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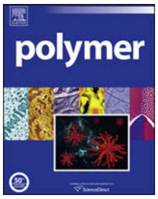

Novel white-light-emitting polyfluorenes with benzothiadiazole and Ir complex on the backbone

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ABSTRACT

Novel white-emitting polyfluorenes were synthesized by mixing fluorescence and phosphorescence emission. Benzothiadiazole(BT) and iridium(III)bis(2-(1-naphthalene)pyridine-$C^{2'}$,*N*)-2,2,6,6-tetramethyl-3,5-heptanedione[$(1\text{-npy})_2$Ir(tmd)] units were incorporated into polyfluorene backbone as green and red chromophores by Suzuki polycondensation. The device from PFG03–IrR07 shows a maximum luminous efficiency (LE) of 5.3 cd/A, a maximum luminance of 9900 cd/m^2 at a current density of 453 mA/cm^2 and a CIE coordinate of (0.32, 0.34) with the configuration: ITO/PEDOT:PSS/PVK/emissive layer/CsF/Al. Besides, the EL efficiencies decline slightly with increasing the current density. All emissions located very close to the equi-energy white point (0.33, 0.33) when applied voltage change from 9 to 14 V. Furthermore, the white emission of devices based on these materials shows very good color quality, with high color rendering index range between 84 and 89. Our results indicate that, by incorporation of singlet and triplet species into polymer backbone, the obtained white-emitting materials and devices are promising candidates for display and solid-state-lighting purpose.

1. Introduction

White polymer light-emitting diodes (WPLEDs) have a great advantage of easy fabrication and processing, because it can be fabricated with wet-processes including spin coating, screen printing, and ink-jet printing techniques which are expected to be low cost in mass production [1]. Various approaches have been developed to fabricate WPLEDs. Light-emitting layers with broad emission spectra can be sought in a polymer doped with various dyes [2], blending polymers with different emissions [3], or a single polymer with broad emission [4]. A single polymer used as an active layer in WPLEDs has the advantages of avoiding phase separation and stable of electroluminescent (EL) spectra upon varying applied voltages [4a,b]. In early years, white-light-emitting polymer with long wavelength emission coming from aggregated states and excimer was reported by Tsai et al. [4c] and Chen et al. [4d]. Wang et al. [4a,b,e,f,g] presented a series of high efficient WPLEDs based on a single polymer with the fluorescent dyes in the conjugated polymer backbone or side chain.

Recently, a new strategy was developed to realize white emission from a single conjugated polymer in which fluorescence- and phosphorescence-emitting species are incorporated. Furuta et al. [5] reported a near-white-emitting polymer with phosphorescent Pt functionalities. Jiang et al. [6], Wang et al. [7] and Wu et al. [8] introduced iridium complexes into the side chain of conjugated polymers, while Zhen et al. [9] and Kappaun et al. [10] introduced the iridium complex into the polymer backbone. Though the efficiencies of these WPLEDs would be theoretically enhanced by introducing phosphorescence-emitting species into polymer, however, the efficiency was not high enough when compared with the devices fabricated using vacuum deposition technologies.

Previously, we introduced bicycloiridium complex iridium(III)-bis(2-(2′-benzo[4,5-*a*]-thienyl)pyridinato-N,$C^{3'}$)-2,2,6,6-tetramethyl-3,5-heptanedioe [$(\text{btp})_2$Ir(tmd)] into the polyfluorene(PFO) backbone and found that [$(\text{btp})_2$Ir(tmd)] peaked at 660 nm is too red for white-light-emitting polymers [9]. In this paper, phosphorescent-emitting species iridium(III)bis(2-(-naphthalene)pyridine-$C^{2'}$,*N*)-2,2,6,6-tetramethyl-3,5-heptanedione [$(1\text{-npy})_2$Ir(tmd)] peaked at 625 nm and 2,1,3-benzothiadiazole (BT) units were introduced into PFO backbone. By adjusting the monomer feed ratios, the white emission from three individual emission species in a single polymer was realized.

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2. Experimental section

2.1. Characterization

^{1}H NMR spectra were recorded on a Bruker DRX 400 spectrometer operating respectively at 400 or 300 MHz, in deuterated chloroform solution with tetramethylsilane as a reference. The molecular weight of the polymers was determined by Waters GPC 2410 in tetrahydrofuran (THF). Number–average (M_n) and weight–average (M_w) molecular weights were estimated by using a calibration curve of polystyrene standards. Elemental analyses were performed on Vario EL Elemental Analysis Instrument (Elementar Co.). Thermogravimetric analysis (TGA) measurements were performed on Netzsch TG 209 under N_2 at a heating rate of 20 °C/min. Differential scanning calorimetric (DSC) measurements were performed on Netzsch DSC204 under N_2 at a heating rate of 10 °C/min.

Cyclic voltammetry (CV) was recorded on a computer-controlled CHI660A electrochemical workstation. The thin polymer film was coated on a platinum electrode as a working electrode at a scan rate of 50 mV/s against calomel reference electrode in a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN). Cyclic voltammetry of model compound DFBT was carried out in the fresh dichloromethane solution. HOMO and LUMO levels were calculated according to an empirical formula ($E_{HOMO} = -e(E_{ox} + 4.4)$ (eV) and $E_{LUMO} = -e(E_{red} + 4.4)$ (eV)) with the ferrocene oxidation potential as the standard for the vacuum energy level [11].

Photoluminescence (PL) spectra of the copolymers in thin film on quartz substrate were recorded on an Instaspec IV CCD spectrophotometer (Oriel Co.) under 325 nm excitation of a HeCd laser. The quantum yields were measured using an Integrating Sphere IS080 (LabSphere) to collect the emitted light in all directions under the excitation of 325 nm line of a HeCd laser (Melles Griot). The thicknesses of the solid films, typically, were 100–200 nm. Phosphorescence spectrum of the iridium complex was determined at 77 K by Edinburgh FLSP920 Combined Fluorescence Lifetime and Steady State Spectrometer.

2.2. LED fabrication and measurement

Polymers were dissolved in *p*-xylene and filtered with a 0.45 μm PTFE syringe filter. Patterned ITO coated glass substrates were cleaned with acetone, detergent, distilled water, and 2-propanol, subsequently in an ultrasonic bath. After treatment with oxygen plasma, 50 nm of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) (Batron-P 4083, Bayer AG) and a layer of poly(vinylcarbazole) (PVK, Aldrich) from 1,1,2,2,-tetrachloroethane solution were spin-coated onto the ITO substrate followed by drying in a vacuum oven at 80 °C for 8 h. A thin film of polymers was cast away onto the cleaned substrate by spin-casting in a glove box. The film thickness of the active layers was determined as 70–80 nm, measured by an Alfa Step 500 surface profiler (Tencor). After spin coating, the films were baked on a hot plate at 80 °C in inert atmosphere for half an hour to remove solvent residue. A thin layer of CsF (1 nm) and subsequent 200 nm layer of Al were thermally evaporated subsequently on the top of an EL polymer layer with a base pressure of 3×10^{-4} Pa. Current–voltage (*I*–*V*) characteristics were recorded with a Keithley 236 source-measurement unit. EL spectra were obtained by Oriel Instaspec IV CCD spectrograph. Luminance was measured by a PR 705 photometer (Photo Research). The external quantum efficiencies were determined by an Si photodiode with calibration in an integrating sphere (IS080, Labsphere).

2.3. Materials

All manipulations involving air-sensitive reagents were performed in the atmosphere of dry argon. The solvents (THF, toluene) were purified by routine procedure and distilled under dry argon before being used. All reagents, unless otherwise specified, were obtained from Aldrich, Chemical Co. and used as received. 2,7-Dibromo-9,9-dioctylfluorene (**1**), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**2**), and 4,7-dibromo-2,1,3-benzothiadiazole($BTBr_2$) (**3**) were synthesized according to the published procedures [12].

2.3.1. 5-Bromo-2-(1-naphthalene)pyridine

5-Bromo-2-(1-naphthalene)pyridine was synthesized according to the procedure as follows. 2,5-Dibromopyridine (2.37 g, 10 mmol), 1-naphthaleneboronic acid (1.72 g, 10 mmol), and tetrakis-(triphenylphosphine)palladium (0.107 g, 0.1 mmol) were dissolved in toluene (15 mL) and ethanol (5 mL). Then an aqueous solution of 2 M Na_2CO_3 (6 mL) was added to the mixture. The result mixture was allowed to stir at 100 °C for 24 h. The reaction mixture was concentrated by evaporation of solvents, and the residue was dissolved in dichloromethane, washed with water, and dried under anhydrous sodium carbonate. After the evaporation of solvent, the obtained product was purified by column chromatography (silica gel, dichloromethane/hexane = 1:4) (yield: 70%). (*m*/*z*) 284. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.86 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 8.00 (d, *J* = 2.9 Hz, 1H), 7.96 (d, *J* = 3.2 Hz, 1H), 7.92 (d, *J* = 3.2 Hz, 1H), 7.62 (d, *J* = 2.6 Hz, 1H), 7.60 (d, *J* = 2.8 Hz, 1H), 7.50 (t, *J* = 6.0 Hz, 1H), 7.49 (t, *J* = 6.0 Hz, 1H), 7.47 (t, *J* = 6.0 Hz, 1H). Element Anal. Calcd for $C_{15}H_{10}BrN$ (%): C, 63.38; H, 3.52; N, 4.93. Found (%): C, 63.30; H, 3.45; N, 4.98.

2.3.2. Iridium(III)bis(5-bromo-2-(1-naphthalene)pyridine-$C^{2'}N$)-2,2,6,6-tetramethyl-3,5-heptanedione [$(1\text{-npyBr})_2\text{Ir(tmd)}$] (*4*)

Iridium(III)bis(5-bromo-2-(1-naphthalene)pyridine-$C^{2'}N$)-2,2,6,6-tetramethyl-3,5-heptanedione [$(1\text{-npyBr})_2\text{Ir(tmd)}$] (**4**) was prepared according to the published procedures [13]. Iridium trichloride hydrate (178 mg, 0.56 mmol), 5-bromo-2-(1-naphthalene)pyridine (477 mg,1.68 mmol), 2-ethoxyethanol (15 mL), and water (5 mL) were added into a three-necked flask (100 mL). The mixture was refluxed under an argon atmosphere for 24 h and then cooled to room temperature. A red precipitate was filtered and washed with water and ethanol several times. The resulted red solid was purified by recrystallization in mixture of CH_2Cl_2 and hexane. Then the dried product (476 mg, 0.078 mmol) was mixed with 2,2,6,6-tetramethyl-3,5-heptanedione (40.5 mg, 0.22 mmol) and sodium carbonate (13 mg) in degassed 2-ethoxyethanol (8 mL) in a three-necked flask. The mixture was refluxed in an argon atmosphere for 13 h. After cooling to room temperature the red precipitate was formed. After being filtered and washed with water and methanol, the precipitate was purified by column chromatography (silica gel, dichloromethane) to get the red needle crystal product (yield: 75%). M-M(tmd), $IrL_2+ = 759.2$. ^{1}H NMR (400 MHz; $CDCl_3$) δ (ppm): 8.53 (s, 2H), 8.44 (d, *J* = 8.6 Hz, 2H), 8.37 (d, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 7.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.0 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.52 (d, *J* = 8.3 Hz, 2H), 5.56 (s, 1H), 0.91 (s, 18H). Element Anal. Calcd for $C_{41}H_{37}Br_2IrN_2O_2$ (%): C, 52.30; H, 3.93; N, 2.98. Found (%): C, 52.12; H, 3.79; N, 3.07.

2.3.3. 2-(1-Naphthalene)pyridine

2-(1-Naphthalene)pyridine was synthesized according to the procedure as follows. 2-Bromopyridine (1.58 g, 10 mmol), 1-naphthaleneboronic acid (1.72 g, 10 mmol), and tetrakis-(triphenylphosphine)palladium (0.107 g, 0.1 mmol) were dissolved in toluene

(15 mL) and ethanol (5 mL). Then an aqueous solution of 2 M Na_2CO_3 (6 mL) was added to the mixture. The resulting mixture was allowed to stir at 100 °C for 24 h. The reaction mixture was concentrated by evaporation of solvents, and the residue was dissolved in dichloromethane, washed with water, and dried under anhydrous sodium carbonate. After the evaporation of solvent, the obtained product was purified by column chromatography (silica gel, dichloromethane/hexane = 1:3) (yield: 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.81 (d, $J = 2.8$ Hz, 1H), 8.12–8.07 (m, 1H), 7.95 (d, $J = 10.0$ Hz, 2H), 7.82 (td, $J = 7.7$, 1.8 Hz, 1H), 7.63–7.45 (m, 5H), 7.35–7.31 (m, 1H).

2.3.4. *Iridium(III)bis(2-(1-naphthalene)pyridine-C$^{2'}$N)-2,2,6,6-tetramethyl-3,5-heptanedione [(1-npy)$_2$Ir(tmd)]*

Iridium(III)bis(2-(1-naphthalene)pyridine-C$^{2'}$N)-2,2,6,6-tetramethyl-3,5-heptanedione [(1-npy)$_2$Ir(tmd)] was synthesized according to the procedure as follows. Iridium trichloride hydrate (212 mg, 0.6 mmol), 2-(1-naphthalene)pyridine (369 mg,1.8 mmol), 2-ethoxyethanol (15 mL), and water (5 mL) were added into a three-necked flask (100 mL). The mixture was refluxed under an argon atmosphere for 24 h and then cooled to room temperature. An orange precipitate was filtered and washed with water and ethanol several times. The resulted orange solid was purified by recrystallization in mixture of CH_2Cl_2 and hexane. Then the dried product (102 mg, 0.08 mmol) was mixed with 2,2,6,6-tetramethyl-3,5-heptanedione (44.2 mg, 0.24 mmol) and sodium carbonate (13 mg) in degassed 2-ethoxyethanol (8 mL) in a three-necked flask. The mixture was refluxed in an argon atmosphere for 13 h. After cooling to room temperature the red precipitate was formed. After being filtered and washed with water and methanol, the precipitate was purified by column chromatography (silica gel, dichloromethane) to get the orange needle crystal product (yield: 60%). ^{1}H NMR (300 MHz; $CDCl_3$) δ (ppm): 8.56 (d, $J = 8.6$ Hz, 2H), 8.49 (t, $J = 6.5$ Hz, 4H), 7.78 (t, $J = 7.9$ Hz, 2H), 7.65 (d, $J = 7.7$ Hz, 2H), 7.47 (td, $J = 7.0$, 1.3 Hz, 2H), 7.25 (t, $J = 7.1$ Hz, 2H), 7.10–7.04 (m, 4H), 6.56 (d, $J = 8.1$ Hz, 2H), 5.52 (s, 1H), 0.89 (s, 18H).

2.3.5. *4,7-Bis-(9,9-dioctyl-9H-fluoren-2-yl)-benzo[1,2,5]thiadiazole (DFBT)*

Into a flask was introduced 20 mL of toluene and 7 mL ethanol, 1.09 g of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene(2.9 mmol), 294 mg of 4,7-dibromo-benzo[1,2,5]thiadiazole (1.1 mmol) and 4 mL of aqueous 2 M Na_2CO_3. This was N_2 purged for 1 h. 230 mg of tetrakistriphenylphosphine palladium (0) (0.03 mmol) then was added under a nitrogen purge. The content of the flask was refluxed for 2 days. The reaction flask was allowed to cool to RT and about 50 mL water added and the organic layer separated. The aqueous layer was extracted with 50 mL toluene. The organic layers were combined and washed successively with water twice and then dried over $MgSO_4$. Concentration gave an oil which was purified by column chromatography (silica gel, dichloromethane/petroleum ether = 1:9) to give 587 mg (64% yield) green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.04 (d, $J = 7.9$ Hz, 2H), 7.96 (s, 2H), 7.88 (d, $J = 7.7$ Hz, 4H), 7.78 (d, $J = 6.3$ Hz, 2H), 7.35 (m, 6H), 2.01 (m, 8H), 1.10 (m, 48H), 0.81 (t, $J = 5.9$ Hz, 12H).

2.3.6. *General procedure of Suzuki polycondensation taking PFG03–IrR07 as an example*

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**1**) (341 mg, 0.5 mmol), 2,7-dibromo-9,9-dioctylfluorene (**2**) (268 mg, 0.49895 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (**3**) (1 mL, 3×10^{-4} M solution in tetrahydrofuran (THF)), (1-npy-Br)$_2$Ir(tmd) (**4**) (0.75 mL, 1×10^{-3} M solution in THF), and bis(tri-*o*-tolyphosphine) palladium(II) dichloride (5 mg) were dissolved in the mixture of toluene/THF (15 mL), 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 in 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 (50 mg) by continuous stirring for 12 h and then bromobenzene (0.25 mL) followed by continuous reacting 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%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.85 (br, 2H), 7.78 (br s, 2H), 7.72 (br, 2H), 1.96 (m, 4H), 1.21–0.97 (m, 24H), 0.82 (br, 6H). Element Anal. Calcd (%): C, 89.16; H, 10.20; N, 0.071. Found (%): C, 88.53; H, 10.69; N, <0.3.

3. Result and discussion

3.1. *Synthesis and characterization*

Polyfluorene (PFO), an excellent blue-light-emitting polymer, has large band gap and good electronic properties. The emission color of PFO can be tuned in entire visible region by incorporating low band gap units into the backbone or attaching emitters onto the side chain [14]. However, phosphor quenching of the triplet emitter by polyfluorene must be considered when a triplet emitter is introduced into polyfluorene.

It is well known that polyfluorene possesses high singlet energy level (3.2 eV), but its triplet energy level is 2.3 eV [15], which is lower than those of most phosphorescent materials [16]. Consequently, the fluorene-based copolymers with phosphorescent emitters usually suffer from the energy back transfer from the triplet level of guest to that of polyfluorene, leading to a serious phosphorescence quenching and poor emission property.

In fact, some efficient electrophosphorescent red-light-emitting devices have been achieved based on physical- or chemical-doping PFO systems [14a,17], but a few green and blue electrophosphorescent light-emitting devices could be achieved based on PFO systems because the triplet energy levels of both green and blue triplet emitters (>2.4 eV) are higher than that of PFO, resulting in the green emission quenching of both green and blue triplet emitters [18].

However, PFO possesses higher singlet energy level and therefore, efficient singlet energy transfer can occur from polyfluorene to singlet emitters. The efficiency enhancement was reported due to the exciton confinement of the narrow-band gap emitters [12]. In principle, to obtain efficient green emission from the fluorene-based copolymers, using fluorescent comonomers as the narrow-band gap emitters should be a good choice. Therefore, efficient white emission is expected from the fluorene-based copolymers by introducing green-fluorescent and red-phosphorescent units into the polymer backbone [19].

Fig. 1 shows the energy transfer among polyfluorene backbone, green- and red-emitting model compound 4,7-bis(9,9-dihexylfluoren-2-yl)-2,1,3-benzothiadiazole(DFBT) and iridium complex (1-npy)$_2$Ir(tmd) in the copolymer. The singlet energy level of PFO is higher than that of DFBT and Ir complex, thus there should be cascade singlet energy transfer from PFO to both DFBT and Ir complex units. The triplet energy levels of PFO, DFBT and (1-npy)$_2$Ir(tmd) are 2.3, 1.6 and 2.1 eV, respectively. Since the triplet energy levels of both DFBT and Ir complex are lower than that of PFO, thus the triplet energy back transfer from both of the DFBT and Ir compolex units to the PFO segment could be well-avoided, and the triplet exitons could be mainly confined in the Ir complex which would lead efficient phosphorescent red emission. However, it can

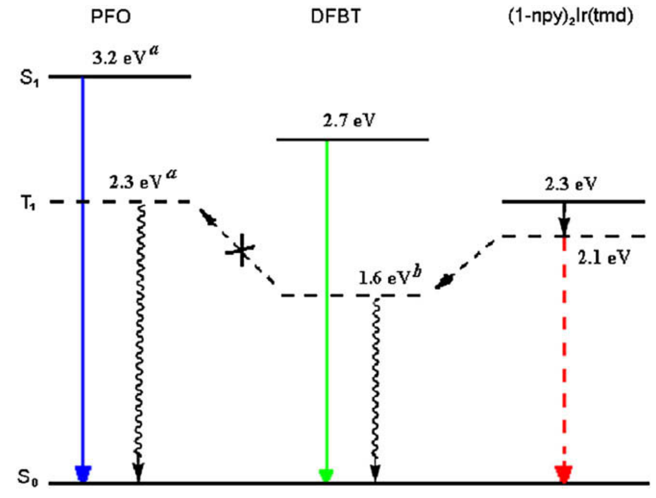


Fig. 1. Schematic energy level diagram showing energy transfer among PFO, DFBT and Ir complex, the data (a) and (b) come from Refs. [20,21], respectively.

be speculated that there should be exothermic energy transfer from Ir complex triplet state to DFBT triplet state from their triplet energy alignments, thus we suppose there should be some energy loss in a certain extent.

The synthetic route of copolymers is shown in Scheme 1. The copolymers containing fluorene, BT and Ir complex units were prepared by Suzuki polycondensation (SPC).

In order to keep the blue-, green-, and red-emission balance, the monomer feed ratios of 4,7-dibromo-2,1,3-benzothiadiazole (**3**) and iridium(III) bis(5-bromo-2-(1-naphthalene)pyridine-$C^{2'}$,N)-2,2,6,6-tetramethyl-3,5-heptanedione [(1-npyBr)$_2$Ir(tmd)] (**4**) were respectively tuned from 0.02 to 0.05 mol% and 0.075 to 0.1 mol% in the polycondensation and the corresponding polymers were named as PFG02–IrR1, PFG04–IrR1, PFG05–IrR1 and PFG03–IrR07. The resulted copolymers are soluble in organic solvents and have number–average molecular weight from 23,300 to 33,700 with polydispersity index (PDI) from 1.6 to 1.8 relative to polystyrene standards.

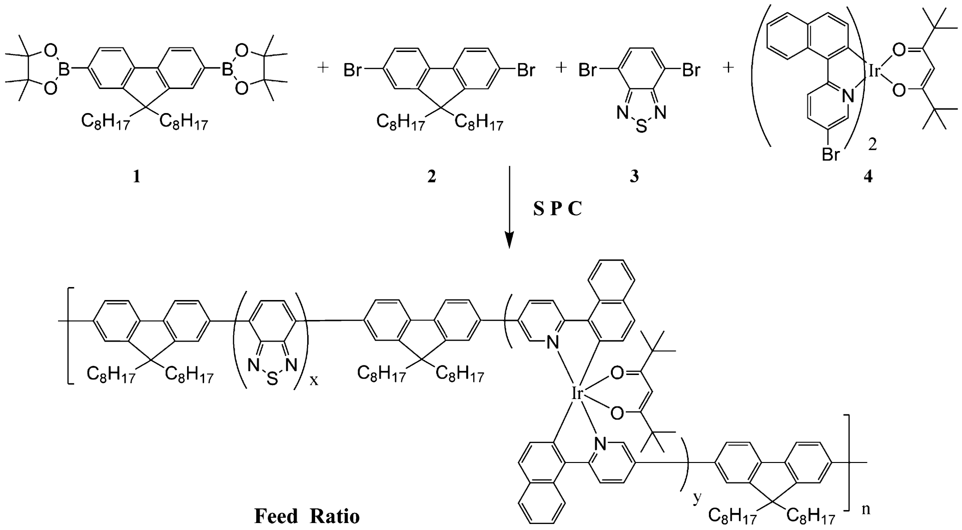
Fig. 2 shows the thermal properties of polymer PFG05–IrR1, which were evaluated by TGA and DSC measurements. The decomposition temperature (T_d) (5% weight loss) and the glass-transition temperature (T_g) are at 420 °C and 117 °C, respectively. Other polymers exhibit similar thermal properties as PFG05–IrR1. This means that introducing such small amount of emitter unit into polyfluorene backbone does not affect the rigidity of the resulting copolymers.

3.2. Photophysical and electrochemical properties

Fig. 3(a) shows the absorption and PL spectra of the copolymer. Compared with PFO, two distinct emissions peaked at 530 nm and 625 nm originated from BT and Ir complex moieties in the polymer backbone were observed, respectively. In Fig. 3(b), there is good overlap between the absorption of Ir complex/BT unit and the PL spectra of PFO and BT unit in the copolymer, respectively, which implies that the efficient energy transfer, mediated by BT unit, readily occurs from the fluorene segment to the Ir compex-based moieties in the copolymer.

Fig. 4a shows the PL spectra of the copolymers with different contents of BT and Ir complex. We can see that the emission from BT unit peaked at 530 nm is much stronger than that from Ir complex although the content of BT is much lower than Ir complex, and increase with the increasing content of BT unit in copolymers. The intensity of the red emission peaked at 625 nm depends not only on the content of Ir complex but also on that of BT unit. By comparing the emissive intensities peaked at 625 nm of PFG02–IrR1 with PFG05–IrR1, the enhancement of emissive intensity of Ir complex can be observed with the increasing content of BT unit in copolymers, which indicates that the BT unit in the copolymer behaves as a bridge to provide a more efficient energy transfer from the fluorene segment to the Ir complex in the PL excitation process [22].

The light-emitting diodes were made with the configuration: ITO/PEDOT:PSS/PVK/emissive layer/CsF/Al, where poly(vinylcarbazole) (PVK) acts as a hole transport layer. In Fig. 4b, the EL spectra of polymers show three balanced blue-, green- and red-emission peaked at 420 and 440, 520 and 625 nm, respectively.



Feed Ratio (mol%)

PFG02-IrR1 x=0.02 y=0.1

PFG05-IrR1 x=0.05 y=0.1

PFG04-IrR1 x=0.04 y=0.1

PFG03-IrR07 x=0.03 y=0.075

Scheme 1. Synthetic route of copolymers.

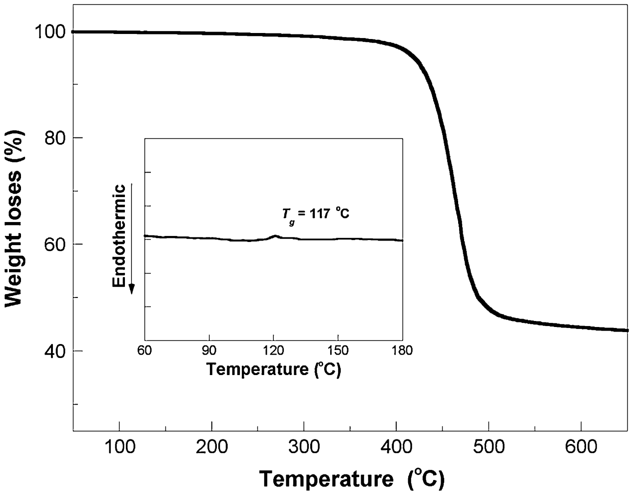


Fig. 2. TGA thermogram (inset: DSC trace) of PFG05–IrR1.

As shown in Fig. 4, comparison of PL spectra from the emitting layers with the EL spectra of the devices reveals that the EL spectra have a much higher contribution from the BT unit and Ir complex, indicating different excitation mechanisms for PL and EL [23].

In PL process, the emission comes from segments which absorb the photon or transferred from the other excitons, so the emission intensity depends on the concentration of emitters in the copolymers. However, charge trapping makes a more important role in EL process. White emission in EL spectra can be attributed to the individual emission from blue-, green- and red-emitters with the partial energy transfer and charge trapping on the narrow-band gap units.

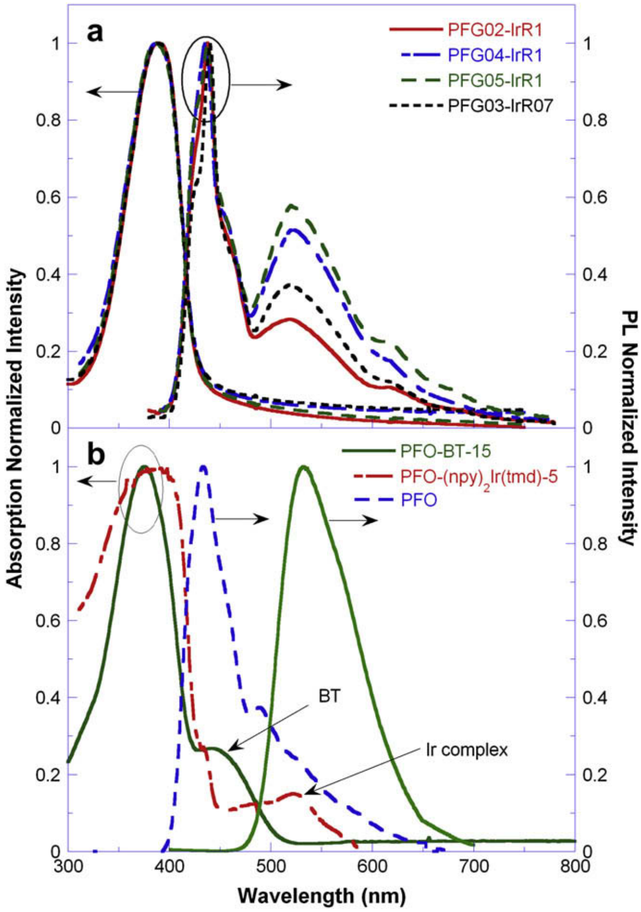


Fig. 3. Absorption and PL spectra of polymers (a), and BT unit (PFO-BT-15, 15 mol% of BT in polymer) and Ir complex (PFO-(npy)$_2$Ir(tmd)-5, 5 mol% of Ir complex) (b).

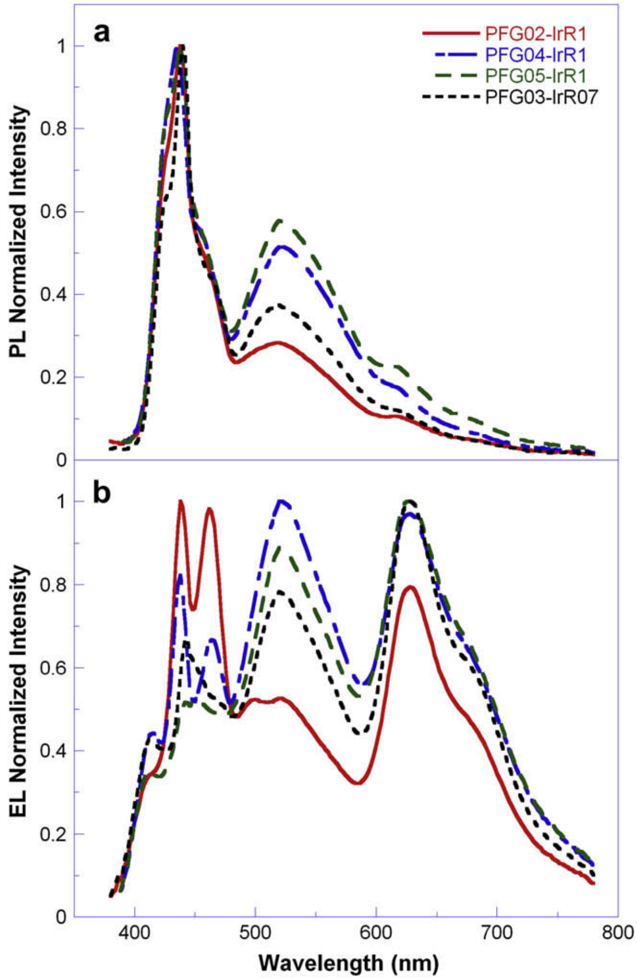


Fig. 4. PL (a) and EL (b) spectra for the polymers.

The trapping mechanism can also be understood from the energy levels. The hole- and electron-trapping is more favorable if the highest occupied molecular orbital (HOMO) level of the guest is above (closer to the vacuum level) than that of the host, and the

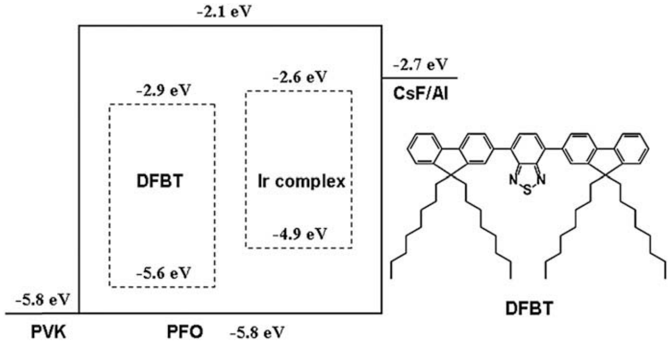


Fig. 5. Energy level scheme of PFO, DFBT(G) and Ir complex (R) units.

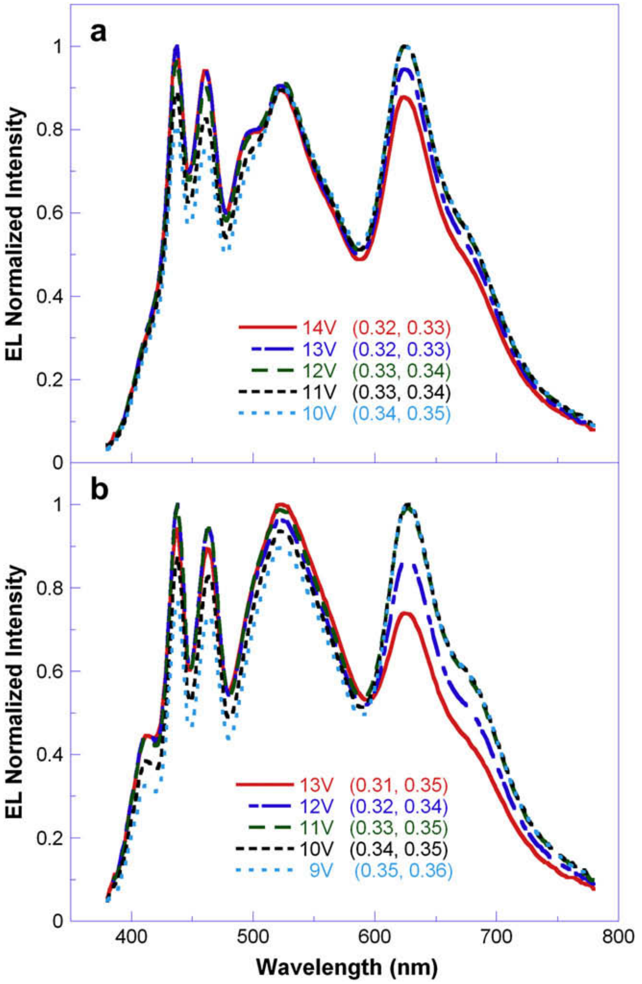


Fig. 6. EL spectra from PFG02-IrR1 (a) and PFG03–IrR07 (b) at different applied voltages.

lowest unoccupied molecular orbital (LUMO) level of the guest is below (farther from the vacuum level) than that of the host. As determined by cyclic voltammetry (shown in Fig. 5), the HOMO and LUMO of PFO, DFBT and [1-(npy)$_2$Ir(tmd)] are −5.8 and −2.1 eV, −5.6 and −2.9 eV, as well as −4.9 and −2.6 eV, respectively. Considering the extended conjugated length of Ir complex unit in conjugation with a neighboring conjugated segment in the polymer backbone [14b], the actual HOMO level of Ir complex unit in the backbone should be above −4.9 eV. Therefore, HOMO and LUMO of the green DFBT and red-emitting Ir complex are within that of the blue-emitting segment (PFO). As a result, the electron injected from CsF/Al and the hole from anode are readily trapped on the site of both green- and red-emitters. In case of the combination of hole and electron at the DFBT and Ir complex, singlet and triplet excited states will be formed and the emission from DFBT and Ir complex will attribute to the overall EL emission. The same observation has also been reported in previous papers [8,24].

According to the above discussion, the EL process of the WPLEDs comprises three main mechanisms. After charges are injected into copolymers from the electrodes, some of them directly recombine on the fluorene segment to produce blue emission, and some are trapped on the DFBT and Ir complex sites to emit green- and red-light, and the others are transferred from fluorene segment to DFBT and Ir complex units to produce green- and red-emission. As a result, the broad white emission combines the emissions from the three-emitting species, fluorene segment, DFBT unit in the singlet state and Ir complex in the triplet state.

By changing the contents of BT unit and Ir complex in the polymers, the EL spectra can be adjusted. When the content of BT unit as well as Ir complex in the polymers are in the region of 0.02–0.05 mol% and about 0.1 mol% respectively, the EL spectra of polymers are in the region of white emission.

3.3. Device performances

Fig. 6 displays the EL spectra at different applied voltages for PFG02–IrR1 and PFG03–IrR07, respectively. With increasing of the applied voltage from 10 V to 14 V, CIE coordinates change slightly from (0.34, 0.35) to (0.32, 0.33) for PFG02–IrR1, and from (0.35, 0.36) to (0.31, 0.35) (9–13 V) for PFG03–IrR07. All of the emissions are located very close to the ideal white point (0.33, 0.33). The color shift could be attributed to the very small content of the Ir complex which readily reaches saturated status even at low bias voltage. Thus when the voltage increases, the relative intensity of red emission from the Ir complex decreased, as a result, the blue emission from fluorene segments was enhanced. However, the emission color of copolymers remains stable upon the variations of applied voltage. The enhanced stability of the white emission of a single copolymer is obviously due to the sufficient isolation of green- and red-chromophores in the polyfluorene backbone.

The performances of the devices from copolymers are summarized in Table 1. PFG02–IrR1 emits pure white light with the efficiency of 4.4 cd/A and CIE coordinates of (0.33, 0.33). The maximum luminous efficiency of 5.3 cd/A, which corresponds to an external quantum efficiency (EQE) of 2.7%, and a maximum luminance of 9900 cd/m^2 with CIE coordinates of (0.34, 0.36) were achieved for PFG03–IrR07. The devices show an appropriate color temperature, as measured by Correlated Color Temperature (CCT), of ca. 5000 K and a color rendering index (CRI) value of 88, which is important for illumination, representing good color quality for displays and solid-state lighting.

Typical current density–luminance–voltage (J–L–V) characteristics from copolymer PFG03–IrR07 is presented in Fig. 7(a). The turn-on voltage (defined as the voltage where 1 cd/m^2 is measured) of 5.3 V is low among PVK-based white PLEDs, where high drive voltages are usually required because of low hole transport mobility, unmatched charge carrier injection barrier heights and

Table 1
Device performances from polymers.

Polymer	Maximum efficiency				L_{max} (cd/m^2)	CIE (x, y)[a]	CRI	CCT (K)
	Bias (V)	J (mA/cm^2)	LE (cd/A)	EQE (%)				
PFG02–IrR1	6.9	4.3	4.4	2.2	3700	(0.33, 0.33)	84	5520
PFG04–IrR1	10	1.3	3.1	1.5	3400	(0.33, 0.36)	89	5460
PFG05–IrR1	10.3	2.6	3	1.5	3100	(0.36, 0.37)	87	4704
PFG03–IrR07	7	1.1	5.3	2.7	9900	(0.34, 0.36)	88	5094

Device structure: ITO/PEDOT:PSS/PVK/emissive layer/CsF/Al.
[a] Obtained at the current of 13 mA cm^{-2}.

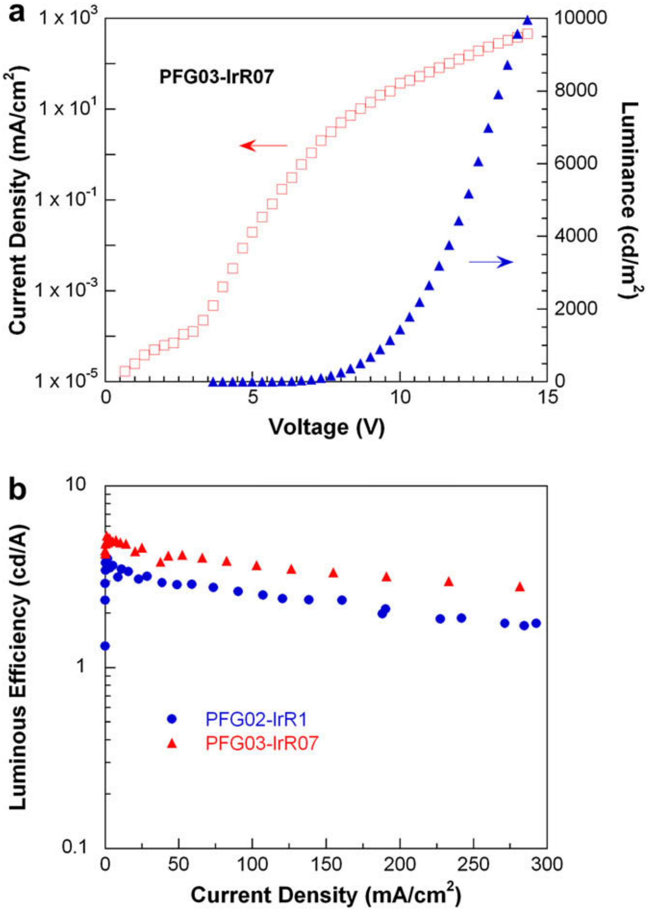


Fig. 7. *J–L–V* (a), and *LE–J* (b) characteristics of the device from polymers.

charge trapping effects. The low operation voltages of the devices are important for reducing power consumption. Furthermore, the device reaches a maximum luminance of 9900 cd/m^2 at 14.3 V and 453 mA/cm^2. As plotted in *LE–J* characteristics (Fig. 7b), the devices possess a fairly slow roll-off in efficiency loss, which can be attributed to the reducing long radiative lifetime of triplet excited states via chemical modification, otherwise multi-particle annihilation processes, such as triplet–triplet annihilation, may cause significant roll-off in efficiency at high current density region [25]. Our results indicate that the obtained white-emitting materials and devices are promising candidates for display and solid-state-lighting purpose.

4. Conclusion

Efficient white emission from fluorene-based copolymers by mixing fluorescence with phosphorescence emission has been demonstrated. The white emission from such copolymers is relatively stable in white-light region at all applied voltages, and the EL efficiencies decline slightly with the increasing current density, indicating that the incorporation of singlet and triplet species into polymer backbone is a promising approach to achieve white emission devices.

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References

[1] (a) Xie ZY, Huang JS, Li CN, Liu SY, Wang Y, Li YQ, et al. Appl Phys Lett 1999;74:641–3;
(b) Ko CW, Tao YT. Appl Phys Lett 2001;79:4234–6;
(c) Zhu L, Yang C, Zhong C, Xu L, Qin J. Polymer 2008;49:3716–21.

[2] (a) Kido J, Hongawa K, Okuyama K, Nagai K. Appl Phys Lett 1994;64:815–7;
(b) Gong X, Wang S, Moses D, Bazan GC, Heeger AJ. Adv Mater 2005;17:2053–8;
(c) Shih PI, Shu CF, Tung YL, Chi Y. Appl Phys Lett 2006;88:251110–3;
(d) Attar HA, Monkman AP, Tavasli M, Bettington S, Bryce MR. Appl Phys Lett 2005;86:121101–3;
(e) Kim TH, Lee HK, Park OO, Chin BD, Lee SH, Kim JK. Adv Funct Mater 2006;16:611–7.

[3] (a) Xu YH, Peng JB, Mo YQ, Hou Q, Cao Y. Appl Phys Lett 2005;86:163502–4;
(b) Shih PI, Tseng YH, Wu FI, Dixit AK, Shu CF. Adv Funct Mater 2006;16:1582–9;
(c) Park JH, Lee TW, Kim YC, Park OO, Kim JK. Chem Phys Lett 2005;403:293–7;
(d) Lee RH, Lin KT, Huang CY. J Polym Sci Part B Polym Phys 2007;45:330–41;
(e) Lin HY, Liou GS, Lee WY, Chen WC. J Polym Sci Part A Polym Chem 2007;45:1727–36;
(f) Huang J, Li G, Wu E, Xu Q, Yang Y. Adv Mater 2006;18:114–7.

[4] (a) Liu J, Zhou Q, Geng Y, Wang L, Ma D, Wang F, et al. Adv Mater 2005;17:2974–8;
(b) Tu G, Mei C, Geng Y, Wang L, Ma D, Wang F, et al. Adv Funct Mater 2006;16:101–6;
(c) Tsai ML, Liu CY, Hsu MA, Chow TJ. Appl Phys Lett 2003;82:550–2;
(d) Lee YZ, Chen X, Chen MC, Chen SA, Hsu JH, Fann W. Appl Phys Lett 2001;79:308–10;
(e) Liu J, Zhou Q, Geng Y, Wang L, Ma D, Wang F, et al. Adv Funct Mater 2006;16:957–65;
(f) Liu J, Xie Z, Geng Y, Wang L, Ma D, Wang F, et al. Adv Mater 2007;19:531–5;
(g) Liu J, Chen L, Geng Y, Wang L, Ma D, Wang F, et al. Adv Mater 2007;19:1859–63;
(h) Paik KL, Baek NS, Kim HK, Lee JH, Lee Y. Macromolecules 2002;35:6782–91;
(i) Lee PI, Hsu SL, Lee RF. Polymer 2007;48:110–5;
(j) Wu FI, Shih PI, Tseng YH, Shu CF, Tung YL, Chi Y. J Mater Chem 2007;17:167–73;
(k) Luo J, Li X, Hou Q, Peng J, Yang W, Cao Y. Adv Mater 2007;19:1113–7.

[5] Furuta PT, Deng L, Garon S, Thompson ME, Fréchet MJ. J Am Chem Soc 2004;126:15388–9.

[6] Jiang J, Xu Y, Yang W, Guan R, Zhen H, Cao Y, et al. Adv Mater 2006;18:1769–73.

[7] Mei C, Ding J, Cheng Y, Xie Z, Geng Y, Wang L, et al. J Polym Sci Part A Polym Chem 2007;45:1746–57.

[8] Wu FI, Yang XH, Neher D, Dodda R, Tseng YH, Shu CF. Adv Funct Mater 2007;17:1085–92.

[9] Zhen H, Xu W, Yang W, Chen Q, Xu Y, Cao Y. Macromol Rapid Commun 2006;27:2095–100.

[10] Kappaun S, Eder S, Saf R, Mereiter K, List EJW, Slugovc C. J Mater Chem 2006;16:4389–92.

[11] Bredas JL, Silbey R, Boudreaux DS, Chance RR. J Am Chem Soc 1983;105:6555–9.

[12] (a) Hou Q, Xu Y, Yang W, Yuan M, Peng J, Cao Y. J Mater Chem 2002;12:2887–92;
(b) Yang W, Hou Q, Niu Y, Huang J, Yang R, Cao Y, et al. J Mater Chem 2003;13:1351–5;
(c) Tang DF, Wen GA, Qi XY, Wang HY, Wei W, Huang W, et al. Polymer 2007;48:4412–8.

[13] (a) Lamansky S, Djurovich P, Murphy D, Kwong R, Bortz M, Thompson ME, et al. Inorg Chem 2001;40:1704–11;
(b) Yao YH, Yang SH, Hsu CS. Polymer 2006;47:8297–308.

[14] (a) Jiang J, Jiang C, Yang W, Zhen H, Huang F, Cao Y. Macromolecules 2005;38:4072–80;
(b) Zhen H, Jiang C, Yang W, Jiang J, Huang F, Cao Y. Chem Eur J 2005;11:5007–16;
(c) Du B, Liu R, Zhang Y, Yang W, Peng JP, Cao Y. Polymer 2007;48:1245–54.

[15] (a) Hertel D, Setayesh S, Nothofer HG, Scherf U, Müllen K, Bässler H. Adv Mater 2001;13:65–70;
(b) Rothe C, Monkman A. Phys Rev B 2002;65:073201–4.

[16] (a) Sandee AJ, Williams CK, Davies JE, Köhler A, Friend RH, Holmes AB. J Am Chem Soc 2004;126:7041–8;
(b) Wu WC, Liu CL, Chen WC. Polymer 2006;47:527–38.

[17] (a) Jiang C, Yang W, Peng J, Xiao S, Cao Y. Adv Mater 2004;16:537–41;
(b) Knaapila M, Almásy L, Garamus VM, Ramos ML, Burrows HD, Monkman AP. Polymer 2008;49:2033–8.

[18] (a) Zhen H, Luo J, Yang W, Chen Q, Ying L, Cao Y, et al. J Mater Chem 2007;17:2824–31;
(b) Li BL, Liu ZT, He YM, Pan J, Fan QH. Polymer 2008;49:1527–37;
(c) Zhu L, Yang C, Zhang W, Qin J. Polymer 2008;49:217–24.

[19] (a) Xu YH, Guan R, Jiang JX, Yang W, Peng JB, Cao Y, et al. J Polym Sci Part A Polym Chem 2008;46:453–63;
(b) Chen SH, Shiau CS, Tsai LR, Chen Y. Polymer 2006;47:8436–43.
[20] Monkman AP, Burrows HD, Hartwell LJ, Horsburgh LE, Hamble I, Navaratnam S. Phys Rev Lett 2001;86:1358–61.
[21] (a) Ford TA, Avilov I, Beljonne D, Greenham NC. Phys Rev B 2005;71:125212–8;
(b) Morgado J, Charas A, Fernandes JA, Goncalves IS, Carlos LD, Alcacer L. J Phys D Appl Phys 2006;39:3582–7.
[22] (a) Baldo MA, Thompson ME, Forrest SR. Nature (London) 2000;403:750–3;
(b) Zhang Y, Huang Z, Zeng W, Cao Y. Polymer 2008;49:1211–9.
[23] (a) Gong X, Ostrowski JC, Moses D, Bazan GC, Heeger AJ. Adv Funct Mater 2003;13:439–44;
(b) Lane PA, Palilis LC, O'Brien DF, Cadby J, Campbell AJ, Bradley DDC. Phys Rev B 2001;63:235206–13.
[24] (a) Gong X, Robinson MR, Ostrowski JC, Moses D, Bazan GC, Heeger AJ. Adv Mater 2002;14:581–5;
(b) Yang CH, Bhongale CJ, Chou CH, Yang SH, Lo CN, Hsu CH. Polymer 2007;48:116–28.
[25] (a) Baldo MA, Lamansky S, Burrows PE, Thompson ME, Forrest SR. Appl Phys Lett 1999;75:4–6;
(b) Baldo MA, Adachi C, Forrest SR. Phys Rev B 2000;62:10967–77.