Design and synthesis of phosphorescent iridium conaining dendrimers for potential applications in organic light-emitting diodes
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Design and Synthesis of Phosphorescent Iridium Containing Dendrimers for Potential Applications in Organic Light-Emitting Diodes[a]

Qin-De Liu, Jianping Lu,* Jianfu Ding,* Ye Tao

Three phosphorescent dendrimers (**IrC1**, **IrC3**, and **IrF2**) with an iridium complex core and oligocarbazole or oligofluorene substituted ligands were synthesized and characterized. The structures of the oligocarbazole were designed to maintain high triplet energy of the ligands so that phosphorescence quenching in the resulting dendrimers can be prevented, while the oligofluorene in **IrF2** resulted in undesired phosphorescence quenching. Best performance was obtained from an **IrC3** based electrophosphorescent light-emitting device with a maximum luminance of $13\,060$ cd $\cdot$ m^{-2} at a driving voltage of 11.5 V and a peak current-efficiency of 4.3 cd $\cdot$ A^{-1} at a luminance of $3\,400$ cd $\cdot$ m^{-2}, owing to its high PL efficiency, and efficient energy transfer between the iridium complex core and the ligands.

n = 1, (**IrC1**)
n = 3, (**IrC3**)

Introduction

For more than a decade, π-conjugated oligomers with well-defined chemical structures have been extensively inves-

Q.-D. Liu, J. Ding
Institute for Chemical Process and Environmental Technology (ICPET), National Research Council of Canada (NRC), 1200 Montreal Road, Ottawa, ON, K1A 0R6, Canada
E-mail: Jianfu.Ding@nrc-cnrc.gc.ca
Q.-D. Liu
Current address: Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602
J. Lu, Y. Tao
Institute for Microstructural Sciences (IMS), National Research Council of Canada (NRC), 1200 Montreal Road, Ottawa, ON, K1A 0R6, Canada
Fax: (613) 991-2384; E-mail: Jianping.Lu@nrc-cnrc.gc.ca

tigated as active materials for the realization of various organic devices ranging from organic light-emitting diodes (OLED), organic field-effect transistors (OFET), to solar cells due to their good film-forming properties, relatively easy purification processes, high thermal and chemical stabilities, and excellent optical and electronic properties.[1–4] In addition, the oligomers can be designed to possess conjugated cores for efficient emission and/or charge transport and to have appropriate terminal groups and/or side chains for good processability. This unique molecular architecture therefore allows independent optimization of the optoelectronic and processing properties.[5–7]

Since the first report on the use of triplet emitters in OLEDs by Forrest and Thompson,[8] electrophosphorescent devices have attracted a great deal of interest, in which metal-organic complexes of Ru(II), Os(II), or Ir(III) are doped into charge transporting host materials as the emitting centers.[9] The advantage of phosphorescent emitters over

the fluorescent counterparts is that they can capture energy from both singlet and triplet excited states so that it is theoretically possible to achieve OLEDs with 100% internal quantum efficiency. This therefore triggered tremendous research activities in the development of phosphorescent metal complex oligomers and dendrimers.[10] In these materials, the core chromophores are various phosphorescent organometallic complexes and jointed by multiple hyperbranched oligomers or dendrons to prevent undesired triplet-triplet annihilation.[11–13] By rational design on the core chromophores and the hyperbranched ligands, phosphorescence from these complexes can be tuned from sky blue to deep red,[14] and a remarkable external quantum efficiency of 16% has been achieved for green phosphorescent dendrimer based devices.[11]

In this study, we prepared a new series of phosphorescent dendrimers (**IrC1**, **IrC3**, and **IrF2**) with an identical iridium complex core consisting of one ancillary and two cyclometalating ligands. Their synthetic routes are outlined in Scheme 1–3. Hyperbranched oligocarbazoles or oligofluorenes were attached to the iridium complex core to minimize the interaction between the phosphorescent cores. In addition, these hyperbranched oligomers also functioned as the charge transporting host for the Ir complex core. Carbazole-based oligomers have been widely used as the host materials for the small molecular iridium complexes due to their relatively high triplet energy.[15,16] Because of the hole transporting nature of the oligomer ligands in the dendrimers in this study, they have to be blended with an electron transporting material, such as 1,3,5-tris(N-phenyl-benzimidazol-2-yl)benzene (TPBI) to form emitting layers with balanced charge transport properties. Meanwhile, a widely used bipolar material for iridium complexes, 4,4′,4″-tris(N-carbazolyl)-triphenylamine (TCTA), may also be blended into the emitting layer as a diluent to maintain the contents of the Ir complex core at the same level in different devices for comparison. Due to the same structure of the Ir complex core, these three dendrimers should have similar phosphorescence spectra. However, the structures and sizes of the surrounding ligands are expected to impose a significant impact on the photophysical and optoelectronic properties, such as photoluminescent (PL) efficiency, energy levels, and charge injection and transport. A device with the best performance was obtained from **IrC3** with a maximum luminance of 13 060 cd · m^{-2} at a driving voltage of 11.5 V and a peak current-efficiency of 4.3 cd · A^{-1} at a luminance of 3 400 cd · m^{-2}, due to its high PL efficiency and suitable energy levels.

Experimental Part

Materials and Characterization

All starting materials were analytical reagents purchased from Sigma-Aldrich Co. and used without further purification except IrCl$_3$ · $\times$ H$_2$O, which was purchased from Strem Chemicals. All solvents used in synthesis and spectroscopic measurements were distilled over appropriate drying and/or degassing reagents. ^{1}H NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrometer. Matrix Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) spectra were acquired using a Voyager-DE STR MALDI-TOF mass spectrometer (PerSeptive Biosystems) in the linear positive mode with delayed extraction. A dichloromethane solution of the sample (1 μL) was mixed with 10 μL of dithranol matrix (10 mg · ml^{-1} in CH$_2$Cl$_2$:EtOH, 7:3) before loading onto a metal plate. Electrochemical measurements were carried out under argon protection in deoxygenated dry acetonitrile solution of 0.10 M Bu$_4$NPF$_6$ at a scan rate of 50 mV · s^{-1} using a Solartron SI1287 Electrochemical Interface equipped with a disc platinum working electrode, a platinum counter electrode, and an Ag quasi-reference electrode. Thin film samples were deposited on the surface of the working electrode by dip-coating the dendrimer solutions (ca. 1%) in toluene. UV-vis absorption spectra were recorded on a Hewlett-Packard 8453 spectrometer. Excitation and emission spectra were obtained with a Spex Fluorolog 3 spectrometer. The DSC analysis and the thermogravimetric analysis (TGA) were performed under a nitrogen atmosphere (50 mL · min^{-1}) on a TA Instruments DSC 2920 and a TGA 2950 thermogravimetric analyzer, respectively, at a heating rate of 10 K · min^{-1}. The absolute PL quantum yields of the thin films were measured at ambient temperature using a commercial fluorimeter in combination with an integrating sphere according to the literature procedure.[17] The starting materials, 2′,7-bis(9,9-dioctylfluorene)-2-boronic acids,[18] 3,6-dibromocarbazole,[19] N-octyl-3,6-dibromocarbazole,[19] and Ir(Br-ppy)$_2$(acac)[20] (Br-ppy = 2-(4-bromophenyl)pyridine, acac = acetyl acetonate) were prepared using the procedures reported previously.

General Syntheses of Boronic Acids

Under Ar protection, the aryl halide (1 equiv.) was dissolved in dry THF. The temperature was cooled to −78 °C using an acetone-dry ice bath, and a 2.5 M n-butyllithium solution in hexane (1.1 equiv.) was added slowly via syringe. The solution was stirred at this temperature for 1 h, and then triisopropylboronate (1.2 equiv.) was added slowly via syringe. After stirring for another hour at −78 °C, the temperature was allowed to warm to ambient temperature by removing the cooling bath. The solution was stirred for 12 h at room temperature before 50 mL of 1 M HCl aqueous solution was added. The mixture was then extracted with diethyl ether (4 × 50 mL), and the organic layers were combined and dried over Mg$_2$SO$_4$. Flash chromatography using CH$_2$Cl$_2$ followed by acetone as the eluent afforded the corresponding boronic acid as foamy white solids. The resulting boronic acids were directly used for the next step Suzuki coupling reactions without further purification.

Synthesis of 1a. A mixture of N-octyl-3,6-dibromocarbazole (18.0 g, 41.2 mmol), carbazole (3.4 g, 20.4 mmol), CuI (0.79 g, 2.0 mmol), 1,10-phenanthroline (0.75 g, 4.1 mmol), and K$_2$CO$_3$ (6.2 g, 45 mmol) was suspended in 20 mL DMF. The mixture was refluxed with vigorous stirring under Ar protection for 24 h and cooled to ambient temperature. The resulting brown mixture was extracted

with CH_2Cl_2 (4 × 50 mL), and the organic layers were combined, dried over $MgSO_4$, and purified by column chromatography (CH_2Cl_2/hexanes, 1:5) to obtain compounds **1a** as white solids (15.7 g, 73%). ^1H NMR (400 MHz; acetone-d_6; Me_4Si): $\delta_H = 8.46$ (1 H, d, $J = 1.8$ Hz), 8.44 (1 H, d, $J = 2.0$ Hz), 8.24 (2H, d, $J = 7.8$ Hz), 7.90 (1H, d, $J = 8.6$ Hz), 7.70–7.62 (3 H, m), 7.44–7.36 (4 H, m), 7.29 (2H, dt, $J_1 = 1.5$ Hz, $J_2 = 8.0$ Hz), 4.56 (2H, t, $J = 7.2$ Hz), 2.00–1.90 (2 H, m), 1.55–1.20 (10 H, m), 0.86 (3 H, t, $J = 7.2$ Hz).

Syntheses of 2a and 3a. To a mixture of corresponding carbazolyl boronic acid (**1b** or **2b**) (1 equiv.), *N*-octyl-3,6-dibromocarbazole (3 equiv.), and tetrakis(triphenylphosphine)-palladium [$Pd(PPh_3)_4$], (5% per C–Br bond), were added a degassed 2 M K_2CO_3 aqueous solution (5 equiv.) and degassed toluene with a ratio of 1:2. The solution was refluxed under argon protection for 24 h. The resulting solution was extracted with CH_2Cl_2 (4 × 50 mL). The organic layers were combined, dried over Mg_2SO_4, and purified by silicon gel column chromatography (CH_2Cl_2/hexanes, 1:4) to obtain the compounds **2a** or **3a** as white solids (yields: 80% for **2a**, 76% for **3a**).

2a ^1H NMR (400 MHz; acetone-d_6; Me_4Si): $\delta_H = 8.70$ (1 H, d, $J = 1.6$ Hz), 8.62 (1 H, d, $J = 1.6$ Hz), 8.48 (1 H, d, $J = 1.9$ Hz), 8.40 (1 H, S), 8.25 (2H, d, $J = 7.8$ Hz), 8.00 (1 H, dd, $J_1 = 1.8$ Hz, $J_2 = 8.6$ Hz), 7.95 (1 H, dd, $J_1 = 1.8$ Hz, $J_2 = 8.6$ Hz), 7.89 (1 H, d, $J = 8.6$ Hz), 7.78 (1 H, d, $J = 8.6$ Hz), 7.70–7.64 (2 H, m), 7.56 (2 H, m), 7.46–7.38(4 H, m), 7.29 (2H, dt, $J_1 = 1.8$ Hz, $J_2 = 8.0$ Hz), 4.61(2 H, t, $J = 7.2$ Hz), 4.45 (2H, t, $J = 7.0$ Hz), 2.03 (2 H, m), 1.89 (2 H, m), 1.53 (2 H, m), 1.45–1.20(18 H, m), 0.87 (3 H, t, $J = 6.8$ Hz), 0.83 (3 H, t, $J = 6.8$ Hz).

3a ^1H NMR (400 MHz; acetone-d_6; Me_4Si): $\delta_H = 8.72$ (1 H, d, $J = 1.8$ Hz), 8.70 (1 H, d, $J = 1.6$ Hz), 8.65 (1 H, d, $J = 1.6$ Hz), 8.61 (1 H, d, $J = 1.8$ Hz), 8.49 (1 H, d, $J = 2.1$ Hz), 8.42 (1 H, S), 8.24 (2H, d, $J = 7.6$ Hz), 8.02 (1 H, dd, $J_1 = 1.8$ Hz, $J_2 = 8.6$ Hz), 7.96–7.88 (4 H, m), 7.79 (1 H, d, $J = 8.6$ Hz), 7.70–7.64 (4 H, m), 7.57 (2 H, m), 7.46–7.38(4 H, m), 7.28 (2H, dt, $J_1 = 1.8$ Hz, $J_2 = 8.0$ Hz), 4.61(2 H, t, $J = 7.2$ Hz), 4.52–4.44 (4 H, m), 2.03–1.85 (6 H, m), 1.6–1.20 (30 H, m), 0.90–0.80 (9 H, m).

Syntheses of 4a and 4b. To a mixture of *N*-octyl-3,6-dibromocarbazole (1 equiv.), corresponding oligocarbazolyl boronic acid (**1b** or **3b**, 2.5 equiv.), and $Pd(PPh_3)_4$, (5% per C–Br bond), was added a degassed 2 M K_2CO_3 aqueous solution (5 equiv.) and degassed toluene with a ratio of 1:2. The solution was refluxed under argon protection for 24 h. The resulting solution was extracted with CH_2Cl_2 (50 mL × 4). The organic layers were combined, dried over Mg_2SO_4, and purified by silicon gel column chromatography (CH_2Cl_2/hexanes, 2:1) to yield the compounds **4a** or **4b** as white solids (yields: 83% for **4a**, 77% for **4b**).

4a ^1H NMR (400 MHz; acetone-d_6; Me_4Si): $\delta_H = 10.35$ (1H s, NH), 8.67 (2 H, d, $J = 1.4$ Hz), 8.62 (2 H, d, $J = 1.8$ Hz), 8.45 (2 H, d, $J = 1.8$ Hz), 8.23 (4 H, d, $J = 7.6$ Hz), 7.95 (2 H, dd, $J_1 = 1.8$ Hz, $J_2 = 8.6$ Hz), 7.84 (4 H, t, $J = 8.4$ Hz), 7.73 (2H, d, $J = 8.6$ Hz), 7.62 (2 H, dd, $J_1 = 1.8$ Hz, $J_2 = 8.6$ Hz), 7.58 (2 H, d, $J = 8.4$ Hz), 7.45–7.35 (8 H, m), 7.35–7.23 (4 H, m), 4.57 (4H, t, $J = 7.0$ Hz), 2.02–1.95 (4 H, m), 1.55–1.20 (20 H, m), 0.86 (6 H, t, $J = 7.2$ Hz).

4b ^1H NMR (400 MHz; C_6D_6): $\delta_H = 8.78$ (2 H, d, $J = 1.6$ Hz), 8.76 (2 H, d, $J = 1.6$ Hz), 8.74 (2 H, d, $J = 1.6$ Hz), 8.70 (2 H, d, $J = 1.5$ Hz), 8.67 (2 H, s), 8.49 (2 H, d, $J = 1.5$ Hz), 8.14 (4 H, d, $J = 7.3$ Hz), 8.08–7.90 (14 H, m), 7.44–7.24 (28 H, m), 3.92 (8 H, t, $J = 6.9$ Hz), 3.86 (4 H, t, $J = 6.7$ Hz), 1.70–1.60 (12 H, m), 1.30–1.10 (60 H, m), 0.90–0.80 (18 H, m, 6-CH_3).

General Syntheses of 5a and 5b

A mixture of the corresponding oligocarbazole compounds (**4a** or **4b**, 1 equiv.), 4,4′-dibromobiphenyl (3 equiv.), CuI (0.1 equiv.), 1,10-phenanthroline (0.2 equiv.), and K_2CO_3 (2.2 equiv.) was suspended in DMF. The mixture was refluxed under Ar protection for 24 h and then cooled to room temperature. The resulting brown sticky solid was extracted with CH_2Cl_2 (4 × 50 mL), and the extracted solutions were combined, dried over $MgSO_4$, and the crude products were purified by column chromatography (CH_2Cl_2/hexanes, 1:2) to obtain compounds **5a** or **5b** as white solids (yields: 85% for **5a**, 80% for **5b**).

5a ^1H NMR400 MHz; C_6D_6): $\delta_H = 8.79$ (2 H, d, $J = 1.4$ Hz), 8.50 (2 H, d, $J = 1.6$ Hz), 8.25–8.15 (4 H, m), 8.02 (2 H, dd, $J_1 = 1.8$ Hz, $J_2 = 8.6$ Hz), 7.96–7.90 (4 H, m), 7.61 (2H, d, $J = 8.6$ Hz), 7.43–7.25 (22 H, m), 7.16 (2 H, d, $J = 8.6$ Hz), 7.09 (2 H, d, $J = 8.6$ Hz), 3.89 (4H, t, $J = 7.0$ Hz), 1.70–1.60 (4 H, m), 1.30–1.10 (20 H, m), 0.88 (6 H, t, $J = 7.0$ Hz).

5b ^1H NMR (400 MHz; C_6D_6): $\delta_H = 8.84$ (2 H, d, $J = 1.2$ Hz), 8.78–8.75 (6 H, m), 8.72 (2 H, d, $J = 1.2$ Hz), 8.49 (2 H, d, $J = 1.6$ Hz), 8.13 (4H, d, $J = 7.6$ Hz), 8.08–7.95 (14 H, m), 7.68 (2 H, d, $J = 8.4$ Hz), 7.49 (2 H, d, $J = 8.4$ Hz), 7.44–7.24 (30 H, m), 7.13 (2 H, d, $J = 8.4$ Hz), 3.95–3.90 (8 H, m), 3.85 (4 H, t, $J = 6.8$ Hz), 1.70–1.60 (12 H, m), 1.30–1.10 (60 H, m), 0.90–0.80 (18 H, m, 6-CH_3).

Synthesis of 7

To a mixture of 3,6-dibromocarbazole (1 equiv.), 2′,7-bis(9,9-dioctylfluorene)-2-boronic acid (**F2**–$B(OH)_2$, 2.5 equiv.), and $Pd(PPh_3)_4$ (5% per C–Br bond), was added degassed 2 M K_2CO_3 aqueous solution (5 equiv.) and degassed toluene with a ratio of 1:2. The solution was refluxed under argon protection for 24 h. The resulting brown solution was extracted with CH_2Cl_2 (4 × 50 mL). The organic layers were combined, dried over Mg_2SO_4, and purified by silicon gel column chromatography (CH_2Cl_2/hexanes, 1.5:1) to obtain the compound **7** as a white solid (yield: 80%).

^1H NMR (400 MHz; acetone-d_6; Me_4Si): $\delta_H = 10.59$ (1H, s, NH), 8.63 (2 H, s), 7.95–7.70 (22 H, m), 7.67 (2 H, t, $J = 8.6$ Hz), 7.47 (2H, d, $J = 7.2$ Hz), 7.40–7.30 (4 H, m), 2.30–2.05 (16 H, m), 1.20–1.05 (80 H, m), 0.90–0.80 (40 H, m).

Synthesis of 8

A mixture of compound **7**, (1 equiv.), 4,4′-diiodobiphenyl (3 equiv.), CuI (0.1 equiv.), 1,10-phenanthroline (0.2 equiv.), and K_2CO_3 (2.2 equiv.) was suspended in DMF. The mixture was refluxed under Ar protection for 24 h and then cooled to room temperature. The resulting brown sticky residue was extracted with CH_2Cl_2 (4 × 50 mL), and the organic layers were combined, dried over $MgSO_4$, and purified by column chromatography (CH_2Cl_2/hexanes, 1:2) to obtain compound **8** as a white solid (yield: 70%).

^1H NMR400 MHz; C_6D_6; Me_4Si) $\delta_H = 8.73$ (2 H, s), 8.05 (2 H, s), 8.03 (2 H, s), 8.00 (2 H, s), 7.92 (2 H, dd, $J_1 = 1.2$ Hz, $J_2 = 8.6$ Hz), 7.88–7.73 (12 H, m), 7.68–7.64 (2 H, m), 7.59 (2H, d, $J = 8.4$ Hz), 7.55 (2H, d, $J = 8.4$ Hz), 7.38–7.22 (10 H, m), 7.00 (2H, d, $J = 8.4$ Hz), 2.23–2.03 (16 H, m), 1.30–0.80 (120 H, m).

General Syntheses of Phosphorescent Oligomers IrF2, IrC1, and IrC3

To a mixture of Ir(Br-ppy)$_2$(acac) (0.22 g, 0.30 mmol), the appropriate boronic acid (0.75 mmol), and Pd(PPh$_3$)$_4$ (0.070 g, 0.061 mmol, 10% per C—Br bond), was added degassed K$_2$CO$_3$ solution (10 mL, 2 M), and degassed toluene (25 mL). The solution was refluxed under Ar protection for 16 h. The resulting brown solution was extracted with CH$_2$Cl$_2$ (4 × 50 mL). The organic layers was combined and dried over MgSO$_4$. Silicon gel chromatography (CH$_2$Cl$_2$/hexanes, 1:4) afforded the products.

IrF2 (0.38 g, 44%). ^{1}H NMR (400 MHz; C$_6$D$_6$): δ_H = 8.87 (2 H, d, J = 5.3 Hz), 8.73 (4 H, s), 8.05 (4 H, s), 8.03 (4 H, s), 8.00 (4 H, s), 7.92–7.74 (28 H, m), 7.70–7.64 (4 H, m), 7.60–7.52 (10 H, d, J = 8.6 Hz), 7.47 (4 H, d, J = 8.6 Hz), 7.43 (4 H, d, J = 8.4 Hz), 7.38–7.18 (20 H, m), 7.08–6.92 (4 H, m), 6.53 (2 H, t, J = 6.8 Hz), 5.27 (1 H, s), 2.25–2.04 (32 H, m), 1.73 (6 H, S), 1.21–0.88 (192 H, m), 0.87–0.79 (48 H, m, 16-CH$_3$). MALDI-TOF: 4 343 (M$^+$).

IrC1 (0.373 g, 45%). ^{1}H NMR (400 MHz; C$_6$D$_6$): δ_H = 8.84 (2 H, d, J = 5.3 Hz), 8.78 (4 H, d, J = 1.6 Hz), 8.50 (4 H, d, J = 1.4 Hz), 8.20 (8 H, d, J = 7.0 Hz), 8.03 (4 H, dd, J_1 = 1.6 Hz, J_2 = 8.6 Hz), 7.95–7.90 (8 H, m), 7.60 (4 H, d, J = 8.6 Hz), 7.51 (6H, t, J = 8.6 Hz), 7.47–7.27 (48 H, m), 7.24 (2 H, dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz), 7.16 (4 H, d, J = 8.6 Hz), 6.92 (2 H, t, J = 8.4 Hz), 6.50 (2 H, t, J = 7.2 Hz), 5.24 (1 H, s), 3.89 (8 H, t, J = 6.8 Hz), 1.71 (6 H, S, 2-CH$_3$), 1.67–1.62 (8 H, m), 1.30–1.10 (40 H, m), 0.89 (12 H, t, J = 6.8 Hz, 4-CH$_3$). MALDI-TOF: 3 004 (M$^+$).

IrC3 (0.557 g, 36%). ^{1}H NMR (400 MHz; C$_6$D$_6$): δ_H = 8.86–8.82 (6 H, m), 8.77 (12 H, s), 8.72 (4 H, d, J = 1.2 Hz), 8.49 (4 H, d, J = 1.2 Hz), 8.13 (8 H, d, J = 7.6 Hz), 8.09–7.95 (28 H, m), 7.66 (4 H, d, J = 8.4 Hz), 7.55–7.23 (72 H, m), 6.95 (2 H, t, J = 7.2 Hz), 6.52 (2 H, t, J = 6.8 Hz), 5.25 (1 H, s), 3.95–3.80 (24 H, m), 1.80–1.60 (30 H, m), 1.30–1.10 (120 H, m), 0.90–0.80 (36 H, m, 12-CH$_3$). MALDI-TOF: 5 224 (M$^+$).

EL Device Fabrication and Testing

Indium tin oxide (ITO)-coated glass substrates (15 $\Omega \cdot \square^{-1}$) were patterned by a conventional wet-etching process using a mixture of HCl (6 M) and HNO$_3$ (0.6 M) as the etchant. The active area of each EL device was 2.5 × 5 mm^2. After patterning, the substrates were rinsed in deionized water, and then ultrasonicated sequentially in acetone and 2-propanol. The ITO substrate was treated in a UV-ozone oven for 15 min immediately prior to device fabrication. A poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS) thin film (60 nm) was spin-coated at 5 000 rpm from its aqueous suspension onto the substrate, and then baked at 130 °C under nitrogen for 30 min. A thin blend film of the phosphorescent oligomer and charge transporting hosts was spin-coated on top of the PEDOT-PSS film from a toluene solution at 1 200 rpm. The thickness of the resulting film was measured using a Dektak III surface profilometer, and found to be around 70 nm. A hole-blocking layer (TPBI, 25 nm) was then vacuum-deposited on top of the emitting layer at 2 × 10^{-7} Torr. Finally, LiF (1 nm) and Al (100 nm) were deposited as the cathode. The devices were tested in air under ambient conditions with no protective encapsulation. The EL spectra, luminance-voltage (L–V) and current-voltage (I–V) characteristics were recorded using a combination of a Photo Research PR-650 SpectraScan and a Keithley 238 Source meter.

Results and Discussion
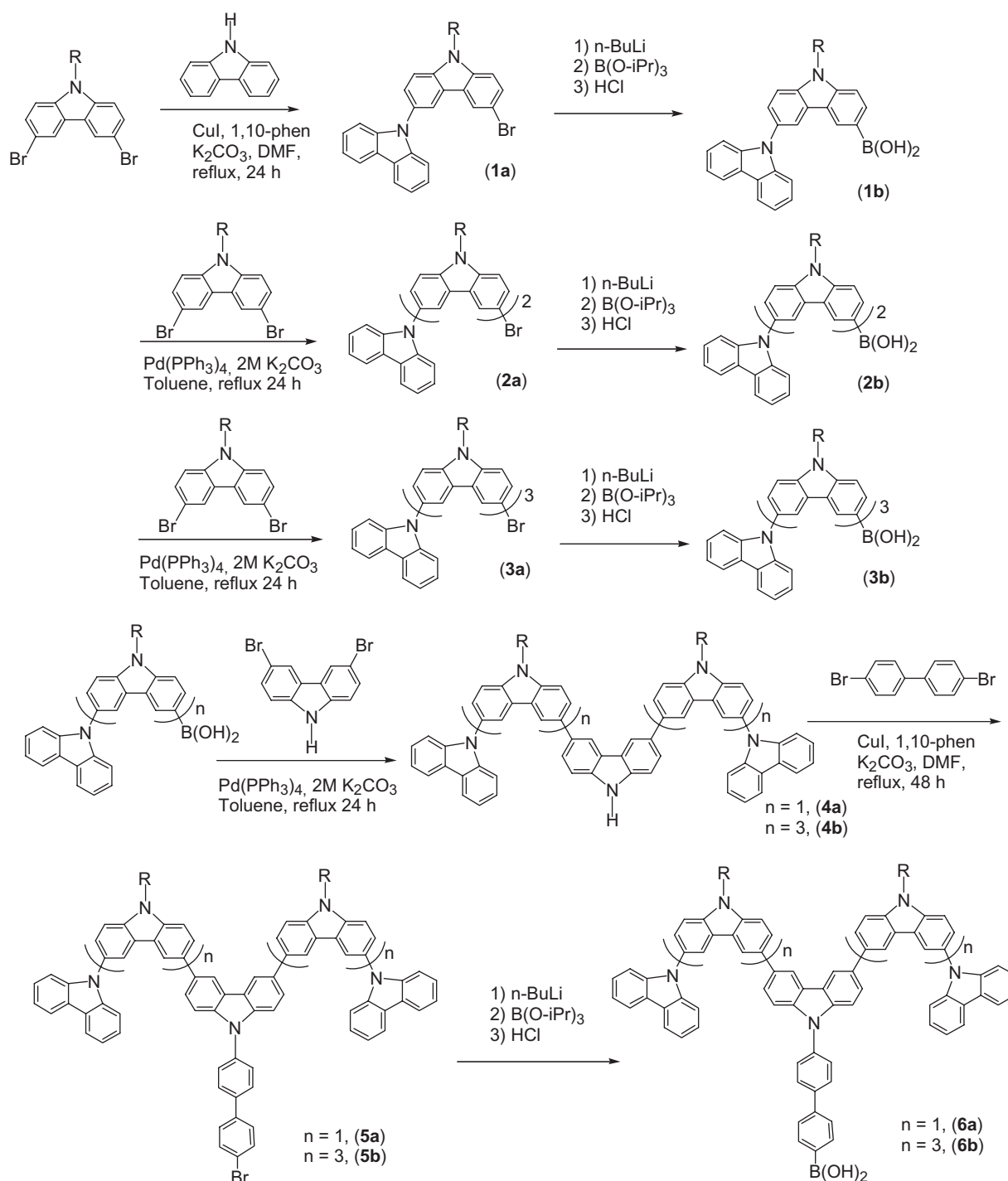
Design and Synthesis

Ir(III) complexes have been extensively studied due to their extremely high luminous efficiency and good stability. In small molecular electrophosphorescent devices, iridium complexes are typically co-deposited with bipolar materials, such as 4,4′-bis(N-carbazolyl)biphenyl (CBP) and TCTA, under well controlled conditions. This process is both complicated and costly. The development of solution-processable phosphorescent materials has become the focus of intense researches in this field.[20–23] Given that carbazole-based materials are widely used as hosts for triplet emitters in OLEDs, it is not surprising that a variety of carbazole oligomers have been attached to iridium complexes.[10,12,24] In this study, we designed and synthesized two branched carbazole oligomers and then attached them to a core iridium complex by Suzuki coupling. The linkage between each carbazole unit was specifically designed to maintain high triplet energy level of the ligand. For comparison purposes, an iridium dendrimer with oligofluorene containing ligands was also synthesized. The photophysical and electrochemical properties, and performance in OLEDs of the three synthesized iridium dendrimers were investigated and compared.

The syntheses of the Ir-containing dendrimers involve rationally designed Ullmann condensation and Suzuki coupling reactions. All of the boronic acids were synthesized via lithiation reactions of the corresponding aryl halide compounds with n-butyllithium, followed by the treatments of triisopropylborate and subsequent hydrolysis, using dilute aqueous hydrochloric acid. It is well known that the boronic acids easily lose water to produce the corresponding 6-membered boroxine anhydride ring.[18] Therefore, all the isolated "boronic acids" actually are a mixture of boronic acids and boroxines. However, the reaction condition of Suzuki coupling will allow the boroxine rings to be hydrolyzed back to boronic acids. Therefore, the presence of boroxine rings has no impact on the Suzuki coupling reaction. Consequently, the term "boronic acids" has been used throughout this paper regardless of the presence of boroxines in the boronic acids.
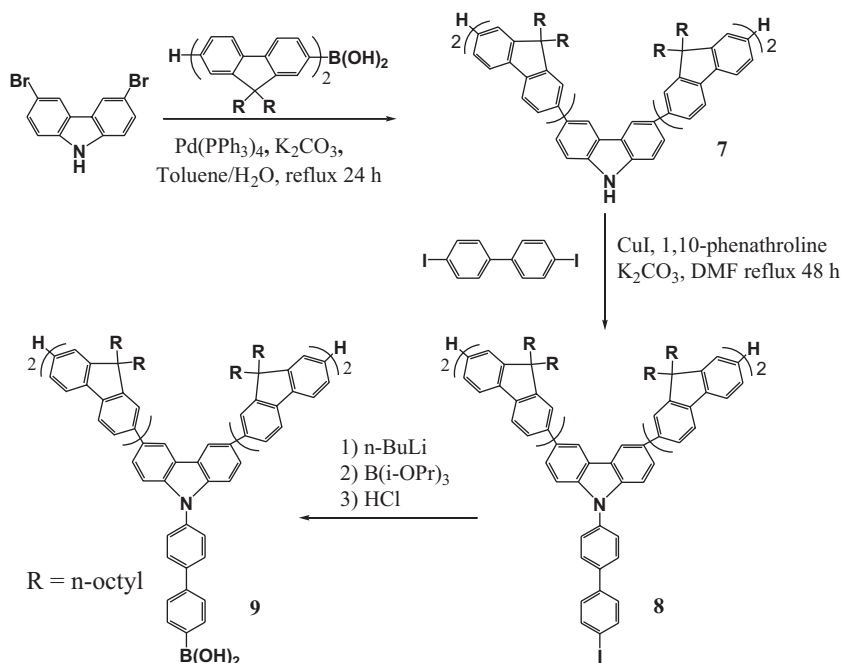
The oligocarbazole boronic acids were synthesized using a repetitive lithiation and Suzuki coupling procedure starting from the monobromo-substituted compound **1a**, which was obtained in good yield by Ullmann condensation between carbazole and excess N-octyl-3,6-dibromo-carbazole (1:2 ratio) in the presence of K$_2$CO$_3$, CuI and 1,10-phenanthroline catalysts (Scheme 1). Then the monobromide was converted to the boronic acid through a lithiation as described above. The subsequent Suzuki coupling between the oligocarbazole boronic acid and excess N-octyl-3,6-dibromocarbazole (1:3 molar ratio)

linked one more carbazole unit to the oligomer. Repeating this lithiation and then Suzuki coupling procedure further extended the oligocarbazole chain by one carbazole unit each time, hence an oligocarbazole chain with different carbazole units can be readily obtained by repeating this procedure.

Then two molecules of the formed oligocarbazole or oligofluorene[18] (4a–b or 7, see Scheme 1 and 2) can be joined together in good yields by Suzuki coupling via a central carbazole bridge, whose NH group can act as a reactive site for the Ullmann condensation with 4,4′-dibromobiphenyl or 4,4′-diiodobiphenyl to form Y-shaped

Scheme 1. Synthetic route to oligocarbazole substituted biphenylylboronic acid.

Scheme 2. Synthetic route to oligofluorene substituted biphenylylboronic acid.
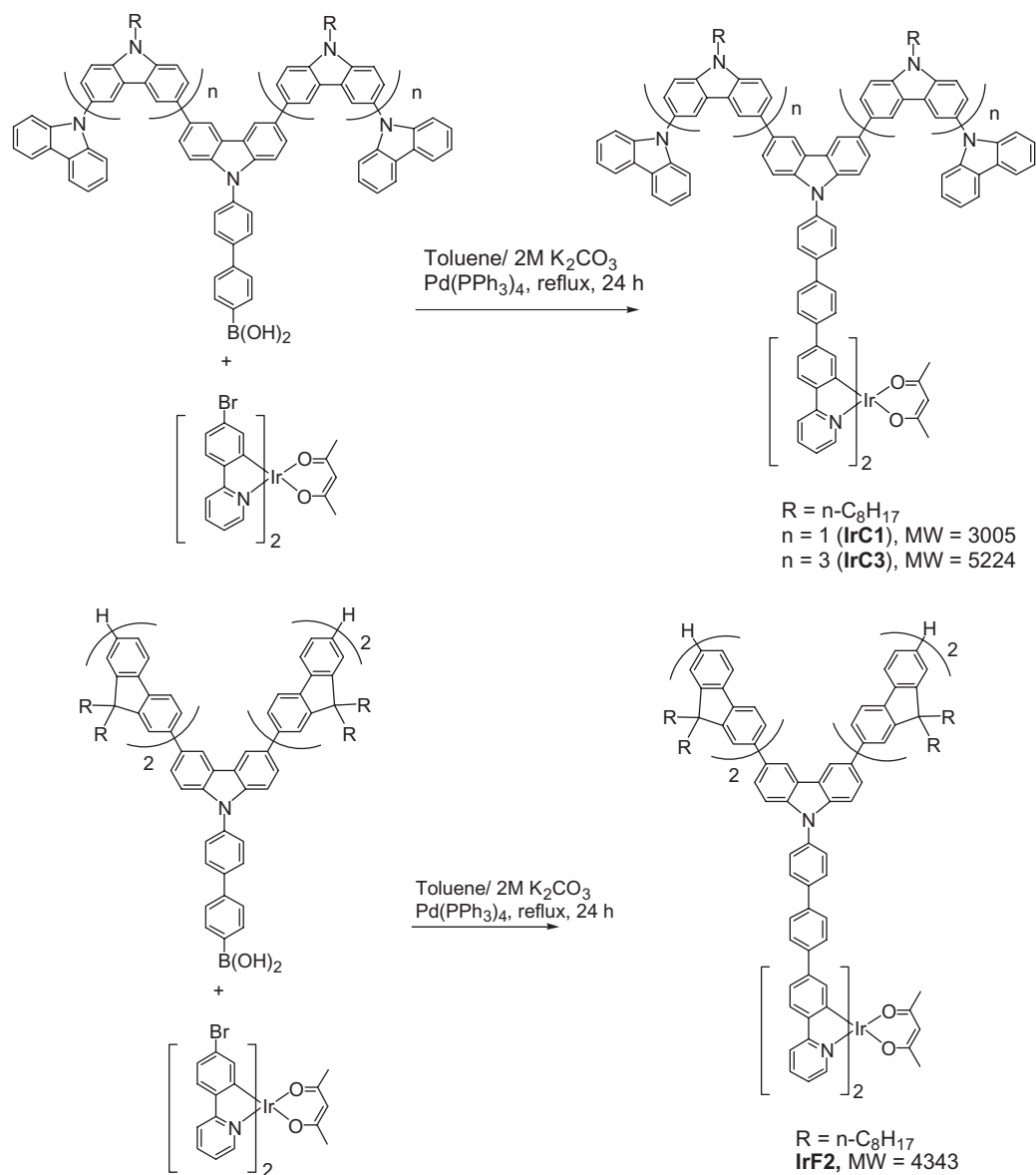
R = n-octyl

182 °C, 223 °C, and 144 °C for **IrC1**, **IrC3** and **IrF2**, respectively. Such amorphous feature is desirable for OLED applications because of the good morphological stability of the resulting films. TGA showed that **IrC1**, **IrC3** and **IrF2** all possess good thermal stability with onset decomposition temperatures (1% weight loss) at 338 °C, 346 °C, and 342 °C, respectively, under nitrogen.

The UV-vis absorption and PL spectra of **IrC1**, **IrC3** and **IrF2** in degassed CH_2Cl_2 are shown in Figure 3. The strong absorption bands in the UV region (below 380 nm) can be assigned to the spin-allowed $^1\pi-\pi^*$ transition of the ligands. In addition, a much weaker and lower energy absorption band was also found well extending into the visible region (between 420–500 nm), which probably correspond to an admixture of metal to ligand charge transfers (^{1}MLCT and ^{3}MLCT), and a $^3\pi-\pi^*$ transition.[20] Compared with widely used Ir(PPy)$_3$, the intensity of the MLCT transitions of these three Ir-containing dendrimers was very low, simply because of the low loading of iridium complex in the materials. A similar phenomenon has been observed by Holmes et al. in Ir-containing oligofluorenes.[20] The phosphorescence yields of **IrC1**, **IrC3** and **IrF2** were measured in degassed CH_2Cl_2 solution under excitation at 375 nm using Ir(PPy)$_3$ ($\Phi_{ph} = 0.40$) as a reference. Among these three dendrimers, **IrC3** showed the highest PL efficiency (0.25). The phosphorescence yield of **IrF2** was as low as 0.10 due to the relatively low triplet energy of the oligofluorene, leading to undesired phosphorescence quenching.[16] At the same time, as can be seen from Figure 3, besides the emission from the Ir core chromophore, a strong blue emission from the oligofluorene substituted ligands was also observed when the **IrF2** solution was excited at 375 nm. On the contrary, negligible blue emission associated with the oligocarbazoles was observed from **IrC1** and **IrC3**. This phenomenon indicates an inefficient energy transfer from the oligofluorene substituted ligands to the iridium complex core, which could be another reason for the low phosphorescence yield of **IrF2.** Table 1 summarizes the thermal and photophysical properties of **IrC1**, **IrC3** and **IrF2.**

oligomers (**5a–b** and **8**). The final Ir-containing dendrimers, **IrC1**, **IrC3**, and **IrF2**, were synthesized in moderate yields by the Suzuki coupling between the Y-shaped boronic acids (**6a–b** and **9**) and Ir(Br-ppy)$_2$(acac), respectively (Scheme 3). As reported earlier in literature,[20] we also find that this synthesis is a better approach than the direct chelation of phenylpyridine containing oligomers with IrCl$_3$.

All of the intermediate compounds were characterized by ^{1}H NMR. The Ir-containing dendrimers were fully characterized by ^{1}H NMR, MALDI-TOF MS and gel-permeation chromatography (GPC). In MALDI-TOF MS, the M$^+$ peaks for all the Ir-containing dendrimers were observed. However, due to the relatively poor stability of these metal complexes under the MALDI-TOF MS condition, other identified fragment peaks were also observed. In spite of the fragment peaks in the MS spectra, the good purity of the dendrimers can be demonstrated by ^{1}H NMR and GPC analysis. As can be seen in Figure 1, all three Ir-containing dendrimers are monodispersed with a very narrow and symmetric peak. It is interesting to note that **IrF2** has a larger "hydrodynamic" size than **IrC3** although the latter has a higher molecular weight.

Thermal and Optical Properties of the Phosphorescent Dendrimers IrC1, IrC3 and IrF2

DSC curves from the second heating scan and TGA curves of the samples are displayed in Figure 2. DSC curves revealed that all three dendrimers are amorphous materials with high glass transition temperatures of

Electrochemical Study

To investigate the electrochemical properties of these three phosphorescent dendrimers and estimate their

■ *Scheme 3.* Synthetic route to phosphorescent dendrimers with an iridium complex core.

HOMO and LUMO energy levels, cyclic voltammetry (CV) measurements were carried out under argon in a three-electrode cell using 0.1 M Bu$_4$NPF$_6$ in anhydrous CH$_3$CN as the supporting electrolyte. The CV curves were referenced to an Ag quasi-reference electrode, which was calibrated using a ferrocene/ferrocenium (Fc/Fc$^+$) redox couple (4.8 eV below the vacuum level) as an external standard. The $E_{1/2}$ of the Fc/Fc$^+$ redoc couple was found to be 0.40 V vs. the Ag quasi-reference electrode. Therefore, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the **Ir** dendrimers can be estimated using the empirical equation $E_{\mathrm{HOMO}} = -(E_{on}^{ox} + 4.40)$ eV and $E_{\mathrm{LUMO}} = -(E_{on}^{red} + 4.40)$ eV,

respectively, where E_{on}^{ox} and E_{on}^{red} stand for the onset potentials for oxidation and reduction relative to the Ag quasi-reference electrode, respectively. The results are summarized in Table 2.

The CVs of the dendrimers are shown in Figure 4. For all three materials, the anodic oxidation processes were reversible, and the CV curves remained unchanged under multiple successive potential scans, indicating their excellent stability against electrochemical oxidation. **IrF2** displayed two reversible anodic redox pairs at 1.13 V and 1.33 V, corresponding to the oxidation of the Ir center and the oligofluorene substituted ligands, respectively. For **IrC1** and **IrC3**, the first anodic oxidation
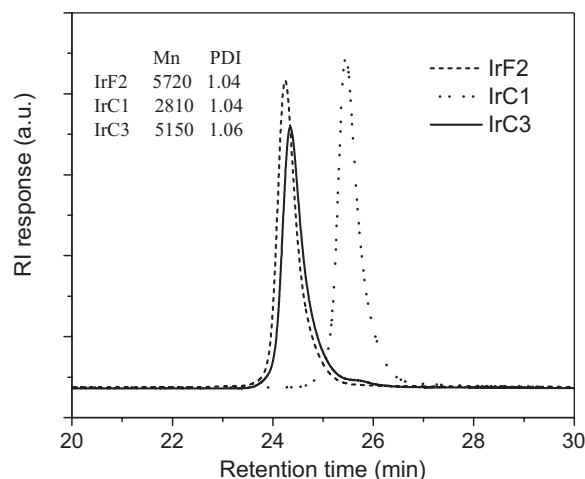
Figure 1. GPC curves of Ir containing dendrimers ($\overline{M}_n$ and PDI values were calculated based on polystyrene standards).

occurred at 0.91 V and 0.82 V, respectively, indicating the oligocarbazole ligands were oxidized first before the Ir core. **IrF2** underwent a reversible cathodic reduction. However, the cathodic reduction waves of **IrC1 and IrC3** were not reversible. This is because the oligocarbazole substituted ligands are difficult to be charged with electrons.
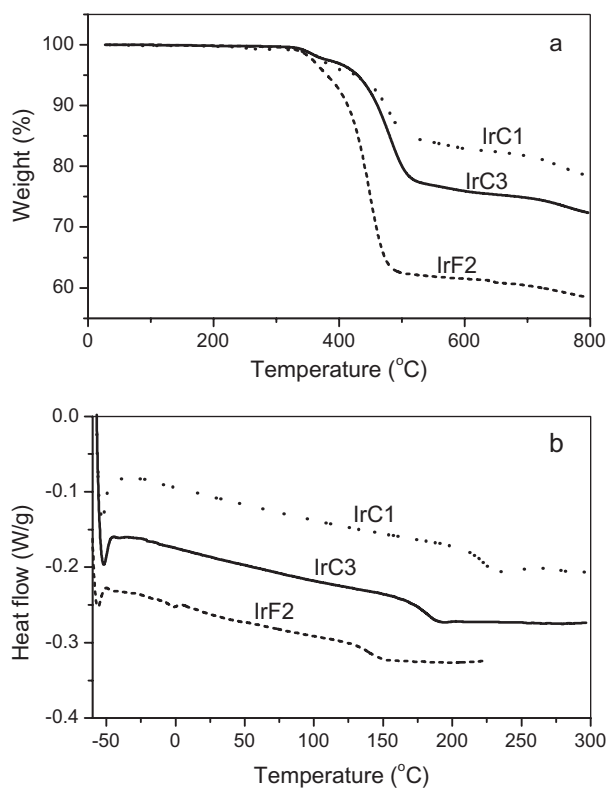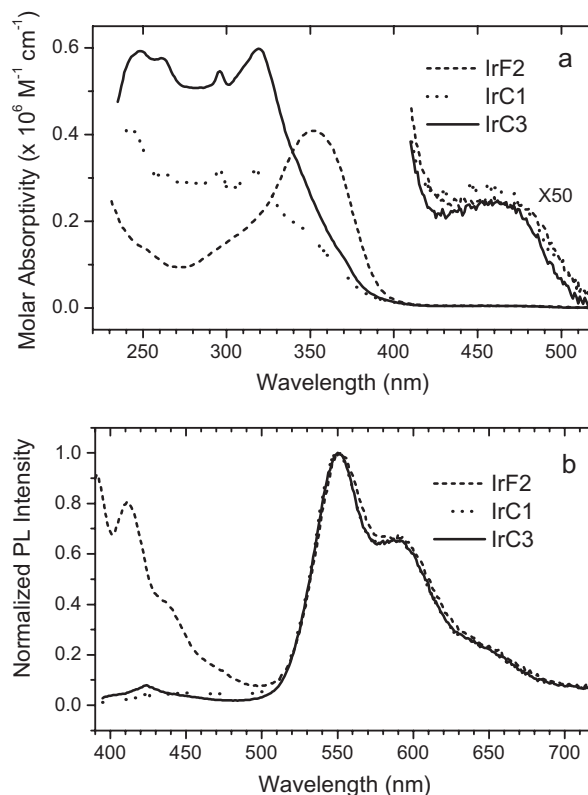

Figure 3. UV-vis absorption spectra (a) and PL emission spectra (b) of **IrC1**, **IrC3** and **IrF2** in degassed CH_2Cl_2.

Electroluminescent Properties of Oligomers IrC1, IrC3, and IrF2

In this work, we investigated the EL performance of the synthesized Ir containing dendrimers as triplet emitters by blending with electron transporting matrix. The device based on **IrC3** with the configuration of ITO/PEDOT-PSS/**IrC3**:TPBI/TPBI//LiF/Al has been fabricated, where TPBI is

Table 1. The thermal and photophysical properties of dendrimers **IrC1**, **IrC3** and **IrF2**.

Complex	T_g	T_d[a]	λ_{em}[b]	Φ_{ph}[b),c]
	°C	°C	nm	
IrC1	182	338	549, 587	0.21
IrC2	223	346	550, 587	0.25
IrF2	144	342	553, 581	0.10

[a] 1% Weight loss temperature under nitrogen; [b] Measured in degassed CH_2Cl_2 at room temperature; [c] Using $Ir(PPy)_3$ ($\Phi_{ph} = 0.40$) as a reference.

Figure 2. TGA (a) and DSC (b, from the second heating scan) curves of Ir containing dendrimers.

Table 2. Electrochemical properties and energy levels of demdrimers **IrC1**, **IrC3**, and **IrF2**.

Complex	E_{on}^{ox} [a]	E_{on}^{red} [a]	E_{HOMO} [b]	E_{LUMO} [b]	E_g [c]
	V	V	eV	eV	eV
IrF2	0.94	−2.28	5.34	2.12	3.22
IrC1	0.64	−2.12	5.04	2.28	2.76
IrC3	0.62	−2.13	5.02	2.27	2.75

[a] E_{on}^{ox} and E_{on}^{red} stand for the onset potentials for oxidation and reduction relative to the Ag quasi-reference electrode, respectively; [b] Estimated from onset potentials; [c] Electrochemical energy gaps.
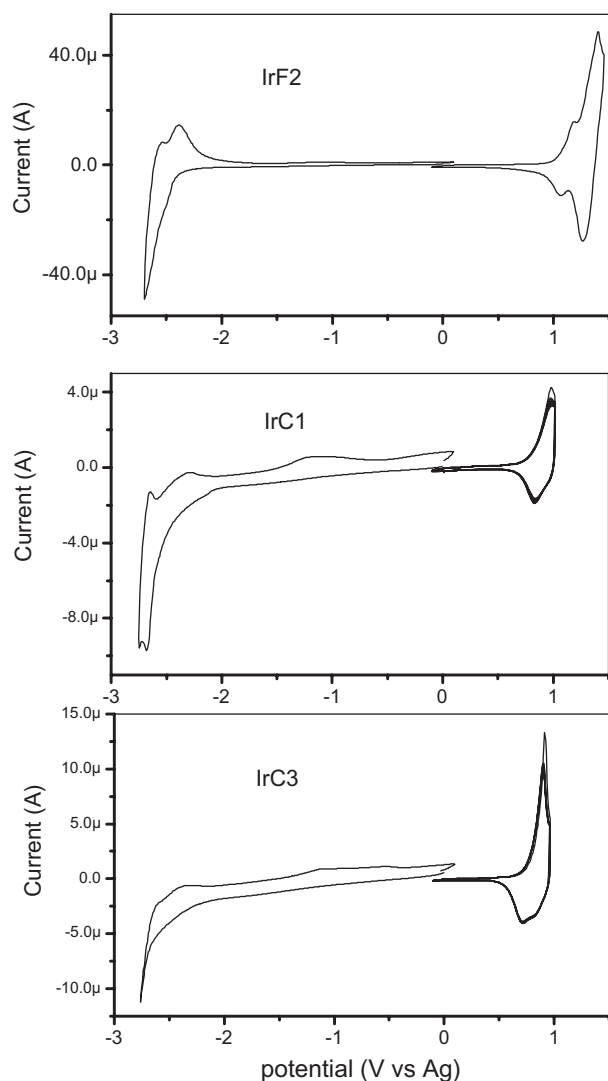

Figure 4. Cyclic voltammograms of the thin films of Ir containing dendrimers in 0.1 M Bu$_4$NPF$_6$ anhydrous CH$_3$CN solutions. Scan rate: 50 mV · s^{-1}.

an electron transporting material used as a host for the electrophosphorescent dendrimer in the emitting layer. Our previous study showed that the charge transport in oligocarbazoles is hole-dominant, so an electron transporting material such as TPBI has to be added to the emitting layer to balance its charge transport.[25] Optimized performance was achieved with the weight ratio of **IrC3**/TPBI at 55/45. Therefore, the content of TPBI in the emitting layer was fixed at 45% by weight for all three dendrimers based devices in this study. Because the other two dendrimers (**IrC1** and **IrF2**) have different weight contents of the Ir complex core compared with **IrC3**, for a reasonable comparison of the performance of the devices, a similar Ir complex core content of ca. 9 wt.-% was used in the emitting layer for all the fabricated devices. Therefore, TCTA, a widely used bipolar material for iridium complexes was also added to the emitting layer to keep the Ir complex core concentration at this level. In this case, the weight ratio of the dendrimer/TCTA/TPBI in the emitting layer of the **IrC1** and **IrF2** based devices is 35/20/45 and 45/10/45, respectively. The photoluminescence efficiency of the emitting layer was measured in an integrating sphere using a modified literature procedure,[17] and found to be 0.84, 0.57, and 0.14 for the **IrC1**, **IrC3** and **IrF2** doped films, respectively. Compared with **IrC1** and **IrC3**, **IrF2** based films have a very low PL yield probably due to the PL quenching by the oligofluorene with low triplet-energy. It should be noted that for all these films, only yellow PL emission from the Ir complex core was observed. PL emission from TCTA, TPBI and oligocarbazole or oligofluorene ligands was completely quenched in the films.

Figure 5 shows the EL spectra and luminance-voltage characteristics of dendrimers **IrC1, IrC3** and **IrF2** based devices. The EL emission of the host was completely quenched, indicating complete energy and/or charge transfer from the host to the iridium core upon electrical excitation. The EL spectra of **IrC1**, **IrC3** and **IrF2** devices remained unchanged within the tested voltage range and were almost identical to their solution PL spectra. All the devices based on the three dendrimers were relatively stable during the device-testing period with reproducible luminance and efficiency at same applied voltages. Since **IrC1**, **IrC3** and **IrF2** possess the same core chromophore, a biscyclometalated iridium complex, they showed quite similar EL spectra. However, the surrounding ligand structures have a big impact on the device performance, as shown in Figure 5. Compared with **IrC1** and **IrC3**, **IrF2** based devices gave a poor performance. This result is not surprising since **IrF2** has low PL efficiency not only in solution but also in the solid film, probably due to undesired phosphorescence quenching by the oligofluorene with a low triplet energy.[16,20] On the other hand, **IrC3** based devices showed the best performance with a maximum luminance of 13 060 cd · m^{-2} at a driving
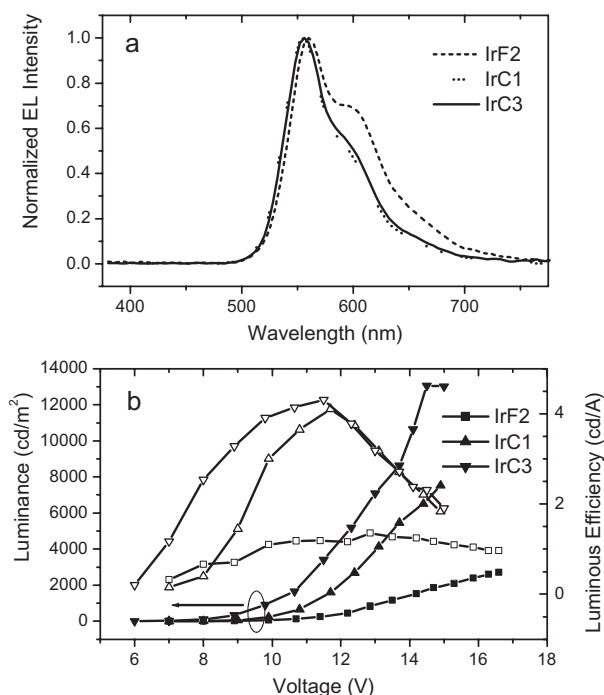
Figure 5. (a) EL spectra, (b) luminance-voltage (filled symbols) and luminous efficiency-voltage (open symbols) characteristics of **IrC1**, **IrC3** and **IrF2** based devices.

voltage of 11.5 V and a peak current-efficiency of 4.3 cd · A^{-1} at a luminance of 3 400 cd · m^{-2}. In the future work, we will work to improve the device performance by further optimizing the emitting layer composition to obtain balanced charge injection and transport.

Conclusion

We have designed and synthesized three new phosphorescent dendrimers with an iridium complex core and investigated their potential applications in electrophosphorescent devices as yellow emitters. Dendrimers **IrC1** and **IrC3** contain hyperbranched oligocarbazole substituted ligands, while dendrimer **IrF2** contains oligofluorene substituted ligands. We found that the ligand structure has significant impacts on the optical, electrochemical, and electroluminescent properties of the resulting dendrimers. Because of the high lowest-excited-triplet energy and efficient Förster energy transfer from oligocarbazole to the Ir complex core, **IrC1** and **IrC3** have demonstrated high PL efficiencies in both solution and solid states. In contrast, **IrF2** with oligofluorene substituted ligands has low PL efficiency. High-efficiency electrophosphorescent LEDs

were fabricated by blending **IrC3** with an electron-transporting material as the triplet emitter.

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