Chem. Mater. **2007,** *19,* 5602−5608

Norbornene-Based Copolymers with Iridium Complexes and Bis(carbazolyl)fluorene Groups in Their Side-Chains and Their Use in Light-Emitting Diodes

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Received July 1, 2007. Revised Manuscript Received August 17, 2007

Solution-processable copolymers with pendant phosphorescent iridium complexes and 2,7-di(carbazol-9-yl)fluorene-type host moieties were synthesized using ruthenium-catalyzed ring-opening metathesis polymerization. Low polydispersity indices and molecular weights around 20 000 Da were obtained for all copolymers. As a result of the living character of the polymerization of the monomer containing the host moiety, a high degree of control over the molecular weights of all copolymers can be obtained. The photo- and electroluminescence properties of the copolymers were investigated. All copolymers retained the photo- and electrophysical properties of the corresponding nonpolymeric iridium complexes. Furthermore, as a proof of principle for the potential use of these materials, organic light-emitting devices were fabricated using the orange-emitting copolymer. A maximum external quantum efficiency of 1.9% at 100 cd/m^2 and a turn-on voltage of 3.7 V were obtained with photoluminescence quantum yield of 0.10 demonstrating the potential of these copolymers as emissive materials for display and lighting applications.

Introduction

Phosphorescent metal complexes are at the center of recent research emphases on organic light-emitting diodes (OLEDs).[1] In these complexes, strong spin−orbit coupling induces the intersystem crossing from the singlet to the phosphorescent triplet excited state.[1] Theoretically, using phosphorescent materials as emission centers for OLEDs allows for the collection of all the singlet and triplet excitons generated upon electrical excitation in an OLED device. Indeed, nearly 100% internal quantum efficiencies have been reported for OLEDs based on phosphorescent transition metal complexes.[2] In particular, third-row transition metal complexes have been used widely in OLEDs as a result of the heavy-atom effect on the spin−orbit coupling.[1] Of these, iridium complexes exhibit the most promising properties in terms of device performance.[2,3] Iridium complexes with emission spectra that span the entire visible spectrum have been synthesized and employed in vacuum-deposited OLEDs with high external quantum efficiencies.[3] For example, external quantum efficiencies as high as 19% have been obtained for a system utilizing a 2-phenylpyridinato-based iridium complex doped into a wide energy gap host.[2b]

The excellent device performances that have been obtained using vacuum-deposited iridium complexes inspired the exploration of solution-processable approaches for incorporation of iridium complexes into OLEDs.[4,5] A promising methodology is the covalent anchoring of small-molecule components to polymer backbones, resulting in materials that can be solution-processed[4−9] and, if desired, photopatterned.[10] Both conjugated and nonconjugated polymer backbones have been employed in this strategy to produce solution-processable iridium-containing materials.[4,5] Although devices based on polymeric materials often have lower performances than equivalent devices based on vacuum-deposited material, they

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10.1021/cm0717357 CCC: $37.00

demonstrate the promise that this new strategy holds for OLEDs.

Over the past 5 years, we have initiated a program of covalently grafting metal complexes onto polymers with a special emphasis on poly(norbornene)s as materials for OLED applications.[5,6] Poly(norbornene)s can be polymerized via ring-opening metathesis polymerization (ROMP), a living polymerization method that allows for a high degree of control over molecular weights.[11] Furthermore, ruthenium-based ROMP initiators are highly functional-group tolerant, allowing for the polymerization of norbornene monomers containing fluorescent and phosphorescent metal complexes.[5a,6a] Finally, the employment of a living polymerization method such as ROMP allows for the synthesis of controlled copolymers ranging from random to block copolymers.[11] The use of poly(norbornene) was based on the assumption that poly(norbornene)-based backbones have relatively little adverse effects on the charge-carrier mobilities in devices. Indeed, higher hole mobilities have been measured for bis-(diarylamino)fluorene-functionalized poly(norbornene)s in comparison to analogous materials based on the more polar poly(acrylate) backbone.[12]

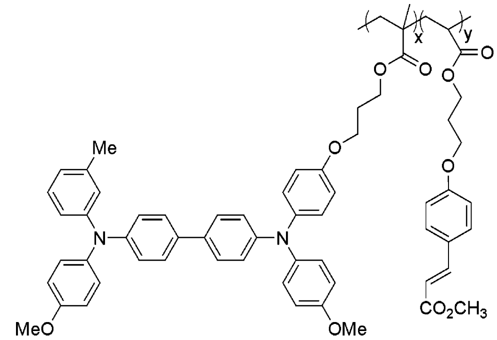

Figure 1. Structure of the cross-linkable hole-transport polymer (x/y = 4:1).

In 2005, we reported the covalent functionalization of iridium complexes onto poly(norbornene)s.[5a] We demonstrated that the poly(norbornene) backbone does not interfere with the photophysical properties of the iridium complexes studied. However, our preliminary contribution did not employ copolymers containing host material-based comonomers, a key requirement for the use of these materials in efficient OLED devices. In this contribution, we describe the synthesis of random copolymers containing 2,7-di-(carbazol-9-yl)fluorene-type host moieties and various iridium complexes in the side-chains that emit in various regions of the visible spectrum and report their solution and solid-state photoluminescence properties and their solid-state electroluminescence properties. Furthermore, we report the first iridium-containing poly(norbornene)-based OLED device to demonstrate the potential of our materials.

Experimental Section

General. Compounds **4**,[13] **5**,[5c] **7**,[5a] **8**,[5c] **10**,[5a] and **13**[14] were synthesized according to published procedures.

Device Fabrication. Previously described TPD-based acrylate copolymers containing 20 mol % of a cinnamate cross-linkable moiety (Figure 1) were used as hole-transport materials.[15] Films of 35−40 nm thickness were prepared by spin coating onto oxygen plasma treated indium tin oxide (ITO) with a sheet resistance of 20 Ω/□ (Colorado Concept Coatings, L.L.C.) from toluene solutions of the polymer. One minute of UV exposure using a standard broadband UV light with a 0.6 mW/cm^2 power density was used to cross-link the hole-transport polymer. The emissive copolymers (**14**, **15**,

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16, or **17**) were then spin-coated from their chloroform solutions onto the cross-linked hole-transport layer to form films with a thickness of 20−30 nm. Electron-transport and hole-blocking layers comprised of a 20 nm thick film of AlQ_3 and a 6 nm thick film of BCP, respectively, were thermally evaporated at rates between 0.4 and 0.7 Å/s under a pressure below 1×10^{-7} torr on top of the emitting layer. LiF (1 nm) and the metal cathode Al (150 nm) were deposited through a shadow mask to define five devices per substrate with an emissive area of 0.1 cm^2 each.

Synthesis of 2,6-Difluoro-3-pyridin-2-yl-benzoic Acid (1). Under an argon atmosphere, 10.5 mL of an ^{n}BuLi solution (1.6 M in hexanes, 16.8 mmol) was added dropwise at −78 °C to a THF (55 mL) solution of 2-(2,4-diflouro-phenyl)pyridine (3.2 g, 16.8 mmol). The mixture was stirred for 20 min, followed by the addition of freshly crushed dry ice. After stirring for an additional 5 min, 10 mL of an aqueous HCl solution (1 M) was added, followed by the addition of diethyl ether (30 mL). The organic layer was collected, and the aqueous layer was washed three times with diethyl ether (30 mL). The combined organic layers were concentrated in vacuo, and the target compound was obtained by precipitation into hexanes (2.7 g, 68% yield). ^{1}H NMR (DMSO): $\delta = 8.72$ (d, 1H, $J = 3.3$ Hz), 8.04 (d, 1H, $J = 6.9$ Hz), 7.91 (m, 1H), 7.76 (m, 1H), 7.41 (m, 1H), 7.33 (t, 1H, $J = 8.7$ Hz). ^{13}C NMR (DMSO): $\delta =$ 162.8, 161.5, 158.9, 158.0, 155.6, 151.8, 150.6, 137.8, 134.1, 124.9, 124.8, 123.9, 113.6, 113.4, 113.1. MS Calcd (M + 1): 236.0. Found (ESI): 236.0 (M + 1).

Synthesis of 2,6-Difluoro-3-pyridin-2-yl-benzoic Acid Bicyclo-[2.2.1]hept-5-en-2-ylmethyl Ester (2). Compound **1** (2.7 g, 11.5 mmol), *exo*-5-norbornene-2-methanol (1.4 g, 11.5 mmol), and dimethylaminopyridine (0.3 g, 2.45 mmol) were combined in 100 mL of THF. A solution of dicyclohexylcarbodiimide (2.7 g, 13.1 mmol) in 10 mL of THF was added, and the reaction was stirred under argon at ambient temperatures for 24 h. The solvent was evaporated, and the residue was purified via column chromatography (silica, 4:1 hexanes/ethyl acetate) to give compound **2** as a clear oil (2.6 g, 66% yield). ^{1}H NMR ($CDCl_3$): $\delta = 8.71$ (d, 1H, $J = 4.8$ Hz), 8.10 (m, 1H), 7.76 (t, 1H, $J = 1.5$ Hz), 7.74 (m, 1H), 7.26 (m, 1H), 7.07 (td, 1H, $J = 8.7$ Hz, 1.5 Hz), 6.09 (m, 2H), 4.45 (dd, 1H, $J = 6.6$ Hz, 10.8 Hz), 4.28 (dd, 1H, $J = 9.3$ Hz, 10.8 Hz), 2.85 (s, 1H), 2.80 (s, 1H), 1.86 (m, 1H), 1.37 (s, 2H), 1.30 (d, 1H, $J = 8.4$ Hz), 1.24 (m, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 162.5$, 162.4, 159.9, 159.1,158.9, 156.5, 151.9, 150.1,137.2, 136.8, 136.4, 134.2, 134.1, 134.0, 124.6, 124.5, 123.0, 112.8, 112.7, 112.5, 112.4, 70.4, 45.2, 43.9, 41.9, 38.1, 29.8. MS Calcd (M): 341.2. Found (EI): 341.2 (M).

Synthesis of *fac*-exo-Bis(2-(4′,6′-difluorophenyl)-pyridinato, N, C$^{2'}$)(2-(5′-bicyclo[2.2.1]hept-5-ene-2-yl ethanoyl-4′,6′-difluorophenyl)pyridinato, N, C$^{2'}$) Iridium(III) (3). Compound **2** (75 mg, 0.22 mmol), $(Ir(ppf)_2Cl)_2$ (90 mg, 0.074 mmol),[3f] and $AgCF_3SO_3$ (38 mg, 0.148 mmol) were combined in 3 mL of ethoxyethanol. The mixture was purged with argon for 30 min followed by stirring at 150 °C for 24 h under an argon atmosphere. The mixture was cooled to room temperature, and water (10 mL) was added to precipitate the product. After filtration, the collected solid was purified via column chromatography (silica, CH_2Cl_2) to yield compound **3** (36 mg, 27% yield). ^{1}H NMR ($CDCl_3$): $\delta = 8.33$ (m, 3H), 7.72 (m, 3H), 7.45 (m, 3H), 6.96 (m, 3H), 6.41 (m, 3H), 6.25 (m, 2H), 6.09 (m, 2H), 4.39 (dd, 1H, $J = 6.6$ Hz, 10.8 Hz), 4.19 (dd, 1H, $J = 9.3$ Hz, 10.8 Hz), 2.84 (s, br, 2H), 1.85 (m, 1H), 1.37 (s, 2H), 1.28 (m, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 163.7$, 163.2, 160.1, 147.3, 147.1, 137.7, 132.6, 123.8, 123.5, 122.9, 122.5, 119.1, 118.2, 97.6, 68.9, 49.6, 44.2, 42.5, 37.9, 29.9, 29.2. MS Calcd (M): 912.9. Found (EI): 912.9 (M). Anal. Calcd ($C_{42}H_{28}F_6IrN_3O_2$): C, 55.26; H, 3.09; N, 4.60. Found: C, 55.11; H, 3.22; N, 4.66.

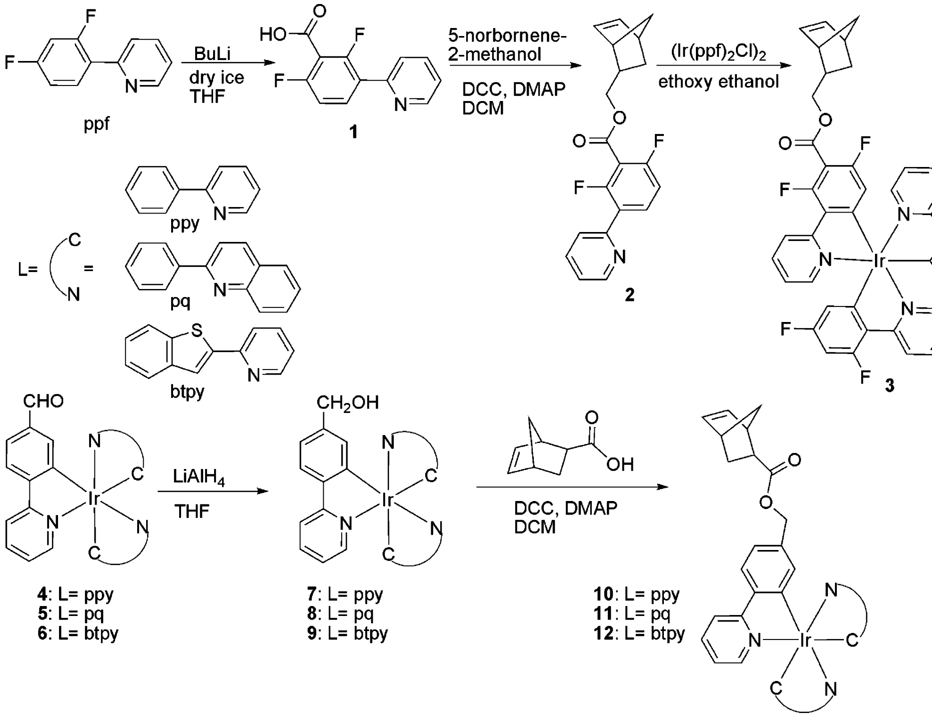
Synthesis of *fac*-Bis(2-(benzo[*b*]thiophen-2-yl)-pyridinato, N, C$^{3'}$)(2-(4′-formylphenyl)pyridinato, N, C$^{2'}$) Iridium(III) (6). $(Ir(btpy)_2Cl)_2$[3a] (1.0 g, 0.77 mmol), 4-(2-pyridyl)benzaldehyde (0.42 g, 2.3 mmol), and $AgCF_3SO_3$ (0.40 g, 1.5 mmol) were combined in 11 mL of ethoxyethanol. The reaction mixture was purged with argon for 30 min and then stirred at 150 °C for 24 h under an argon atmosphere. The solution was cooled to room temperature, and water (20 mL) was added to precipitate the product. After filtration, the collected solid was purified via column chromatography (silica, CH_2Cl_2) to yield compound **6** (0.18 g, 15% yield). ^{1}H NMR ($CDCl_3$): $\delta = 9.62$ (s, 1H), 7.78 (m, 4H), 7.51(m, 7H), 7.39 (d, 1H, $J = 5.7$ Hz), 7.33 (d, 1H, $J = 1.8$ Hz), 7.24 (d, 1H, $J = 5.4$ Hz), 7.09 (m, 2H), 6.93 (td, 1H, $J = 5.9$ Hz, 1.5 Hz), 6.78 (t, 1H, $J = 7.6$ Hz), 6.68 (m, 5H). ^{13}C NMR ($CDCl_3$): $\delta = 194.7$, 165.6, 163.2, 162.6, 160.8, 156.6, 155.9, 150.7, 148.9, 148.1, 147.6, 146.9, 143.7, 143.3, 142.6, 137.6, 137.1, 136.2, 134.6, 134.4, 128.7, 125.2, 124.3, 123.8, 123.7, 122.5, 122.3, 119.9, 119.7, 118.9, 118.8. MS Calcd (M + 1): 796.1. Found (ESI): 796.1 (M + 1).

Synthesis of *fac*-Bis(2-(benzo[*b*]thiophen-2-yl)-pyridinato, N, C$^{3'}$)(2-(4′-hydroxymethylphenyl)pyridinato, N, C$^{2'}$) Iridium(III) (9). Compound **6** (50 mg, 0.062 mmol) was dissolved in 5 mL of THF, and 0.08 mL of lithium aluminum hydride (1 M in diethyl ether) was added dropwise. The reaction mixture was stirred at ambient temperatures for 45 min and then quenched by the addition of excess water. The crude product, which showed no remaining aldehyde signals by ^{1}H NMR spectroscopy, was dissolved in dichloromethane, washed three times with water, dried with $MgSO_4$, and used without further purification.

Synthesis of fac-exo-Bis(2-phenyl-quinolinato, N, C$^{2'}$)(2-(4′-methyl bicyclo[2.2.1]hept-5-ene-2-carboxylphenyl)pyridinato, N, C$^{2'}$) Iridium(III) (11). Compound **8** (1.220 g, 1.55 mmol), *exo*-5-norbornene-2-carboxylic acid (0.245 g, 1.77 mmol), and dimethylaminopyridine (0.100 g, 0.82 mmol) were combined in 60 mL of CH_2Cl_2. A solution of dicyclohexylcarbodiimide (0.370 g, 1.79 mmol) in 10 mL of CH_2Cl_2 was added, and the reaction was stirred under argon at ambient temperatures for 24 h. The solvent was evaporated, and the residue was purified via column chromatography (silica, CH_2Cl_2) to give compound **11** as an orange powder (1.07 g, 76% yield). ^{1}H NMR ($CDCl_3$): $\delta = 8.09$ (m, 5H), 7.91 (d, 1H, $J = 8.4$ Hz), 7.86 (d, 1H, $J = 6.9$ Hz), 7.70 (m, 2H), 7.62 (d, 2H, $J = 9.0$ Hz), 7.57 (d, 1H, $J = 9.0$ Hz), 7.46 (td, 1H, $J =$ 9.0 Hz, 3.0 Hz), 7.40 (d, 1H, $J = 9.0$ Hz), 7.22 (t, 1H, $J = 7.8$ Hz), 7.16 (t, 1H, $J = 7.8$ Hz), 6.95 (m, 3H), 6.71 (m, 7H), 6.50 (d, 1H, $J = 1.2$ Hz), 6.14 (m, 2H), 4.82 (m, 2H), 2.97 (s, br, 1H), 2.91(s, br, 1H), 2.20 (dd, 1H, $J = 7.2$, 4.2), 1.88 (m, 1H), 1.44 (m, 1H), 1.33 (m, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 176.2$, 167.5, 167.4, 165.8, 163.2, 160.6, 158.4, 149.2, 148.8, 148.2, 146.4, 144.9, 143.7, 138.3, 137.6, 137.2, 137.1, 136.3, 136.1, 135.9, 133.3, 133.2, 130.4, 129.8, 129.7, 129.2, 128.4, 127.9, 127.8, 127.7, 127.1, 126.4, 126.3, 125.9, 125.3, 123.6, 122.3, 120.6, 120.2, 119.8, 119.2, 118.4, 118.1, 66.9, 46.8, 43.5, 41.9, 30.6, 30.5. MS Calcd (M): 905.3. Found (EI): 905.3 (M). Anal. Calcd ($C_{50}H_{38}IrN_3O_2$): C, 66.35; H, 4.23; N, 4.64. Found: C, 66.21; H, 4.38; N, 4.67.

Synthesis of *fac*-Bis(2-benzo[*b*]thiophen-2-yl-pyridinato, N, C$^{3'}$)(2-(4′-methylbicyclo[2.2.1]hept-5-ene-2-carboxylphenyl)pyridinato, N, C$^{2'}$) Iridium(III) (12). Compound **9** (143 mg, 0.18 mmol), *exo*-5-norbornene-2-carboxylic acid (29 mg, 0.21 mmol), and dimethylaminopyridine (10 mg, 0.08 mmol) were combined in 15 mL of CH_2Cl_2. A solution of dicyclohexylcarbodiimide (42 mg, 0.21 mmol) in 5 mL of CH_2Cl_2 was added, and the reaction was stirred under argon at ambient temperatures for 24 h. The solvent was evaporated, and the residue was purified via column chromatography (silica, CH_2Cl_2) to give compound **12** (81 mg, 49% yield). ^{1}H NMR ($CDCl_3$): $\delta = 7.76$ (d, 2H, $J = 8.1$ Hz), 7.69 (d,

Scheme 1. Syntheses of Iridium Complex Containing Monomers 3 and 10−12



1H, $J = 8.1$ Hz), 7.62 (d, 1H, $J = 8.4$ Hz), 7.47 (m, 6H), 7.36 (d, 1H, $J = 6.0$ Hz), 7.26 (d, 1H, $J = 5.1$ Hz), 7.12 (td, 1H, $J = 7.2$ Hz, 1.5 Hz), 7.05 (m, 1H), 6.93 (dd, 1H, $J = 6.3$ Hz, 1.5 Hz), 6.85 (m, 3H), 6.67 (m, 5H), 6.06 (m, 2H), 4.87 (s, 2H), 2.83 (m, 2H), 2.01 (m, 1H), 1.55 (m, 1H), 1.34 (m, 1H), 1.23 (m, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 176.2$, 166.7, 163.4, 162.7, 161.8, 157.4, 155.3, 149.3, 147.8, 147.7, 147.5, 147.1, 144.6, 143.2, 142.6, 138.5, 138.0, 137.2, 136.9, 136.7, 136.2, 129.2, 128.8, 125.1, 124.9, 124.1, 123.7, 122.4, 122.3, 122.2, 120.4, 119.8, 118.8, 118.7, 66.7, 46.6, 43.3, 41.8, 30.4. MS Calcd (M) 917.2. Found (EI): 917.2 (M). Anal. Calcd ($C_{46}H_{34}IrN_3O_2S_2$): C, 60.24; H, 3.74; N, 4.58. Found: C, 58.53; H, 3.62; N, 4.59.

General Polymerization Procedure. A solution of Grubbs' third-generation initiator[16] in chloroform (0.05 M) was added to a chloroform solution (0.01 M) containing a mixture of **13** and the desired iridium-containing monomer (**3**, **10**−**12**) in a ratio of 9:1, respectively. The reaction mixture was stirred for 20 min at ambient temperatures. After 20 min, the polymerization was quenched by the addition of ethyl vinyl ether. The reaction mixture was concentrated and precipitated into methanol. The resulting solid was collected by filtration, redissolved in CH_2Cl_2, and reprecipitated into methanol. This procedure was repeated until the methanol solution was clear to yield copolymers **14**−**17** for which ^{1}H NMR spectra showed no remaining monomer or other impurity peaks. All copolymers were >97% pure by ^{1}H NMR (Supporting Information). The copolymers were synthesized with a total monomer to catalyst ratio of 50:1.

Copolymer 14. ^{1}H NMR ($CDCl_3$): $\delta = 8.07$ (br), 7.78 (br), 7.42 (br), 7.22 (br), 6.85 (br), 6.38 (br), 6.26 (br), 4.97 (br), 2.98 (br), 2.00 (br), 1.68 (br), 1.44 (br). ^{13}C NMR ($CDCl_3$): $\delta = 163.5$, 163.0, 162.3, 154.0, 147.1, 141.1, 138.8, 137.6, 137.1, 134.1, 129.9, 126.3, 123.6, 121.8, 121.4, 120.6, 120.3, 118.2, 110.0, 97.4, 73.1, 71.0, 51.2, 42.7, 41.6, 37.1, 29.9, 26.8, 25.3. Anal. Calcd: Ir, 2.75. Found: Ir, 2.16.

Copolymer 15. ^{1}H NMR ($CDCl_3$): $\delta = 8.05$ (br), 7.76 (br), 7.38 (br), 7.20 (br), 6.76 (br), 4.98 (br), 2.98 (br), 2.16 (br), 1.92 (br), 1.67 (br), 1.43 (br). ^{13}C NMR ($CDCl_3$): $\delta = 166.8$, 166.3, 161.7, 161.2, 160.9, 154.1, 147.1, 143.7, 141.1, 138.7, 137.3, 137.0, 136.0, 134.6, 134.1, 133.1, 130.7, 130.1, 129.9, 127.9, 126.2, 124.1, 123.6, 121.8, 121.4, 120.6, 120.2, 118.9, 110.0, 73.0, 71.0, 51.2, 44.1, 42.3, 41.7, 38.9, 37.1, 29.9, 26.7, 25.4. Anal. Calcd: Ir, 2.79. Found: Ir, 3.06.

Copolymer 16. ^{1}H NMR ($CDCl_3$): $\delta = 8.07$ (br), 7.81 (br), 7.42 (br), 7.21 (br), 6.82 (br), 6.63 (br), 4.98 (br), 3.05 (br), 1.98 (br), 1.68 (br), 1.42 (br). ^{13}C NMR ($CDCl_3$): $\delta = 167.4$, 165.8, 160.4, 158.3, 154.0, 149.1, 148.4, 143.5, 141.1, 138.7, 137.0, 135.9, 133.3, 129.8, 128.3, 126.2, 125.2, 123.6, 121.8, 121.4, 120.6, 120.2, 119.3, 110.0, 72.9, 71.0, 51.2, 42.6, 41.5, 39.2, 37.1, 26.8, 25.4. Anal. Calcd: Ir, 2.75. Found: Ir, 2.99.

Copolymer 17. ^{1}H NMR ($CDCl_3$): $\delta = 8.06$ (br), 7.77 (br), 7.40 (br), 7.21 (br), 6.82 (br), 6.65 (br), 4.97 (br), 2.98 (br), 1.92 (br), 1.68 (br), 1.43 (br). ^{13}C NMR ($CDCl_3$): $\delta = 167.5$, 161.8, 157.8, 155.2, 154.0, 149.2, 147.8, 143.2, 142.6, 141.1, 138.7, 137.0, 134.1, 129.9, 126.2, 125.1, 123.6, 121.8, 121.4, 120.6, 120.2, 118.6, 110.0, 73.0, 71.0, 51.2, 46.0, 42.7, 39.2, 37.1, 26.8, 25.3. Anal. Calcd: Ir, 2.75. Found: Ir, 2.77.

Results and Discussion

Synthesis. The coupling of 2-phenyl-pyridine (ppy) to *exo*-norbornene carboxylic acid is the key step for the synthesis of the iridium complex-based monomers **10**−**12** (Scheme 1). The emission color of the iridium complexes and therefore, that of the monomers and polymers, can be tuned through variation of the ligand. In our case, we utilized either 2-phenyl-pyridine, 2-phenylquinoline (pq), or 2-benzo[*b*]-thiophen-2-yl-pyridine (btpy) as ligands. This synthetic strategy could not be applied to the synthesis of a blue/green-emitting monomer based on the 2-(2,4-difluoro-phenyl)-pyridinato (ppf) ligand since we anticipated that the emission would be red-shifted by the presence of the functionalized

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[16] Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035.

ppy ligand relative to that expected for an Ir(ppf)$_3$-type complex.[13] Therefore, monomer **3** consisting of three ppf-type ligands was synthesized according to the route shown in Scheme 1.

Key to our strategy is the possibility of covalently linking host materials to the polymer backbone along with the emissive compound, combining the properties of both in a single material by copolymerizing two functional monomers randomly in a controlled fashion, thus mimicking host−guest molecular glasses obtained by coevaporation of metal complexes and host molecules in vacuum-deposited phosphorescent OLEDs. In this study, we employed a 2,7-di-(carbazol-9-yl)fluorene-based material[14] as the host material in monomer **13**, which has similar emission spectra and quantum yields as 4,4′-di(carbazol-9-yl)biphenyl (CBP).[17a] CBP is one of the most widely used host materials in OLEDs due to its high triplet energy which enables it to transfer both singlet and triplet excitation to a wide range of iridium complexes.[3a,3d,3e] Density functional theory (DFT) calculations suggest that use of the fluorene-diyl bridge, which can be readily functionalized with polymerizable groups such as norbornene, in place of the biphenyl bridge of CBP does not significantly affect the energy of lowest triplet state.[17b]

Compounds **4**,[13] **5**,[5c] **7**,[5a] **8**,[5c] **10**,[5a] and **13**[14] were prepared according to literature procedures. Compound **1** was obtained by taking advantage of the most acidic hydrogen in the benzene ring of ppf through the reaction of ppf with BuLi, followed by treatment with CO$_2$ (Scheme 1).[18] Coupling of **1** to 5-norbornene-2-methanol yielded **2**, which was metalated to yield the Ir(ppf)$_3$-based monomer **3**. Complex **6** was synthesized by the reaction of the iridium dimer (Ir(btpy)$_2$Cl)$_2$ with 4-(2-pyridine)benzaldehyde. The aldehyde group in **6** was reduced to an alcohol using LiAlH$_4$ to give **9**, which was esterified with *exo*-5-norbornene-2-carboxylic acid to yield monomer **12**. Monomer **11** was prepared in the same manner starting with compound **8**.

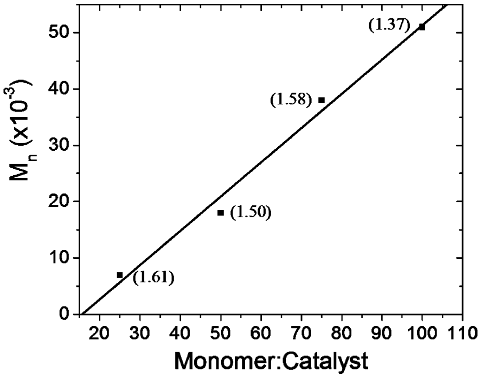
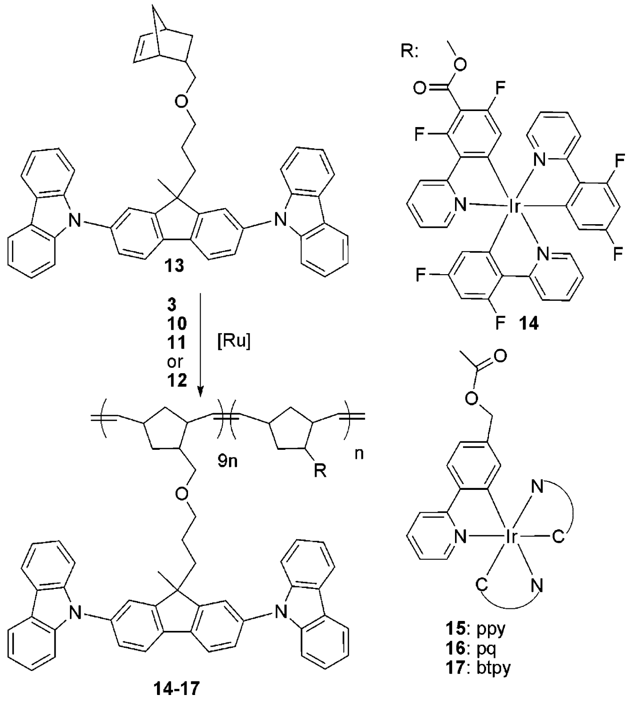


Figure 2. Plot of M_n vs monomer to catalyst ratio for the homopolymerization of **13**. Numbers in parentheses are the polydispersity indices of the polymers.

Scheme 2. Synthesis of Copolymers 14−17



A living polymerization is key to the successful reproducibility of all desired copolymers. Therefore, we investigated the living character of the homopolymerization of **13**. In order to verify the living character of the polymerizations of **13**, four different polymerizations were carried out with monomer to catalyst ratios of 25:1, 50:1, 75:1, and 100:1 using Grubbs' third-generation initiator. Figure 2 shows the plot of the molecular weights of these homopolymers versus the monomer to catalyst ratios. The linear relationship indicates that the polymerization is controlled. Furthermore, ^{1}H NMR spectroscopy experiments showed the complete disappearance of the carbene signal of the initiator around 19.1 ppm, and the formation of a new, broad carbene signal around 18.5 ppm, indicating complete initiation. Both experiments strongly suggest that the polymerization of **13** proceeds in a living fashion. Attempts to investigate the living character of the homopolymerization of **3** and **10**−**12** were not possible because the addition of the ruthenium initiator to the monomer solutions resulted in precipitation of insoluble materials. We have previously proposed that aggregation may occur in homopolymers or oligomers of iridium complex-based materials, due to the close proximity of the iridium complexes to each other along the polymer backbone.[5a] Therefore, in our materials, comonomer **13** also serves as a spacer and solubilizing unit between the metal complexes in addition to its role in accepting electrons and holes.

Copolymerizations of **3**, **10**, **11**, or **12** with **13** were carried out in chloroform at room temperature using Grubbs' third-generation initiator (Scheme 2).[16] All copolymerizations were complete within 10 min. In all copolymers, a 9:1 ratio of **13** to the iridium complex containing monomer was employed and the target degree of polymerization was 50, i.e., monomer to catalyst ratios of 50:1 were employed. As mentioned, attempts to homopolymerize **3** and **10**−**12** resulted in precipitation of insoluble materials. In our previous study, attempts at block copolymerizations of iridium-containing

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(17) (a) Hreha, R. D.; George, C. P.; Haldi, A.; Domercq, B.; Malagoli, M.; Barlow, S.; Bredas, J.-L.; Kippelen, B.; Marder, S. R. *Adv. Funct. Mater.* **2003**, *13*, 967. (b) Marsal, P.; Avilov, I.; da Silva Filho, D. A.; Brédas, J.-L.; Beljonne, D. *Chem. Phys. Lett.* **2004**, *392*, 521.

(18) (a) Schlosser, M.; Heiss, C. *Eur. J. Org. Chem.* **2003**, 4618. (b) Coe, P. L.; Waring, A. J.; Yarwood, T. D. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2729. (c) Bridges, A. J.; Patt, W. C.; Stickney, T. M. *J. Org. Chem.* **1990**, *55*, 773.

Table 1. Polymer Characterization Data

compd	M_w ($\times 10^{-3}$)	M_n ($\times 10^{-3}$)	PDI	T_d (°C)[a]
14	23.5	18.5	1.24	318
15	25.5	19.5	1.31	324
16	24.5	19.0	1.29	302
17	23.0	19.0	1.22	303

[a] Temperature at 5% weight loss.

Table 2. Photophysical and Electroluminescence Characterization of Copolymers 14−17

compd	λ_{abs} (nm)[a]	λ_{em} (nm)[a,b]	λ_{em} (nm)[b,c]	Φ[d]	τ (μs)[e]	τ (μs)[f]	λ_{el} (nm)[g]
14	296, 343, 379	468	474	0.41	0.0637	1.30	511
15	295, 343, 382	512	517	0.33	0.0848	1.43	521
16	295, 342, 408	591	595	0.10	0.1936	1.34	603
17	297, 339, 408	600	600	0.07	0.1664	3.71	602

[a] In chloroform solutions. [b] All polymers were excited at 400 nm. [c] Peak emission in the solid state. [d] In degassed solutions using *fac*-Ir(ppy)$_3$ (Φ = 0.40, in toluene). [e] Luminescence lifetimes in THF solution. [f] Luminescence lifetimes in degassed THF solution. [g] Peak EL emission.

monomers and a solubilizing monomer (i.e., monomer with long alkyl chain) caused the same phenomena,[5a] indicating that a random distribution of the monomers is necessary for solubility. Therefore, the high solubilities of copolymers **14**−**17** in common organic solvents suggest a random distribution of the two monomers along the backbone. Table 1 lists the polymer properties of copolymers **14**−**17**. All copolymers have molecular weights around 20 kDa and polydispersities between 1.22 and 1.31. The low polydispersity indexes (PDIs) of the copolymers indicate some degree of control of the polymerizations and ensure that the approximate lengths of the polymer chains are reproducible, minimizing potentially adverse effects of chain length differences on device performance. We observed no glass-transition temperatures for any of the copolymers. All copolymers underwent 5% weight loss at temperatures slightly higher than 300 °C as measured by thermal gravimetric analysis.

Photophysical Properties. The photophysical and electroluminescence properties of the small-molecule analogues of the iridium complexes used in this study have been well-characterized in the literature, and devices based on these complexes exhibit promising performances.[3] Therefore, we compared the basic photophysical properties of our copolymers to their small-molecule analogues to evaluate their potential as materials for OLEDs. Table 2 lists the photophysical properties of copolymers **14**−**17**. In solution, the high-energy regions of the absorption spectra of the copolymers are dominated by monomer **13** since its concentration is 9 times higher than those of the iridium complex-containing monomers. Thus, the ligand-centered (LC) $\pi-\pi^*$ transitions typically observed for iridium complexes in the region of 250−350 nm are obscured by transitions attributable to **13** at around 295 and 340 nm. In the lower energy region, starting around 380 nm, broad features assignable to metal-to-ligand charge-transfer (MLCT) transitions of the iridium complexes are observed.

The solid-state emissions of the copolymers are slightly red-shifted compared to the solution emissions with the exception of **17**. Figure 3 shows the solid-state emission spectra of the copolymers. The tunability of the emission of cyclometalated iridium species is well-established; relative to Ir(ppy)$_3$, a blue-shifted emission can be obtained by employing electron-withdrawing groups such as fluorine, whereas the emission of the complexes with extended conjugation is red-shifted.[3] The shapes of the peaks and the emission maxima of our copolymers are identical to those of the corresponding small-molecule iridium complexes, indicating that polymer backbones do not interfere with the emission.

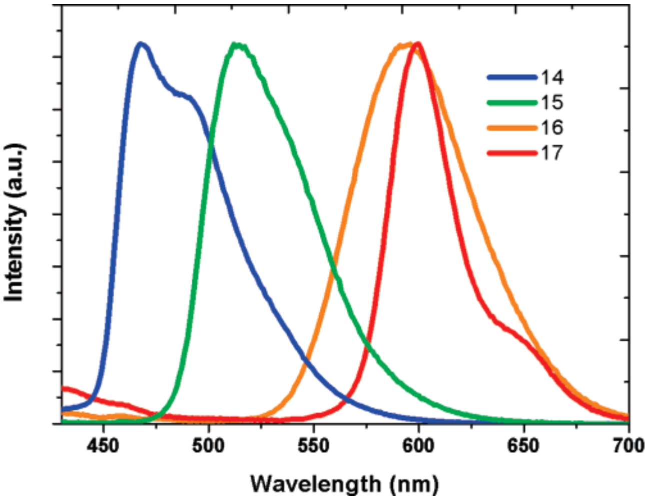

Figure 3. Solid-state photoluminescence emission spectra of all copolymers.

The solution phosphorescence quantum efficiencies of **14**−**17** were measured using *fac*-Ir(ppy)$_3$ as reference (Φ = 0.40, in toluene) and range from 0.07 to 0.41. The emission lifetimes are strongly affected by the presence of oxygen due to the quenching of the ^{3}MLCT state by oxygen.[19] In degassed solutions, the lifetimes are in the microsecond region. The measured values of the emission efficiencies and the lifetimes are comparable to those of the corresponding small-molecule complexes.

Electroluminescence Properties and Device Performance. Figure 4 shows the electroluminescence spectra of devices in which the copolymers **14**−**17** have been used as emitting layers between the cross-linked TPD-based copolymer (Figure 1) as the hole-transport material and vacuum-deposited BCP and AlQ$_3$ as hole-blocking and electron-transport materials, respectively. Devices fabricated using copolymers **14**−**17** show electroluminescence spectra with emission maxima that are similar to those measured in photoluminescence experiments performed in solid state (see Figure 3), suggesting that the emission stems from the iridium complex. Note, however, that the electroluminescence (EL) spectrum of devices fabricated using copolymer **14** shows a shift toward longer wavelengths with a maximum at 511 nm compared to a maximum of 465 nm in photoluminescence spectra. Figure 5 shows the electrical characteristics of devices fabricated using copolymer **16** and **17** as emitting layers. Current density as a function of applied voltage shows a leak-free behavior at low voltage and could be measured over 6 orders of magnitude. The turn-on voltage

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(19) *Fluorescence and Phosphorescence Analysis: Principles and Applications*; Hercules, D. M., Ed.; Interscience Publishers: New York, 1966.

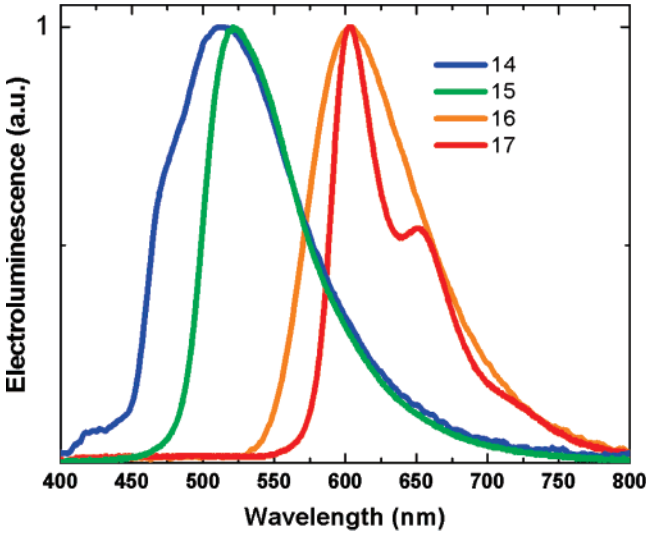

Figure 4. Electroluminescence spectra for devices with the structure ITO/**18**/(**14**−**17**)/BCP/AlQ$_3$/LiF/Al (35 nm/25 nm/6 nm/20 nm/1 nm/150 nm).

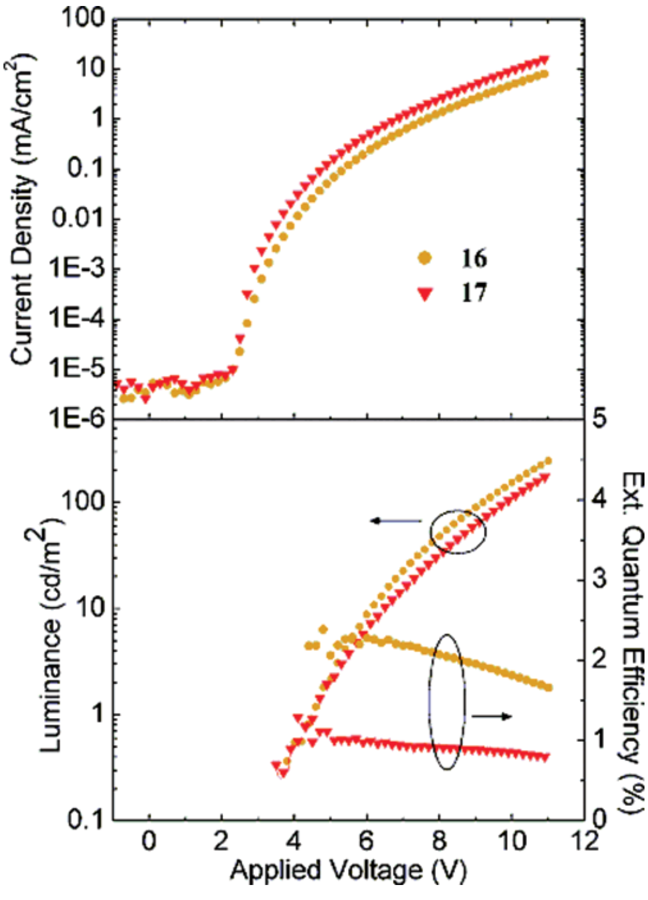

Figure 5. Current density, luminance, and external quantum efficiency as a function of applied voltage for a device with the structure ITO/**18**/(**16** or **17**)/BCP/AlQ$_3$/LiF/Al (35 nm/25 nm/6 nm/20 nm/1 nm/150 nm).

for the current density is low (ca. 2.4 V) for both devices, and the turn-on voltage for the light for both devices is 3.7 V. External quantum efficiencies at 100 cd/m^2 are 1.9% and 0.9% for devices fabricated using copolymer **16** and **17**, respectively. These results are encouraging given the low photoluminescence quantum efficiency of these two copolymers (10% and 7% for copolymers **16** and **17**, respectively) compared to that of Ir(ppy)$_3$ (40% in solution and 97% in doped thin films).[2c,3d] Devices fabricated from copolymers **14** and **15** yielded low light output. This behavior may be due to less efficient triplet energy transfer from the host material in the copolymer to phosphorescent moieties with longer wavelength emission. Previous studies on small-molecule devices fabricated from the vapor phase on mixtures of CBP and Ir(ppy)$_3$ have shown that efficient energy transfer occurs between CBP to the phosphor.[20] The origin of the lower performance in our red-emitting copolymer materials compared to their molecular counterparts is not well understood at this stage and will be further investigated.

Conclusions

We have synthesized a series of norbornene-based copolymers via ROMP that combine emissive iridium complexes with a host material. This design allows for solution processibility and prevents phase separation. NMR spectroscopy and gel permeation chromatography (GPC) studies proved that the polymerizations are controllable, and the low PDIs assured that molecular weight differences of the polymer chains are minimized to prevent any possible adverse effect of chain length difference on the device performance. By comparing the iridium-containing copolymers to their small-molecule analogues, we established that the polymer backbones do not interfere with the basic photophysical properties of the iridium complexes. Furthermore, we employed these copolymers as the emissive layer in OLED devices. Devices based on the orange-emitting copolymer gave encouraging results despite the low phosphorescence quantum yields of the copolymer. These results demonstrate that our methodology allows for the solution-based fabrication of OLED devices from functionalized poly(norbornene)s. Current emphases are the fabrication of OLED devices with improved device performance by using polymer-supported iridium complexes with higher phosphorescence quantum yields as well as employing more suitable (i.e., wider band gap) host materials for the blue/green-emitting polymeric materials.

Acknowledgment. Financial support has been provided by Solvay SA. Part of this work is supported by the STC Program of the National Science Foundation under Agreement No. DMR-0120967 and the Office of Naval Research through a MURI program. M.W. gratefully acknowledges a DuPont Young Professor Award, an Alfred P. Sloan Fellowship, and a Camille Dreyfus Teacher−Scholar Award.

Supporting Information Available: General experimental methods and ^{1}H NMR spectra of copolymers **14**−**17** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) (a) Baldo, M. A.; Lamansky, S.; Burrows, P. E.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *75*, 4. (b) Pfeiffer, M.; Forrest, S. R.; Leo, K.; Thompson, M. E. *Adv. Mater.* **2002**, *14*, 1633.