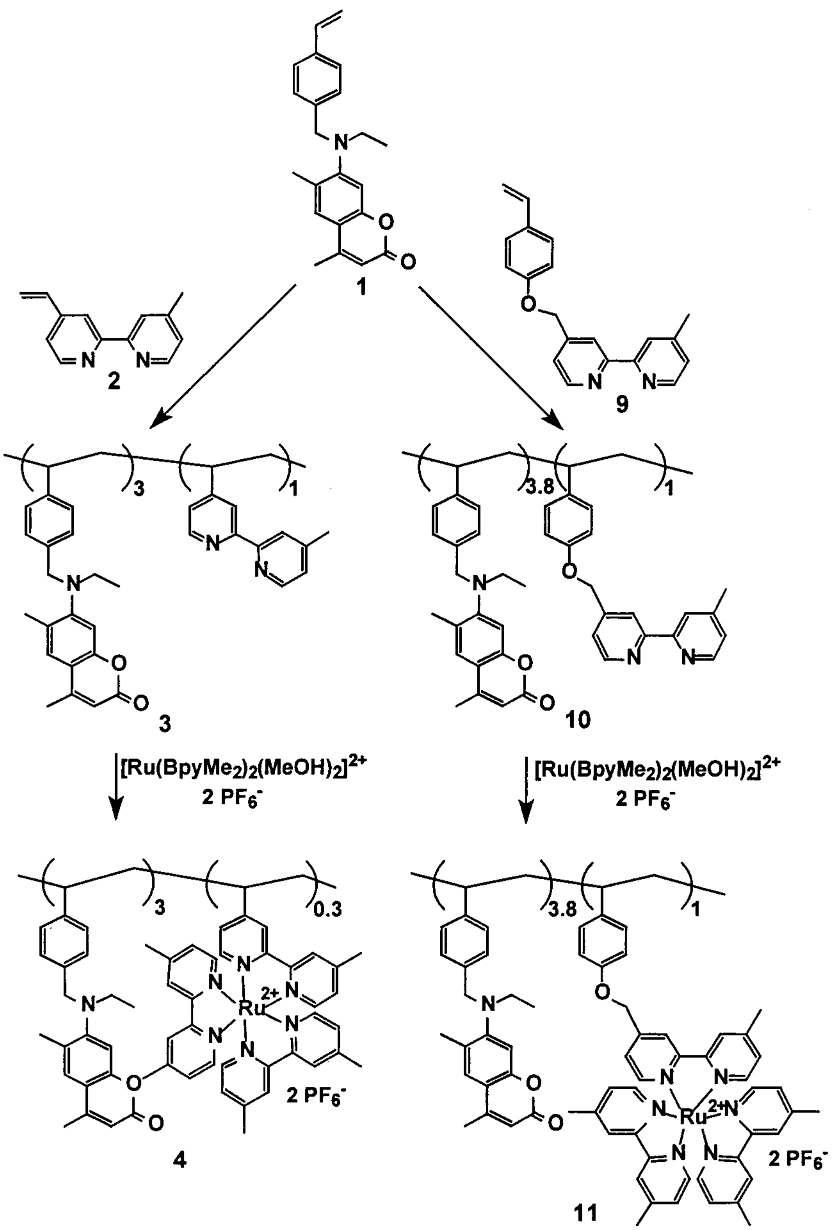
* Corresponding author. Telephone: (510) 643-3077. Fax: 643-3079. E-mail: frechet@cchem.berkeley.edu.

[†] University of California, Berkeley.

[‡] McMaster University. Telephone: (905) 525-9140 ext. 23514. Fax: (905) 522-2509. E-mail: adronov@mcmaster.ca.

10.1021/ma020265t CCC: $22.00

Scheme 1



Results and Discussion

A series of coumarin-2/Ru(BpyMe$_2$)$_3^{2+}$ copolymers was prepared through the polymerization of coumarin-2- and bipyridine-functionalized monomers followed by complexation of Ru(BpyMe$_2$)$_2$(MeOH)$_2^{2+}$·2PF$_6^-$ (Scheme 1). In a first attempt, **1** and **2** were polymerized in a 3:1 ratio, respectively, in chlorobenzene with AIBN as initiator.[19] A copolymer (**3**) was obtained with a composition reflecting the monomer feed. The Ru(BpyMe$_2$)$_2$(MeOH)$_2^{2+}$·2PF$_6^-$ intermediate, obtained by refluxing Ru(BpyMe$_2$)$_2$Cl$_2$[20] with AgPF$_6$ in methanol overnight,[21] was then refluxed with **3** in dimethoxyethane for 48 h. The UV–vis spectrum of the resulting polymer (**4**) exhibited a new absorption band at 465 nm due to the formation of the ruthenium complex (Figure 1). The efficiency of Ru incorporation, calculated using the extinction coefficients of both chromophores and comparing the relative absorption of both chromophores within the polymer, was estimated to be only 30%. However, a significant energy transfer was observed between coumarin-2 and the ruthenium complex as determined from the quenching of the coumarin-2 emission in Figure 2. On the basis of our earlier work with similar chromophores,[14,15] we believe this to be a through-space Förster type energy transfer[2d,22] made possible by the overlap of the emission spectrum of the coumarin dye with the Ru(BpyMe$_2$)$_3^{2+}$ metal-to-ligand charge transfer (MLCT) band at 465 nm. An energy transfer efficiency of 70% was calculated by comparing the fluorescence of the coumarin-2 chromophore before and after grafting of the ruthenium complex.[19] A significant antenna effect was observed, which resulted in a 5-fold increase of the ruthenium emission at 630 nm when **4** was excited at 350 nm (the coumarin-2 maximum absorption wavelength) relative to 465 nm, which corresponds to the direct excitation of the ruthenium chromophore (Figure 2, inset).

It has previously been observed that the grafting of Ru(Bpy)$_2$Cl$_2$ on a bipyridine containing poly(acrylate) was drastically improved when a spacer group was introduced between the bipyridine and the polymer backbone.[23] Therefore, we synthesized monomer **9** by

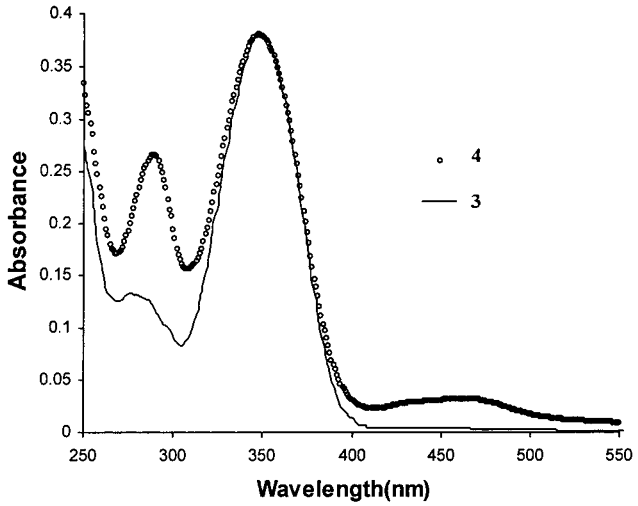


Figure 1. UV−vis spectra of **3** and **4** normalized at the coumarin-2 maximum absorption.

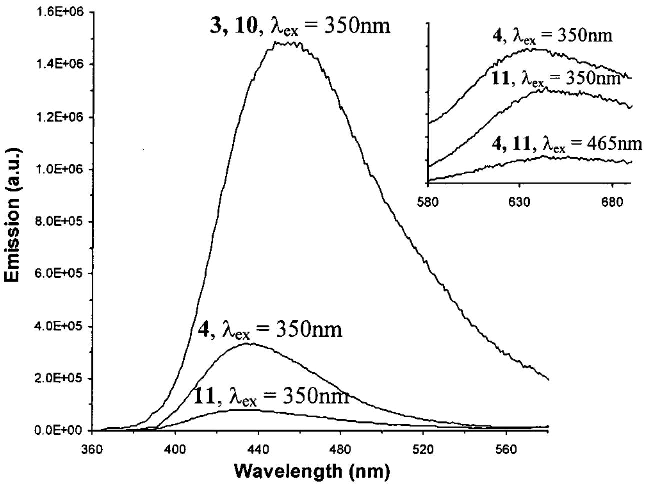
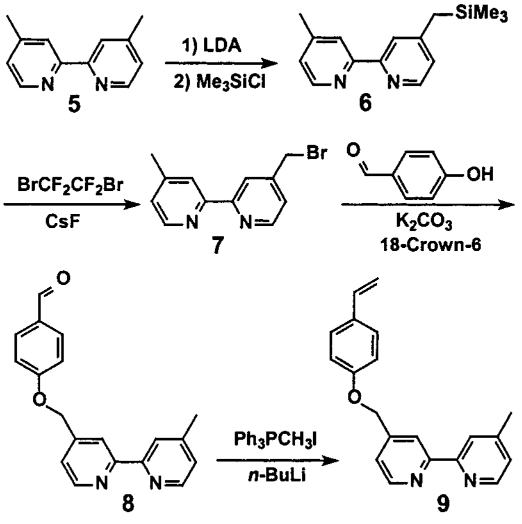


Figure 2. Luminescence spectra of **3**, **4**, **10**, and **11** in the coumarin-2 emission region. The inset shows the antenna effect observed in the region where the Ru(BpyMe$_2$)$_3^{2+}$ emits.

first deprotonating a single benzylic position of **5** with lithium diisopropylamide (LDA) followed by anion trapping with trimethylsilyl chloride (TMSCl) to form **6**. Subsequent bromination using 1,2-dibromotetrafluoroethane gave compound **7** in 74% overall yield, which was previously prepared using a three-step synthesis in 31% overall yield.[24] Compound **7** was then coupled to *p*-hydroxybenzaldehyde to form **8**. Monomer **9** was synthesized from **8** using a standard Wittig reaction (Scheme 2). Polymerization of **9** with **1** using a 1:3 ratio (**9**:**1**) in a minimum amount of dichlorobenzene containing 2% AIBN was then performed (Scheme 1). After two successive precipitations in Et$_2$O, **10** was obtained as a white powder. The composition of **10** (Table 1) was determined by integrating the methylene protons at the benzyl positions of both monomers in the ^{1}H NMR spectrum. The ratio of **9** to **1** in the polymer was found to be 0.8:3, respectively. The UV−vis spectrum of **10** displays two bands at 290 and 350 nm, characteristic of the bipyridine and the coumarin-2 units (Figure 3). Grafting of the Ru(BpyMe$_2$)$_2$(MeOH)$_2^{2+}$•2PF$_6^-$ complex was performed (vide supra; Scheme 1) to afford a red polymer (**11**) exhibiting the characteristic UV absorption of the ruthenium MLCT at 465 nm (Figure 3). As expected, although the ratio of bipyridine to coumarin-2 in **10** is slightly lower than in **7**, the introduction of the aryl ether spacer leads to an improved grafting efficiency (>95%) of the ruthenium complex (as determined from the UV−vis spectrum of **11** in Figure 3). Fluorescence measurements showed an energy-transfer efficiency of better than 95%, as calculated by comparing the emission of coumarin-2 at 450 nm in both **10** and **11** when exciting the polymer at 350 nm (Figure 2). At this excitation wavelength (as opposed to 465 nm), the emission of the ruthenium chromophore is amplified by a factor of 3.6 as a result of an antenna effect (Figure 2, inset). This increase of the ruthenium emission is lower than in the case of **4** as a result of the higher Ru content and therefore higher Ru(BpyMe$_2$)$_3^{2+}$:coumarin-2 ratio in **11**.

Scheme 2



Although these macromolecular complexes display high energy-transfer efficiencies resulting in an enhanced excitation of the ruthenium chromophore, they are only slightly soluble in common organic solvents. Therefore, the terpolymerization of monomers **1**, **9**, and styrene was performed in order to “dilute” the polymer with styrene moieties used as solubilizing groups. These monomers were polymerized to 37% conversion in a feed ratio of 1:1:10 (**1**:**9**:styrene) to produce polymer **12** with

Table 1. Composition of the Studied Coumarin/Ruthenium Polymers

compound	monomer feed[a]	polymer composition[a]	M_w; PDI	yield (%)
3	**1** (0.75); **2** (0.25)	**1** (0.75); **2** (0.25)	15400; 1.6	70
10	**1** (0.75); **9** (0.25)	**1** (0.79); **9** (0.21)	41300; 1.4	76
12	**1** (0.083); **9** (0.083); styrene (0.83)	**1** (0.083); **9** (0.083); styrene (0.83)	33 000; 1.3	37
16	**1** (0.75); **14** (0.25)	**1** (0.75); **14** (0.25)	nd[b]	60
17	**1** (0.25); **14** (0.75)	**1** (0.36); **14** (0.64)	nd[b]	20
21	**14** (0.2); **1** (0.4); **20** (0.4)	**14** (0.41); **1** (0.29); **20** (0.3)	nd[b]	42
22	**2** (0.2); **1** (0.4); **20** (0.4)	**2** (0.42); **1** (0.32); **20** (0.26)	22800; 1.7	36

[a] The number in parentheses represents the mole fraction of the monomer in the feed and in the polymer. [b] nd = not determined (see Experimental Section).

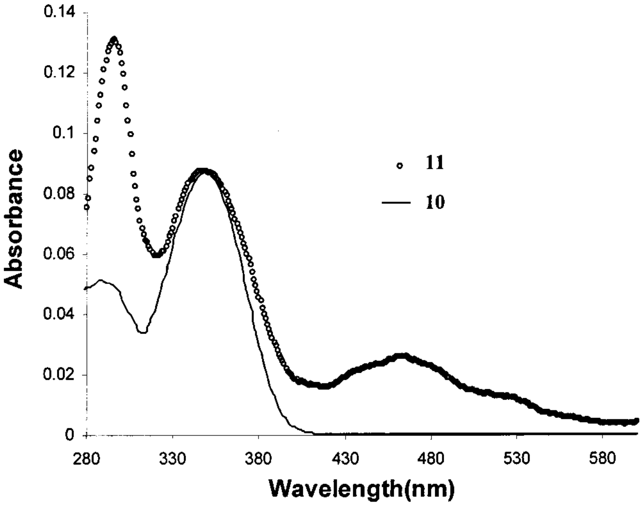
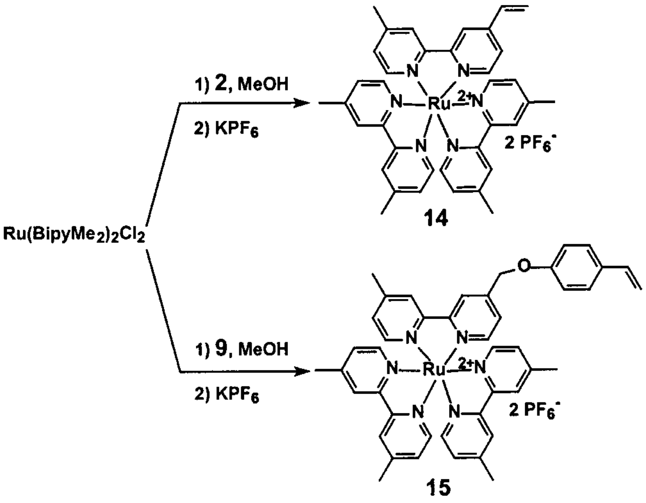


Figure 3. UV–vis spectra of **10** and **11** normalized at the coumarin-2 maximum absorption.

Scheme 3



a repeat unit composition of 1:1:10 (**1**:**9**:styrene) as determined by ^{1}H NMR and elemental analysis. Grafting of the Ru complex was performed as described above. Although the resulting terpolymer **13** demonstrated improved solubility in DMF and DMSO, its solubility remained low. The energy transfer efficiency and the $\mathrm{Ru(BpyMe_2)_3}^{2+}$ functionalization in **13** were found to be ca. 86%, and 60%, respectively.

We believe that the low solubility of **4**, **11**, and **13** arises from secondary reactions resulting in a partial cross-linking of the polymers.[25] To circumvent this limitation, we studied the synthesis and polymerization of two ruthenium-containing monomers. Monomers **14** and **15** were obtained in 95% and 90% yield, respectively, by reaction of the corresponding bipyridine-functionalized monomers **2** and **9** with $\mathrm{Ru(BpyMe_2)_2Cl_2}$ in MeOH, followed by ion exchange with $\mathrm{KPF_6}$ (Scheme 3). Copolymerization of these monomers with **1** was attempted in DMF with AIBN as the initiator. After 12 h at 90 °C, the reaction mixture was precipitated twice in $\mathrm{Et_2O}$ and washed with MeOH to remove the unreacted ruthenium monomer. When monomer **14** was polymerized with **1** in a 1:3 ratio, a red solid (**16**) was obtained, which exhibited enhanced solubility properties in organic solvents ($\mathrm{CH_2Cl_2}$, DMF) and also displayed a near quantitative energy-transfer efficiency between the coumarin-2 and the ruthenium complex. This is clearly seen in the quenching of donor emission (Figure 4). The significant change in solubility of **16** supports the theory that cross-linking led to the low solubility of **4**, **11**, and **13**. This is particularly clear for terpolymer **13** for which solubility remained low despite the incorporation of 83 mol % of styrene.

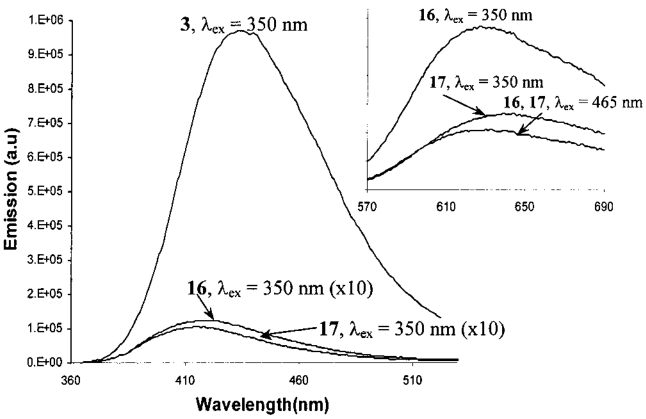


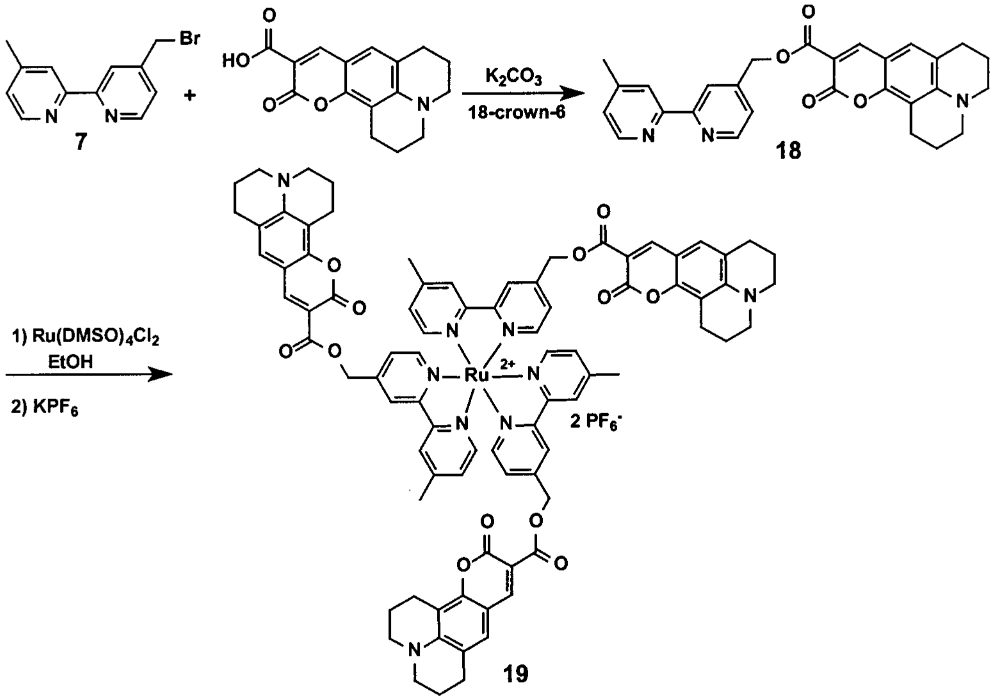
Figure 4. Luminescence spectra of **3**, **16**, and **17**. The inset shows the antenna effect when exciting the donors (λ_{ex} = 350 nm) vs the acceptors (λ_{ex} = 465 nm).

To study the impact of the ruthenium content on the solubility of the polymer and on the antenna effect, a different copolymer (**17**) was prepared from a 3:1 feed ratio of **14** and **1**, respectively, using the same polymerization conditions as for **16** (Table 1). The lower isolated yield (20%) obtained for this copolymerization was due to product loss during purification of the copolymer. As incorporation of the ruthenium monomer into the copolymer increases, so does its solubility in MeOH. Therefore, a portion of **17** dissolves in MeOH along with the unreacted monomer **14** during the purification step. Although more than 50% of this copolymer is composed of highly ionic $\mathrm{Ru(BpyMe_2)_3}^{2+}$ units, the copolymer still remains soluble in solvents of low polarity ($\mathrm{CH_2Cl_2}$, $\mathrm{CHCl_3}$). For both of these copolymers, a high energy-transfer efficiency from the coumarin-2 donors to the Ru-containing acceptors was observed upon excitation at 350 nm (Figure 4). This results in an increased emission at 630 nm when exciting the donor chromophores (λ_{ex} = 350 nm) vs the acceptor chromophores (λ_{ex} = 465 nm, Figure 4, inset). As expected, since the ratio of the donor to acceptor decreases from **16** to **17**, so does the antenna effect. The emission at 630 nm is amplified by a factor of 2.7 in **16** as opposed to 1.3 in **17** when exciting at 350 nm vs 465 nm.

While polymerization of monomer **1** with **14** proved successful, all attempts to polymerize **15** with **1** failed. It is believed that, due to the proximity of the ruthenium center, the benzylic protons in **15** are more labile relative to those in monomer **9**, thereby encouraging chain transfer termination pathways.

To further enhance the emission properties of these ruthenium macromolecular complexes, the introduction of a third chromophore capable of efficient light harvesting and energy transfer was studied. Coumarin-343 exhibits a relatively high extinction coefficient (ϵ = 4.9×10^4 $\mathrm{M^{-1}{\cdot}cm^{-1}}$ at 450 nm) and an intense emission band between 450 and 500 nm (Φ_f = 0.8). Therefore, this chromophore should be a good energy-donor candidate for a ruthenium tris(bipyridine) complex. Model compound **19** was prepared to study energy transfer between these two dyes (Scheme 4). Coupling of cou-

Scheme 4



marin-343 with **7** in the presence of K_2CO_3 and 18-crown-6 afforded **18** in 86% yield. Reaction of this ligand with $Ru(DMSO)_4Cl_2$[26] produced model compound **19** in 35% yield. The normalized luminescence spectra of **18** and **19** are shown in Figure 5. As can be seen in this figure, the emission of **18** at 470 nm ($\lambda_{ex} = 400$ nm) is completely quenched after complexation with $Ru(DMSO)_4Cl_2$. Furthermore, a 5.8-fold increase in the ruthenium emission at 630 nm is observed when **19** is excited at 400 nm as opposed to 480 nm. Since the absorbance of the $Ru(BpyMe_2)_3{}^{2+}$ complex in **19** at 480 nm is slightly lower than at 465 nm ($A_{480}/A_{465} = 0.9$), extrapolation of the data at 465 nm suggests that the antenna effect provided by the coumarin-343 dyes results in a 5.2-fold increase of the ruthenium emission when excited at its maximum absorption (assuming that the luminescence quantum yield remains constant between 465 and 480 nm). Both the quenching of the coumarin emission and the resulting antenna effect confirm that this dye is an excellent energy donor for the ruthenium tris(bipyridine) complex. As a result of this model study, the synthesis of a ruthenium-functionalized polymer containing the coumarin-2 and coumarin-343 donor dyes (Figure 6) was carried out in order to obtain a macromolecule with improved light-harvesting properties between 300 and 450 nm.

Terpolymerization of **1** and **14** along with a styrenic coumarin-343 monomer[15] (**20**) in a ratio of 2:1:2, respectively, gave terpolymer **21** (Scheme 5). In addition, model terpolymer **22** was also synthesized from a mixture of **1**, **2**, and **20** (2:1:2) in order to determine the energy transfer efficiency of the two coumarin dyes in the ruthenium-containing polymer. The UV−vis spectra of both polymers are shown in Figure 7. The presence of the ruthenium MLCT band accounts for the broadening of the coumarin-343 absorption band between 400 and 500 nm. Monomers **2** and **14** are readily incorporated to the same extent in **22** and **21**, respectively, suggesting that the introduction of ruthenium does not affect significantly the reactivity of the vinyl group. The emission spectrum of model polymer **22** (Figure 8) shows a nearly quantitative quenching of the coumarin-2 fluorescence and the appearance of the coumarin-343

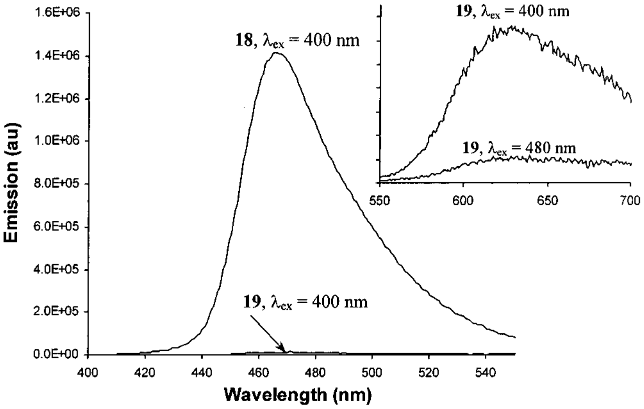


Figure 5. Luminescence spectra of **18** and **19**. The inset shows the antenna effect when exciting the ruthenium center through the donor chromophore ($\lambda_{ex} = 400$ nm).

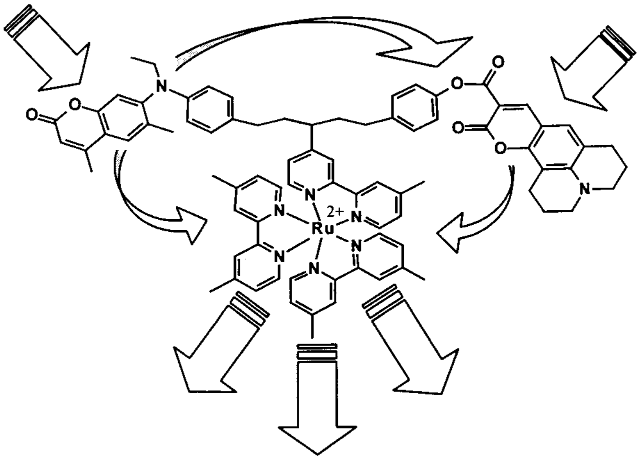
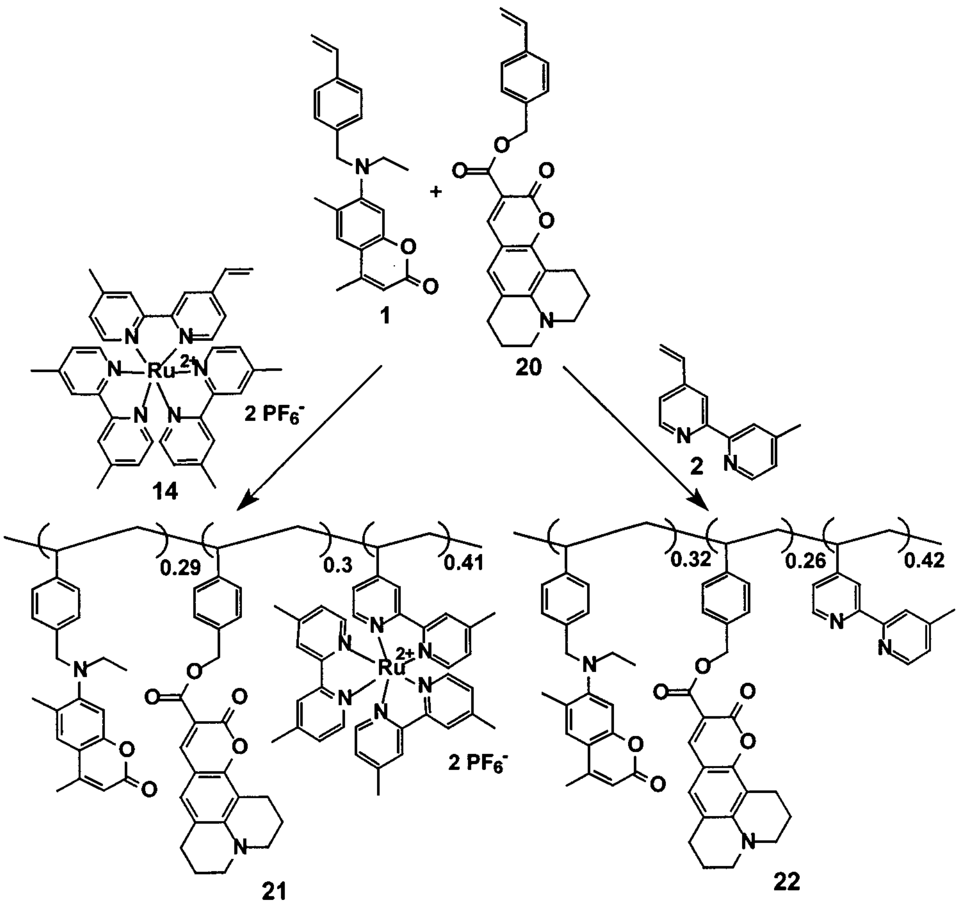


Figure 6. Graphic representation of the light-harvesting system containing two-donor chromophores.

Scheme 5



fluorescence band at 480 nm, as well as a broad band between 510 and 700 nm resulting from excimer formation due to the lack of an appropriate acceptor.[15] Significant attenuation of these two bands is observed for **21** as a result of energy transfer between the two coumarin dyes and the ruthenium complex. The efficiency of this process is above 95% for both laser dyes. Extrapolating from the values obtained at 480 nm excitation (Figure 8), the antenna effect observed when exciting **21** at 350 and 400 nm is 1.5× and 3.1×, respectively, when compared to direct excitation at 465 nm. As a result of the efficient transfer of the additional energy absorbed by the coumarin dyes between 300 and 450 nm, the macromolecular complex **21** exhibits highly enhanced absorption and luminescence properties.

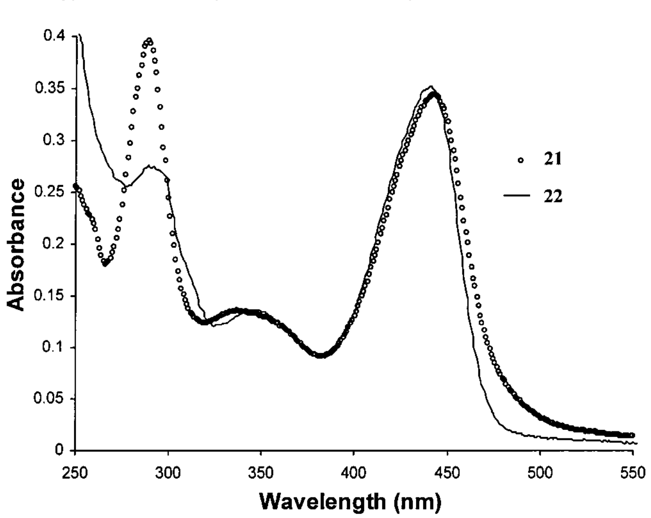


Figure 7. UV–vis spectra of polymer **21** and **22** normalized to the coumarin-2 maximum absorption.

Conclusion

Polymers containing coumarin laser dyes (energy donors) and a $Ru(BpyMe_2)_3^{2+}$ chromophore (energy acceptor) have been synthesized. These macromolecules efficiently concentrate absorbed energy through energy transfer at the acceptor and display a significant antenna effect. A grafting approach led to polymers that displayed low solubility, which could not be improved

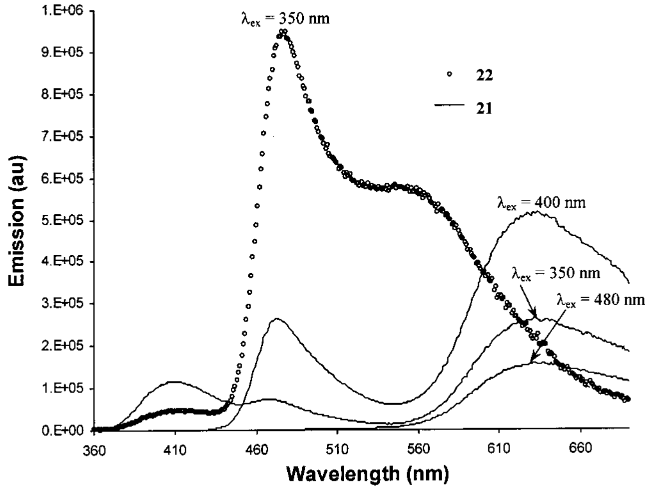


Figure 8. Luminescence spectra of **21** and **22** showing the quenching of the coumarin-2 and coumarin-343 donor emission and the resulting antenna effect when exciting **21** at 350 and 400 nm.

by either the addition of styrene into the polymer backbone or the placement of a spacer between the backbone and the acceptor chromophore. However, the solubility was improved by copolymerizing the donor monomer(s) with a $Ru(BpyMe_2)_3^{2+}$ acceptor monomer. The antenna effect observed in these systems was easily tuned by changing the ratio of donor to acceptor within the copolymer. The absorption and luminescence properties of these macromolecular compounds were further improved by introducing a second coumarin dye. In light of these findings, the application of these metallopolymers to photonic[27] and photovoltaic devices as well as ruthenium-promoted photoreactions is of continuing interest.

Experimental Section

THF was dried over Na/benzophenone before use. All solvents used for absorption and luminescence measurements were spectroscopic grade. All the other solvents were anhydrous and reagent grade. Absorption spectra were recorded on a Cary 50 UV−vis spectrometer in chloroform. Emission and excitation spectra were obtained using an ISA/SPEX Fluorolog 3.22 equipped with a 450W Xe lamp, double excitation and double emission monochromators, and a digital photon-counting photomultiplier. Samples for luminescence experiments were dissolved in chloroform or in DMF in standard 1 cm quartz cells. The optical density was kept below 0.1, and the samples were degassed by bubbling argon for 5 min before each measurement. All measurements were performed at room temperature. The compositions of the polymers in Table 1 were determined by elemental analysis and/or by UV−vis spectroscopy using the extinction coefficients of monomers **1** ($\epsilon = 1.5 \times 10^4$ $M^{-1}\cdot cm^{-1}$ at 350 nm), **20** ($\epsilon = 4.9 \times 10^4$ $M^{-1}\cdot cm^{-1}$ at 450 nm), and **14** ($\epsilon = 1.4 \times 10^4$ $M^{-1}\cdot cm^{-1}$ at 465 nm) to determine the relative concentrations of each monomer within the copolymers or terpolymers. The molecular weights of **3**, **10**, **12**, and **22** were determined by GPC in DMF at a flow rate of 1 mL/min using a 2690 XE Alliance separation module (Waters) equipped with a column set comprising two 300 × 7.5 mm i.d. 10^3 and 10^5 Å Polymer Labs gel columns thermostated at 55 °C. Unfortunately, the GPC method could not be applied to the ruthenium-containing polymers **4**, **11,** **13**, **16**, **17**, and **21**. Similar problems have already been reported in the literature[28] and arise from the strong interaction of ruthenium with the stationary phase used in the GPC columns. However, it should be mentioned that several examples for the successful GPC characterization of metal-containing polymers have been reported.[29] Attempts at characterizing the polymer through MALDI−TOF MS using a variety of matrices were also unsuccessful. Monomers **1**, **2**, **14**, and **20** were synthesized as previously described in the literature.[15,19,30] The composition, molecular weight, polydispersity, and yield of the various polymerizations are reported in Table 1. High-resolution mass spectra (HRMS) were obtained on a Micromass ProSpec using electron impact (EI) and a Micromass LCT using electrospray (ES). Matrix-assisted laser desorption ionization time-of-flight (MALDI−TOF) mass spectrometry was performed on a PerSeptive Biosystems Voyager-DE spectrometer using a delayed extraction mode and with an acceleration voltage of 20 keV. Samples were prepared from a solution of DMF using 2-(4-hydroxyphenylazo)benzoic acid (HABA) as the matrix.

Synthesis of 4-Bromomethyl-4′-methyl-2,2′-bipyridine (7). A solution of 1.80 mL of diisopropylamine (128 mmol, 1.18 equiv) in 20 mL of THF at 0 °C was treated with 4.80 mL of 2.28 M *n*-BuLi (hexane solution, 109 mmol, 1.00 equiv), and the mixture was stirred for 30 min under Ar. A solution of **5** (2.00 g, 109 mmol) in 75 mL of THF was quickly added to the reaction mixture, and the dark brown solution was allowed to warm to room temperature and stirred for 2 h. It was then cooled to −78 °C, and 1.5 mL of chlorotrimethylsilane (118 mmol, 1.09 equiv) was quickly injected. After 30 s, 5 mL of ethanol was injected to quench the reaction and the mixture was stirred for 10 min. A saturated aqueous solution of sodium bicarbonate (50 mL) was added, and the mixture turned yellow upon formation of a precipitate. The mixture including the precipitate was poured into a separatory funnel and extracted with ethyl acetate (3 × 200 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and evaporated to dryness to yield a yellow solid (**6**) (2.79 g, 99%). This product was used without further purification. ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 2.17$ (s, 2), 2.39 (s, 3), 6.90 (d, $J = 5$ Hz, 1), 7.08 (d, $J = 5$ Hz, 1), 8.02 (s, 1), 8.19 (s, 1), 8.44 (d, $J = 5$ Hz, 1), 8.49 (d, $J = 5$ Hz, 1).

To a mixture of the crude product (2.00 g, 780 mmol) and dibromotetrafluoroethane (2.00 mL, 167 mmol, 2.1 equiv) in 100 mL of DMF was added CsF (3.15 g, 207 mmol, 2.7 equiv). The suspension was stirred at room temperature for 3 h and then poured into a separatory funnel containing 200 mL of H_2O. The mixture was extracted with ethyl acetate (3 × 200 mL), and the organic layers were combined, washed with brine (3 × 200 mL), dried over Na_2SO_4, filtered, and evaporated to dryness to yield a clear, colorless oil, which solidified overnight under vacuum (1.55 g, 75%). ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 2.44$ (s, 3), 4.48 (s, 2), 7.15 (d, $J = 4$ Hz, 1), 7.33 (d, $J = 4$ Hz, 1), 8.24 (s, 1), 8.42 (s, 1), 8.54 (d, $J = 4$ Hz, 1), 8.65 (d, $J = 4$ Hz, 1). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 21.09$, 30.66, 120.87, 121.95, 123.40, 124.89, 147.07, 148.14, 148.92, 149.55, 155.21, 156.85. UV ($CHCl_3$): $\lambda_{max} = 285$ nm. HRMS (EI): calcd for $C_{12}H_{11}N_{2}79Br_{1}$ $m/z = 262.0117$, found $m/z = 262.0105$; calcd for $C_{12}H_{11}N_{2}81Br_{1}$ $m/z = 264.0087$, found $m/z = 264.0085$.

Synthesis of 4-Methyl-4′-(*p*-benzaldehyde)methyl-2,2′-bipyridine Ether (8). A solution of **7** (1.06 g, 4.03 mmol) in 10 mL of acetone was treated with *p*-hydroxybenzaldehyde (541 mg, 4.43 mmol), K_2CO_3 (1.11 g, 8.06 mmol), and 18-crown-6 (106 mg, 0.443 mmol). The solution was stirred at reflux for 7 h. The resulting pink solution was concentrated, redissolved in a minimum of CH_2Cl_2, and filtered through Celite. The product was concentrated, dissolved in a minimum of CH_2Cl_2, and purified by column chromatography on silica gel first passivated with 9:1 hexanes:Et_3N using first 7:3 hexanes:EtOAc and then 7:3 CH_2Cl_2:EtOAc as the eluents to yield 1.15 g of a white solid (94%). ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 2.43$ (s, 3), 5.23 (s, 2), 7.08 (d, $J = 9$ Hz, 2), 7.15 (d, $J = 5$ Hz, 1), 7.37 (d, $J = 5$ Hz, 1), 7.84 (d, $J = 8$ Hz, 2), 8.24 (s, 1), 8.44 (s, 1), 8.53 (d, $J = 5$ Hz, 1), 8.68 (d, $J = 5$ Hz, 1), 9.88 (s, 1). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 21.11$, 68.49, 115.04, 118.80, 121.24, 122.00, 124.92, 130.40, 131.95, 146.07, 148.21, 148.92, 149.49, 155.35, 156.65, 163.00, 190.61. UV ($CHCl_3$): $\lambda_{max} = 283$ nm. mp 95−96 °C. MS (EI): $m/z = 304$ (M^+), 183. Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 74.69; H, 5.33; N, 8.81.

Synthesis of 4-Methyl-4′-(*p*-vinylaryl ether)methyl-2,2′-bipyridine (9). To a flame-dried flask charged with argon was added Ph_3PCH_3I (173 mg, 427 μmol) and 1 mL of THF. The solution was cooled to 0 °C, and *n*-BuLi (23 mg, 3.6×10^2 μmol, 1.1 equiv) was added with a syringe while stirring. The resulting bright yellow-orange solution was warmed to room temperature, allowed to equilibrate for 40 min, and again cooled to 0 °C. To another flame-dried flask charged with argon was added **8** (100 mg, 281 μmol) and 1 mL of THF. This solution was added to the first flask via cannula. The mixture was stirred at room temperature for 2.5 h, and 1 mL of MeOH was added to quench the reaction. A saturated aqueous $NaHCO_3$ (10 mL) solution was added, and the solution was poured into a separatory funnel containing 10 mL of H_2O. The mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, and evaporated to dryness. The product was then taken up in a minimum of CH_2Cl_2 and purified by column chromatography on silica gel first passivated with 9:1 CH_2Cl_2:Et_3N using 7:3 CH_2Cl_2:EtOAc as the eluent, to yield 64 mg of a white solid (64%). ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 2.43$ (s, 3), 5.13 (d, $J = 12$ Hz, 1), 5.15 (s, 2), 5.61 (d, $J = 18$ Hz, 1), 6.61−6.68 (dd, $J = 12$, 18 Hz, 1), 6.92 (d, $J = 8$ Hz, 2), 7.13 (d, $J = 5$ Hz, 1), 7.34 (d, $J = 9$ Hz, 2), 7.39 (d, $J = 5$ Hz, 1), 8.25 (s, 1), 8.43 (s, 1), 8.54 (d, $J = 5$ Hz, 1), 8.66

(d, $J = 5$ Hz, 1). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 21.05$, 68.02, 111.98, 112.78, 117.85, 121.38, 121.99, 124.90, 127.43, 130.92, 134.01, 147.13, 148.16, 148.87, 149.39, 155.61, 156.48, 157.82. UV ($CHCl_3$): $\lambda_{max} = 266$ nm. mp 117−121 °C. MS (EI): $m/z = 302$ (M^+), 277, 201, 183, 152, 77. Anal. Calcd for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26. Found: C, 79.08; H, 5.91; N, 9.21.

Synthesis of Ruthenium Bis(4,4′-dimethyl-2,2′-bipyridine) 4-Methyl-4′-(*p*-vinylaryl ether)methyl-2,2′-bipyridine (15). To a solution of **9** (100 mg, 330 μmol) dissolved in 16 mL of MeOH was added Ru(4,4′-dimethyl-2,2′-bipyridine)$_2$Cl$_2$ (162 mg, 300 μmol), and the solution was stirred at reflux for 12 h. The solution was concentrated, dissolved in a minimum amount of H_2O, and added to 20 mL of a saturated solution of KPF_6. The resulting precipitate was filtered, washed with H_2O, and dried under vacuum to yield 285 mg of a red solid (90%). ^{1}H NMR (400 MHz, DMF-d_7): $\delta = 2.45{-}2.56$ (m, 15), 5.14 (m, 1), 5.39 (m, 2), 5.73 (m, 1), 6.73 (m, 1), 7.09 (d, $J = 7$ Hz, 2), 7.32−7.49 (m, 8), 7.67 (s, 1), 7.84 (m, 4), 8.56 (s, 1), 8.72 (s, 1), 8.81 (s, 3), 8.90 (s, 1), 9.02 (s, 1). ^{13}C NMR (100 MHz, DMF-d_7): $\delta = 19.41$, 19.43, 66.74, 110.64, 110.92, 114.13, 114.16, 121.31, 124.25, 126.72, 126.76, 127.64, 127. 83, 130.40, 135.38, 147.69, 149.01, 150.09, 150.89, 155.87, 156.02, 157.17. MS (ES): $m/z = 917$ $(M^{2+} - PF_6^-)^+$, 385 $(M^{2+} - 2PF_6^-)^{2+}$. Anal. Calcd for $C_{44}H_{42}F_{12}N_6OP_2Ru$: C, 49.77; H, 3.99; N, 7.91. Found: C, 49.92; H, 4.14; N, 7.72.

Synthesis of Coumarin-343-Functionalized 4,4′-Dimethyl-2,2′-bipyridine (18). A mixture of coumarin-343 (215 mg, 754 μmol), **7** (125 mg, 503 μmol), K_2CO_3 (380 mg, 2.74 mmol), and 18-crown-6 (28.0 mg, 114 μmol) was refluxed in 11 mL CH_3CN. After 3 h, the solution was cooled to room temperature, poured into a separatory funnel containing 300 mL of H_2O, and extracted with CH_2Cl_2 (3 × 200 mL). The organic layers were combined, washed with brine (200 mL), dried over Na_2SO_4, and evaporated to dryness. The resulting solid was then taken up in a minimum of CH_2Cl_2, and the product was isolated by column chromatography on silica gel, first passivated with 9:1 hexanes:Et_3N, using 9:1 CH_2Cl_2:CH_3OH as the eluent, to yield 190 mg of a dark yellow solid (86%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 1.96{-}1.99$ (m, 4), 2.45 (s, 3), 2.75−2.77 (m, 2), 2.87−2.91 (m, 2), 3.32−3.37 (m, 4), 5.44 (s, 2), 6.96 (s, 1), 7.14 (d, $J = 4$ Hz, 1), 7.53 (d, $J = 4$ Hz, 1), 8.24 (s, 1), 8.40 (s, 1), 8.41 (s, 1), 8.54 (d, $J = 4$ Hz, 1), 8.68 (d, $J = 4$ Hz, 1). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 8.56$, 19.87, 19.95, 20.92, 21.07, 27.24, 45.95, 49.77, 50.17, 64.60, 70.44, 110.39, 119.16, 119.30, 121.82, 121.93, 124.72, 127.07, 144.96, 148.84, 149.39, 149.54. Anal. Calcd for $C_{28}H_{29}N_3O_6 \cdot 2H_2O$: C, 66.79; H, 5.80; N, 8.34. Found: C, 66.51; H, 5.87; N, 8.23.

Synthesis of Ru(Bpy-C343)$_3$(PF$_6$)$_2$ (19). A solution of **18** (60.0 mg, 128 μmol) and Ru(DMSO)$_4$Cl$_2$[26] (20 mg, 41 μmol) in 5 mL of ethanol was stirred at reflux for 4 days. The reaction mixture was then concentrated, dissolved in a minimum amount of H_2O, and added dropwise to 20 mL of a saturated solution of KPF_6 in H_2O. The precipitate was filtered and washed with 200 mL of H_2O. The resulting solid was dissolved in a minimum amount of CH_2Cl_2 and precipitated into 20 mL of Et_2O twice. It was then stirred in 20 mL of MeOH at room temperature for 24 h. The mixture was filtered, washed with 200 mL of MeOH, and dried under reduced pressure to yield 26 mg of a yellow solid (35%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 1.97$ (s, 12), 2.59 (s, 9), 2.77 (m, 6), 2.87 (m, 6), 3.35 (s, 12), 5.50 (s, 6), 7.06 (m, 3), 7.3 (m, 3), 7.52−7.68 (m, 9), 8.31 (s, 3), 8.47 (m, 3), 8.69 (s, 3). No ^{13}C NMR data could be obtained due to the low solubility of **5**. UV/vis ($CHCl_3$): $\lambda_{max} = 283$, 447 nm. MS (MALDI): $m/z = 1504.3$ $(M^{2+} - 2PF_6^- - H^+)^+$, 1649.9 $(M^{2+} - PF_6^-)^+$, calcd $m/z = 1502.63$, 1648.61. MS (ES): calcd for $m/z = 751.7296$ $(M^{2+} - 2H^+ - 2e^- - 2PF_6^-)$; found $m/z = 751.7155$.

Polymerization. In a typical experiment, **1** (331 mg, 990 μmol), **9** (100 mg, 330 μmol), and AIBN (0.87 mL of a 3×10^{-2} M solution in chlorobenzene) were placed in a 2 mL flask. The solution was degassed (freeze−thawed) twice, purged with argon, and heated at 90 °C for 14 h. The solution was then precipitated twice in 20 mL of Et_2O, filtered and washed with 100 mL of MeOH giving 337 mg of a white powder (**10**) (76%). M_w: 41 300 Da. PDI: 1.43. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 0.84$ (br s, $-CH_2CH_3$), 1.32−1.60 (br m, $-CH_2-$ & $-CH-$), 2.26−2.38 (br m, aromatic $-CH_3$), 2.85 (br s, $N-CH_2-CH_3$), 3.98 (br s, $N-CH_2-$, 3), 4.95 (br s, $O-CH_2-$, 0.8), 6.03 (br s, aromatics), 6.12−7.15 (br m, aromatics), 7.17−7.35 (br m, aromatics), 8.12−8.55 (br m, aromatics). Anal. Calcd for $C_{79}H_{82}N_5O_6$: N, 5.85. Found: N, 5.68. M_w: 15 400 Da. PDI: 1.6.

The same procedure was used for **3**, **12**, **16**, **17**, **21**, and **22** except that **16**, **17**, **21**, and **22** were obtained in DMF and further purified by overnight trituration in MeOH to remove the unreacted ruthenium monomers.

Grafting Procedure. In a general procedure, 75 mg of **10** was added to 38 mL of a solution of Ru(**5**)$_2$(MeOH)$_2$ (PF$_6$)$_2$ (94 mg, 1.14 mmol) in dimethoxyethane (60 mL, 3.1 mM). The reaction vessel was fitted with a reflux condenser and a mechanical stirrer, heated at reflux for ca. 48 h, and cooled to room temperature. The mixture was filtered, diluted with dichloromethane, and washed with water to remove the unreacted ruthenium complex. The dichloromethane solution was then concentrated and precipitated in ether to afford 96 mg of a dark red powder (79%). ^{1}H NMR (500 MHz, DMF-d_7): $\delta = 1.04$, 1.26, 1.44, 1.77, 2.14, 2.59, 2.75, 3.90, 3.92, 6.85, 7.30, 7.62, 8.00, 8.38, 8.45, 9.00.

The same procedure was used for **4** and **13**.

Acknowledgment. Financial support of this research comes from the AFOSR (No. FDF-49620-01-1-0167) program and the Office of Naval Research (No. N00014-98-F-0402) through the U.S. Department of Energy (No. DE-AC03-76SF00098). A graduate fellowship from the Eastman Kodak Co. (A.A.) is gratefully acknowledged.

References and Notes

(1) Merrigan, J. A. *Prospects for solar energy conversion by photovoltaics*; MIT press: Cambridge, MA, 1975.
(2) (a) Sauvage, J. P.; Collin, J. P.; Chambron, J. C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelotti, F.; Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993. (b) Plevoets, M.; Vögtle, F.; De Cola, L.; Balzani, V. *New. J. Chem.* **1999**, *1*, 63. (c) Vögtle, F.; Plevoets, M.; Nieger, M.; Azzellini, G. C.; Credi, A.; De Cola, L.; De Marchis, V.; Venturi, M.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 6290. (d) Zhou, X.; Tyson, D. S.; Castellano, F. N. *Angew. Chem., Int. Ed.* **2000**, *39*, 4301.
(3) Newkome, G. R.; He, E.; Godinez, L. A.; Baker, G. R. *J. Am. Chem. Soc.* **2000**, *122*, 9993.
(4) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689.
(5) Zhou, M.; Roovers, J. *Macromolecules* **2001**, *34*, 244.
(6) Kirch, M.; Lehn, J. M.; Sauvage, J. P. *Helv. Chem. Acta* **1979**, *62*, 1345.
(7) Seddon, E. A.; Seddon, K. R. In *The Chemistry of ruthenium*; Clark, R. J. H., Ed.; Elsevier: Amsterdam, 1984; Chapter 15, p 1221.
(8) Suzuki, M.; Kobayashi, S.; Uchida, S.; Kimura, M.; Hanabusa, K.; Shirai, H. *Polymer* **1998**, *39*, 1539.
(9) Fendler, J. H. In *Nanoparticles and Nanostructured Films*; Fendler, J. H., Ed.; Fendler; Wiley: 1998; Chapter 9, p 207.
(10) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49.
(11) O'Regan, B.; Grätzel, M. *Nature (London)* **1991**, *353*, 737.
(12) (a) Suzuki, M.; Bartels, O.; Gerdes, R.; Schneider, G.; Wöhrle, D.; Schulz-Ekloff, G.; Kimura, M.; Hanabusa, K.; Shirai, H. *Phys. Chem. Chem. Phys.* **2000**, *2*, 109. (b) Bourdelande, J. L.; Font, J.; Marques, G.; Abdel-Shafi, A. A.; Wilkinson, F.; Worrall, D. R. *J. Photochem. Photobiol. A: Chem.* **2001**, *138*, 65.
(13) (a) Nazeeruddin, M. K.; Kay, A.; Radicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382. (b) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
(14) (a) Adronov, A.; Gilat, S. L.; Fréchet, J. M. J.; Ohta, K.; Neuwahl, F. V. R.; Fleming, G. R. *J. Am. Chem. Soc.* **2000**,

122, 1175. (b) Gilat, S. L.; Adronov, A.; Fréchet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1422.
(15) Adronov, A.; Robello, D. R.; Fréchet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1366.
(16) (a) Sauvage, J. P. *Transition Metals in Supramolecular Chemistry*; Perspectives in Supramolecular Chemistry Series; Wiley: New York, 1999; Vol VI. (b) Pickup, P. G. *J. Mater. Chem.* **1999**, *9*, 1641.
(17) (a) Wu, X.; Collins, J. E.; McAlvin, J. E.; Cutts, R. W.; Fraser, C. L. *Macromolecules* **2001**, *34*, 2812. (b) Corbin, P. S.; Webb, M. P.; McAlvin, J. E.; Fraser, C. L. *Biomacromolecules* **2001**, *2*, 223.
(18) (a) Strouse, G. F.; Worl, L. A.; Younathan, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 9101. (b) Friesen, D. A.; Kajita, T.; Danielson, E.; Meyer, T. J. *Inorg. Chem.* **1998**, *37*, 2756. (c) Fleming, C. N.; Maxwell, K. A.; DeSimone, J. M.; Meyer, T. J.; Papanikolas, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 10336.
(19) Schultze, X.; Serin, J.; Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2001**, 1160.
(20) Jones, W. E.; Smith, R. A.; Abramo, M. T.; Williams, M. D.; Houten, J. V. *Inorg. Chem.* **1989**, *28*, 2281.
(21) Wu, X.; Fraser, C. *Macromolecules* **2000**, *33*, 4053.
(22) (a) Förster, T. *Ann. Phys.* **1948**, *2*, 55; (b) Förster, T. *Z. Naturforsch.* **1949**, *4*, 321.
(23) Yoshinaga, K.; Toyofuku, I.; Yamashita, K.; Kanehara, H.; Ohkubo, K. *Colloid Polym. Sci.* **2000**, *278*, 481.
(24) Ciana, L. D.; Hamachi, I.; Meyer, T. J. *J. Org. Chem.* **1989**, *54*, 1731.
(25) Trouillet, L.; De Nicola, A.; Guillerez, S. *Chem. Mater.* **2000**, *12*, 1611.
(26) Treadway, J. A.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 2267.
(27) (a) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789. (b) Kocher, M.; Däubler, T. K.; Harth, E.; Scherf, U.; Gügel, A.; Neher, D. *Appl. Phys. Lett.* **1998**, *72*, 650. (c) Nierengarten, J. F. *Mater. Tod.* **2001**, *4*, 16.
(28) (a) Lee, J. K.; Yoo, D.; Rubner, M. F. *Chem. Mater.* **1997**, *9*, 1710. (b) Laguitton-Pasquier, H.; Martre, A.; Deronzier, A. *J. Phys. Chem. B.* **2001**, *105*, 4801.
(29) (a) Chujo, Y.; Sada, K.; Saegusa, T. *Macromolecules* **1993**, *26*, 6320. (b) Heller, M.; Schubert, U. S. *Macromol. Rapid Commun.* **2001**, *22*, 1358.
(30) (a) Wörner, M.; Greiner, G.; Rau, H. *J. Phys. Chem.* **1995**, *99*, 14161.(b) Ghosh, P. K.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 5543.

MA020265T