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High-Efficiency Electrophosphorescent Fluorene-*alt*-carbazole Copolymers N-Grafted with Cyclometalated Ir Complexes

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ABSTRACT: A series of electrophosphorescent conjugated fluorene-*alt*-carbazole copolymers are synthesized by Suzuki polycondensation. A diketone-ended alkyl chain which is grafted in the N-position of carbazole serves as a ligand to form a pendant cyclometalated Ir complex with 1-phenylisoquinoline (Piq), 2-naphthylpyridine (Napy), and 2-phenylquinoline (Phq). The PL efficiencies of PFCzIrPiq and PFCzIrPhq copolymers are around 60% and 70%, respectively. EL emission from the backbone of PFCzIrPiq and PFCzIrPhq copolymers is completely quenched even though the Ir complex contents in the polymers are as low as 0.5 mol %. The device of PFCzIrPiq05 copolymer shows the highest external quantum efficiency of 4.9% ph/el and the luminous efficiency of 4.0 cd/A with 240 cd/m^2 at a bias voltage of 7.7 V and a peak emission of 610 nm. The device efficiency of PFCzIrPiq05 copolymer still remains high (QE $_{\text{ext}}$ = 3.4% ph/el and LE = 2.9 cd/A) with a luminance of 2978 cd/m^2 even at a current density of 100 mA/cm^2. The enhancement of the device performance could be due to the higher triplet energy and meanwhile to suitable HOMO and LUMO levels for efficient charge injection by introducing a carbazole unit into the polyfluorene backbone at the 3,6-linkage and blending PBD into the copolymers.

Introduction

Electrophosphorescent light-emitting diodes (LEDs) have been attracting much attention because of their high quantum efficiency.[1] Unlike electrofluorescence, electrophosphorescence can make full use of both singlet and triplet excitons owing to strong spin−orbital coupling of heavy-metal ions in phosphorescent complexes. As a result, electrophosphorescence can theoretically approach 100% internal quantum efficiency.[1b] The green OLEDs with bis(2-phenylpyridine)iridium(III) acetylacetonate [(ppy)$_2$Ir(acac)] doped into 3-phenyl-4-(1′-naphthyl)-5-phenyl-1,2,4-triazole (TAZ) show a high external quantum efficiency of 19% ph/el (photo/election) and a power efficiency of 60 lm/W.[2] Phosphorescent dyes can also be doped into polymer host materials to use the dopants as emissive centers since it allows light-emitting diodes (LEDs) to be made with a spin-coating or printing technique. The yellow-green PLEDs with tris(9,9-dihexyl-2-(pyridinyl-2′)fluorene)iridium(III) [Ir(dpf)$_3$] doped into a blend of nonconjugated poly(vinylcarbazole) (PVK) with 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole show an external quantum efficiency of 10% ph/el and a luminous efficiency (LE) of 36 cd/A.[3] O'Brien and co-workers[4] achieved an external quantum efficiency of 3.5% and a luminous efficiency of <1.0 cd/A with a maximum emission at 646 nm by doping platinum(II) porphyrins (PtOEP) into conjugated poly(9,9-dioctylfluorene). Jiang et al.[5] achieved an external quantum efficiency of 12% ph/el and a luminous efficiency of 5.2 cd/A, with a maximum emission at 624 nm for electrophosphorescent PLEDs by doping iridium(III) bis(1-phenylisoquinolyl)-N,C$^{2'}$) acetylacetonate [(piq)$_2$Ir(acac)] into conjugated poly(9,9-dioctylfluorene) (PFO) and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD). These results demonstrate that high external quantum efficiency can also be realized by using conjugated polymer as host materials.

Although the devices with phosphorescent dye doped into a small molecule or polymer host are successful in the realization of high-efficiency O(P)LEDs, there exist serious problems, such as complexity in fabrication procedure and fast decay of efficiency with the increase in current density which might become more serious during a long-term operation due to the intrinsic instability of such blend systems. A solution to this problem is to introduce a phosphorescent dye into the polymer chain. Lee et al.[6] synthesized nonconjugated polyethylene main chain with directly attached phenylpyridine to side chain as a ligand and pendant *N*-vinylcarbazole as host materials. High external quantum efficiency of 4.4% ph/el was achieved at current density of 6.4 mA/cm^2. A similar approach of using nonconjugated main chain with pendant diketone was reported by Tokito et al.[7] By carefully designing the multilayer device structure, selecting the electron transport material for the emissive layer and optimizing the content of the iridium complex unit in the phosphorescent polymer chain, high external quantum efficiencies of 5.5%, 9%, and 3.5% in red, green, and blue PLEDs were respectively achieved. The phosphorescent conjugated polymers based on polyfluorene backbone with diketone pendant attached to the 9-carbon position of fluorene were reported by Chen et al.[8] The device from polymer grafted with 1.3 mol % iridium(III) bis(2-(2′-benzothienyl)pyridinato-N,C$^{3'}$) acetylacetonate complex [(btp)$_2$Ir(acac)] in diketone pedant attached to the 9-position of fluorene unit has shown a high external quantum efficiency of 1.59% ph/el and a power efficiency of 2.8 cd/A at 7.0 V with luminance of 65 cd/m^2 and peak emission at 610 nm. Recently, a series of main-chain-type well-defined oligo- and polyfluorenyl bis-cyclo-

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metalated Ir complexes was reported by Sandee et al.[9] An external quantum efficiency of 1.5% ph/el with a peak emission of 610 nm was obtained by introducing the $(btp)_2Ir(acac)$ complex covalently into the poly(9,9′-dioctylfluorene) backbone.

In this paper, a series of alternating copolymers from fluorene and *N*-alkylcarbazole at the 3,6-linkage were synthesized by Suzuki polycondensation. A part of *N*-alkylcarbazole units were replaced by a diketone group ended to provide a ligand for the formation of Ir complexes in side chain in the presence of 1-phenylisoquinoline (Piq), 2-naphthylpyridine (Napy), and 2-phenylquinoline (Phq). We expect that the incorporation of diketone−alkyl group into the N-position of a carbazole unit can substantially raise the flexibility and reactivity of a diketone group to the iridium core due to more rotating freedom of diketone−alkyl around the nitrogen atom. On the other hand, the fluorene-*alt*-carbazole segment is used as a polymer backbone because the HOMO level of carbazole-based copolymers can be tuned by the substitution at the 3-, 6-, and 9-position, while the triplet level remains sufficiently high to accommodate even blue triplet emitters.[10]

Experimental Section

Materials and Measurements. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. All reagents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Co. and were used as they were received. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 spectrometer operating respectively at 400 and 100 MHz, with tetramethylsilane as a reference. Direct injection mass spectra were recorded by the electron spray impact (ESI) method on a LCQ DECA XP liquid chromatograph−mass spectrometer (Thremo Co.). Molecular weight determination was obtained using a Waters GPC 2410 in tetrahydrofuran via a calibration curve of polystyrene standards. Elemental analyses were performed on Vario EL elemental analysis instrument (Elementar Co.). The iridium contents analyses were determined by using a Philips (Magix PRO) sequential X-ray fluorescence spectrometry (XRF), with a rhodium tube operated at 60 kV and 50 mA, a LiF 200 crystal, and a scintillation counter. Iridium(III) 2,4-pentanedionate (from Alfa Aesar Co.) was used as a standard. Samples were pressed as homogeneous tablets (diameter = 30 mm) of compressed (375 MPa) powder of the copolymers. UV−vis absorption spectra were recorded on a HP 8453 spectrophotometer. Cyclic voltammetry was carried out on a potentiostat/galvanostat model 283 (Princeton Applied Research) with platinum electrode at a scan rate of 50 mV/s against Ag/AgCl reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN).

12-Bromo-2-dodecaneone (1). 11-Bromoundecane acid (10 g, 37.7 mmol) was dissolved in 300 mL of THF. The solution was cooled to −78 °C, and a 1.6 M solution of CH_3Li (47.1 mL, 75.4 mmol) in diethyl ether was added dropwise. After stirring for 2 h, the reaction mixture was allowed to warm to 0 °C and quenched with saturated ammonium chloride followed by extraction with ether. The ether phase was separated, dried with $MgSO_4$, and concentrated. Purification by silica column chromatography gave the product in colorless oil (7.0 g, yield 70%). ^1H NMR ($CDCl_3$) δ (ppm): 3.35 (t, 2H, Br−CH_2), 2.36 (t, 2H), 2.10 (s, 3H, −CH_3), 1.85−1.25 (m, 16H). ^{13}C NMR ($CDCl_3$) δ (ppm): 209.1 (C-keto form), 43.61, 34.13, 33.92, 32.71, 29.72, 29.22, 29.18, 29.02, 28.60, 28.03, 23.72 (−CH_3). Anal. Calcd for $C_{12}H_{23}OBr$: C, 54.75; H, 8.74. Found: C, 55.28; H, 8.70.

3,6-Dibromocarbazole (2) was prepared according to the published procedure.[11] ^1H NMR ($CDCl_3$) δ (ppm): 8.12 (s, 1H, N−H), 8.05 (d, 2H), 7.54 (m, 2H), 7.25 (t, 2H) (carbazole ring). ^{13}C NMR ($CDCl_3$) δ (ppm): 138.73, 129,72, 124.54, 123.69, 113.05, 112.66.

3,6-Dibromo-9-(11-dodecaneone)carbazole (3). To a solution of sodium hydride (2.5 g, 61.6 mmol, 60%) in 50 mL of THF, 3,6-dibromocarbazole (10 g, 30.8 mmol) in 20 mL of THF was added dropwise. The mixture was refluxed for 1.5 h under a N_2 atmosphere, and then 12-bromodo-2-decaneone **(1)** (8 g, 30.8 mmol) in 10 mL of THF was added dropwise to the mixture. The mixture was refluxed for another 12 h and cooled to room temperature. Then it was extracted with dichloromethane followed by washing with water. The oil phase was separated and dried overnight with $MgSO_4$. The solvent was removed by evaporation, and the crude products were purified by silica column chromatography to give 9.4 g of white solid (yield, 60%). ^1H NMR ($CDCl_3$) δ (ppm): 8.11 (s, 2H), 7.53 (d, 2H), 7.22 (m, 2H) (carbazole ring), 4.21 (t, 2H, N−CH_2), 2.37 (t, 2H), 2.10 (s, 3H, −CH_3), 1.82−1.19 (m, 16H) (aliphatic). ^{13}C NMR ($CDCl_3$) δ (ppm): 209.21 (C-keto form), 139.25, 128.95, 123.38, 123.16, 111.89, 110.36 (carbazole ring), 43.75 (N−CH_2), 43.27, 29.83, 29.34, 29.30, 29.24, 29.14, 29.09, 28.81, 27.15, 23.81 (−CH_3) (aliphatic). Anal. Calcd for $C_{24}H_{29}NOBr_2$: C, 56.81; H, 5.72; N, 2.76. Found: C, 56.27; H, 5.63; N, 2.71.

3,6-Dibromo-9-(14-trifluoro-11,13-tetradecyldiketone)-carbazole (4). Sodium methoxide (1.7 g, 31.6 mmol) in 5 mL of methanol was added dropwise to a solution of 3,6-dibromo-9-(11-dodecaneone)carbazole **(3)** (8 g, 15.8 mmol) in 50 mL of methyl *tert*-butyl ether. The mixture was refluxed for 1.5 h under a N_2 atmosphere, and then ethyl trifluoroacetate (20 mL) was added dropwise to the mixture. The mixture was refluxed for another 12 h, cooled to room temperature, and poured into ice water. The aqueous layer was acidified with diluted acetic acid. The diketone was extracted with dichloromethane followed by neutralization with a solution of $NaHCO_3$. The organic phase was separated and dried overnight with $MgSO_4$. The solvent was removed by evaporation, and the crude products were purified by silica column chromatography to give 5.0 g of white solid (yield, 80%). ^1H NMR ($CDCl_3$) δ (ppm): 14.42 (s, 1H, enol form, −OH), 8.12 (d, 2H), 7.51 (m, 2H), 7.25 (t, 2H) (carbazole ring), 5.88 (s, 1H, enol form, −CH), 4.23 (t, 2H, keto form, −CH_2), 2.37 (t, 2H), 1.82−1.20 (m, 16H) (aliphatic). ^{13}C NMR ($CDCl_3$) δ (ppm): 197.55 (C-keto form), 175.77, 175.41 (C-enol form), 118.49, (keto form, −CF_3), 115.68, (enol form, −CF_3), 139.36, 129.05, 123.51, 123.31, 111.99, 110.41, (carbazole ring), 95.69 (enol form, −CH), 43.31 (N−CH_2), 38.44 (keto form, −CH_2), 29.73, 29.34, 29.30, 29.24, 29.15, 29.02, 28.85, 27.21, 25.46 (aliphatic). Anal. Calcd for $C_{26}H_{28}NO_2Br_2F_3$: C, 51.74; H, 4.64; N, 2.32. Found: C, 51.21; H, 4.32; N, 2.28.

2-Naphthylpyridine (5). To a solution of α-naphthalene (10.36 g, 50 mmol) in 50 mL of THF, *n*-BuLi (32 mL, 50 mmol) was added dropwise at −80 °C. The mixture was warmed to −50 °C, and stirring was continued for 0.5 h. $ZnCl_2$ (6.8 g, 50 mmol) with 50 mL of THF was added dropwise. The mixture was allowed to warm to 25 °C and stirred for another 1.5 h. The mixture solution of 2-bromopyridine (8 g, 50 mmol) and tetrakis(triphenylphosphine)palladium (0.9 g) in 50 mL of THF was added dropwise. The reaction mixture was stirred for 2 h at room temperature. Then it was neutralized by 10% $NaHCO_3$ to make the solution neutral followed by extracting with ethyl acetate. The combined organic layers were washed by water and dried overnight with $MgSO_4$. The solvent was removed by a rotary evaporator, and the crude products were purified by silica chromatography to give 3.0 g (yield, 60%) of yellow oil product. ^1H NMR ($CDCl_3$) δ (ppm): 8.78 (d, 1H, pyridine ring), 8.06 (d, 1H), 7.91, (d, 1H), 7.81, (m, 1H), (naphthalene ring), 7.76 (t, 2H) (pyridine ring), 7.67 (m, 2H), 7.52 (m, 1H), 7.48 (m, 1H), 7.31 (t, 2H), (naphthalene ring), 7.28 (m, 1H, pyridine ring). ^{13}C NMR ($CDCl_3$) δ (ppm): 159.21, 149.12, 136.32, 123.21, 121.92 (pyridine ring), 138.40, 133.91, 131.12, 128.83, 128.31, 127.42, 126.41, 125.82, 125.51, 125.21 (naphthalene ring). Anal. Calcd for $C_{15}H_{11}N$: C, 87.81; H, 5.36; N, 6.83. Found: C, 87.46, H, 5.84; N, 6.80.

1-Phenylisoquinoline (6). 1-Chloroisoquinoline (8.0 g, 48.9 mmol) was added into a solution of tetrakis(triphenylphosphine)palladium (1.7 g, 1.4 mmol) in 100 mL of ethylene glycol dimethyl ether. The mixture was stirred for 10 min under an argon atmosphere to give a yellow/green solution. Benzeneboronic acid (6.0 g, 48.9 mmol) in 10 mL of ethanol was added to the mixture to give a light red solution. The sodium carbonate solution (97.8 mmol, 2 M) was added to the mixture and refluxed for 16 h. Then the mixture was allowed to cool to room temperature and extracted by dichloromethane. The oil phase was washed with water and dried overnight with $MgSO_4$. The solvent was removed by rotary evaporator, and the crude products were purified by silica chromatography to give 5.4 g (yield, 52%) of yellow needle product. ^1H NMR ($CDCl_3$) δ (ppm): 8.59 (d, 1H, isoquinoline ring, N−CH), 8.09 (d, 1H, benzene ring), 7.84 (d, 1H), 7.67 (d, 1H), 7.62 (t, 1H), 7.52 (m, 1H) 7.48 (m, 1H) (isoquinoline ring), 7.36−7.23 (m, 4H, benzene ring). ^{13}C NMR ($CDCl_3$) δ (ppm): 160.75, 142.23, 136.87, 129.98, 127.58, 127.15, 126.98, 126.73, 119.89 (isoquinoline ring), 139.61, 129.92, 128.57, 128.33 (benzene ring). Anal. Calcd for $C_{15}H_{11}N$: C, 87.81; H, 5.36; N, 6.83. Found: C, 87.52; H, 5.75; N, 6.78.

Chloride-Bridged Dimers [$(Piq)_2Ir$-(μ-Cl)$_2$Ir$(Piq)_2$ (7a), Piq = 1-Phenylisoquinoline], [$(Napy)_2Ir$-(μ-Cl)$_2$Ir$(Napy)_2$ (7b), Napy = 2-Naphthylpyridine], and [$(Phq)_2Ir$-(μ-Cl)$_2$Ir$(Phq)_2$ (7c), Phq = 2-Phenylquinoline] (7a, 7b, and 7c) were synthesized according to the published procedures.[12]

3,6-Dibromo-9-(iridium(III)bis(1-phenylisoquinoline-N,C$^{2'}$))-14-trifluoro-11,13-tetradecyldiketone)carbazole (8a). Chloride-bridged dimer (**7a**) (0.45 g, 0.354 mmol), **4** (0.54 g, 0.885 mmol), and sodium carbonate (100 mg) were mixed and refluxed in 2-ethoxyethanol (30 mL) for 16 h under a N_2 atmosphere. The solution was cooled to room temperature and filtered before washing with water and hexane. The crude products were purified by silica chromatography (40% dichloromethane and 60% petroleum ether). ^1H NMR ($CDCl_3$) δ (ppm): 8.95 (d, 2H, isoquinoline ring), 8.36 (d, 2H), 8.25 (d, 2H), (benzene ring), 8.13 (m, 1H, carbazole ring), 7.85 (m, 1H), 7.71 (m, 1H), (benzene ring), 7.64−6.36 (m, 16H), 5.53 (s, 1H, −CH), 4.20 (t, 2H, N−CH_2), 2.12 (t, 2H), 1.77−0.76 (m, 16H). ^{13}C NMR ($CDCl_3$) δ (ppm): 195.11, 185.51 (C-keto form), 173.05, 168.98, 149.01, 146.43, 127.25, 126.92, 126.72, 123.48, 123.36 (isoquinoline ring), 140.18, (−CF_3), 139.34, 137.28, 134.04, 130.81, 129.67, 129.03 (benzene ring), 123.29, 121.15, 120.81, 119.96, 111.98, 110.38 (carbazole ring), 95.57 (−CH), 43.34 (N−CH_2), 34.13, 31.24, 29.18, 28.98, 28.81, 28.57, 27.16, 26.25, 22.62. Anal. Calcd for $C_{56}H_{47}Br_2N_3F_3O_2Ir$: C, 55.91; H, 3.91; N, 3.49. Found: C, 57.06; H, 4.49; N, 3.30. Mass (ESI), *m/z*: 1202.2 (M^+).

3,6-Dibromo-9-(iridium(III)bis(2-(1′-naphthylpyridine-N,C$^{2'}$))-14-trifluoro-11,13-tetradecyldiketone)carbazole (8b) was synthesized by a similar method for **8a**. Chloride-bridged dimer (**7b**) (0.7 g, 0.551 mmol), **4** (0.83 g, 1.377 mmol), and sodium carbonate (100 mg) were used for the preparation. ^1H NMR ($CDCl_3$) δ (ppm): 8.55 (d, 2H), 8.47 (m, 2H), 8.12 (d, 2H),7.80 (m, 2H), 7.62−6.24 (m, 18H), 5.59 (s, 1H), 4.21 (t, 2H), 2.05 (t, 2H), 1.77−0.83 (m, 16H). ^{13}C NMR ($CDCl_3$) δ (ppm): 193.25, 184.35 (C-keto form), 160.12, 148.51, 137.73, 123.48, 121.21 (pyridine ring), 139.34, 132.19, 131.56, 131.25, 129.71, 129.02, 128.58, 126.42, 125.12 (naphthalene ring), 140.15 (−CF_3), 139.23, 123.28, 122.62, 122.41, 111.97, 110.39 (carbazole ring), 94.48 (−CH), 42.25 (N−CH_2), 34.15, 31.74, 29.71, 29.45, 28.97, 28.57, 27.16, 26.26, 22.52. Anal.Calcd for $C_{56}H_{47}Br_2N_3F_3O_2Ir$: C, 55.91; H, 3.91; N, 3.49. Found: C, 57.28; H, 4.60; N, 3.16. Mass (ESI), *m/z*: 1202.4 (M^+).

3,6-Dibromo-9-(iridium(III)bis(2-phenylquinoline-N,C$^{2'}$))-14-trifluoro-11,13-tetradecyldiketone)carbazole (8c) was synthesized by using chloride-bridged dimer **(7c)** (0.5 g, 0.393 mmol), **4** (0.593 g, 0.983 mmol), and sodium carbonate (100 mg) by the method as mentioned above. ^1H NMR ($CDCl_3$) δ (ppm): 8.31 (d, 1H, quinoline ring), 8.17 (d, 1H, benzene ring), 8.13 (m, 2H), 8.06 (m, 2H) (carbazole ring), 7.92−7.23 (m, 14H), 6.93 (t, 2H), 6.62 (m, 2H), 6.54 (d, 1H), 6.48 (d, 1H), 5.29 (s, 1H, −CH), 4.24 (t, 2H, N−CH_2), 2.37 (t, 2H), 1.79−0.84 (m, 16H). ^{13}C NMR ($CDCl_3$) δ (ppm): 194.12, 186.68 (C-keto form), 160.05, 151.98, 141.01, 132.43, 124.25, 123.92, 122.72, 121.48, 121.32 (quinoline ring), 142.14, 129.83, 129.75, 128.58, 127.79, 126.46 (benzene ring), 141.15 (−CF_3), 139.33, 123.88, 123.52, 122.61, 121.97, 110.45 (carbazole ring), 96.42 (−CH), 43.23 (N−CH_2), 34.14, 31.46, 29.70, 28.12, 28.04, 27.15, 25.58, 22.61, 22.49. Anal. Calcd for $C_{56}H_{47}Br_2N_3F_3O_2Ir$: C, 55.91; H, 3.91; N, 3.49. Found: C, 56.60; H, 4.29; N, 3.43. Mass (ESI), *m/z*: 1202.3 (M^+).

3,6-Dibromo-9-hexanecarbazole (9) was prepared according to the published procedures.[11] ^1H NMR ($CDCl_3$) δ (ppm): 8.09 (s, 2H), 7.53 (d, 2H), 7.24 (d, 2H) (carbazole ring), 4.17 (t, 2H, N−CH_2), 1.81−1.24 (m, 8H), 0.85 (t, 3H, −CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 139.2, 128.9, 123.4, 123.1, 111.9, 110.3 (carbazole ring), 43.3 (N−CH_2), 31.4, 28.8, 26.8, 22.5, 13.9 (−CH_3). Anal. Calcd for $C_{18}H_{19}Br_2N$: C, 52.81; H, 4.64; N, 3.42. Found: C, 52.72; H, 4.83; N, 3.22.

2,7-Dibromofluorene (10) and 2,7-dibromo-9,9-dioctylfluorene (11) were prepared according to the published procedures.[13]

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (12) was prepared following the published procedure from 2,7-dibromo-9,9-dioctylfluorene (**11**).[14] The resulted boronic ester was recrystallized from methanol and further purification by column chromatography (silica gel, 10% ethyl acetate in hexane) to give a white solid product (yield, 50%); mp 128−131 °C. ^1H NMR ($CDCl_3$) δ (ppm): 7.81 (d, 2H), 7.76 (s, 2H), 7.72 (d, 2H) (fluorene ring), 1.97 (m, 4H), 1.37 (s, 24H, −CH_3), 1.22−0.98 (m, 20H), 0.81 (t, 6H), 0.54 (m, 4H) (aliphatic). ^{13}C NMR ($CDCl_3$) δ (ppm): 150.85, 144.32, 134.06, 129.27, 121.67, 119.75 (fluorene ring), 84.12, 55.56 (C_9-fluorene ring), 40.49, 32.15, 30.32, 29.57, 25.33, 23.97, 22.98, 14.47 (aliphatic). Anal. Calcd for $C_{41}H_{64}O_4B_2$: C, 76.74; H, 10.04. Found: C, 76.43; H, 9.95.

General Procedures of Suzuki Polycondensation, Taking PFCzIrPiq05 as an Example. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**12**) (642 mg, 1.0 mmol), 3,6-dibromo-9-(iridium(III)bis(1-phenylisoquinoline-N,C$^{2'}$))-14-trifluoro-11,13-tetradecyldiketone)carbazole (**8a**) (12 mg, 0.01 mmol), 3,6-dibromo-9-hexanecarbazole (**9**) (405 mg, 0.99 mmol), and tetrakis(triphenylphosphine)palladium (5 mg) were dissolved in the mixture of toluene/THF(10 mL) and stirred for 0.5 h, and then Et_4NOH (20%) aqueous solution (4 mL) was added. The mixture was heated to 100 °C and stirred for 2 days under an argon atmosphere. Then the polymer was capped by adding 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (100 mg) by stirring for 12 h and then bromobenzene (1 mL) followed by heating for another 12 h. The whole mixture was poured into methanol. The precipitated polymer was recovered by filtration and purified by silica column chromatography with toluene to remove small molecular complex and catalyst residue (yield, 50%). ^1H NMR ($CDCl_3$) δ (ppm): 8.52 (s, 2H), 7.87 (d, 2H), 7.85 (m, 2H) (fluorene ring), 7.79 (d, 2H), 7.75 (m, 2H), 7.27 (s, 2H) (carbazole ring), 4.25 (s, 2H, N−CH_2), 2.25 (t, 2H), 1.93 (m, 4H), 1.55−1.14 (t, 20H), 0.92−0.77 (m, 16H) (aliphatic). ^{13}C NMR ($CDCl_3$) δ (ppm): 151.69, 140.84, 140.65, 139.55, 133.10, 126.14, 125.53, 123.63, 121.67, 119.88, 118.96, 109.04 (fluorene and carbazole ring), 55.35 (C_9-fluorene ring), 43.42, 40.63, 31.79, 31.63, 30.10, 29.23, 29.05, 27.02, 23.90, 22.58, 14.01 (aliphatic). Anal. Calcd for $(C_{29}H_{40})_{50}(C_{18}H_{19}N)_{49.5}(C_{56}H_{47}N_3F_3O_2Ir)_{0.5}$: C, 88.16; H, 9.19; N, 2.21. Found: C, 8 8.02; H, 9.38; N, 1.79.

PFCzIrPiq1. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**12**) (642 mg, 1.0 mmol), 3,6-dibromo-9-(iridium(III)bis(1-phenylisoquinoline-N,C$^{2'}$))-14-trifluoro-11,13-tetradecyldiketone)carbazole (**8a**) (24 mg, 0.02 mmol), and 3,6-dibromo-9-hexanecarbazole (**9**) (411 mg, 0.98 mmol) were used in the polymerization. ^1H NMR ($CDCl_3$) δ (ppm): 8.52 (s, 2H), 8.49 (d, 2H), 7.86 (m, 2H) (fluorene ring), 7.76 (d, 2H), 7.53 (m, 2H), 7.37 (d, 2H) (carbazole ring), 4.39 (s, 2H, N−CH_2), 2.15 (t, 2H), 1.97 (m, 4H), 1.52−1.09 (t, 20H), 0.93−0.76 (m, 16H) (aliphatic). ^{13}C NMR ($CDCl_3$) δ (ppm): 151.71, 141.05, 140.86, 140.42, 139.57, 133.11, 126.17, 125.54, 123.65, 121.69, 119.90, 118.97, 109.06 (fluorene and carbazole ring), 55.37 (C_9-fluorene ring), 40.65, 40.51, 31.81, 31.65, 30.12, 29.25, 29.08, 27.04, 23.92, 23.83, 22.61, 14.04 (aliphatic). Anal. Calcd for $(C_{29}H_{40})_{50}(C_{18}H_{19}N)_{49}(C_{56}H_{47}N_3F_3O_2Ir)_1$: C, 87.78; H, 9.12; N, 2.23. Found: C, 87.14; H, 9.38; N, 1.60.

PFCzIrPiq2. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**12**) (642 mg, 1.0 mmol), 3,6-dibromo-9-(iridium(III)bis(1-phenylisoquinoline-N,C$^{2'}$))-14-trifluoro-11,13-tetradecyldiketone)carbazole **(8a)** (48 mg, 0.04 mmol), and 3,6-dibromo-9-hexanecarbazole (**9**) (402 mg, 0.96 mmol) were used in the polymerization. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.52 (s, 2H), 7.85 (t, 2H), 7.78 (d, 2H) (fluorene ring), 7.75 (d, 2H), 7.53 (m, 2H), 7.25 (s, 2H) (carbazole ring), 4.41 (s, 2H, N−CH$_2$), 2.16 (t, 2H), 1.97 (d, 4H), 1.51−1.10 (m, 20), 0.93−0.77 (m, 16H) (aliphatic). ^{13}C NMR (CDCl$_3$) δ (ppm): 151.72, 140.87, 140.42, 139.58, 133.12, 126.18, 125.55, 123.66, 121.69, 119.89, 118.97, 109.06 (fluorene and carbazole ring), 55.37 (C$_9$-fluorene ring), 43.43, 40.65, 31.81, 31.65, 30.12, 29.26, 29.08, 27.04, 23.92, 22.61, 14.03 (aliphatic). Anal. Calcd for $(C_{29}H_{40})_{50}(C_{18}H_{19}N)_{48}(C_{56}H_{47}N_3F_3O_2Ir)_2$: C, 87.07; H, 8.99; N, 2.26. Found: C, 87.20; H, 9.29; N, 1.92.

PFCzIrNapy05. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**12**) (1.0 mmol), 3,6-dibromo-9-hexanecarbazole (**9**) (0.99 mmol), and 3,6-dibromo-9-(iridium(III)bis(2-(1′-naphthylpyridine-N,C$^{2'}$))-9-(14-trifluoro-11,13-tetradecyldiketone)carbazole **(8b)** (0.01 mmol) were used in the polymerization. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.52 (s, 2H), 7.84 (d, 2H), 7.78 (t, 2H) (fluorene ring), 7.74 (t, 2H), 7.52 (d, 2H), 7.24 (s, 2H) (carbazole ring), 4.39 (s, 2H, N−CH$_2$), 2.16 (t, 2H), 1.97 (m, 4H), 1.58−1.09 (m, 20H), 0.92−0.76 (m, 16H) (aliphatic). ^{13}C NMR (CDCl$_3$) δ (ppm): 151.71, 140.86, 140.42, 139.57, 133.11, 126.17, 125.54, 123.65, 121.69, 119.91, 118.97, 109.06 (fluorene and carbazole ring), 55.37 (C$_9$-fluorene ring), 40.65, 31.81, 31.65, 30.12, 29.26, 29.08, 27.04, 23.92, 22.61, 14.04 (aliphatic). Anal. Calcd for $(C_{29}H_{40})_{50}(C_{18}H_{19}N)_{49.5}(C_{56}H_{47}N_3F_3O_2Ir)_{0.5}$: C, 88.16; H, 9.19; N, 2.21. Found: C, 87.78; H, 8.85; N, 1.60.

PFCzIrNapy1. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**12**) (0.5 mmol), 3,6-dibromo-9-hexanecarbazole (**9**) (0.49 mmol), and 3,6-dibromo-9-(iridium(III)bis(2-(1′-naphthylpyridine-N,C$^{2'}$))-9-(14-trifluoro-11,13-tetradecyldiketone)carbazole (**8b**) (0.01 mmol) were used in the polymerization. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.52 (d, 2H), 7.86 (t, 2H), 7.78 (m, 2H) (fluorene ring), 7.74 (d, 2H), 7.53 (t, 2H), 7.24 (s, 2H) (carbazole ring), 4.40 (s, 2H, N−CH$_2$), 2.16 (t, 2H), 1.97 (m, 4H), 1.48−1.09 (m, 20), 0.93−0.76 (m, 16) (aliphatic). ^{13}C NMR (CDCl$_3$) δ (ppm): 151.72, 140.86, 140.42, 139.57, 133.11, 126.18, 125.54, 123.65, 121.69, 119.90, 118.97, 109.06 (fluorene and carbazole ring), 55.37 (C$_9$-fluorene ring), 40.65, 31.81, 31.65, 30.12, 29.25, 29.08, 27.04, 23.92, 22.60, 14.03 (aliphatic). Anal. Calcd for $(C_{29}H_{40})_{50}(C_{18}H_{19}N)_{49}(C_{56}H_{47}N_3F_3O_2Ir)_1$: C, 87.78; H, 9.12; N, 2.23. Found: C, 87.50; H, 9.46; N, 1.56.

PFCzIrNapy2. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**12**) (0.5 mmol), 3,6-dibromo-9-hexanecarbazole (**9**) (0.48 mmol), and 3,6-dibromo-9-(iridium(III)bis(2-(1′-naphthylpyridine-N,C$^{2'}$))-9-(14-trifluoro-11,13-tetradecyldiketone)carbazole (**8b**) (0.02 mmol) were used in the polymerization. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.52 (s, 2H), 7.87 (d, 2H), 7.86 (d, 2H) (fluorene ring), 7.79 (m, 2H), 7.75 (d, 2H), 7.27 (s, 2H) (carbazole ring), 4.38 (s, 2H, N−CH$_2$), 2.15 (t, 2H), 1.95 (t, 4H), 1.52−1.13 (m, 20H), 0.92−0.77 (m, 16H) (aliphatic). ^{13}C NMR (CDCl$_3$) δ (ppm): 151.69, 148.16, 140.84, 140.40, 139.55, 133.09, 126.17, 125.50, 123.63, 121.67, 119.88, 118.95, 109.04 (fluorene and carbazole ring), 55.35 (C$_9$-fluorene ring), 40.62, 31.79, 31.63, 30.10, 29.23, 29.06, 27.02, 23.90, 22.58, 14.09 (aliphatic). Anal. Calcd for $(C_{29}H_{40})_{50}(C_{18}H_{19}N)_{48}(C_{56}H_{47}N_3F_3O_2Ir)_2$: C, 87.07; H, 8.99; N, 2.26. Found: C, 87.32; H, 9.02; N, 1.99.

PFCzIrPhq05. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**12**) (1.0 mmol), 3,6-dibromo-9-hexanecarbazole (**9**) (0.99 mmol), and 3,6-dibromo-9-(iridium(III)bis(2-phenylquinoline-N,C$^{2'}$))-14-trifluoro-11,13-tetradecyldiketone)carbazole **(8c)** (0.01 mmol) were used in this polymerization. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.52 (s, 2H), 7.86 (d, 2H), 7.78 (t, 2H) (fluorene ring), 7.74 (m, 2H), 7.53 (d, 2H), 7.24 (s, 2H) (carbazole ring), 4.40 (s, 2H, N−CH$_2$), 2.16 (t, 2H), 1.97 (t, 4H), 1.58−1.13 (m, 20H), 0.92−0.76 (m, 16H) (aliphatic). ^{13}C NMR (CDCl$_3$) δ (ppm): 151.72, 140.86, 140.42, 139.57, 133.11, 126.17, 125.55, 123.65, 121.69, 119.91, 118.96, 109.06 (fluorene and carbazole ring), 55.37 (C$_9$-fluorene ring), 43.42, 40.65, 31.81, 31.65, 30.12, 29.25, 29.08, 27.04, 23.92, 22.61, 14.03 (aliphatic). Anal. Calcd for $(C_{29}H_{40})_{50}(C_{18}H_{19}N)_{49.5}(C_{56}H_{47}N_3F_3O_2Ir)_{0.5}$: C, 88.16; H, 9.19; N, 2.21. Found: C, 87.56; H, 9.40; N, 1.75.

PFCzIrPhq1. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**12**) (0.50 mmol), 3,6-dibromo-9-hexanecarbazole (**9**) (0.49 mmol), and 3,6-dibromo-9-(iridium(III)bis(2-phenylquinoline-N,C$^{2'}$))-14-trifluoro-11,13-tetradecyldiketone)carbazole **(8c)** (0.01 mmol) were used in this polymerization. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.52 (s, 2H), 7.87 (t, 2H), 7.79 (m, 2H) (fluorene ring), 7.75 (d, 2H), 7.55 (t, 2H), 7.25 (s, 2H) (carbazole ring), 4.41 (s, 2H, N−CH$_2$), 2.17 (t, 2H), 1.97 (t, 4H), 1.48−1.14 (m, 20H), 0.93−0.77 (m, 16H) (aliphatic). ^{13}C NMR (CDCl$_3$) δ (ppm): 151.72, 140.87, 140.43, 139.58, 133.12, 126.18, 125.56, 123.66, 121.71, 119.91, 118.97, 109.06 (fluorene and carbazole ring), 55.37 (C$_9$-fluorene ring), 43.41, 40.66, 31.82, 31.66, 30.13, 29.26, 29.08, 27.04, 23.93, 22.61, 14.04 (aliphatic). Anal. Calcd for $(C_{29}H_{40})_{50}(C_{18}H_{19}N)_{49}(C_{56}H_{47}N_3F_3O_2Ir)_1$: C, 87.78; H, 9.12; N, 2.23. Found: C, 87.20; H, 9.24; N, 1.69.

PFCzIrPhq2. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**12**) (0.50 mmol), 3,6-dibromo-9-hexanecarbazole (**9**) (0.48 mmol), and 3,6-dibromo-9-(iridium(III)bis(2-phenylquinoline-N,C$^{2'}$))-14-trifluoro-11,13-tetradecyldiketone)carbazole **(8c)** (0.02 mmol) were used in this polymerization. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.85 (s, 2H), 7.87 (d, 2H), 7.79 (d, 2H) (fluorene ring), 7.75 (d, 2H), 7.56 (d, 2H), 7.26 (s, 2H) (carbazole ring), 4.23 (s, 2H, N−CH$_2$), 2.15 (t, 2H), 1.92 (t, 4H), 1.55−1.14 (m, 20H), 0.93−0.77 (m, 16H) (aliphatic). ^{13}C NMR (CDCl$_3$) δ (ppm): 151.69, 140.82, 140.40, 139.55, 133.09, 126.15, 125.54, 123.63, 121.67, 119.87, 118.95, 109.04 (fluorene and carbazole ring), 55.34 (C$_9$-fluorene ring), 40.62, 31.79, 31.63, 30.10, 29.23, 29.06, 27.02, 23.90, 22.58, 14.01 (aliphatic). Anal. Calcd for $(C_{29}H_{40})_{50}(C_{18}H_{19}N)_{48}(C_{56}H_{47}N_3F_3O_2Ir)_2$: C, 87.07; H, 8.99; N, 2.26. Found: C, 87.28; H, 9.34; N, 1.94.

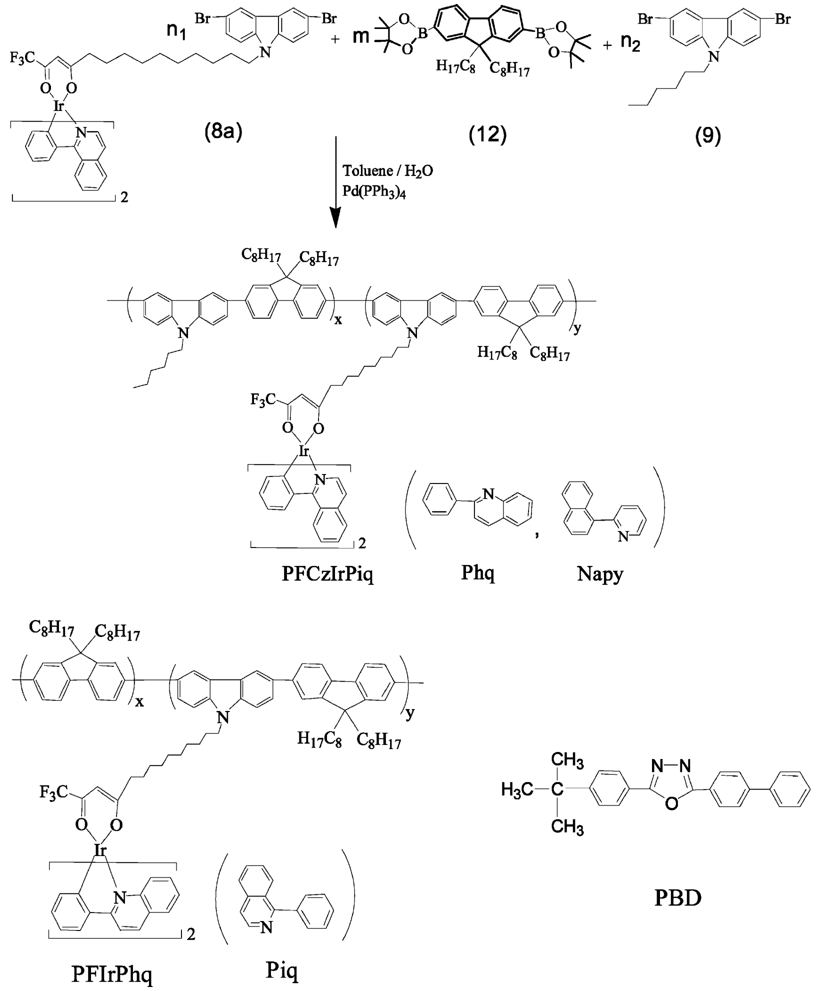
PFCz. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**12**) (0.50 mmol) and 3,6-dibromo-9-hexanecarbazole (**9**) (0.50 mmol) were used in this polymerization. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.52 (s, 2H), 7.84 (d, 2H), 7.79 (d, 2H) (fluorene ring), 7.72 (m, 2H), 7.53 (d, 2H), 7.24 (m, 2H) (carbazole ring), 4.38 (s, 2H, N−CH$_2$), 2.13 (d, 2H), 1.95 (t, 4H), 1.52−0.74 (m, 24 H) (aliphatic). ^{13}C NMR (CDCl$_3$) δ (ppm): 151.69, 140.83, 140.40, 139.55, 133.09, 126.14, 123.63, 121.66, 119.87, 118.93, 109.04 (fluorene and carbazole ring), 56.94 (N$_9$-carbazole ring), 55.34 (C$_9$-fluorene ring), 40.62, 31.78, 31.62, 30.11, 29.23, 29.05, 27.02, 23.89, 22.57, 14.01 (aliphatic). Anal. Calcd for $(C_{29}H_{40})_{50}(C_{18}H_{19}N)_{50}$: C, 88.54; H, 9.26; N, 2.19; Found: C, 88.03; H, 9.33; N, 1.88.

PFO. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**12**) (0.50 mmol) and 2,7-dibromo-9,9-dioctylfluorene **(11)** (0.50 mmol) were used in this polymerization. ^{1}H NMR (CDCl$_3$) δ (ppm): 7.85 (d, 2H), 7.78 (s, 2H), 7.73 (d, 2H) (fluorene ring), 1.95 (m, 4H), 1.22−0.98 (m, 20H), 0.83 (t, 6H), 0.55 (m, 4H) (aliphatic). ^{13}C NMR (CDCl$_3$) δ (ppm): 150.92, 144.52, 134.16, 129.31, 121.17, 119.84 (fluorene ring), 55.58 (C$_9$-fluorene ring), 40.42, 32.11, 30.27, 29.47, 25.24, 23.87, 22.86, 14.53 (aliphatic). Anal. Calcd for $C_{29}H_{40}$: C, 89.69; H, 10.31. Found: C, 88.78; H, 9.63.

PFIrPiq05. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctyl-fluorene (**12**) (642 mg, 1.0 mmol), 3,6-dibromo-9-(iridium(III) bis(1-phenylisoquinoline-N,C$^{2'}$))-14-trifluoro-11,13-tetradecyldiketone)carbazole (**8a**) (12 mg, 0.01 mmol), and 2,7-dibromo-9,9-dioctylfluorene (**11**) (543 mg, 0.99 mmol) were used in this polymerization. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.52 (s, 2H), 7.84 (d, 2H), 7.79 (d, 2H) (fluorene ring), 2.13 (d, 2H), 1.95 (t, 4H), 1.52−0.74 (m, 24 H) (aliphatic). ^{13}C NMR (CDCl$_3$) δ (ppm): 151.69, 139.55, 133.09, 126.14, 118.93, 109.04 (fluorene ring), 55.34 (C$_9$-fluorene ring), 31.78, 31.62, 30.11, 29.23, 29.05, 27.02, 23.89, 22.57, 14.01 (aliphatic). Anal. Calcd for $(C_{29}H_{40})_{99.5}(C_{56}H_{47}N_3F_3O_2Ir)_{0.5}$: C, 89.36; H, 10.23. Found: C, 89.03; H, 9.53.

PFIrPhq2. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**12**) (642 mg, 1.0 mmol), 3,6-dibromo-

Scheme 1. Synthetic Route for the Copolymers and Molecular Structures of Different Backbone-Based Copolymers and PBD



9-(iridium(III)bis(2-phenylquinoline-N,C$^{2'}$))-14-trifluoro-11,13-tetradecyldiketone)carbazole (**8c**) (48 mg, 0.04 mmol), and 2,7-dibromo-9,9-dioctylfluorene (**11**) (526 mg, 0.96 mmol) were used in this polymerization. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.53 (s, 2H), 7.83 (d, 2H), 7.81 (d, 2H) (fluorene ring), 2.12 (d, 2H), 1.96 (t, 4H), 1.51−0.73 (m, 24 H) (aliphatic). ^{13}C NMR (CDCl$_3$) δ (ppm): 151.66, 139.51, 133.08, 126.15, 118.93, 109.02 (fluorene ring), 55.32 (C$_9$-fluorene ring), 31.75, 31.62, 30.11, 29.23, 29.05, 27.02, 23.88, 22.53, 14.02 (aliphatic). Anal. Calcd for $(C_{29}H_{40})_{98}(C_{56}H_{47}N_3F_3O_2Ir)_2$: C, 88.34; H: 10.01. Found: C, 88,17; H, 9.45.

Results and Discussion

Synthesis and Characterization of Polymers. The synthetic route of the copolymers is shown in Scheme 1. The monomers with Ir complex monomers were synthesized from 3,6-dibromo-9-(14-trifluoro-11,13-tetradecyldiketone)carbazole **(4)** and the corresponding iridium chloride-bridged dimers. The copolymers from fluorene, carbazole, and iridium complex-attached carbazole units were prepared by Suzuki polycondensation. The feed ratios of Ir complexes in the polycondensation are 0, 0.5, 1, and 2 mol %, and the corresponding polymers are named PFO, PFCz, PFIrPiq05, PFCzIrPiq05, PFCzIrPiq1, PFCzIrPiq2, PFCzIrNapy05, PFCzIrNapy1, PFCzIrNapy2, PFCzIrPhq05, PFCzIrPhq1, PFCzIrPhq2, and PFIrPhq2, respectively.

Table 1. Structural Properties of the Copolymers

			DOF/Cz/CzIr (molar ratio)	
copolymers	M_w ($\times 10^3$)	PDI	comonomer in feed ratio	composition in copolymer[a]
PFO	51.3	2.0		
PFCz	12.5	1.9	50:50	56.5:43.5
PFCzIrPiq05	11.5	2.1	50:49.5:0.5	50:49.6:0.4
PFCzIrPiq1	5.1	1.7	50:49:1	50:49.2:0.8
PFCzIrPiq2	13.2	2.1	50:48:2	50:48.8:1.2
PFCzIrNapy05	12.4	2.1	50:49.5:0.5	50:49.8:0.2
PFCzIrNapy1	7.1	1.8	50:49:1	50:49.6:0.4
PFCzIrNapy2	11.8	2.1	50:48:2	50:48.7:1.3
PFCzIrPhq05	12.3	2.1	50:49.5:0.5	50:49.8:0.2
PFCzIrPhq1	14.1	2.0	50:49:1	50:49.3:0.7
PFCzIrPhq2	18.8	2.2	50:48:2	50:48.7:1.3
PFIrPiq05	16.7	2.1	99.5:0:0.5	99.6:0:0.4
PFIrPhq2	16.5	1.9	98:0:2	98.8:0:1.2

[a] Calculated from the nitrogen and iridium content in copolymers.

The iridium content in the copolymers was approximately estimated by using of the sequential X-ray fluorescence spectrometry (XRF). Therefore, the molar ratios of Ir complexes in the copolymers were calculated by combining elemental analysis with XRF data. Actual compositions of the copolymers and the feed ratios of the comonomers are listed in Table 1. The results indicate that actual Ir complex content in the copolymer is substantially lower than that of the feed ratio of the monomers. The weight-average molecular weights of these copolymers are from 5100 to 18 000 with a polydispersity index (PDI) from 1.7 to 2.2, which is consistent with a polycondensation reaction.

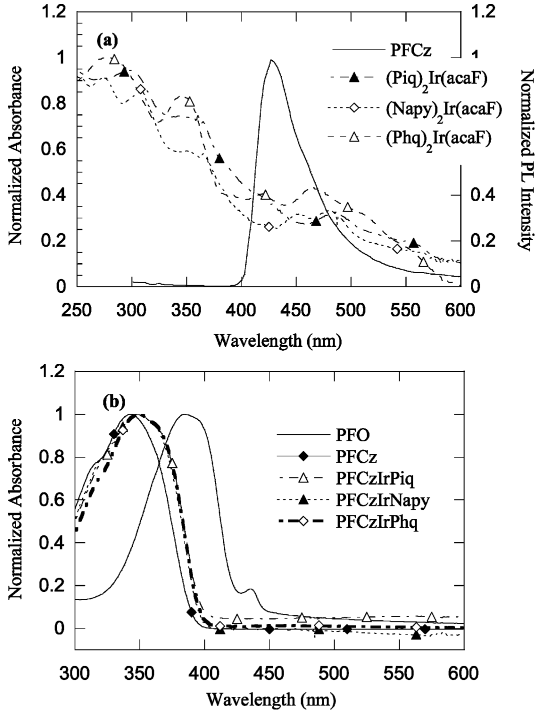


Figure 1. (a) UV–vis absorption spectra of Ir complexes and PL spectrum of PFCz in film. (b) UV–vis absorption spectra of PFO, PFCz, and copolymers in film.

Optical and Electrochemical Properties. Figure 1a shows the UV–vis absorption spectra of the Ir complexes [(Piq)$_2$Ir(acaF), (Napy)$_2$Ir(acaF), and (Phq)$_2$Ir(acaF)] and the PL spectrum of fluorene-*alt*-carbazole copolymer (PFCz). The Ir complexes have similar absorption spectra with broad bands from 270 to 490 nm. The intense absorption peaks below 350 nm are attributed to the spin-allowed singlet state $^1\pi-\pi^*$ transition of cyclometalated ligands, and the weak absorption peaks around 420 nm can be assigned to the spin-allowed singlet metal-to-ligand charge-transfer (^{1}MLCT) transition.[15] The strong absorption peaks of 465 nm for (Phq)$_2$Ir(acaF), 478 nm for (Napy)$_2$Ir(acaF), and 488 nm for (Piq)$_2$Ir(acaF) are due to the triplet metal-to-ligand charge-transfer (^{3}MLCT) transition.[16] The spin-forbidden ^{3}MLCT transition is gained by mixing it with the higher spin-allowed ^{1}MLCT transition through the strong spin–orbit coupling of iridium. Figure 1a indicates that the PL emission spectrum of the host polymer (PFCz) and the absorption spectra of the guests (Ir complexes) show good spectra overlap. Therefore, the efficient Förster energy transfer from the PFCz host to the Ir complex guests can be expected. Figure 1b shows the absorption spectra of the electrophosphorescent copolymers and that of the host polymers (PFO and PFCz). The absorption spectrum of PFCz shows a blue shift of 40 nm compared to that of PFO. This is due to the interruption of delocalization of the π-electrons along the polymer backbone by the 3,6-carbazole linkages.[10b] These absorption spectra show no essential differences among these complex copolymers with low Ir complex contents. The absorption of the complex copolymers red shifts around 10 nm in comparison with that of the host copolymer (PFCz). From the onset of the absorption peaks, the optical band gap of the complex copolymers was estimated at 3.12 eV, which is a little less than that of the host copolymer (3.14 eV) (Table 2).

The electrochemical behavior of the Ir complexes and the polymers was investigated by cyclic voltammetry (CV) in the solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) in acetonitrile (CH$_3$CN). The CV curves were referenced to an Ag quasi-reference electrode, which was calibrated using the ferrocene/ferrocenium redox couple (0.35 V vs Ag/AgCl) as an internal standard prior to measurements. The photophysical and electrochemical properties of the Ir complexes and the redox potentials of the copolymers derived from the onset in the cyclic voltammetry are summarized in Table 2. The onset of oxidation potentials of PFO and PFCz is observed respectively at 1.38 and 1.07 V. The HOMO and LUMO levels of polymers can be estimated using the equations $E_{\mathrm{HOMO}} = -e(E_{\mathrm{ox}} + 4.38)$ (eV) and $E_{\mathrm{LUMO}} = -e(E_{\mathrm{red}} + 4.38)$ (eV).[17a] Therefore, the HOMO levels of PFO and PFCz are respectively estimated at −5.76 and −5.45 eV. The results show that the introduction of a carbazole unit into the polyfluorene main chain leads to the rise in HOMO, which implies a much lower barrier for the hole injection. The onset of oxidation potential of the carbazole-based copolymers with Ir complexes is almost constant at about 1.1 V against Ag/AgCl reference electrode, which is consistent with that of the PFCz. This peak is attributed to p-doping of the fluorene-*alt*-carbazloe backbone. HOMO and LUMO levels are respectively estimated at −5.5 and −2.2 eV (Table 2). That the cabarzole-based copolymers have an irreversible n-doping process indicates that the electron-charged (n-doped) state of these polymers is unstable. The similar behavior has been reported for the polymer with the same backbone of P(F-*alt*-Cz).[17] Unfortunately, the redox peaks failed to be recorded corresponding to the Ir complex in all of the copolymers, obviously due to the low Ir complex content. The oxidation potentials for the Ir complexes (Piq)$_2$Ir(acaF), (Napy)$_2$Ir(acaF), and (Phq)$_2$Ir(acaF) were observed respectively at 0.85, 0.90, and 0.95 V (Table 2). Suppose there are no great changes in the HOMO level of the Ir complexes grafted into host polymer chains; the HOMO level of the Ir complexes must fall within the band gap of the host polymer. Therefore, the grafted Ir complexes will function as both a hole and an electron trap.[18]

The photoluminescent (PL) spectra of the copolymers are shown in Figure 2. All of the copolymers emit light of $\lambda_{\max} = 580-610$ nm. Slight emission differences in these copolymers are related to the nature of the ligands. In Figure 2, the intense emission peaked at about 420 nm from host unit can be observed for those copolymers with low Ir complex content of 0.5 mol %. This indicates that the energy transfer from main chain to the Ir complex connected on the alkyl side chain is incomplete because the average distance from a photoexcited polymer chain to the nearest Ir complex is too large.[19] The relative intensities at the peak of 420 nm vary with the Ir complex contents in the copolymers. With the increase of Ir complex content in copolymers, the emission intensity of 420 nm from the main chain descends. The emission of PFCz segments in copolymers almost quenched completely for the copolymers with the Ir complex content of 2 mol %, which indicates that energy transfer from the main chain to the Ir complex becomes complete. The PL efficiencies and the maximum emission wavelength of the copolymers are listed in Table 2. The PL efficiencies of PFCzIrPiq and PFCzIrPhq copolymers are as high as 60–70%, much higher than that of the host polymers (PFCz), which should be owed to the full energy transfer from the PFCz segments to the Ir complexes in the copolymers. How-

Table 2. Optical and Electrochemical Properties of Polymers and Ir Complexes

copolymers	λ_{max} abs [nm]	E_g[a] (eV)	E_{ox} (V)	E_{red} (V)	HOMO (eV)	LUMO (eV)	photoluminescence λ_{PL} (nm)	photoluminescence Q_{PL} (%)
PFO	385	2.85	1.38	−2.16	−5.76	−2.22	435	45
PFCz	345	3.14	1.07	−2.11	−5.45	−2.27	420	42
PFCzIrPiq05	350	3.12	1.11	−2.12	−5.49	−2.26	420, 610	56
PFCzIrPiq1	350	3.12	1.14	−2.15	−5.52	−2.23	610	58
PFCzIrPiq2	350	3.12	1.09	−2.07	−5.47	−2.31	610	61
PFCzIrNapy05	350	3.12	1.08	−2.14	−5.46	−2.24	415, 595	29
PFCzIrNapy1	350	3.12	1.11	−2.12	−5.49	−2.26	415, 595	21
PFCzIrNapy2	350	3.12	1.09	−2.10	−5.47	−2.28	415, 595	20
PFCzIrPhq05	350	3.12	1.15	−2.18	−5.53	−2.20	420, 580	65
PFCzIrPhq1	350	3.12	1.08	−2.13	−5.46	−2.25	580	74
PFCzIrPhq2	350	3.12	1.15	−2.10	−5.53	−2.28	580	75
PFIrPiq05	385	2.88	1.36	−2.17	−5.74	−2.21	435, 610	60
PFIrPhq2	350	3.12	1.37	−2.18	−5.75	−2.20	580	62
$(Piq)_2Ir(acaF)$[b]	303, 358, 488		0.85		−5.23		610	
$(Napy)_2Ir(acaF)$[b]	300, 356, 478		0.90		−5.28		595	
$(Phq)_2Ir(acaF)$[b]	280, 350, 465		0.95		−5.33		580	

[a] Estimated from the onset of absorption edge responsible for copolymers. [b] Data in CH_2Cl_2 solution (10^{-5} mol/L) of 0.1 mol/L n-Bu_4NPF_6.

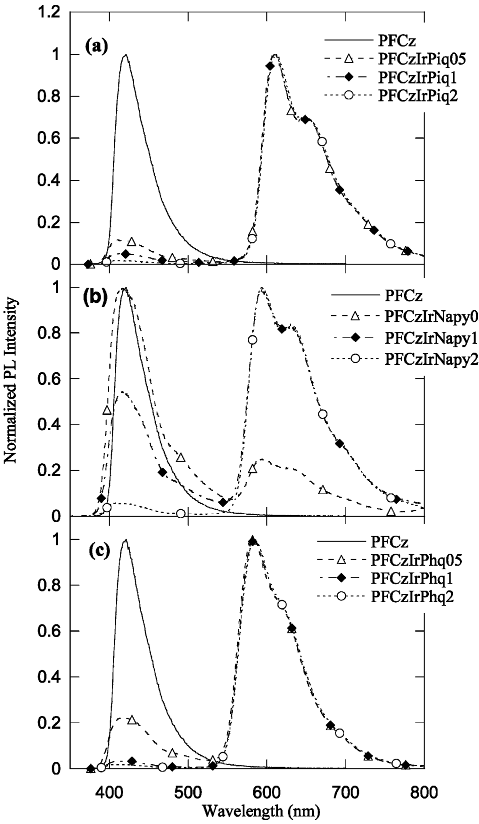


Figure 2. PL spectra of copolymers in film for PFCzIrPiq (a), PFCzIrNapy (b), and PFCzIrPhq (c).

ever, PFCzIrNapy shows much lower PL efficiency (20%) than that of the other two copolymers, which should be owed to the incomplete energy transfer (Figure 2b).

Device Performances. The devices were fabricated in the configuration below. ITO/PEDOT/copolymer + PBD (30 wt %)/Ba/Al. PBD was blended with copolymers to improve the electron-transporting capability of the copolymers.[20] The EL spectra of the copolymers are shown in Figure 3. In the case of PFCzIrPiq and PFCzIrPhq, EL emission from the backbone of the copolymers completely quenches even though the Ir complex content is as low as 0.5 mol % in the feed ratio. There is only one emission peak at 610 nm for PFCzIrPiq and 580 nm for PFCzIrPhq due to the corresponding Ir complex emission. This indicates that there occurs the efficient energy transfer from the host to the guest. Like the case of PL emission, PFCzIrNapy shows less efficient energy transfer. The PFCzIrNapy05 copolymer shows clearly the emission peaked at 420 nm from the main chain, which completely quenches at the Ir complex content of 2 mol % in the feed ratio. The substantial difference of energy transfer efficiencies between the PL and EL for the copolymers implies that different mechanisms are involved.[19] Under photoexcitation, the singlet excited states are created on the main chain and subsequently transfer to the metal−organic complex by Förster energy transfer. In contrast, the electrons and holes are trapped on the Ir complex after

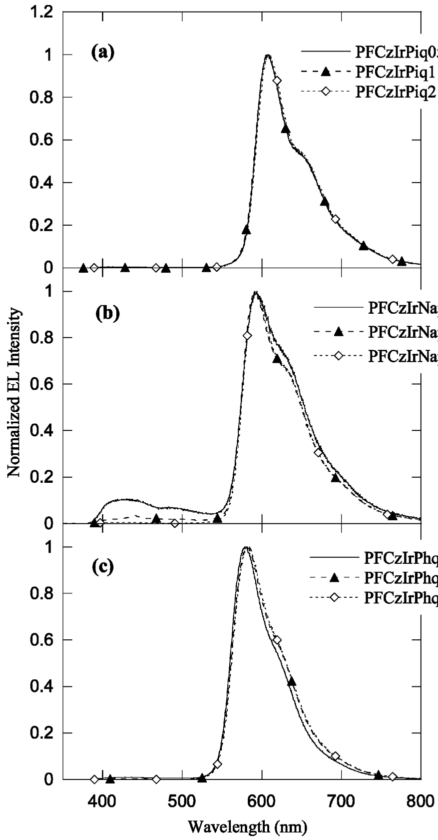


Figure 3. EL spectra of copolymers for PFCzIrPiq (a), PFCzIrNapy (b), and PFCzIrPhq (c). Device structure: ITO/PEDOT/copolymer + PBD(30 wt %)/Ba/Al.

Table 3. Device Performances of the Copolymers[a]

	maximal QE_{ext}[b]					$J = 100$ mA/cm^2 [c]			
copolymers	bias (V)	J (mA/cm^2)	L (cd/m^2)	QE_{ext} (%)	LE (cd/A)	bias (V)	L (cd/m^2)	QE_{ext} (%)	LE (cd/A)
PFCzIrPiq05	7.7	5.9	240	4.9	4.0	10.7	2978	3.4	2.9
PFCzIrPiq1	8.0	6.1	127	2.4	2.1	12.1	1089	1.3	1.1
PFCzIrPiq2	9.5	21.8	228	1.5	1.2	11.0	826	1.2	0.8
PFCzIrNapy05	6.0	11.8	55	0.4	0.5	7.5	352	0.2	0.3
PFCzIrNapy1	7.5	35.8	325	0.6	0.9	8.2	854	0.5	0.7
PFCzIrNapy2	5.2	3.5	53	1.1	1.6	7.1	912	0.6	1.0
PFCzIrPhq05	6.5	6.1	108	1.1	1.5	8.0	1053	0.5	1.1
PFCzIrPhq1	5.7	1.5	55	1.7	2.3	8.2	1492	0.7	1.5
PFCzIrPhq2	8.0	10.6	448	2.7	3.1	10.1	2546	1.3	2.5

[a] Device structure: ITO/PEDOT/copolymer + PBD(30 wt %)/Ba/Al. [b] Device performances at the maximal external quantum efficiency. [c] Device performances when the current density is 100 mA/cm^2.

Table 4. Device Performances of Different Backbone-Based Copolymers

					efficiency	
copolymers	$\lambda_{EL\ max}$ (nm)	bias (V)	J (mA/cm^2)	L (cd/m^2)	QE_{ext} (%)	LE (cd/A)
PFCzIrPiq05[a]	610	7.1	5.3	80	2.3	1.9
PFCzIrPiq05: PBD[b]	610	7.7	5.9	240	4.9	4.0
PFIrPiq05[a]	610	5.4	6.3	44	0.7	0.6
PFIrPiq05: PBD[b]	610	4.7	5.9	62	1.5	1.3
PFCzIrPhq2[a]	580	7.2	5.4	234	1.2	1.4
PFCzIrPhq2: PBD[b]	580	8.0	10.6	448	2.8	3.1
PFIrPhq2[a]	580	6.5	4.5	112	0.4	0.5
PFIrPhq2: PBD[b]	580	6.7	7.4	126	1.1	1.2

[a] Device structure: ITO/ PEDOT/copolymer/Ba/Al. [b] Device structure: ITO/ PEDOT/copolymer + PBD(30 wt %)/Ba/Al.

the injection of the electrons from the cathode and the holes from the opposite anode in the device.[3,19]

The device performances of the copolymers are listed in Table 3. Like other phosphorescent PLEDs,[4a,21,22] the device performance shows a strong dependence on the Ir complex content. The best device performance is observed for PFCzIrPiq05 with Ir complex content of 0.5 mol % in the feed ratio, which is much lower than that of the same Ir complex doped system.[5] A maximum external quantum efficiency of 4.9% ph/el and a luminous efficiency of 4.0 cd/A with a luminance of 240 cd/m^2 are achieved at a current density of 5.9 mA/cm^2. The efficiency of this device remains as high as $QE_{ext} = 3.4\%$ pl/el and LE = 2.9 cd/A with a luminance of 2978 cd/m^2 at a current density of 100 mA/cm^2 (Table 3). The device of PFCzIrPhq2 shows $QE_{ext} = 2.7\%$ ph/el and LE = 3.1 cd/A with a luminance of 448 cd/m^2 at the current density of 10.6 mA/cm^2. At the current density of 100 mA/cm^2, the efficiency of this device still remained $QE_{ext} = 1.3\%$ pl/el and LE = 2.5 cd/A with a luminance of 2546 cd/m^2. The device based on PFCzIrNapy2 shows much lower external quantum efficiencies of 1.1% with luminous efficiencies of 1.6 cd/A.

The fluorene-based copolymer PFIrPiq05 and PFIrPhq2 were synthesized for comparison. The molecular structures are shown in Scheme 1. Table 4 shows that the quantum efficiencies of the devices with PBD are higher than those of the device without PBD. It is a fact that the buildup of space-charge due to trapping of holes on the Ir complex is largely inhibited by supplying a large number of electrons via efficient injection and transport from blended with PBD.[18] The device performances of the carbazole-based copolymers PFCzIrPiq05 and PFCzIrPhq2 are superior to those of the fluorene-based copolymer PFIrPiq05 and PFIrPhq2. This indicates that carbazole unit in the backbone is necessary due to the raised HOMO level of the copolymer making the hole injection easier and having a higher triplet level than phosphorscent guest to prevent triplet energy transfer from the guest to the host by the introduction of carbazole unit at the 3,6-linkage into polyfluorene main chain.[10] Therefore, the device performances were improved.

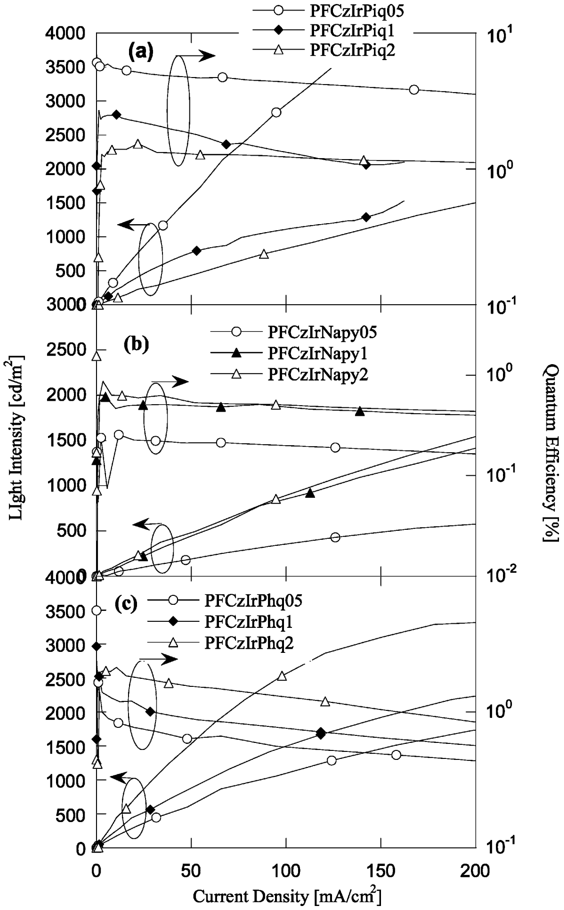


Figure 4. Luminance and external quantum efficiency vs current density for PFCzIrPiq (a), PFCzIrNapy (b), and PFCzIrPhq (c). Device structure: ITO/PEDOT/copolymer + PBD(30 wt %)/Ba/Al.

Figure 4 shows the luminance and the external quantum efficiency of the devices as a function of current density for PFCzIrPiq, PFCzIrNapy, and PFCzIrPhq copolymers with different Ir complex content in the polymers. Unlike other electrophosphorescent PLEDs, the external quantum efficiencies of phosphorescent grafting copolymers show a gentle decay with the increasing in current density due to the depressing triplet−triplet annihilation of the copolymers.[21,22] That less decay in the device performances with the increase in current density than that in devices with Ir complex blended into polymer host indicates that grafting of phosphorescent complexes into host copolymer backbone could inhibit the concentration quenching at the high current density due to the complex aggregation.[21]

Conclusion

The high-efficiency electrophosphorescent copolymers were synthesized based on carbazole-*alt*-fluorene as a main chain and Ir complex as a side group. The efficient energy transfer from the main chain to the Ir complex connected on the side chain of the polymers was observed. EL emission from the main chain is completely quenched even at Ir complex content as low as 0.5 mol % for PFCzIrPiq and PFCzIrPhq copolymers. The device of PFCzIrPiq05 copolymer shows the highest external quantum efficiency of 4.9% ph/el and the luminous efficiency of 4.0 cd/A with 240 cd/m^2 at a bias voltage of 7.7 V and peak emission at 610 nm. The device of PFCzIrPhq2 shows $QE_{ext} = 2.7\%$ ph/el and LE = 3.1 cd/A with the luminance of 448 cd/m^2 at a current density of 10.6 mA/cm^2. The device efficiency of PFCzIrPiq05 copolymer remains high ($QE_{ext} = 3.4\%$ ph/el and LE = 2.9 cd/A) at the current density of 100 mA/cm^2. The enhancement of the device performance could be due to the higher triplet energy and meanwhile to suitable HOMO and LUMO levels for efficient charge injection by introducing the carbazole unit into polyfluorene backbone at the 3,6-linkage and blending PBD into the copolymers.

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Supporting Information Available: ^{1}H NMR spectra of monomers (**4**, **8a**−**8c**) and representative polymers, cyclic voltammetry (CV) curves, and X-ray fluorescence (XRF) spectra of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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