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Articles

Ruthenium Bipyridine-Containing Polymers and Block Copolymers via Ring-Opening Metathesis Polymerization

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ABSTRACT: We present the direct and efficient synthesis of homopolymers and block copolymers bearing a dense arrangement of ruthenium(II) tris(bipyridine) complexes as pendant groups via ring-opening metathesis polymerization. UV/vis absorbance and luminescence studies as well as cyclic voltammetry show that the properties of the monomer are retained in the homopolymers and block copolymers. Our studies suggest that the polymers can be described as an array of independent chromophores, whose properties remain essentially unchanged upon linking to the polymer backbone. The Ru-containing block copolymers can self-assemble in selective solvents to generate large compound micellar aggregates, which retain their luminescence upon micellization.

Introduction

Ruthenium bipyridine-containing polymers have recently been the subject of increasing attention, owing to the unique photophysical, photochemical, and electrochemical properties of the Ru(II) diimine moiety.[1] Numerous potential applications have been proposed for these polymers, namely as photosynthesis mimics, polymer-supported electrodes, photosensitizers, emission sensitizers, photovoltaic cells, conducting and photoresponsive materials, as well as in metal ion sensing, catalysis, and supramolecular chemistry.[1] A number of ruthenium diimine-containing polymeric materials, containing the ruthenium moiety in either the polymer main chain or the side chain, have been reported in the literature.[2] For example, polymers based on polystyrene,[3] polypyrroles,[4] π-conjugated poly(2,2′-bipyridine-5,5′-diyl),[5] poly(vinylbipyridine),[6] polyesters,[7] poly(1-vinylimidazole),[8] poly(*p*-phenylenevinylene) with pendant terpyridine,[9] electropolymerized bipyridine or terpyridine derivatives,[10] and metallo-supramolecular block copolymers[11] have been generated. Star polymers with ruthenium−polypyridine complexes in the core[12] or on branches[13] have been prepared. Ruthenium(II) diimine-containing polymers can be prepared either directly from monomers containing the ruthenium complex or by coordination of preformed polymers with ruthenium complexes.[6] However, most synthetic approaches to date have involved the construction of systems with broad molecular weight distributions and lack of control over polymer architecture or have required tedious postfunctionalization of precursor polymers. In addition, there has been no previous report of direct generation of block copolymers containing Ru(II) diimine units.

The ring-opening metathesis polymerization (ROMP) has recently played a major role in the controlled construction of functional polymers because of its living nature and its remarkable functional group tolerance.[14,15] In this work, we present the direct and efficient synthesis of homopolymers and block copolymers containing a dense arrangement of ruthenium(II) tris(bipyridine) units via ROMP. Examination of their photophysical and electrochemical properties shows that these polymers behave as an array of independent Ru(II) chromophores, whose properties remain essentially unchanged upon loading onto the polymer backbone. The Ru-containing block copolymers can self-assemble in selective solvents to generate large compound micellar aggregates, with retention of their luminescence.

Results and Discussion

Synthesis of Monomer 3, Homopolymer 4, and Copolymer 6. The ruthenium-based monomer **3** was prepared as shown in Scheme 1. Reaction of exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride with excess 2,2-(ethylenedioxy) bis(ethylamine) at 80 °C gave monoamine **1** in 25% yield. Coupling of amine **1** with the succinimidyl ester of [(bpy)$_2$Ru(4-carboxyl-4′-methyl-2,2′-bipyridyl)] [PF$_6$]$_2$ (compound **2**)[16] in acetonitrile gave monomer **3** as a dark red powder in 74% yield. Monomer **3** was characterized using ^{1}H and ^{13}C NMR as well as HR-FAB mass spectral analysis.

We first studied the ring-opening metathesis polymerization of monomer **3** with the ruthenium alkylidene initiator [(H$_2$IMes)(3-Br-Py)$_2$Cl$_2$Ru═CHPh], **7**[17] (10:1 ratio), in acetone at room temperature (Scheme 1). The reaction was complete within 20 min (monitored by thin-layer chromatography and ^{1}H NMR). This results in the formation of homopolymer **4**, with conversions above 97% (by ^{1}H NMR). The reaction was quenched with the addition of ethyl vinyl ether, and polymer **4** can be isolated by precipitation with ether (90% yield).

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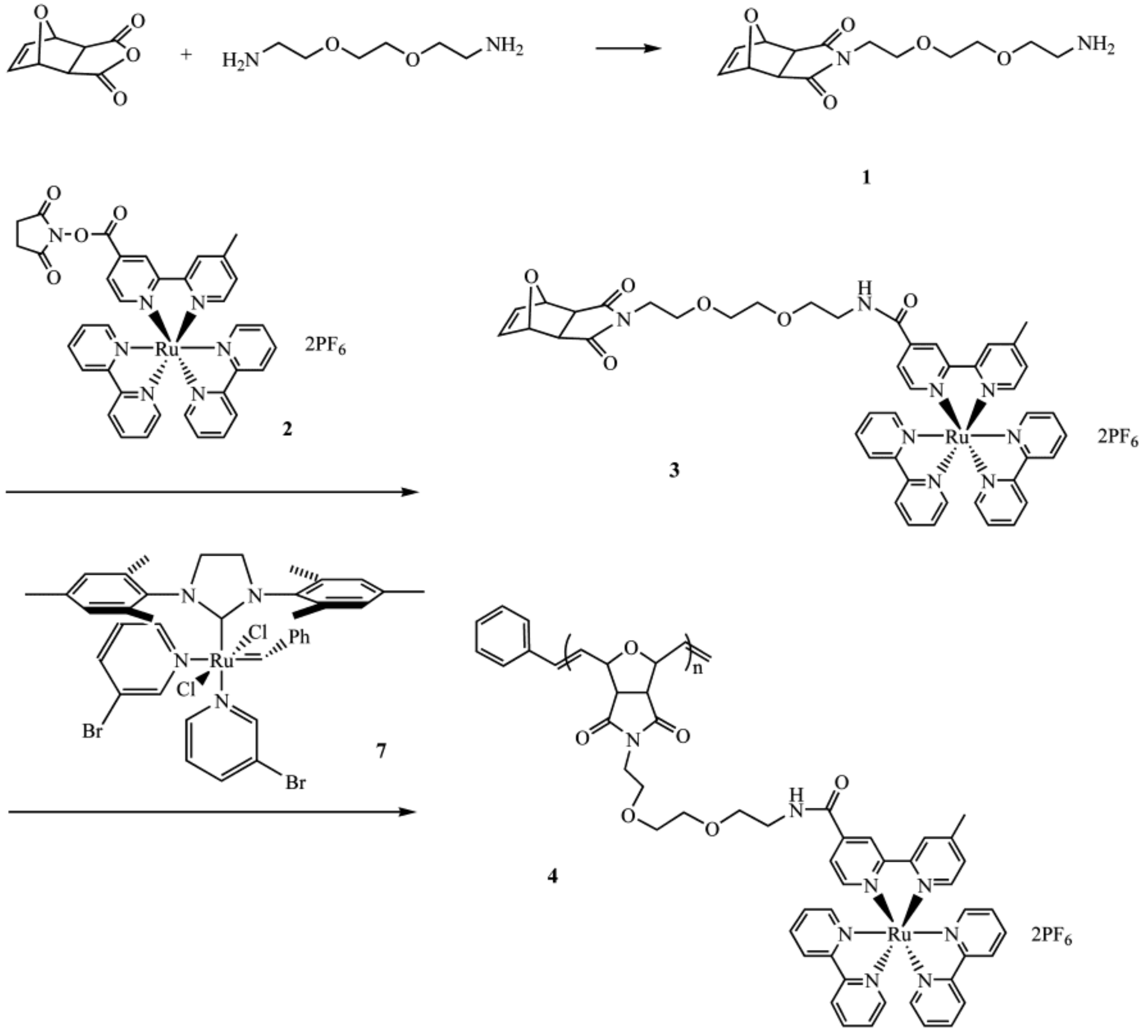
Scheme 1. Synthesis of Monomer 3 and Homopolymer 4



^{1}H NMR monitoring of the polymerization of monomer **3** at room temperature in d_6-acetone reveals the rapid disappearance of the alkylidene peak (19.1 ppm) of the initiator and the appearance of a broad signal at 18.5 ppm, corresponding to the Ru−alkylidene proton of the propagating polymer chain. The latter resonance persists throughout the entire polymerization process at room temperature and does not diminish even upon allowing the resulting solution to stand at room temperature overnight. This suggests that chain termination/transfer is slow for this reaction. To evaluate the living nature of this polymerization, the ROMP reaction of monomer **3** with catalyst **7** was monitored by ^{1}H NMR in d_6-acetone at 0 °C under an inert atmosphere. At this temperature, the kinetics were slower, and monomer conversion was 80% complete after ca. 60 min (Figure 1). Analysis of the spectra revealed a clear linear dependence of the monomer conversion on reaction time (i.e., the kinetics are first-order in monomer concentration). Thus, the persistence of the alkylidene peaks throughout the polymerization, the ability to generate block copolymers from **3**,[18] and the first-order kinetics with respect to monomer concentration[19] are all consistent with living character of the ROMP of monomer **3** with catalyst **7**. Homopolymer **4** is soluble in a range of polar organic solvents (e.g., acetone, DMSO, DMF, acetonitrile) and has been characterized by ^{1}H and ^{13}C NMR (64% trans double bonds).

The ROMP reaction is a powerful tool for the synthesis of block copolymers through the sequential addition of monomers. This block polymer architecture would provide the opportunity to create multifunctional Ru(II) diimine assemblies, with precise positioning of the chromophores along the polymer backbone, an especially

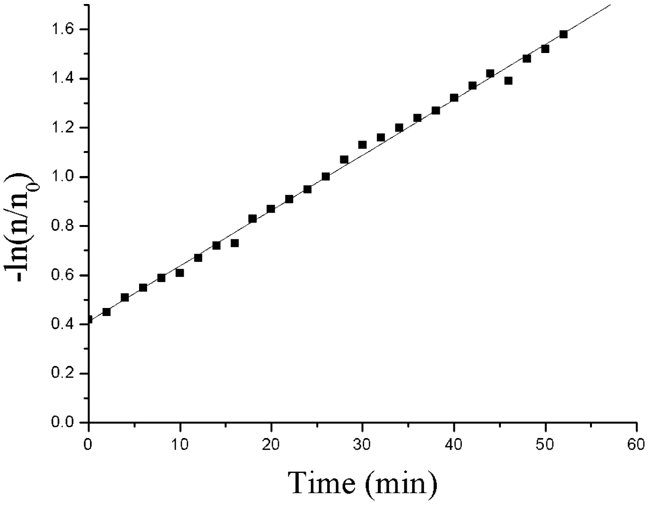
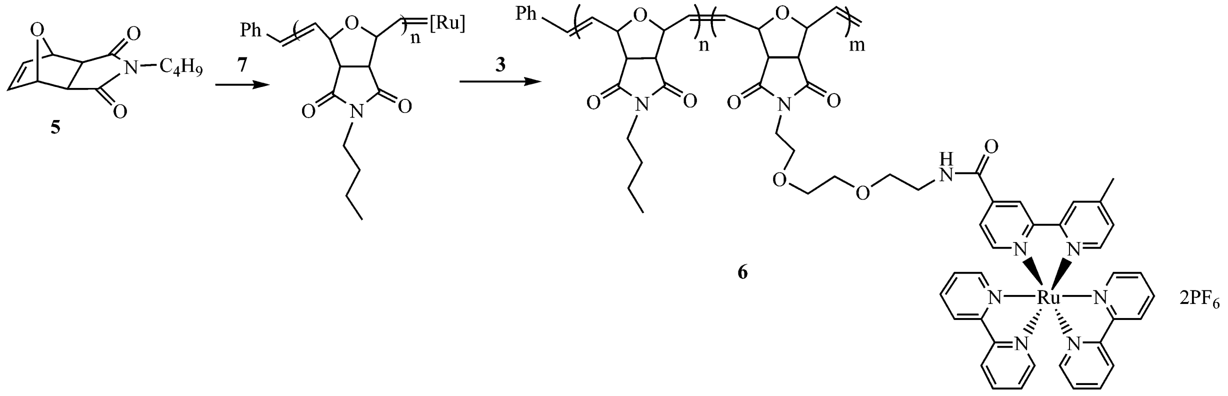


Figure 1. Linear dependence of monomer **3** conversion vs time. n = ^{1}H NMR integration of the remaining monomer concentration at time t; n_0 = ^{1}H NMR integration of the initial monomer concentration (see Experimental Section).

Scheme 2. Synthesis of Block Copolymer 6



useful feature for applications of these polymers as photosynthesis mimics.[3] As a first step, exo-*N*-butyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**5**)[20] (15 equiv) was reacted with initiator **7** in acetone at room temperature for 40 min (Scheme 2). An aliquot of this solution was removed, and its ^{1}H NMR spectrum revealed quantitative conversion of monomer **5** as well as broad peaks corresponding to poly(**5**). End-group analysis of the polymer (phenyl group signal at 7.2–7.5 ppm) gives an average number of repeat units of 14, corresponding to the original monomer/initiator ratio (15:1). To the remaining solution of poly(**5**), an acetone solution of monomer **3** (20 equiv) was added. ^{1}H NMR showed more than 98% conversion of monomer **3** after 2 h at room temperature. After quenching with ethyl vinyl ether and precipitation in ether, block copolymer **6** was further purified by preparative size exclusion chromatography (SEC) in 85% yield. Interestingly, SEC revealed the presence of only one polymer band and the absence of a band corresponding to poly(**5**). This is consistent with quantitative formation of block copolymer **6** from all poly(**5**) chains present in the reaction, in agreement with the living nature of ROMP reactions with initiator **7**.[17] The resulting copolymer **6** was characterized by ^{1}H and ^{13}C NMR, which showed the presence of the two polymer blocks, poly(**5**) and poly(**3**). Using the ^{1}H NMR peaks of poly(**5**) at 0.95, 1.30, and 1.53 ppm, corresponding to the butyl group, and the aromatic signals at 8.06 ppm, corresponding to the hydrogens ortho to the bpy nitrogens (4H per repeat unit), the average degree of polymerization of poly(**3**) was calculated as 21, resulting in an average molecular weight of diblock copolymer **6** (poly(**5**)$_{14}$-*block*-(**3**)$_{21}$) of approximately $M_n = 28\,000$. (The expected ratio based on complete conversion of **3** and **5** is 14:18.) GPC analysis could not be performed on ruthenium-containing polymers **4** and **6**, possibly due to strong interactions with the stationary phase.[7,21]

UV/Vis Absorption and Emission Spectra. Absorption and room temperature emission spectra of monomer **3**, homopolymer **4**, and block copolymer **6** were obtained in acetonitrile solution and are shown in Figures 2 and 3. Data are summarized in Table 1, where molar absorptivity values per Ru center for the homopolymer and copolymer are given. For monomer **3**, the UV region is dominated by intense ligand-centered $\pi-\pi^*$ absorptions bands. The spectra also exhibits a broad absorption in the visible region assigned to the dπ (Ru)–π^*(bpy) metal-to-ligand change-transfer (MLCT) transition.[22] The UV/vis spectra of the homopolymer **4** and copolymer **6**, including the molar absorptivity values for the MLCT bands, are quite similar to those of the monomer (Table 1). This is consistent with the absence of a strong electronic interaction between the chromophores in the multinuclear homopolymer and copolymer.[3,13]

Emission spectra for monomer **3**, homopolymer **4**, and copolymer **5** were obtained upon excitation of the 455 nm band in CH$_3$CN at 298 K, and the data are summarized in Table 1. The principal emission peak of monomer is centered at 627 nm. Homopolymer **4** and copolymer **6** show nearly identical emission maxima and profiles to that of the monomer, consistent with mutually independent Ru(II) centers. The emissive ^{3}MLCT excited states thus likely lie at the same energy for all

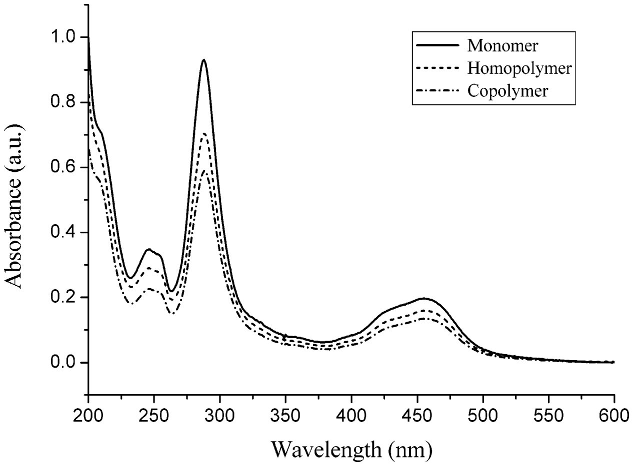


Figure 2. UV/vis absorbance spectra of monomer, homopolymer, and copolymer in acetonitrile.

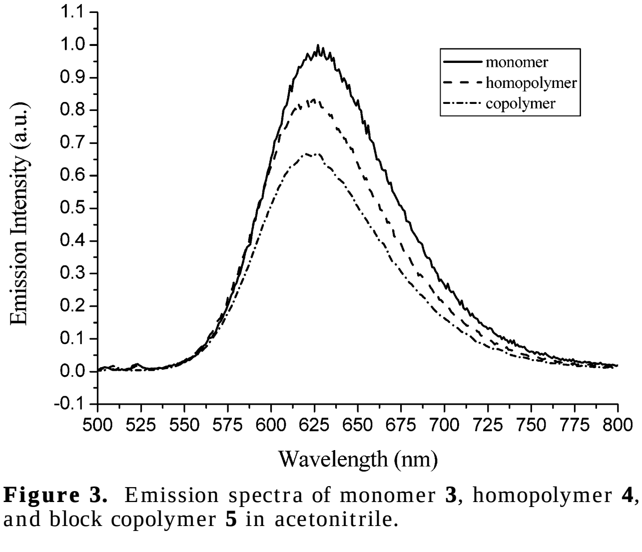


Figure 3. Emission spectra of monomer **3**, homopolymer **4**, and block copolymer **5** in acetonitrile.

Table 1. Absorption and Luminescence Data

compound	λ_{max} (nm)	ϵ (M^{-1} cm^{-1} $\times 10^4$)[a]	λ_{em} (nm)	quantum yield[b]
monomer **3**	246	1.79	627	0.066
	288	4.78		
	455	1.02		
homopolymer **4**	246	1.72	625	0.068
	288	4.45		
	455	1.01		
block copolymer **6**	246	1.70	625	0.066
	288	4.50		
	455	1.02		

[a] The molar absorptivity is reported per mole of ruthenium units. [b] Emission quantum yield, compared to Ru(bpy)$_3$(PF$_6$)$_2$ (Φ_{em} = 0.062) in CH$_3$CN (error approximately ±10%).

three complexes,[13] suggesting that the attachment of Ru(II) complexes to the ROMP polymer with long ethylene glycol linkers has a negligible effect on their electronic properties. The quantum yield for the monomer, homopolymer, and diblock copolymer were calculated using literature procedures, using the total counts of the principal emission peak, combined with the known quantum yield of Ru(bpy)$_3$(PF$_6$)$_2$.[3] For all three systems, the quantum yields are nearly identical, consistent with the behavior of the Ru(II) centers as independent chromophores on the polymer backbone. This lack of interaction between the Ru(II) chromophores is similar to the behavior of previously reported Ru(II)-containing polymers, with low loading of Ru(II) units on a polystyrene backbone as well as lower-generation Ru(II) dendrimers.[3,13] However, more densely packed ruthenium polypyridine-based polystyrene homopolymers[3] or higher-generation dendrimers with ruthenium polypyridine complexes[13] have displayed lowering of the emission quantum yield, as compared to the monomers, because of chromophore−chromophore interactions.[13] In our Ru(II)-containing homopolymer **4** and block copolymer **6**, the lack of interchromophore interaction is likely due to the long ethylene glycol linkers, which make the ruthenium sites far enough to behave independently.

Redox Characteristics. Cyclic voltammetry was recorded on solutions of monomer **3**, homopolymer **4**, and block copolymer **6** in CH$_3$CN (using 0.1 M tetrabutylammonium hexafluorophosphate). In this study, the concentrations of monomer, homopolymer, and copolymer solutions were adjusted so that the concentration of ruthenium(II) redox sites were equivalent (0.1 mM of Ru(II) centers) in all solutions. For the monomer, a quasi-reversible oxidation couple at $E_{1/2}$ = 1.39 V (vs NHE) occurred in the range typical of ruthenium(II/III) couples. Three reduction couples at −1.07, −1.33, and −1.56 V were observed and assigned as ligand-based, sequential one-electron reductions. Similar electrochemical data were obtained for the metallopolymers. Single reversible Ru$^{II/III}$ redox waves at 1.34 V for homopolymer **4** and 1.35 V for block copolymer **6** were obtained. The presence of this single Ru$^{II/III}$ redox wave implies simultaneous one-electron oxidation processes for the Ru(II) centers on the ruthenium complex polymer.[13] In addition, the lack of significant peak broadening indicates that the ground-state interactions between the Ru(II) centers are negligible.[13] The ligand-based reductions of the monomer, homopolymer, and copolymer are also similar (Table 2), again indicating little interaction between the Ru(II) moieties in the metallopolymers.[23]

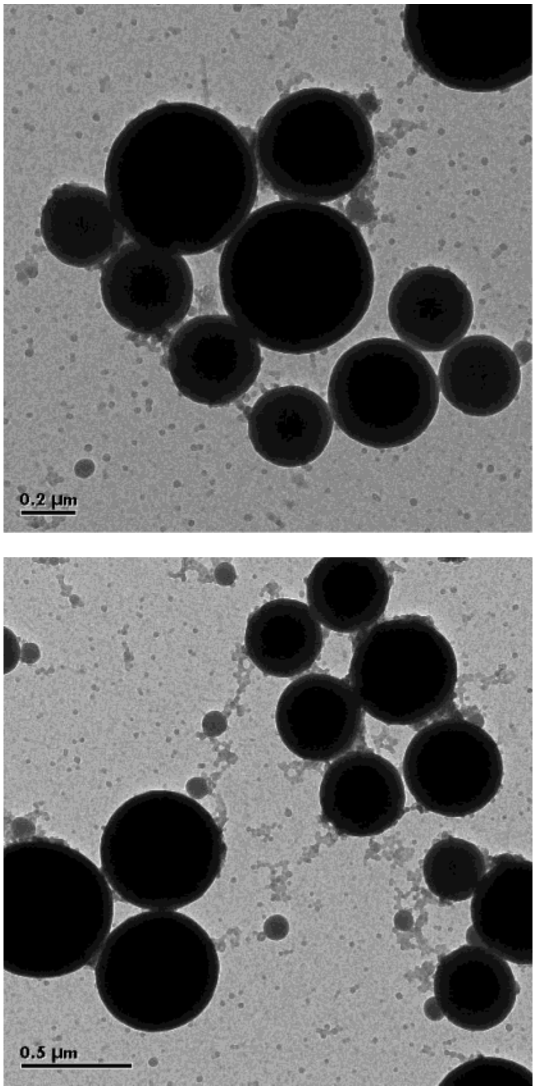


Figure 4. Transmission electron micrographs of block copolymer **6** in acetonitrile/toluene (1:2.5).

Table 2. Electrochemical Data at Room Temperature in Acetonitrile

compound	Ru$^{II/III}$, V	$E^{red}_{1/2}$, V
monomer **3**	1.39	−1.07, −1.33, −1.56
homopolymer **4**	1.36	−1.04, −1.32
block copolymer **6**	1.36	−1.03, −1.34

Preliminary Studies on Micelle Formation. With block copolymer **6** containing ruthenium(II) bipyridine units with in hand, studies were performed on their self-organization into micellar aggregates. In copolymer **6**, the two blocks possess different solubility behaviors. Both blocks are soluble in polar solvents, such as acetonitrile or acetone. Poly(**5**) is soluble in less polar solvents, such as toluene or chloroform, while poly(**3**) is not soluble in these solvents. Micellar aggregates of copolymer **6** were prepared by adding toluene slowly to a solution of the copolymer in acetonitrile (1 mg/mL), until the observed turbidity indicated the onset of aggregation (acetonitrile:toluene 1:2.5). Transmission electron micrographs (TEM) of the resulting solution of copolymer **6** are shown in Figure 4.[24] The TEM studies show that spherical particles of large diameter (from 200 to 600 nm) are obtained. The particle size is too large for individual micelles, indicating that these spherical aggregates may be large compound micelles (LCM).[25] In the 1:2.5 acetonitrile/toluene, it is expected that copolymer **6** self-assembles to expose the hydro-

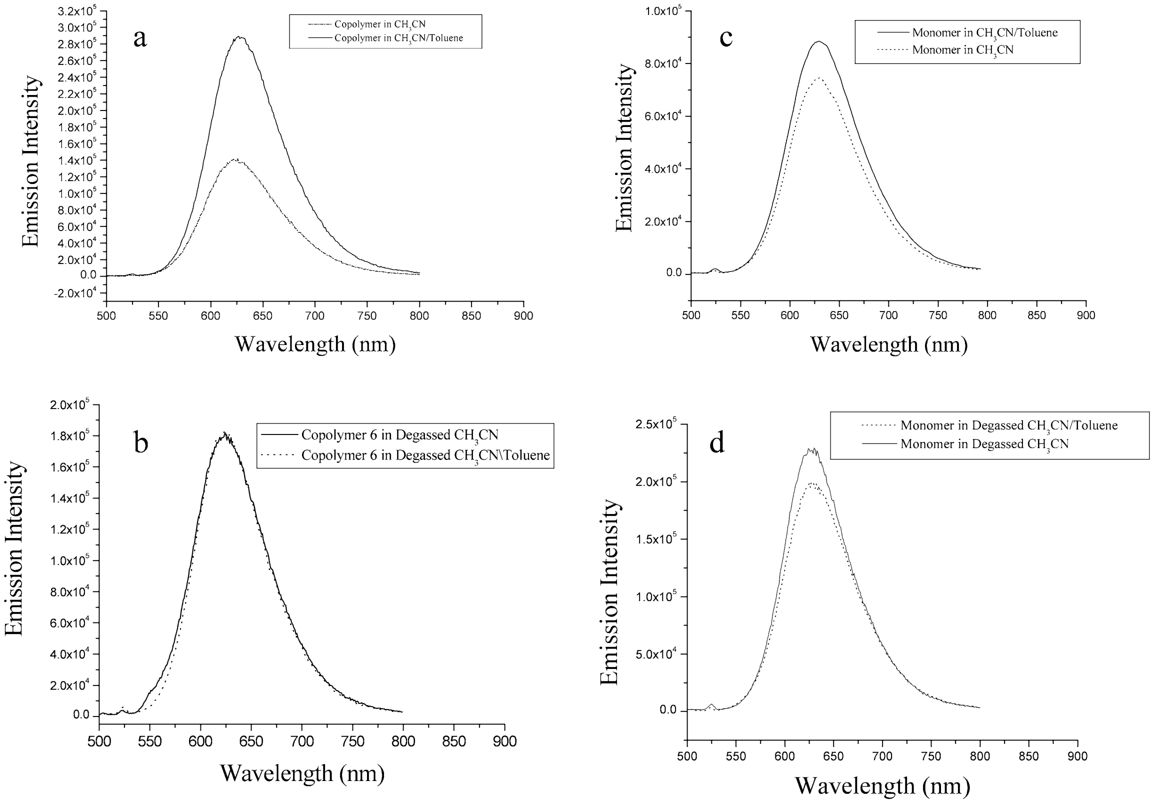


Figure 5. Emission spectra of monomer **3** and copolymer **6** in acetonitrile and acetonitrile/toluene (1:500).

phobic poly(**5**) block to the solvent and to minimize the interaction between poly(**3**) and the toluene-rich medium. Thus, the core of these aggregates is expected to be the ruthenium(II)-containing polymer. To test this assumption, ^{1}H NMR studies were carried out using d_8-toluene and CD_3CN as solvents. The ^{1}H NMR of copolymer **6** in CD_3CN showed signals corresponding to both poly(**3**) and poly(**5**). When d_8-toluene was gradually added until turbidity was observed, the peaks corresponding to poly(**3**) (2.42 ppm corresponding to methyl group, 3.54 ppm corresponding to ethylene glycol linker, and 7.0−9.0 ppm corresponding to aromatic protons) were significantly decreased or even disappeared, consistent with lower mobility and decreased solvation for poly(**3**).[26] On the other hand, the butyl group signals of poly(**5**) (0.88, 1.27, and 1.45 ppm, corresponding to butyl group) were still strong, indicating that the poly(**5**) block constitutes the corona of these LCM, and poly(**3**) block is located in their core. Slow addition of a few drops of CD_3CN until turbidity disappeared restored the signals of poly(**3**).[26]

Figure 5 shows the luminescence of the micellar aggregates of copolymer **6** formed in acetonitrile/toluene. Copolymer **6** was first dissolved in acetonitrile, and toluene was added dropwise until turbidity was observed. The addition was continued until the acetonitrile:toluene ratio was 1:500, and luminescence spectra were recorded upon each toluene addition. No shift of the emission peak (centered at 627 nm with excitation at 455 nm at 298 K) was observed, compared to copolymer **6** in acetonitrile. The luminescence intensity of copolymer **6** nearly doubled in 1:500 acetonitrile:toluene as compared to pure acetonitrile (Figure 5a). In comparison, the luminescence of monomer **3** increased by approximately 15% upon replacement of acetonitrile with acetonitrile:toluene (1:500) as solvent (Figure 5c). The enhancement in emission in the copolymer **6** may be due to exposure of the Ru(II) centers to toluene, consistent with the behavior of $Ru(bpy)_3^{2+}$ complexes, whose quantum yields increase with decrease of solvent polarity.[27] However, considering that the Ru(II) block resides at the core of these micellar structures and that the luminescence increase is greater in the case of copolymer **6** than for monomer **3**, this enhancement may also be the result of effective shielding and thus protection of the Ru(II) centers from oxygen quenching[1] (Figure 5). To probe this phenomenon further, the emission spectra of copolymer **6** were measured in carefully degassed CH_3CN and CH_3CN/toluene (Figure 5b). In this case, no increase in the emission intensity was observed upon micellization, consistent with shielding of the Ru(II) units from oxygen in the micellar aggregates in aerated acetonitrile/toluene. While we are currently investigating the photophysical properties of polymers **4** and **6** further, these results show that the luminescence of the $Ru(bpy)_3^{2+}$ moiety is retained in homopolymer **4**, block copolymer **6**, and the micellar aggregates obtained in acetonitrile/toluene.

Conclusion

In summary, we have shown the first synthesis of ruthenium bipyridine-containing polymers via ring-opening metathesis polymerization. This straightforward synthetic approach allows ready access to well-defined ruthenium bipyridine-containing polymers containing a dense arrangement of chromophores. The photophysical and electrochemical behaviors of these polymers suggest that they can be described as an array of noncoupled Ru(II) units, whose properties remain essentially unchanged upon linking to the polymer backbone. In addition, we have shown the first synthesis and characterization of a Ru(II) tris(bipyridine)-containing block copolymer. This copolymer self-assembles into large compound micelles in acetonitrile/toluene. After micellization, the luminescence properties of the copolymers do not change significantly. This synthesis of block copolymers with exact positioning of luminescent chromophores along the polymer backbone can open the door to the creation of multichromophoric polymeric materials, capable of performing complex functions. This is an especially useful feature, for instance in the area of artificial photosynthesis.[3] Further work is focused on examining the self-assembly of these and related block copolymers, and its consequences on the photophysical and electrochemical properties of these materials as well as the applications of these highly luminescent micellar aggregates as probes in biological assays.

Experimental Procedures

General Considerations. All reactions were carried out under a dry nitrogen atmosphere. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian M400 spectrometer operated at 400.140 MHz. Chemical shifts are reported in ppm relative to the deuterated solvent resonance. UV/vis spectra were recorded on a Varian Cary 300 spectrophotometer. Luminescence experiments were carried out on a PTI (Photon Technology International) TimeMaster model C-720F spectrofluorimeter. Electrochemical experiments were performed using a Solatran 1255/1286 potentiostat/galvanostat. Three electrodes were utilized in this system: a platinum disk working electrode, a platinum wire auxiliary electrode, and Ag/AgCl as the reference electrode. The platinum disk working electrode was manually cleaned with 1 μm diamond polish prior to each scan. The supporting electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate (TBAH), was recrystallized twice from ethanol and vacuum-dried at 110 °C overnight. GPC experiments were carried out on Phenogel 5000 Å GPC columns and on a Viscotek GPC equipment (dual piston pump, VE 7510 GPC vacuum degasser, column oven, differential pressure viscometer, right angle laser light scatter (RALLS) detector, refractive index detector). DMF, 10 mM NH_4PF_6, 50 °C, 1 mL/min flow rate.

Luminescence Quantum Yield Measurements. Acetonitrile used in the photophysical measurements was distilled over CaH_2 and degassed (three freeze−pump−thaw cycles). Optically dilute samples were purged with argon for 20 min prior to use. Emission quantum yields were calculated using the equation $\Phi_{sam} = \Phi_{ref}(I_{sam}/I_{ref})(A_{ref}/A_{sam})$, where Φ is the emission quantum yield (sample or reference compound), I is the integrated emission profile, and A is the absorbance in a 1 cm quartz cuvette. The reference was $[Ru(bpy)_3](PF_6)_2$, for which $\Phi_{em} = 0.062$ in acteonitrile at 298 K.

NMR Monitoring of the ROMP of 3 and 5. Monomers **3** or **5** (40 equiv) were dissolved in degassed d_6-acetone (0.8 mL) and transferred to an NMR tube under inert atmosphere. The solution was frozen with liquid N_2. A solution of catalyst **7** (1 equiv) in degassed d_6-acetone (0.1 mL) was then added to the above reagents. ^{1}H NMR spectra were immediately recorded at 2 min intervals at 0 °C for monomer **3** and at −20 °C for monomer **5**. The n/n_0 values were obtained by integration of the olefin peaks of the monomer/(monomer plus polymer). Linear regression analysis of the graph of Figure 1 gave $R = 0.998\,27$. The intercept of the graph of Figure 1 is not zero because the NMR experiment started at a time later than the actual start of the reaction.

Transmission Electron Microscopy. The diblock copolymer **6** was first dissolved in acetonitrile (1 mg/mL), and then toluene was added dropwise until the turbidity of the solution indicated the onset of aggregation. Samples were prepared by placing a drop of this solution (final concentration of copolymer **6** after addition of toluene is 0.28 mg/mL) onto transmission electron microscopy (TEM) copper grids (400 mesh, carbon-coated, purchased from Electron Microscopy Sciences). The grids were air-dried for 12 h. The aggregates were then examined using a JEOL 2000FX electron microscope operated at 80 kV.

Materials. All reagents were purchased from Aldrich and used as received. Monomer **5**,[20] $[(H_2IMes)(3\text{-Br-py})_2(Cl)_2Ru{=}CHPh]$,[17] was synthesized according to literature procedures. Acetonitrile (CH_3CN) was distilled from CaH_2, degassed, and placed under argon prior to use. Acetone was degassed before use as solvent for polymerization. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification.

Synthesis of 1. Exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (1.0 g, 6.0 mmol) and 2,2-(ethylenedioxy)bis(ethylamine) (7.5 g, 51 mmol) were mixed at room temperature, and the mixture was stirred at 80 °C for 3 h, upon which the solid anhydride gradually dissolved. After cooling to room temperature, the reaction mixture was poured into 200 mL of CH_2Cl_2 and washed with water to remove excess diamine. The organic phase was washed with brine and concentrated in a vacuum. The pure sticky colorless product was obtained by chromatography on alumina with CH_2Cl_2/methanol (v/v = 5:1) as eluent (25%). ^{1}H NMR ($CDCl_3$), δ ppm: 2.86 (m, 4H, $-CH_2NH_2$, −COCHCHCO−), 2.96 (b, 2H, $-NH_2$), 3.58 (m, 10H, $-NCH_2CH_2OCH_2CH_2OCH_2-$), 5.25 (s, 2H, −CHOCH−), 6.49 (s, 2H, −CH=CH−). ^{13}C NMR ($CDCl_3$), δ ppm: 38.52, 41.76, 47.83, 67.49, 70.26, 70.54, 72.89, 81.24, 136.70, 176.31. HR-FAB MS: theoretical calculated for $[C_{14}H_{20}N_2O_5 + H]^+$: 297.1451; found: 297.1450.

Synthesis of Monomer 3. The succinimidyl ester of $[(bpy)_2Ru(4\text{-carboxyl-}4'\text{-methyl-}2,2'\text{-bipyridyl})][PF_6]_2$ (compound **2**, 82 mg, 0.08 mmol)[16] was synthesized and directly filtered into an acetonitrile solution containing **1** (30 mg, 0.1 mmol) as well as triethylamine (25 mg, 0.25 mmol). After stirring this solution at 40 °C for 2 h, the solvent was removed by rotary evaporation. Pure product was obtained by chromatography on alumina with acetonitrile:toluene (4:1) as eluent, followed by pure acetonitrile. (74%). ^{1}H NMR (CD_3CN), δ ppm: 2.57 (s, 3H, $-CH_3$), 2.85 (s, 2H, −COCHCHCO−), 3.60 (m, 12H, $-NCH_2CH_2OCH_2CH_2OCH_2CH_2NH-$), 5.07 (s, 2H, −CHOCH−), 6.47 (s, 2H, −CH=CH−), 7.28 (dd, 1H, $J = 5.7$ Hz, $J = 0.9$ Hz), 7.41 (m, 4H), 7.57 (d, 1H, 5.7 Hz), 7.66 (dd, 1H, $J = 5.7$ Hz, $J = 1.8$ Hz), 7.73 (m, 4H), 7.87 (d, 1H, $J = 5.7$ Hz), 8.06 (m, 4H), 8.52 (m, 5H), 8.84 (d, 1H, $J = 1.2$ Hz). ^{13}C NMR (CD_3CN), δ ppm: 20.72, 38.47, 40.28, 47.80, 67.07, 69.04, 70.21, 81.16, 121.84, 124.47, 124.67, 125.76, 127.75, 127.80, 128.89, 136.63, 138.03, 138.06, 142.72, 150.85, 150.96, 151.73, 151.78, 151.82, 151.89, 152.52, 156.15, 156.93, 157.04, 157.10, 157.13, 158.10, 163.47, 176.67. HR-ESI-MS: theoretical calculated for $[C_{46}H_{44}F_6N_8O_6PRu]^+$: 1051.2069; found: 1051.2064.

Synthesis of Homopolymer 4. Monomer **3** (15.0 mg, 0.0125 mmol) was dissolved in 1 mL of degassed acetone and transferred to an acetone solution of catalyst **7** (1.1 mg, 0.00125 mmol). The mixture allowed to stir for 1 h at room temperature. Ethyl vinyl ether (100 equiv) was added, and the solution was stirred for 30 min, followed by precipitation in ether (3 times), and then purified by size exclusion chromatography (Bio-Beads SX-1), eluted with a 4:1 mixture of toluene and acetonitrile (90%). ^{1}H NMR (CD_3CN), δ ppm: 2.55 (br, 3H), 3.28 (br, 2H), 3.50 (br, 12H), 4.31 (br, 1.1H), 4.83 (br, 0.6H), 5.65 (br, 0.6H), 5.87 (br, 1H), 7.24 (br, 1H), 7.38 (br, 4H), 7.58 (br, 1H), 7.73 (br, 5H), 7.83 (br, 1H), 8.03 (br, 4H), 8.51 (br, 4H), 8.0 (br, 1H), 9.04 (br, 1H). ^{13}C NMR (d_6-acetone), δ ppm: 20.82, 38.28, 39.98, 52.67, 66.78, 69.08, 70.21, 121.20, 124.71, 125.85, 126.58, 128.16, 128.18, 129.09, 138.24, 142.32, 150,-79, 151.78, 151.91, 152.06, 152.08, 152.46, 156.64, 157.16, 157.26, 157.34, 158.28, 162.86, 175.92.

Synthesis of Copolymer 6. Monomer **5** (20 mg, 0.09 mmol) was dissolved in 9 mL of acetone. The solution of monomer **5** was added to a catalyst **7** (5.0 mg, 0.0056 mmol) solution in 1 mL of acetone. The mixture was allowed to stir at room temperature. After 1 h, 90% of the solution was removed and quenched with excess ethyl vinyl ether. Monomer **3** (13.4 mg, 0.0112 mmol) in 2 mL of acetone was added to the remaining solution. The solution was stirred at room temperature overnight. Excess ethyl vinyl ether was added and stirred for 30 min. The copolymer was precipitated with ether, purified by size exclusion chromatography (Bio-Beads SX-1), and eluted with a 4:1 mixture of toluene and acetonitrile. The first orangered band was collected, concentrated under vacuum, and precipitated in ether to afford a dark red solid, which was centrifuged, collected, and dried under vacuum (85%). (The other bands were small impurities which were present in monomer **3** itself.) ^{1}H NMR (CD_3CN), δ ppm: 0.94 (br, 2H), 1.31 (br, 1.4H), 1.54 (br, 1.4H), 2.53 (br, 3H), 3.2−3.6 (br, 16H), 4.2−4.5 (br, 1.6H), 4.88 (br, 1.4H), 5.5−6.1 (br, 3H), 7.28 (br, 1H), 7.40 (br, 4H), 7.60 (br, 1H), 7.66 (br, 1H), 7.75 (br, 4H), 7.86 (br,1H), 8.06 (br, 4H), 8.50 (br, 4H), 8.60 (br, 1H), 8.90 (br, 1H). ^{13}C NMR (CD_3CN) δ ppm: 13.49, 20.20, 20.79, 29.84, 30.33, 38.64, 40.10, 52.68, 53.78, 53.92, 66.78, 69.05, 70.11, 70.12, 77.56, 81.24, 121.78, 124.50, 124.91, 125.85, 127.84, 128.94, 131.99, 138.06, 142.38, 150.82, 150.97, 151.69, 151.77, 151.80, 151.87, 152.48, 152.58, 156.13, 156.91, 157.05, 157.10, 158.10, 163.48, 176.13.

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Supporting Information Available: HR-FAB-MS of compound **1** and HR-ESI-MS of monomer **3**; ^{1}H NMR and ^{13}C NMR of compound **1**, monomer **3**, homopolymer **4**, and copolymer **6** and ^{1}H NMR of copolymer **6** in CD_3CN/d_8-toluene before and after formation of the micelles; CV of monomer **3**, homopolymer **4**, and copolymer **6**. This material is available free of charge via the Internet at http:// pubs.acs.org.

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