Macromolecules **2005,** *38,* 8671−8678

Infrared-Emitting Poly(norbornene)s and Poly(cyclooctene)s

Amy Meyers, Alpay Kimyonok, and Marcus Weck*

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Received May 2, 2005; Revised Manuscript Received August 15, 2005

ABSTRACT: Poly(norbornene)- and poly(cyclooctene)-based copolymers, bearing carbazole and 8-hydroxyquinoline side chains, were prepared. Upon complexation of the pendant quinoline ligands in the side chain with ytterbium followed by the addition of 2 equiv of additional quinolines, infrared-emitting copolymers that emit around 970 nm were obtained. The emission intensities increased linearly as the density of lanthanide−quinolate complexes increased in the copolymers. Finally, we were able to prove that the polymer backbones do not interfere with the optical properties of the polymers, suggesting that these polymers are outstanding materials as IR emitters.

Introduction

The trend in the development of future technologies, such as molecular electronics and electrooptics for display technologies, is moving toward the use of organic materials. Over the past two decades, electrooptical materials with emissions in the visible region have been well established (for examples see refs 1−13). In contrast, organic materials that emit light in the infrared region have only recently started to be explored.[14−26] Infrared-emitting materials have potential applications in electronic devices, such as organic light-emitting diodes, and in photonic communication networks, especially silica optical fibers.[14−20,24−28] Optical fibers based on these materials are potentially useful for high-speed data transmission by confining light in a region of high refractive index between regions of low refractive index.[28] The optimal wavelength of light traveling through the fibers that coincides with the least amount of transmission loss is in the infrared region between 1.3 and 1.5 μm.[18−20,25,26,28,29]

Recent literature reports of materials emitting infrared radiation include conjugated polymers and compounds containing lanthanide complexes.[14−20,24−28] Lanthanide complexes have low band gaps and narrow emission bands due to their f−f transitions that are shielded from external forces by the 5s and 5p electrons.[17−19,30,31] However, because of the forbidden nature of the f−f transitions, in most cases, the lanthanide metal is excited by intramolecular energy transfer from its surrounding ligands. Since this energy transfer is usually through the triplet state of the ligands, the theoretical internal quantum efficiencies can reach 100%, which is significantly higher than systems based only on the recombination of singlet excitons.[18,19,30]

The design of lanthanide-based infrared emitters includes ligands with energy levels that overlap with the energy levels of the lanthanide metal in order for the energy transfer to occur. This is known as the “antenna effect”.[18−21,25,27,28,30] A wide variety of ligands have been coordinated to different lanthanide metals in order to optimize this antenna effect.[18−21,25,27,28,30] One ligand that has been used repeatedly in these studies is 8-hydroxyquinoline.[14,16,25,29−31] Lanthanide−quinolate complexes have been sublimed into thin films and doped into polymer matrices, producing emission ranging from 0.98 μm for ytterbium complexes to 1.53 μm for erbium complexes, with lifetimes as long as 230 μs.[30] However, one of the challenges in the optimization of lanthanide−quinolate materials is the limited processability of the material. We recently reported a polymer−quinolate material that can be solution processed, suggesting a new strategy to overcome this limitation.[32−34]

In this contribution, we report the utilization of the next generation of our polymer−quinolate material to fabricate polymer-supported lanthanide−quinolate complexes. The research design includes the attachment of one 8-hydroxyquinoline ligand to a norbornene or cyclooctene monomer that can then be polymerized using ring-opening metathesis polymerization (ROMP), a polymerization method that allows for controlled polymerizations under mild conditions at room temperature. Furthermore, the tolerance of the Grubbs’ ruthenium-based ROMP catalysts toward most functional groups and the ability to form copolymers make this polymerization method highly desirable.[35−39] The quinolate monomers are copolymerized with a carbazole-based comonomer in order to alleviate solubility problems while providing another potential route for energy transfer to the lanthanide complex.

We demonstrate our new strategy by employing two diverse polymerizable units, norbornene and cyclooctene. By changing the polymer backbone from a poly(norbornene) to a poly(cyclooctene), we can potentially tune the refractive index of the material, thereby giving us yet another means for adjusting the properties of the polymers. Furthermore, by altering the polymer backbone, we will alter the polymer morphology that has a direct effect on the polymer properties such as processability and might have a profound effect on the emission properties of the polymers. While poly(cyclooctene)s are known to have a random coil configuration, poly(norbornene)s are significantly more rigid.[40] This contribution describes the synthesis and detailed characterization of poly(norbornene)s and poly(cyclooctene)s containing ytterbium−quinolate complexes.

Experimental Section

General. All chemicals were purchased from Acros Organics or Aldrich and used without further purification. Flash column chromatography was carried out on silica gel 60, 230−400 mesh (Sorbent Technology). NMR spectra were acquired

---

* Corresponding author. E-mail: marcus.weck@chemistry.gatech.edu.

10.1021/ma050923k CCC: $30.25

with a Varian Mercury 400 (^{1}H, 400.0 MHz; ^{13}C, 100.6 MHz) spectrometer. Chemical shifts are reported in ppm and referenced to the corresponding residual nuclei in deuterated solvents. Gel-permeation chromatography (GPC) analyses were carried out using a Shimadzu instrument and linear mixed bed column packed with 10 μm AM gel using THF as the eluent and a multidiode array UV detector. All GPC data were standardized against poly(styrene). Differential scanning calorimetry (DSC) was performed under nitrogen using a Mettler Toledo DSC 822e cooled by liquid nitrogen. The temperature program provided heating and cooling cycles between −50 and 360 °C at 10 °C/min. UV/vis spectra were obtained on a Perkin-Elmer Lambda 19 UV/vis/NIR spectrometer. The fluorescence spectra were obtained on a Spex FluoroLog-3 spectrofluorimeter.

Synthesis of 5-(Bicyclo[2.2.1]hept-5-en-2-yl-methoxymethyl)quinolin-8-ol (3). Chloromethylhydroxyquinoline hydrochloride (**2**) was prepared from 8-hydroxyquinoline (**1**) according to literature procedures.[41] Monomer **3** was prepared by stirring **2** (2.0 g, 8.7 mmol) and sodium bicarbonate (0.8 g, 9.5 mmol) in a large excess of norbornene methanol (10 mL) at 90 °C for 1 h. The excess alcohol was distilled off, and the remaining solid was dissolved in water. The aqueous solution was extracted with CH_2Cl_2; the organic layer was collected, washed with a brine solution, and dried over sodium sulfate. The solvent was removed, leaving a greenish-yellow solid that was purified by column chromatography (silica gel, 4:1 hexanes/ethyl acetate) yielding an off-white solid (1.8 g, 72% yield). Monomer **3** is an 80:20 mixture of the *endo*−*exo* isomers. These isomers can be separated by column chromatography. While we used both isomers for all polymerization studies, for clarification and proof of purity, we report the ^{1}H and ^{13}C NMR data of only the *exo* isomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.81 (1H, dd, J = 1.65, 4.39); 8.53 (1H, dd, J = 1.65, 8.79); 7.52 (1H, dd, J = 4.39, 8.79); 7.42 (1H, d, J = 7.69); 7.11 (1H, d, J = 7.69); 6.07 (2H, m); 4.84 (2H, s); 3.56−3.01 (2H, m); 2.86−2.70 (2H, m); 1.74 (1H, m); 1.29 (3H, m); 1.19 (1H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.5, 147.8, 138.8, 136.8, 136.7, 133.7, 128.7, 127.6, 124.9, 122.0, 108.9, 75.0, 71.5, 45.3, 44.1, 41.8, 39.1, 30.1. MS (EI): m/z = 281.2. Anal. Calcd for $C_{18}H_{19}O_2N_1$: C, 76.87; H, 6.76; N, 4.98. Found: C, 77.02; H, 7.01; N, 4.72.

Synthesis of 9-(4-Bromobutyl)-9*H*-carbazole (5). Carbazole **4** (3.2 g, 0.020 mol) was combined with an excess of potassium carbonate and dissolved in 20 mL of acetone. An acetone solution of 1,4-dibromobutane (10 g, 1.5 mmol/mL) was added dropwise to the carbazole solution, and the combined mixture was refluxed overnight. The solvent was removed, and the remaining solid was purified by column chromatography (silica gel, 3:1 hexanes/methylene chloride) yielding a white solid (4.8 g, 81% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.19 (2H, d, J = 7.69); 7.56 (2H, dd, J = 7.14, 15.38); 7.45 (2H, d, J = 8.24); 7.35 (2H, dd, J = 7.14, 14.83); 4.36 (2H, t, J = 7.14); 3.40 (2H, t, J = 6.59); 2.11 (2H, m); 1.96 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 140.4; 126.0; 123.1; 120.7; 119.2; 108.8; 42.5; 33.7; 30.6; 28.0. MS (EI): m/z = 301. Anal. Calcd for $C_{16}H_{16}N_1Br_1$: C, 63.78; H, 5.31; N, 4.65. Found: C, 64.02; H, 5.01; N, 4.71.

Synthesis of 9-(5-(Bicyclo[2.2.1]hept-5-en-2-yl-pentyl)-9*H*-carbazole (7). 5-Bromomethylnorbornene (**6**), prepared according to literature procedures[42] (3.0 g, 0.015 mol), was dissolved in 10 mL of anhydrous THF and added dropwise to dried magnesium turnings (0.5 g, 0.020 mol) in 10 mL of anhydrous THF under argon. After the addition was complete, the mixture was warmed to 50 °C and stirred overnight under argon. The resulting solution was then added dropwise to an ice-cold solution of **5** (3.78 g, 0.012 mol), Li_2CuCl_4 (5 mL, 0.1 M solution in THF), and 10 mL of anhydrous THF. After the addition was complete, the solution was warmed to room temperature and stirred under argon overnight. The solution was diluted with ether, washed with an aqueous solution of NH_4Cl and brine, and dried over Na_2SO_4. After removal of the solvent, the yellow oil was purified by column chromatography (silica gel, 5:1 hexanes/ethyl acetate) yielding a yellow solid (3.5 g, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.26 (2H, d, J = 7.69); 7.63 (2H, dd, J = 8.24, 15.38); 7.52 (2H, d, J = 7.69); 7.40 (2H, dd, J = 7.69, 14.83); 6.25 (1H, endo, m); 6.17 (2H, exo, m); 6.04 (1H, endo, m); 4.37 (2H, t, J = 7.14); 2.87 (2H, s, broad); 2.08 (4H, m); 1.56 (6H, m); 1.18 (2H, m); 0.62 (1H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 140.7; 137.2; 132.6; 125.9; 123.1; 120.6; 119.0; 109.1; 50.0; 45.9; 43.4; 39.2; 35.1; 32.9; 29.5; 28.9; 28.0. MS (EI): m/z = 329.3. Anal. Calcd for $C_{24}H_{27}N_1$: C, 87.53; H, 8.21; N, 4.30. Found: C, 88.30; H, 7.93; N, 4.50.

Copolymerization of Monomers 3 and 7 (Ratios of 3/7 = 1:5, 1:10, 1:20). Monomers **3** and **7** were dissolved in 5 mL of chloroform. A chloroform solution of ruthenium catalyst **8** (5 mol % in 1 mL) was added to the monomer solution and stirred for 5 min, followed by the addition of ethyl vinyl ether (1 mL). After stirring for an additional 10 min, the solution was concentrated down to 1 mL and added dropwise to 100 mL of methanol. The polymer, which precipitated out of solution, was collected and redissolved in 1 mL of chloroform and reprecipitated into methanol. This purification procedure was repeated three times. The final product was collected as a brown solid (**9a**−**c**).

*Quinoline-co-carbazole Copolymer **9a** (1:5).* ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.72 (1H, broad); 8.42 (1H, broad); 8.12 (10H, broad); 7.45 (14H, broad); 7.05 (1H, broad); 5.14 (12H, m); 4.69 (2H, broad); 4.25 (10H, m); 3.35 (2H, m); 2.95 (5H, m); 2.65 (8H, m); 1.85 (20H, m); 1.30 (40H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.4; 147.8; 140.5; 138.7; 137.2; 133.8; 132.6; 128.7; 127.5; 125.7; 124.9; 122.9; 120.5; 118.9; 108.8; 50.0; 45.9; 43.3; 39.2; 35.1; 31.9; 29.3; 28.7; 27.8.

*Quinoline-co-carbazole Copolymer **9b** (1:10).* ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.72 (1H, broad); 8.42 (1H, broad); 8.12 (20H, broad); 7.45 (28H, broad); 7.05 (1H, broad); 5.14 (22H, m); 4.69 (2H, broad); 4.25 (20H, m); 3.35 (2H, m); 2.95 (10H, m); 2.65 (16H, m); 1.85 (40H, m); 1.30 (80H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.4; 147.7; 140.4; 138.7; 137.1; 133.7; 132.7; 128.5; 127.5; 125.7; 124.8; 122.8; 120.5; 118.8; 108.9; 50.2; 45.8; 43.2; 39.2; 35.3; 31.9; 29.5; 28.6; 27.7.

*Quinoline-co-carbazole Copolymer **9c** (1:20).* ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.72 (1H, broad); 8.42 (1H, broad); 8.12 (40H, broad); 7.45 (54H, broad); 7.05 (1H, broad); 5.14 (42H, m); 4.69 (2H, broad); 4.25 (40H, m); 3.35 (2H, m); 2.95 (20H, m); 2.65 (32H, m); 1.85 (80H, m); 1.30 (160H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.3; 147.9; 140.4; 138.6; 137.2; 133.9; 132.5; 128.7; 127.4; 125.6; 124.8; 122.9; 120.5; 118.8; 108.8; 50.1; 45.8; 43.3; 39.1; 35.2; 31.8; 29.4; 28.7; 27.8.

Formation of Ybq_3 Copolymers 10a−c. Excess Ybq_3, prepared according to literature procedures[23] was dissolved in a minimum amount of methanol and added to a chloroform solution of **9** (0.1 g/10 mL). After stirring overnight, the solution was concentrated down to 1 mL and added dropwise to 100 mL of methanol. The polymer, which precipitated out of solution, was collected and redissolved in 1 mL of chloroform and precipitated into methanol. This purification procedure was repeated three times. The final product was collected as a brown solid **10a**−**c**.

*Ytterbium Tris(8-hydroxyquinoline)-co-carbazole Copolymer **10a** (1:5). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.75 (m); 8.39 (m); 8.12 (10H, m); 7.83 (m); 7.45 (15H, m); 6.96 (m); 5.28 (12H, m); 4.25 (10H, m); 2.89 (5H, m); 2.52 (8H, m); 1.85 (20H, m); 1.32 (40H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 140.4; 137.1; 132.7; 125.7; 122.8; 120.5; 118.8; 108.9; 50.2; 45.8; 43.2; 39.2; 35.3; 31.9; 29.5; 28.6; 27.7.*

*Ytterbium Tris(8-hydroxyquinoline)-co-carbazole Copolymer **10b** (1:10).* ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.75 (m); 8.38 (m); 8.11 (20H, m); 7.82 (m); 7.44 (30H, m); 6.98 (m); 5.25 (22H, m); 4.24 (20H, m); 2.87 (10H, m); 2.51 (16H, m); 1.82 (40H, m); 1.30 (80H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 140.5; 137.2; 132.6; 125.7; 122.9; 120.5; 118.9; 108.8; 50.0; 45.9; 43.3; 39.2; 35.1; 31.9; 29.3; 28.7; 27.8.

*Ytterbium Tris(8-hydroxyquinoline)-co-carbazole Copolymer **10c** (1:20). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.72 (m); 8.42 (m); 8.12 (40H, broad); 7.45 (54H, broad); 7.05 (m); 5.24 (42H, m); 4.25 (40H, m); 2.95 (20H, m); 2.65 (32H, m); 1.84 (80H, m); 1.32 (160H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 140.4; 137.2; 132.5; 125.6; 122.9; 120.5; 118.8; 108.8; 50.1; 45.8; 43.3; 39.1; 35.2; 31.8; 29.4; 28.7; 27.8.*

Synthesis of 5-(Cyclooct-4-enyloxymethyl)quinolin-8-ol (12). 5-Hydroxycyclooctene (**11**) was prepared according to literature procedure.[43] Monomer **12** was synthesized by stirring chloromethylhydroxyquinoline hydrochloride (**2**) (1.5 g, 0.0065 mol) and **11** (6.8 g, 0.054 mol) in the presence of excess $NaHCO_3$ at 110 °C for 1.5 h. Upon cooling, a solid precipitated that was dissolved in CH_2Cl_2 and washed with water. The solvent and the excess alcohol were removed by distillation. The resulting green solid was recrystallized from hexanes to give a white solid (0.87 g, 46% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.79 (1H, dd, J = 1.65, 4.12); 8.49 (1H, dd, J = 1.65, 8.52); 7.47 (1H, dd, J = 4.12, 8.52); 7.40 (1H, d, J = 7.69); 7.10 (1H, d, J = 7.69); 5.62 (2H, m); 4.80 (2H, dd, J = 11.26, 22.25); 3.51 (1H, m); 2.35−1.40 (10H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.4, 147.6, 138.6, 133.9, 130.2, 129.6, 128.7, 127.7, 125.2, 121.9, 109.2, 80.1, 68.7, 34.6, 33.6, 26.1, 25.9, 23.1. MS *m/z* Calcd (M^+): 284.2. Found (ESI): 284.2 (M^+).

Synthesis of 6-Bromohexanoic Acid Cyclooct-4-enyl Ester (13). Dicyclocarbodiimide (7.5 g, 0.036 mol) and *N*,*N*-(dimethylamino)pyridine (0.4 g, 0.0033 mol) were dissolved in 40 mL of anhydrous CH_2Cl_2 and added dropwise to a solution of **11** (3.9 g, 0.031 mol) and 6-bromohexanoic acid (7.6 g, 0.039 mol) in 40 mL of anhydrous CH_2Cl_2 under argon. The solution was stirred overnight at room temperature. The white precipitate that formed during the reaction was filtered off, the filtrate was reduced, and the remaining oil was purified by column chromatography (silica gel, 4:1 hexanes/ethyl acetate) to yield a colorless oil (7.5 g, 79% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.61 (2H,m); 4.80 (1H,m); 3.37 (2H, t, J = 6.87); 2.36−1.40 (18H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.8; 129.9; 129.7; 75.7; 34.8; 34.1; 34.0; 33.8; 32.7; 27.9; 25.9; 25.2; 24.5; 22.7.

Synthesis of 6-Carbazol-9-ylhexanoic Acid Cyclooct-4-enyl Ester (14). Carbazole **4** (3.7 g, 0.022 mol) was dissolved in anhydrous THF and added dropwise to an ice-cold mixture of NaH (0.5 g, 0.021 mol) in THF and stirred for 1 h. Then, **13** (4.8 g, 0.016 mol), dissolved in 50 mL of anhydrous THF, was added dropwise to the reaction mixture. After the addition was complete, the mixture was refluxed overnight. After filtration, the solution was diluted with ether, washed with an aqueous solution of $NaHCO_3$ and brine, and dried over Na_2SO_4. The solvent was removed, and the crude product was purified by column chromatography (silica gel, 9:1 hexanes/ethyl acetate) yielding a viscous, colorless oil (3.7 g, 60% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.12 (2H, d, J = 7.69); 7.48 (2H, dd, J = 6.89, 15.11); 7.40 (2H, d, J = 7.97); 7.26 (2H, dd, J = 6.89, 14.83); 5.65 (2H, m); 4.81 (1H, m); 4.31 (2H, t, J = 7.14); 2.32−1.44 (18H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.9, 140.5, 129.9, 129.8, 125.8, 123.0, 120.6, 118.9, 108.8, 75.8, 75.7, 43.2, 34.8, 34.1, 33.9, 29.1, 27.2, 25.9, 25.2, 22.7. MS *m/z* Calcd (M^+): 390.2. Found (ESI): 390.2 (M^+).

Copolymerization of 12 and 14 (Ratios of 12/14 = 1:5, 1:10, 1:20). Monomer **12** was dissolved in 1 mL of chloroform. A chloroform solution of the ruthenium catalyst **8** in 1 mL of chloroform was added to the monomer solution and stirred for 30 s, followed by the addition of monomer **14** (in 5 mL of chloroform). After stirring for 10 min, ethyl vinyl ether (1 mL) was added. After stirring for an additional 10 min, the solution was concentrated down to 1 mL and added dropwise to 100 mL of cold methanol. The polymer, which precipitated out of solution, was collected and redissolved in 1 mL of chloroform and reprecipitated into cold methanol. This purification procedure was repeated three times. The final product was collected as a brown solid (**15a**−**c**).

*Quinoline-co-carbazole Copolymer **15a** (1:5).* ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.79 (1H, broad); 8.51 (1H, broad); 8.14 (10H, broad); 7.48 (22H, broad); 7.28 (10H, broad); 7.17 (1H, broad); 5.43 (12H, broad); 4.94 (7H, broad); 4.29 (10H, broad); 3.57 (1H, m); 2.2−1.4 (100H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.3, 152.5, 147.8, 140.5, 138.8, 133.9, 130.6, 130.4, 130.0, 129.8, 129.6, 128.9, 128.7, 127.7, 126.2, 125.9, 125.3, 123.0, 121.9, 120.6, 119.0, 108.9, 73.8, 68.8, 60.3, 43.1, 34.7, 34.4, 34.1, 33.5, 33.2, 33.0, 32.8, 29.1, 28.9, 27.4, 27.2, 25.7, 25.2, 23.7.

*Quinoline-co-carbazole Copolymer **15b** (1:10).* ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.78 (1H, broad); 8.49 (1H, broad); 8.14 (20H, broad); 7.45 (42H, broad); 7.26 (20H, broad); 7.14 (1H, broad); 5.40 (22H, broad); 4.91 (12H, broad); 4.31 (20H, broad); 3.57 (1H, m); 2.2−1.4 (190 H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.3, 152.5, 147.8, 140.5, 138.8, 133.9, 130.6, 130.4, 130.0, 129.8, 129.6, 128.9, 128.7, 127.7, 126.2, 125.9, 125.3, 123.0, 121.9, 120.6, 119.0, 108.9, 73.8, 68.8, 60.3, 43.1, 34.7, 34.4, 34.1, 33.5, 33.2, 33.0, 32.8, 29.1, 28.9, 27.4, 27.2, 25.7, 25.2, 23.7.

*Quinoline-co-carbazole Copolymer **15c** (1:20).* ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.77 (1H, broad); 8.44 (1H, broad); 8.13 (40H, broad); 7.45 (82H, broad); 7.26 (40H, broad); 7.14 (1H, broad); 5.38 (42H, broad); 4.89 (22H, broad); 4.28 (40H, broad); 3.54 (1H, m); 2.2−1.4 (370H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.3, 152.5, 147.8, 140.5, 138.8, 133.9, 130.6, 130.4, 130.0, 129.8, 129.6, 128.9, 128.7, 127.7, 126.2, 125.9, 125.3, 123.0, 121.9, 120.6, 119.0, 108.9, 73.8, 68.8, 60.3, 43.1, 34.7, 34.4, 34.1, 33.5, 33.2, 33.0, 32.8, 29.1, 28.9, 27.4, 27.2, 25.7, 25.2, 23.7.

Formation of Ybq_3 Copolymers 16a−c. Excess Ybq_3 was dissolved in a minimum amount of methanol and added to a chloroform solution of **15** (0.1 g/10 mL). After stirring overnight, the solution was concentrated down to 1 mL and added dropwise to 100 mL of cold methanol. The polymer, which precipitated out of solution, was collected and redissolved in 1 mL of chloroform and precipitated into cold methanol. This purification procedure was repeated three times. The final product was collected as a brown solid **16a**−**c**.

*Ytterbium Tris(8-hydroxyquinoline)-co-carbazole Copolymer **16a** (1:5). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.79 (broad); 8.13 (broad); 7.37 (broad); 5.40 (broad); 4.85 (broad); 4.30 (broad); 3.64 (broad); 2.4−1.2 (broad). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.3, 151.8, 147.6, 140.5, 138.1, 133.6, 130.7, 130.6, 130.5, 130.4, 130.1, 130.0, 129.9, 129.7, 126.2, 125.8, 122.9, 120.6, 118.9, 108.8, 73.8, 66.4, 43.1, 37.3, 34.7, 34.3, 34.1, 32.8, 29.0, 28.8, 27.2, 25.6, 25.2.*

*Ytterbium Tris(8-hydroxyquinoline)-co-carbazole Copolymer **16b** (1:10). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.79 (broad); 8.13 (broad); 7.37 (broad); 5.40 (broad); 4.85 (broad); 4.30 (broad); 3.64 (broad); 2.4−1.2 (broad). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.3, 151.8, 147.6, 140.5, 138.1, 133.6, 130.7, 130.6, 130.5, 130.4, 130.1, 130.0, 129.9, 129.7, 126.2, 125.8, 122.9, 120.6, 118.9, 108.8, 73.8, 66.4, 43.1, 37.3, 34.7, 34.3, 34.1, 32.8, 29.0, 28.8, 27.2, 25.6, 25.2.*

*Ytterbium Tris(8-hydroxyquinoline)-co-carbazole Copolymer **16c** (1:20). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.79 (broad); 8.13 (broad); 7.37 (broad); 5.40 (broad); 4.85 (broad); 4.30 (broad); 3.64 (broad); 2.4−1.2 (broad). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.3, 151.8, 147.6, 140.5, 138.1, 133.6, 130.7, 130.6, 130.5, 130.4, 130.1, 130.0, 129.9, 129.7, 126.2, 125.8, 122.9, 120.6, 118.9, 108.8, 73.8, 66.4, 43.1, 37.3, 34.7, 34.3, 34.1, 32.8, 29.0, 28.8, 27.2, 25.6, 25.2.*

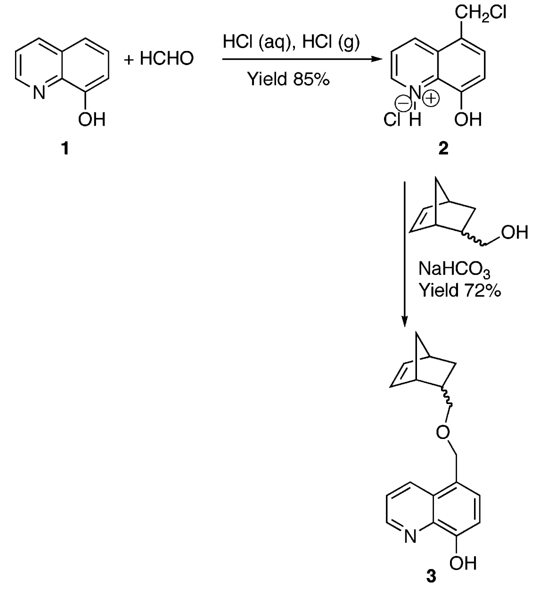
Solution Photoluminescence Studies. Approximately 5 mg of each copolymer was dissolved in a minimum amount of chloroform. The solution was then diluted with DMSO until a precipitate formed followed by the addition of chloroform until the solution became clear again. This procedure was repeated as necessary until a volume of 3 mL was reached. Note that the amount of chloroform and DMSO was different for each copolymer ratio.

Results and Discussion

Synthesis. Scheme 1 outlines the synthesis of monomer **3**. The chloromethylhydroxyquinoline salt **2** was stirred over sodium bicarbonate in the presence of a large excess of the norbornene methanol to yield the target monomer **3**. Monomer **3** was then polymerized using the third generation Grubbs ruthenium catalyst. The homopolymer was isolated and purified, followed by the addition of freshly prepared ytterbium tris(8-hydroxyquinoline) (Ybq_3).

However, upon purification, we were not able to redissolve the isolated Ybq_3 polymer in any common solvents. We have reported before that the metalation (using aluminum and zinc) of polymer-supported quino-

Scheme 1. Synthesis of Quinoline Monomer 3

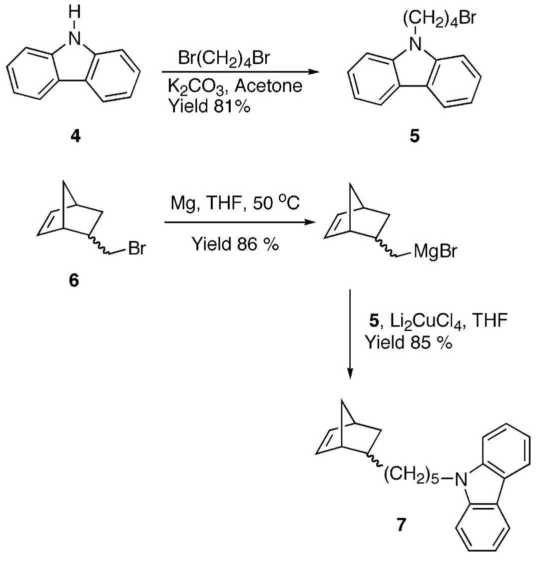


line ligands (these ligands can be viewed as macroligands) can yield to inter- and intramolecular cross-linking of polymers by incorporating more than one polymer-supported quinoline unit in a single metal quinolate complex.[32−34] This results in the formation of a cross-linked three-dimensional polymer network, thereby lowering the solubility of the functionalized polymers. In our previous contributions, we have shown that the incorporation of a nonfunctionalized spacer molecule (in all cases an alkyl-containing norbornene monomer) reduces the quinoline density along the polymer backbone and ultimately the cross-linking density after metalation. This strategy resulted in the synthesis of fully soluble polymers in a variety of organic solvents.[32−34] We rationalize that the same cross-linking phenomenon takes place using Yb metalation and that this solubility problem can be overcome by simply diluting the quinoline side chains along the polymer backbone.

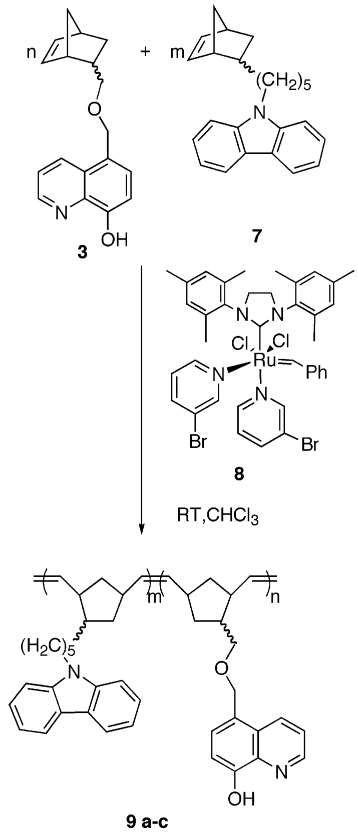
It is essential that the comonomer is moderately conductive and allows for energy transfer to the lanthanide metal center. Both requirements need to be fulfilled to allow for the potential use of the material in electronic devices. We rationalized that a carbazole-based monomer would fulfill these requirements. Poly(*N*-vinylcarbazole) (PVK) has been used previously as a polymer host for erbium quinolates, with results suggesting that the PVK not only acts as a hole-transporting polymer but also allows for energy transfer into the erbium center.[18]

The synthesis of carbazole monomer **7** is shown in Scheme 2. Commercially available carbazole **4** was functionalized with 1,4-dibromobutane and attached to bromomethylnorbornene **6** using a Grignard coupling to yield **7**. The copolymerization of **3** and **7** is shown in Scheme 3. The percentage of **3** in the copolymer was varied systematically from 5% up to 20%, giving ratios of **3/7** of 1:5 in **9a**, 1:10 in **9b**, and 1:20 in **9c**. The resulting purified copolymers were further functionalized by reacting them with Ybq$_3$, yielding the Ybq$_3$ copolymer **10** as shown in Scheme 4. The molecular weights of the copolymers are given in Table 1. Copolymers **9a**−**c** showed glass transition temperatures around 100 °C; however, no glass transition temperatures were detected upon the formation of the lanthanide complex on the side chains of the copolymers. All copolymers decomposed around 260 °C.

Scheme 2. Synthesis of Carbazole Monomer 7



Scheme 3. Copolymerization of 3 with 7



The syntheses of the cyclooctene-based quinoline monomer **12** and carbazole monomer **14** are shown in Scheme 5. Compound **11** was reacted with **2** in the presence of sodium bicarbonate to yield monomer **12**. Esterification of compound **11** with 6-bromohexanoic acid yielded compound **13**. Carbazole monomer **14** was obtained from the reaction of **13** with commercially available carbazole **4**.

The copolymerization of **12** and **14** is shown in Scheme 6. Ratios of **12** to **14** in copolymers **15a**, **15b**, and **15c** are 1:5, 1:10, and 1:20, respectively. Reactions of **15a**−**c** with Ybq$_3$ yielded copolymers **16a**−**c**. Again,

Scheme 4. Formation of the Norbornene-Based Ybq$_3$ Copolymers

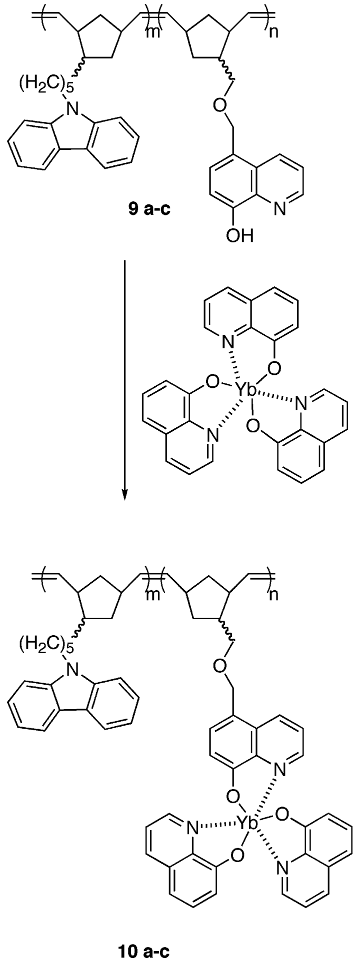


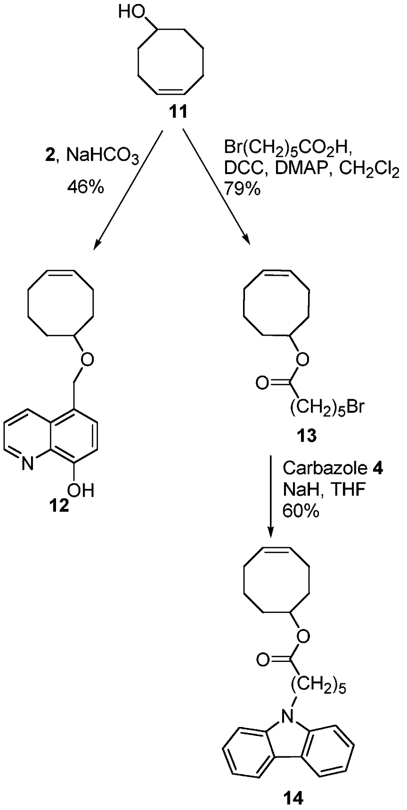
Table 1. Characterization Data for All Monomers and Polymers

	photophysical data		mol wt data		
compd	UV/vis $\lambda_{\max}$(nm)	emission[a] $\lambda_{\max}$ (nm)	M_n [1×10^3]	M_w [1×10^3]	PDI
3	316	n/a	n/a	n/a	n/a
7	346, 295	425	n/a	n/a	n/a
9a	347, 321, 295	511	10	14	1.4
9b	347, 322, 296	510	3.5	4.5	1.4
9c	346, 321, 294	509	3.5	4.5	1.4
10a	386, 347, 293	510, 971	9.5	13.5	1.4
10b	384, 344, 295	509, 970	3.5	4.5	1.4
10c	384, 346, 295	510, 971	3.5	4.5	1.4
12	319	n/a	n/a	n/a	n/a
14	346, 294	435	n/a	n/a	n/a
15a	346, 331, 294	501	16.5	71	4.3
15b	346, 331, 297	481	12.5	53.5	4.3
15c	346, 331, 294	496	15	61.5	4.0
16a	400, 346, 294	517, 971	11.5	49.5	4.2
16b	402, 346, 297	516, 970	13.5	49.5	3.7
16c	399, 346, 294	518, 975	15	53	3.6

[a] The emission spectrum for all compounds was collected at an excitation wavelength of 380 nm.

the molecular weights of the copolymers are given in Table 1. Copolymers **15a**−**c** showed glass transition temperatures around −15 °C a clear indication of the significant more flexible polymer backbone, in contrast to the above-described poly(norbornene)s. Upon formation of the lanthanide complex, glass transition temperatures of the copolymers increased to around −5 °C. All cyclooctene-based copolymers decomposed around 335 °C.

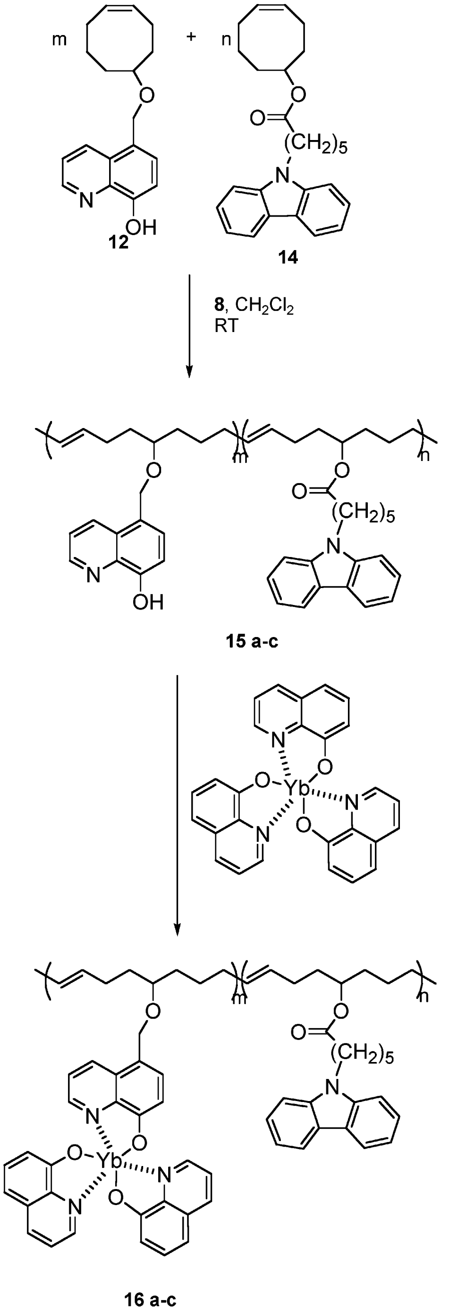
Scheme 5. Synthesis of Cyclooctene Monomers 12 and 14



We used elemental analysis methods to determine the metal contents of polymers **10a,b** and **16a,b**. We carried out ICP analyses of all four polymers. In all cases, the metal contents were only 10−35% of the theoretical values (for **10a**: theoretical value 7.24%, measured value (ICP) 2.55% (35% of theoretical value) and for **10b**: theoretical value 4.29%, measured value (ICP) 0.544% (13% of theoretical value)). These results suggest that only every third to every tenth quinoline unit along the polymer backbone is metalated. To verify these numbers, we also carried out elemental analysis (C, H, N, and O) of **10a**. Since the polymer contains only the elements C, H, N, and O but for the metal, one can calculate the metal contents by subtracting the C, H, N, and O contents from 100%. The remaining contents must be the metal complex. Using this method, we measured a metal content of 6.88% (95% of the theoretical value), suggesting a nearly quantitative metalation of all quinoline units along the polymer backbone.

While one should expect both methods of metal contents characterization to agree, we found that both methods diverse from the theoretical expected metal contents values. We attribute the error of the two analytical methods to the small sample sizes and the low metal percentage of all polymers. Nevertheless, both methods clearly indicate that metalation of the quinoline units along the polymer backbone took place and that the metal contents along the polymers cannot be characterized conclusively. Our data suggest that the polymer containing a high density of quinoline units along the polymer backbone have a higher metal contents (35−95% depending on the characterization method) than the polymers with the lower quinoline density.

Scheme 6. Copolymerization of 12 with 14 and Formation of the Corresponding Ybq$_3$ Copolymers



UV/Vis Absorption. The absorption spectra of **3**, **7**, **9a**, and **10a** are shown in Figure 1 and are tabulated in Table 1. The absorption spectrum of the copolymer **9a** is a combination of both monomers **3** and **7**. The absorption of the ytterbium-containing copolymer **10a** is almost identical to that of **9a** as a result of the shielding effect of the ligands surrounding the ytterbium–metal center. Because of this shielding effect, the metal center itself cannot be excited directly. Instead, the quinoline ligands that are coordinated to the metal center and show absorption maxima around 385 nm and were excited, and the energy transfer to the lanthanide metal centers was recorded as photoluminescence spectra. The same behavior was observed for cyclooctene compounds. Table 1 tabulates the absorption characteristics of **12**, **14**, **15a–c**, and **16a–c**. Complexation of compounds **15a–c** with ytterbium produced absorption bands around 400 nm that indicate the coordination of the metal to the polymers through side chain quinoline ligands. This absorption characteristic was used to excite the copolymers **16a–c** for the photoluminescence study.

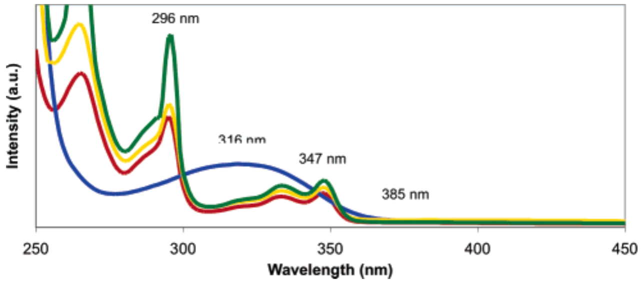


Figure 1. UV/vis absorption spectra of **3** (blue), **7** (red), **9a** (green), and **10a** (yellow).

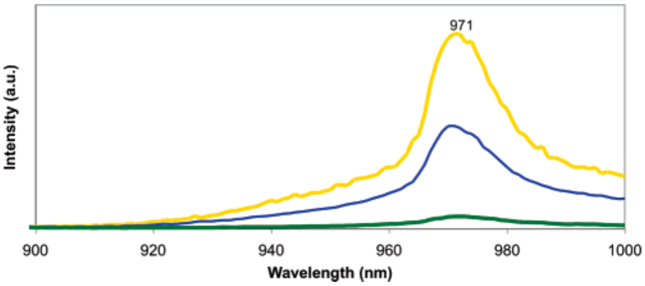


Figure 2. Photoluminescence of Ybq$_3$ copolymers: **10a** 1:5 (yellow), **10b** 1:10 (blue), and **10c** 1:20 (green).

Photoluminescence. The solution photoluminescence of the Ybq$_3$ copolymers (**10a–c, 16a–c**) was measured to determine the effect of the concentration of Ybq$_3$ in the polymer on the emission properties. While all metalated copolymers were soluble in chloroform, no emission was detected in pure chloroform. However, emission was observed when a mixture of chloroform and DMSO was used. As previously reported, DMSO replaces any water molecules coordinated to the lanthanide metal.[23] The emission of lanthanide-containing compounds in chloroform is dramatically lower than the emission of the same compound in DMSO. In solutions of lanthanide complexes, relatively small energy contents of the long wavelength electronic gap can be readily dissipated by solvent. If the energy of the gap between the lowest fluorescence-emitting level and the nearest nonfluorescence level is dissipated, radiationless decay occurs. In water, the O–H stretching vibration is very efficient in dissipating energy. If the O–H vibration can be replaced by a less energetic vibration, quenching becomes less efficient. For example, deuterated water is a less efficient quencher due to the lower energy of the O–D vibration. The same holds true for the S=O stretching vibrations of DMSO that are less efficient in quenching the emission than the O–H stretch of water.[23,44–47]

Table 1 and Figures 2 and 3 (only infrared region) show the emission spectra of polymers **10** and **16**. In all cases two emission maxima were observed for the metalated polymers. One maximum was in the visible region (green emission around 510–515 nm) that stems from the emission of the hydroxyquinoline ligand. The second maxima are in the near-infrared region (around 970 nm) and can be attributed to the ytterbium–hydroxyquinoline complex. In contrast, the nonmetalated polymers **9** and **15** showed only green emission in the visible. It is important to note that the polymers

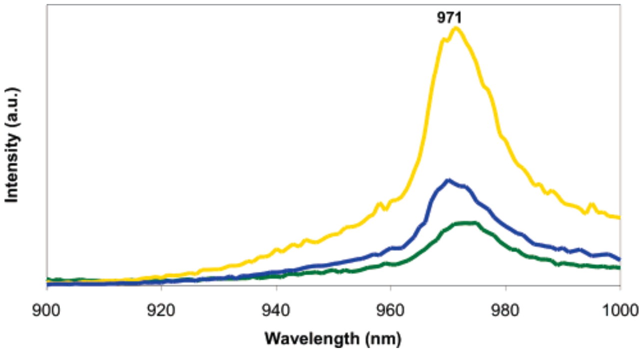


Figure 3. Photoluminescence of Ybq_3 copolymers: **16a** 1:5 (yellow), **16b** 1:10 (blue), and **16c** 1:20 (green).

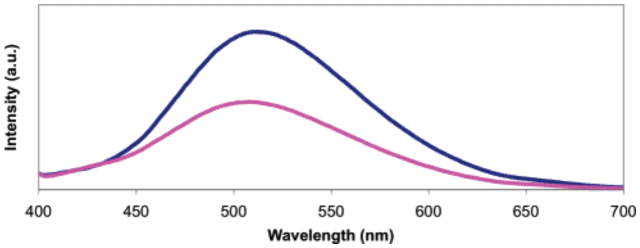


Figure 4. Visible region of the photoluminescence of copolymers **9a** (black) (before) and **10a** (red) (after metalation with ytterbium).

were excited at the hydroxyquinoline excitation at 380 nm. As described in the introduction, no direct excitation of the metal center is possible. Therefore, any observed emission from the metal center must stem from energy transfer between the ligands and the Yb metal center. To quantify this energy transfer, we carried out photoluminescence studies of **9a** and **10a** under identical conditions (solvent, concentration, etc.) and compared the relative intensities of the green emission maxima at 510 nm (Figure 4). After attachment of the lanthanide, we expected a decrease in the intensity of the quinoline emission and the observation of a new emission band in the infrared region due to energy transfer from the quinoline ligand into the metal center. Indeed, as outlined in Figure 4, the emission intensity at 510 nm for the 1:5 Ybq_3 copolymer **10a** was ∼40% lower in comparison to its nonmetalated 1:5 copolymer analogous **9a**. This result suggests that a significant portion of the energy was transferred to the lanthanide metal instead of radiatively relaxing back to the ground state.

As shown in Figures 2 and 3, as the chromophore density in the polymer decreases, the emission intensity also decreases. The integrated emission signal of the 1:20 copolymer was approximately half of that of the 1:10 copolymer, which was half of that of the 1:5 copolymer, indicating a linear relationship between the concentration of lanthanide−quinolate in the copolymer and the emission intensity. Note that the curves shown in Figures 2 and 3 are corrected for concentration. However, when measuring the photoluminescence of a nonsupported Ybq_3 molecule (not shown for clarity), the emission intensity was significantly lower than the emission of the 1:20 Ybq_3 copolymer. This indicates that not only does the polymer backbone not interfere with the emission properties of the lanthanide quinolate, but the polymer backbone actually prevents self-quenching of the Ybq_3 chromophore, a reported occurrence for lanthanide-based materials.[30]

Conclusions

In this contribution, we have demonstrated the attachment of lanthanide complexes that have been suggested as important materials for electronic applications, to poly(norbornene) and poly(cyclooctene) backbones. In particular, we have prepared and studied poly(norbornene) and poly(cyclooctene) copolymers with pendant carbazole and tris(8-hydroxyquinoline)ytterbium complexes. The two polymer backbones investigated have different and distinct physical properties. While copolymers of poly(norbornene) have low polydispersity indices and high glass transition temperatures, copolymers of poly(cyclooctene) displayed significantly higher polydispersity indices as a result of the less controlled polymerization and significantly lower glass transition temperatures. Upon excitation of the quinoline ligands of the metal complexes, all metalated copolymers emit light in the infrared region. We have shown that neither of the two backbones studied interferes with the emission of the lanthanide complex. Comonomers containing pendant carbazole groups were incorporated into the copolymers to potentially increase charge mobility and to also improve the solubility of the final polymeric material. Finally, since carbazole is also a known hole-transport material, it may enhance the performance of future electronic devices made with our copolymeric material.

Acknowledgment. Financial support has been provided by the National Science Foundation (ChE-0239385) and Albemarle Corp. M.W. gratefully acknowledges a 3M Untenured Faculty Award, a DuPont Young Professor Award, A Camille Dreyfus Teacher/Scholar Award, an Alfred P Sloan Fellowship, and a Blanchard Assistant Professorship.

References and Notes

(1) Adachi, C.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1990**, *56*, 799−801.
(2) Antoniadis, H.; Roitman, D.; Miller, J. U.S. Patent 5,719467, 1998.
(3) Baigent, D. R.; Greenham, N. C.; Gruner, J.; Marks, R. N.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Synth. Met.* **1994**, *67*, 3−10.
(4) Berggren, M.; Inganas, O.; Gustafsson, G.; Rasmusson, J.; Andersson, M. R.; Hjertberg, T.; Wennerstrom, O. *Nature (London)* **1994**, *372*, 444−446.
(5) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; MacKay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539−541.
(6) Cacialli, F.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Synth. Met.* **1994**, *67*, 157−160.
(7) Chen, C. H.; Shi, J. *Coord. Chem. Rev.* **1998**, *171*, 161−174.
(8) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Santos, D. A. D.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature (London)* **1999**, *397*, 121−128.
(9) Greiner, A. *Polym. Adv. Technol.* **1998**, *9*, 371−389.
(10) Howard, W. E.; Prache, O. F. *IBM J. Res. Dev.* **2001**, *45*, 115−127.
(11) Kido, J.; Kimura, M.; Nagai, K. *Science* **1995**, *267*, 1332−1334.
(12) Sheats, J. R.; Antoniadis, H.; Hueschen, M.; Leonard, W.; Miller, J.; Moon, R.; Roitman, D.; Stocking, A. *Science* **1996**, *273*, 884−888.
(13) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913−915.
(14) Khreis, O. M.; Curry, R. J.; Somerton, M.; Gillin, W. P. *J. Appl. Phys.* **2000**, *88*, 777−780.
(15) Gillin, W. P.; Curry, R. J. *Appl. Phys. Lett.* **1999**, *74*, 798−799.
(16) Curry, R. J.; Gillin, W. P. *Appl. Phys. Lett.* **1999**, *75*, 1380−1381.

(17) Hong, Z. R.; Liang, C. J.; Li, R. G.; Zhao, D.; Fan, D.; Li, W. L. *Thin Solid Films* **2001**, *391*, 122−125.

(18) Sun, R. G.; Wang, Y. Z.; Zheng, Q. B.; Zhang, H. J.; Epstein, A. J. *J. Appl. Phys.* **2000**, *87*, 7589−7591.

(19) Kawamura, Y.; Wada, Y.; Yanagida, S. *Jpn. J. Appl. Phys.* **2001**, *40*, 350−356.

(20) Slooff, L. H.; Polman, A.; Cacialli, F.; Friend, R. H.; Hebbink, G. A.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Appl. Phys. Lett.* **2001**, *78*, 2122−2124.

(21) Harrison, B. S.; Foley, T. J.; Knefely, A. S.; Mwaura, J. K.; Cunningham, G. B.; Kang, T.-S.; Bouguettaya, M.; Boncella, J. M.; Reynolds, J. R.; Schanze, K. S. *Chem. Mater.* **2004**, *16*, 2938−2947.

(22) Vicinelli, V.; Ceroni, P.; Maestri, M.; Balzani, V.; Gorka, M.; Vögtle, F. *J. Am. Chem. Soc.* **2002**, *124*, 6461−6468.

(23) van Deun, R.; Fias, P.; Nockemann, P.; Schepers, A.; Parac-Vogt, T. N.; van Hecke, K.; van Meervelt, L.; Binnemans, K. *Inorg. Chem.* **2004**, *43*, 8461−8469.

(24) Baigent, D. R.; Hamer, P. J.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Synth. Met.* **1995**, *71*, 2175−2176.

(25) Suzuki, H.; Hattori, Y.; Iizuka, T.; Yuzawa, K.; Matsumoto, N. *Thin Solid Films* **2003**, *438−439*, 288−293.

(26) Desurvire, E. *Phys. Today* **1994**, *47*, 20−27.

(27) Rizzo, F.; Papagni, A.; Meinardi, F.; Tubino, R.; Ottonelli, M.; Musso, G. F.; Dellepiane, G. *Synth. Met.* **2004**, *147*, 143−147.

(28) Pitois, C.; Vestberg, R.; Rodlert, M.; Malmström, E.; Hult, A.; Lindgren, M. *Opt. Mater.* **2002**, *21*, 499−506.

(29) Curry, R. J.; Gillin, W. P. *Synth. Met.* **2000**, *111−112*, 35−38.

(30) Curry, R. J.; Gillin, W. P. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 481−486.

(31) Iwamuro, M.; Adachi, T.; Wada, Y.; Kitamura, T.; Nakashima, N.; Yanagida, S. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1359−1363.

(32) Meyers, A.; Weck, M. *Macromolecules* **2003**, *36*, 1766−1768.

(33) Meyers, A.; Weck, M. *Chem. Mater.* **2004**, *16*, 1183−1188.

(34) Meyers, A.; South, C.; Weck, M. *Chem. Commun.* **2004**, 1176−1177.

(35) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041.

(36) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903−2906.

(37) Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 749−750.

(38) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035−4037.

(39) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29.

(40) *Handbook of Metathesis*; Wiley VCH: Weinheim, 2003; Vol. 3.

(41) Burckhalter, J. H.; Leib, R. I. *J. Org. Chem.* **1961**, *26*, 4078−4083.

(42) Stubbs, L. P.; Weck, M. *Chem.−Eur. J.* **2003**, *9*, 992−999.

(43) Hillmyer, M. A.; Laredo, W. R.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 6311−6316.

(44) Hasegawa, Y.; Kimura, Y.; Murakoshi, K.; Wada, Y.; Kim, J.-H.; Nakashima, N.; Yamanaka, T.; Yanagida, S. *J. Phys. Chem.* **1996**, *100*, 10201−10205.

(45) Stein, G.; Würzberg, E. *J. Chem. Phys.* **1975**, *62*, 208−213.

(46) Kawa, M.; Takahagi, T. *Chem. Mater.* **2004**, *16*, 2282−2286.

(47) Hasegawa, Y.; Yamamuro, M.; Wada, Y.; Kanehisa, N.; Kai, Y.; Yanagida, S. *J. Phys. Chem. A* **2003**, *107*, 1697−1702.

MA050923K