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Novel, blue light-emitting polyfluorenes containing a fluorinated quinoxaline unit

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ABSTRACT

A series of fluorinated quinoxaline containing polyfluorenes were synthesized by Suzuki polycondensation. The polymer light emitting diodes based on the resulting copolymers emitted blue light, and no green emission was observed either in the photoluminescence spectra when the film had been annealed at 80–160 °C nor in the electroluminescence spectra when the current densities increased from 5 to 200 mA cm^{-2}. The fluorescence quantum yields decreased from 79% to 36% with increasing content of BPFQ from 1 to 20 mol%. Peak external quantum efficiency and luminous efficiency were 2.99% and 2.39 cd A^{-1}, respectively, with CIE coordinates of (0.16, 0.10).

1. Introduction

Polymer light-emitting diodes (PLEDs) have attracting increasing interest due to their ease of fabricating large area lighting panel, and low-cost display production [1–3]. For the full color PLED applications, green and red light-emitting polymers can fulfil commercial needs while efficient and stable blue electroluminescence still remains a great challenge. Among currently available blue light-emitting polymers, poly(9,9-dialkylfluorene)s have attracted much attention because of their high photoluminescence quantum efficiencies and excellent solubility in common organic solvents [4–7]. However, the undesirable low-energy emission band located at 530–540 nm was always generated during long-term device operation. To achieve stable and pure blue electroluminescence, the incorporation of kink, heterocyclic aromatic moieties [8–15] into the polyfluorene backbone has been considered as relatively effective approaches. For example, Yang et al. [16] incorporated 3,5-pyridine to the backbone of polyfluorene, which could significantly depress the formation of excimer by controlling the chain rigidity and effective conjugation length, thereby the color purity of blue emission was distinctly enhanced. Zhu et al. [17] incorporated dibenzo[*a*,*c*]phenazine segments into the backbone of polyfluorenes, and achieved the efficient blue electroluminescence from intramolecular charge-transfer emission of a conjugated donor–acceptor system. However, only a few of these reported copolymers could obtain stable spectra while simultaneously achieve high efficiency.

Generally, to improve light-emitting efficiency, the balance of hole and electron injected into the emitting layer is necessary [18]. Since polyfluorene was a kind of typical p-type polymer whose hole transport ability was about three orders of that of electron [19,20], thereby introducing electron deficient n-type moiety to polymer main chain could improve electron injection and transport. Heterocyclic aromatic polyquinoxalines exhibit good electron affinity as effective n-type materials and could be employed as electron injection materials [21–26]. Kulkarni et al. [27] prepared the quinoxaline-containing polyfluorenes and obtained stable blue light-emitting devices, but the device efficiencies remained in low level and need to be further improved. It is well known that fluorinated materials exhibit high electron affinity and electron-transport capability, and could be used as n-type semiconductors in OLEDs, field-effect transistors (FETs) and thin-film transistors (TFTs) [28–30]. Sakamoto et al. [28,29] reported that the organic n-type semiconductors with improved the device performances could be obtained based on such fluorinated phenylene oligomers and dendrimers.

In this contribution, we chose fluorinated monomer 2,3-bisphenyl-6-fluoroquinoxaline (BPFQ) to copolymerize with alkylfluorene essentially for the reasons that, on the one hand, the electron injection would be facilitated by the electron affinity of electron deficient BPFQ moiety; and on the other hand, the

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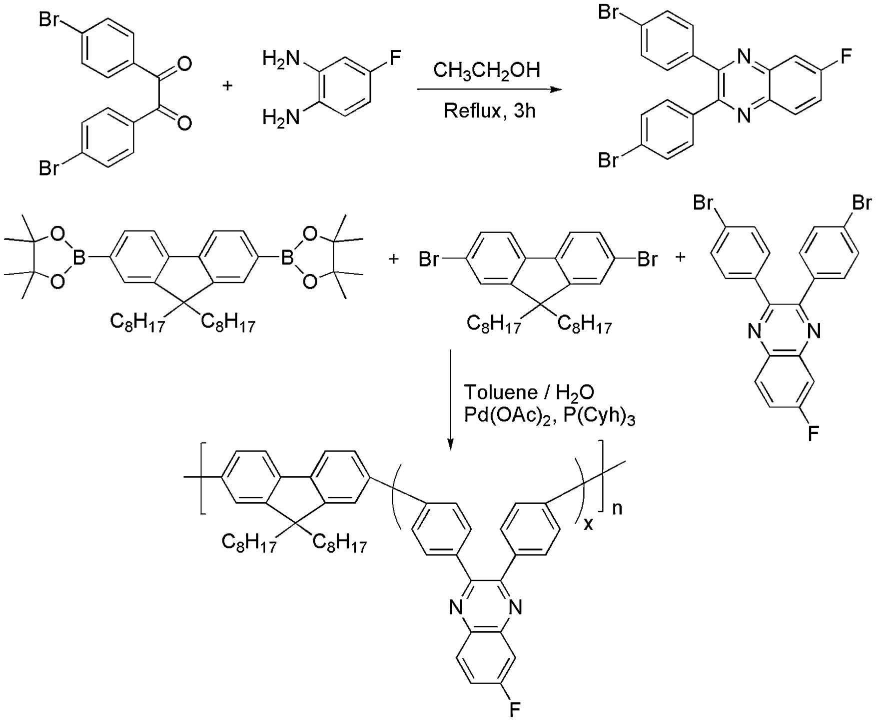

Scheme 1. Synthetic routes for monomer BPFQ and polymers.

electronegative fluorine will further facilitate the electron transportation because of its strong electron-drawn properties.

2. Experimental section

2.1. 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 received. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 300 spectrometer operating respectively at 300 and 75 MHz, respectively, with tetramethylsilane as a reference. Direct injection mass spectra were recorded by the electron spray impact (ESI) method on a LCQ DECA XP Liquid Chromatography–Mass Spectrometer (Thremo Co.). Glass transition temperatures (T_gs), taken as the midpoint of the change in the slope of the baseline, were measured on a TA 5200 M DSC instrument at a heating rate of 10 °C min^{-1} in nitrogen. Thermogravimetric analysis (TGA) of the polymers was measured on a DuPont 2000 SDT-2960 instrument at a heating rate of 20 °C min^{-1} in nitrogen, and T_d were reported as the temperatures at 5% weight losses. Mr determination was undertaken using a Waters GPC 2410 in tetrahydrofuran using polystyrene standard calibration curves. Elemental analyses were performed on Vario EL Elemental analysis instrument (Elementar Co.). Samples were pressed as homogeneous tablets ($\varnothing = 30$ mm) of compressed (375 MPa) powder of the copolymers. UV–vis absorption spectra were recorded on a HP 8453 spectrophotometer. The PL quantum yields were determined in an integrating sphere ISO80 (Labsphere) with 325 nm excitation of HeCd laser (Mells Griot). Cyclic voltammetry was carried out on a CHI660A electrochemical workstation with platinum at a scan rate of 50 mV s^{-1} against a saturated calomel reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN).

2.2. Device fabrication and characterization

Polymers were dissolved in *p*-xylene and filtered with a 0.45 μm filter. Patterned ITO coated glass substrates were cleaned with acetone, detergent, distilled water and 2-propanol followed by an ultrasonic bath. After treating with oxygen plasma, 150 nm of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS, Batron-P 4083, Bayer AG) was spin-coated onto the ITO substrates followed by drying in a vacuum at 80 °C for 18 h. A thin film of polymers was coated onto the anode by spin-casting inside a dry box. The film thickness of the active layers was around 75–80 nm, measured with an Alfa Step 500 surface profiler (Tencor). A thin layer of 1,3,5-tri(*N*-phenyl-benzimidizol-2-yl)benzene (TPBI) (25–30 nm) and Ba (4–5 nm) was subsequently evaporated on the top of an EL polymer layer in a vacuum of 1×10^{-4} Pa. Device performances were measured inside a dry box. Current–voltage (*I*–*V*) characteristics were recorded with a Keithley 236 source meter. 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 a Si photodiode with calibration in an integrating sphere (ISO80, Labsphere).

2.3. Synthesis of monomers

2,7-Dibromo-9,9-dioctylfluorene (**1**) was synthesized according to reported procedures [12].

Table 1
Molecular weights and thermal properties of polymers.

Polymer	$M_n \times 10^4$	PDI	T_g (°C)	T_d (°C)
PFO	10.80	1.66	67	430
PF–BPFQ1	12.65	1.79	69	431
PF–BPFQ5	11.12	1.52	75	431
PF–BPFQ10	6.60	1.50	88	433
PF–BPFQ20	5.64	1.63	106	439

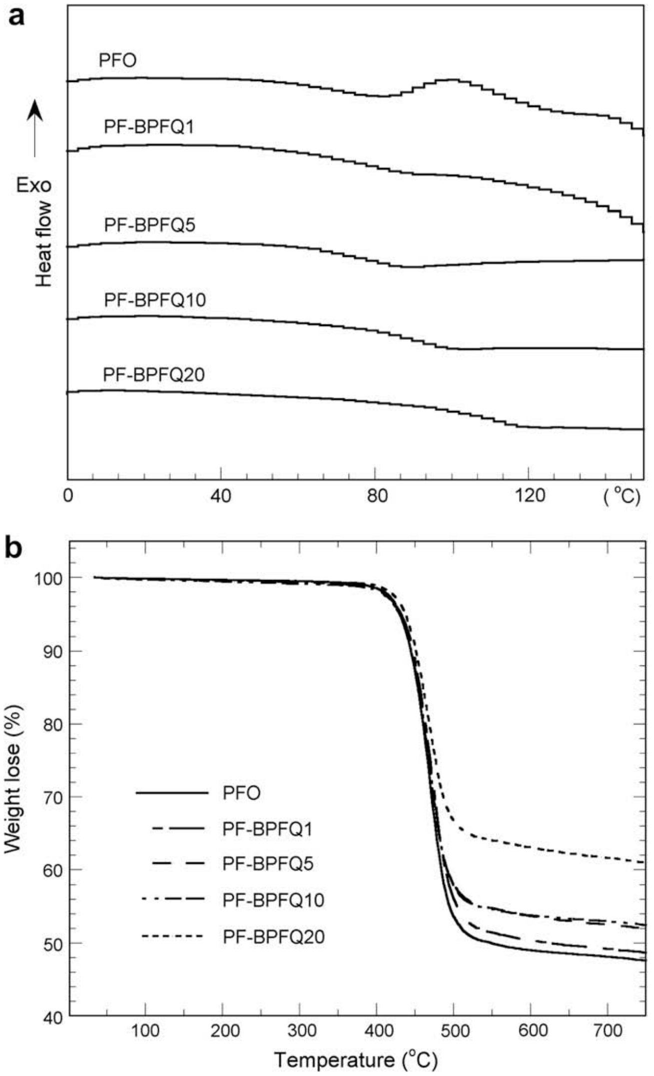

Fig. 1. DSC curves (a) and thermal gravimetrical properties (b) of polymers.

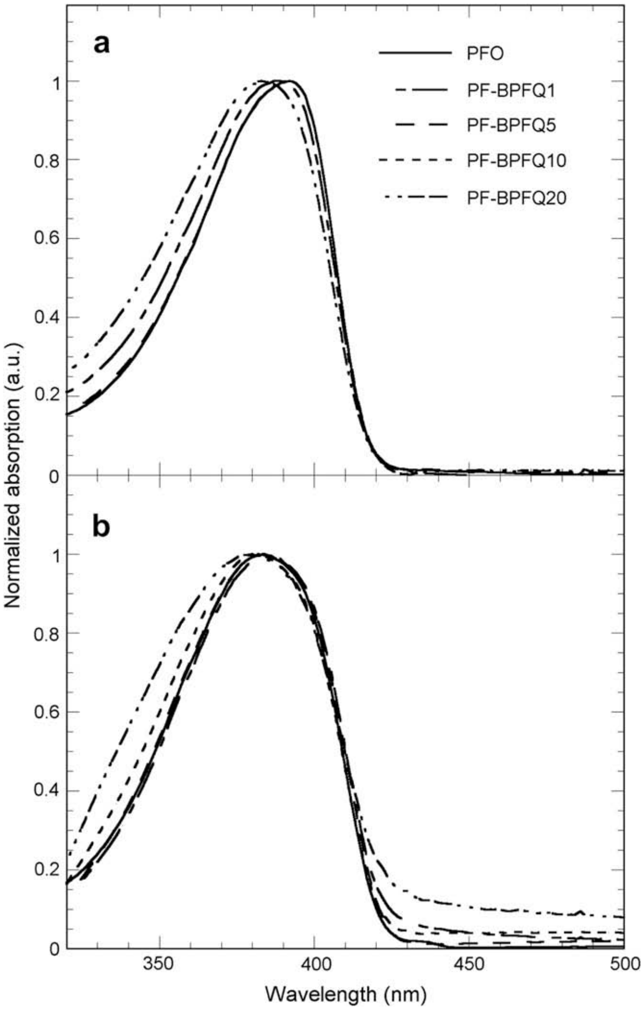

Fig. 2. UV absorption spectra of polymers in toluene solution (a), and in film (b).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.53 (d, 2H), 7.46 (d, 2H), 7.44 (d, 2H), 1.91 (m, 4H), 1.24–1.04 (m, 20 H), 0.83 (t, 6H), 0.58 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 152.95, 139.47, 130.54, 126.57, 121.88, 121.53, 56.08, 40.52, 32.17, 31.35, 30.27, 29.54, 24.02, 23.01, 14.50. Element Anal. Calcd for $C_{29}H_{40}Br_2$: C, 63.51%; H, 7.35%. Found: C, 63.41%; H, 6.68%.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**2**) was synthesized according to reported procedures [12].

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.81 (d, $J = 7.5$ Hz, 2H), 7.74 (s, 2H), 7.71 (d, $J = 7.5$ Hz, 2H), 1.99 (m, 4H), 1.39 (s, 24H), 1.22–1.00 (m, 20H), 0.81 (t, $J = 6.8$ Hz, 6H), 0.56 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 150.86, 144.30, 134.04, 129.29, 119.77, 84.11, 55.57, 40.49, 32.18, 30.33, 29.58, 25.33, 23.98, 22.99, 14.48. Element Anal. Calcd for $C_{41}H_{64}B_2O_4$: C, 76.64%; H, 10.04%. Found: C, 76.49%; H, 9.82%.

*2,3-Bis(4-bromophenyl)-6-fluoroquinoxaline (**3**).* To a 100 ml flask, 4,4-dibromobenzil (1.84 g, 5 mmol) and 4-fluoro-1,2-phenylenediamine (0.70 g, 5.5 mmol) was added in 30 ml ethanol with argon purged. The mixture was heated to reflux in dark for 5 h. After the ethanol was evaporated, the crude product was separated by silica column with petrol ether/ethyl acetate of 20/1 (v/v) to give white powder in very high yield of 98%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.14 (dd, $J = 5.70$ Hz and 9.30 Hz, 1H), 7.77 (dd, $J = 2.70$ Hz and 9.30 Hz, 1H), 7.66 (td, $J = 2.70$ Hz and 5.70 Hz, 1H), 7.53 (d, $J = 3.84$ Hz, 4H), 7.40 (dd, $J = 2.85$ Hz and 6.18 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 164.75, 161.40, 152.65, 151.28, 142.07, 141.89, 138.44, 138.00, 137.40, 137.30, 131.72, 131.40, 131.35, 131.22, 123.99, 123.78, 121.02, 120.67, 112.76, 112.48. EIMS: m/z 457.8 $(m+1)^+$. Element Anal. Calcd for $C_{20}H_{11}Br_2FN_2$: C, 52.43%; H, 2.42%; N, 6.11%. Found: C, 52.65%; H, 2.39%; N, 5.80%.

2.4. Polymerization

2.4.1. General procedures of Suzuki polycondensation, taking PF–BPFQ1 as an example

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**2**) (0.3213 g, 0.5 mmol), 2,3-bis(4-bromophenyl)-6-fluoroquinoxaline (**3**) (4.6 mg, 0.01 mmol), 2,7-dibromo-9,9-dioctylfluorene (**1**) (0.2687 g, 0.49 mmol), palladium(II) acetate [$Pd(OAc)_2$, 1.5–2 mol% equivalent] and tricyclohexylphosphine [$P(Cyh)_3$, 4–6 mol% equivalent] were dissolved in the mixture of toluene (8 ml), after stirred for 0.5 h, deionized H_2O (2 ml) and Et_4NOH (35 wt%) aqueous solution (0.2 ml) was added. The mixture was heated to 90 °C and stirred for 48 h under argon atmosphere. Then the reaction was capped by adding phenyl boric acid (25 mg) by stirring for 12 h to remove the bromine end groups, and then bromobenzene (1 ml) was added as a monofunctional end-capping reagent by heating for another 12 h to remove the resident boronic ester end groups. The whole mixture was poured into methanol. The precipitated polymer was recovered by filtration and purified by silica column chromatography with toluene as eluent to remove

Table 2
Photophysical and electrochemical properties of polymers.

Polymer	In solution		In film			E_{ox} (V)	HOMO (eV)	LUMO[a] (eV)	E_g^{opt} (eV)
	λ_{abs} (nm)	λ_{PL} (nm)	λ_{abs} (nm)	λ_{PL} (nm)	QE_{PL} (%)				
PFO	392	417	384	432	79	1.32	−5.77	−2.16[b]	2.93
PF–BPFQ1	392	417	384	424	72	1.33	−5.73	−2.80	2.93
PF–BPFQ5	391	419	383	426	69	1.36	−5.76	−2.82	2.94
PF–BPFQ10	388	419	382	427	52	1.38	−5.78	−2.83	2.95
PF–BPFQ20	380	425	380	438	36	1.45	−5.85	−2.88	2.97

[a] Calculated from LUMO = HOMO + E_g^{opt}.
[b] Estimated from $E_{LUMO} = -(E_{red} + 4.4)$ eV.

small molecular fraction and catalyst residue (yield 89%). ^{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, 89.88%; H, 10.08%. Found: C, 88.28%; H, 11.60%.

3. Results and discussion

3.1. Synthesis of monomers and polymers

As shown in Scheme 1, 2,7-dibromo-9,9-dioctanefluorene (**1**) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**2**) were prepared according to reported procedures [17]. 2,3-Bis(4-bromophenyl)-6-fluoroquinoxaline (**3**) was facilely synthesized from 4,4′-dibromobenzil and 4-fluoro-1,2-phenyldiamine in high yield of 98%. Copolymers derived from these monomers were prepared by Suzuki polycondensation with 2:1:3 in feed ratio of 50:49:1, 50:45:5, 50:40:10 and 50:30:20, respectively, and the corresponding resulted polymers were named as PF–BPFQ1, PF–BPFQ5, PF–BPFQ10 and PF–BPFQ20. All of the resulted copolymers exhibited good solubility in common organic solvents such as toluene, chloroform and tetrahydrofuran (THF), etc. The molecular structures of the synthesized copolymers were found to be in good agreement with ^{1}H NMR spectra and element analysis (EA). The number average molecular weight (M_n) of polymers estimated by gel permission chromatography (GPC) against the polystyrene standard with THF as eluent solvent ranged from 56,400 to 126,500 with a polydispersity index (PDI) (M_w/M_n) from 1.50 to 1.79, as summarized in Table 1.

3.2. Thermal properties of polymers

The thermal properties of copolymers were evaluated by DSC and TGA measurements and the data of the glass transition temperatures (T_gs) and the decomposition temperatures of 5% weight loss (T_ds) are summarized in Table 1. As can be seen clearly from Fig. 1, compared with the T_g of PFO (67 °C), the T_gs of copolymers gradually increase from 69 to 106 °C with increasing the content of BPFQ moiety from 1 to 20 mol%. Indeed, the non-linear aromatic heterocyclic BPFQ moiety could effectively hinder the motion of molecular segments, and likewise the fluorine in BPFQ could also significantly enhance the interaction among polymer backbones, thereby the T_gs were distinctly improved [31]. In addition, as can be seen in Fig. 2, all of these copolymers exhibited excellent thermal properties, with the T_d of over 430 °C.

3.3. Electrochemical properties

The electrochemical properties of copolymers were investigated by cyclic voltammetry, however, only the p-doping waves (oxidation potentials, E_{ox}) can be recorded for copolymers. The highest occupied molecular orbital (HOMO) levels were calculated according to the empirical formula $E_{HOMO} = -e(E_{ox} + 4.4)$ eV and $E_{LUMO} = -e(E_{red} + 4.4)$ eV [32] with the ferrocene oxidation potential as the standard for the vacuum energy level. The lowest unoccupied molecular orbital (LUMO) levels of copolymers were estimated from HOMO levels and the optical band gaps (E_gs). As can be seen from Table 2, with the increasing content of BPFQ unit in the copolymers, the E_gs of copolymers did not change obviously while quite similar with those of PFO. However, the LUMO levels of the copolymers decreased progressively compared to the PFO, which indicated that the electron-accepting ability could be improved by introducing the electron deficient moiety into the PFO backbone.

3.4. Photophysical properties

Fig. 2 illustrates the absorption spectra of copolymer in toluene solution with the concentration of 10^{-5} mol L^{-1} (a) and in thin

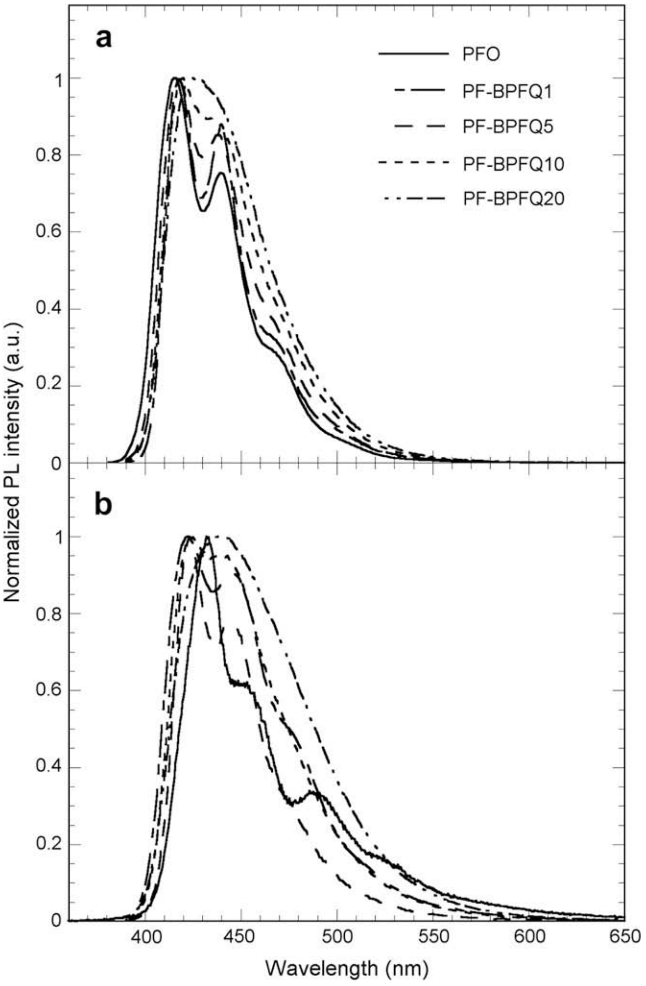

Fig. 3. PL spectra of polymers in toluene solution (a), and in film (b).

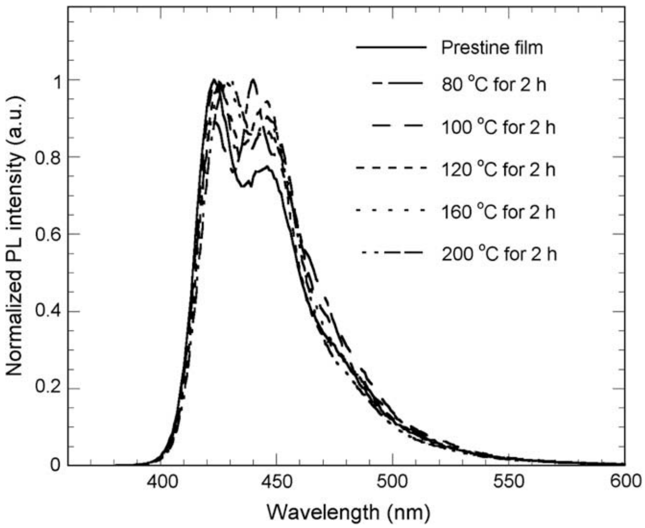

Fig. 4. PL spectra of PF–BPFQ5 annealed at different temperatures in nitrogen.

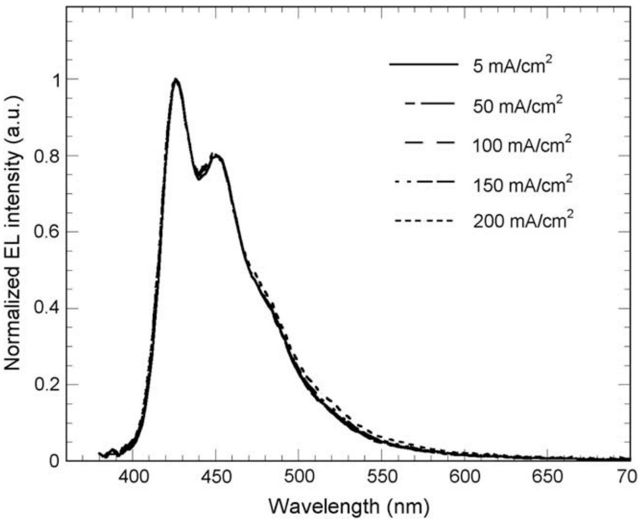

Fig. 6. EL spectra of PF–BPFQ5 at the varied current densities.

film (b). As shown in Fig. 3a, the peak absorption gradually shifted from 393 nm to 380 nm with increasing the BPFQ content from 1 mol% to 20 mol%, which might attribute that the effective π-conjugated length was progressively decreased with the increasing content of BPFQ moiety. Besides, the full width at half-maximum of the absorption spectra increased with the increasing of BPFQ content, which demonstrated the greater inhomogeneous broadening owing to the local disorder induced by the kink BPFQ moiety. In addition, even though it can be seen clearly that all of the copolymers have similar absorption profile in solution and in film, there was only 4 nm shift in film when BPFQ fractions change from 1 to 20 mol%. The fact suggested that the bulk intrachain electronic delocalization for all copolymer backbone might be formed in film, given that the electron deficient BPFQ can form donor–acceptor system with p-type fluorene segments [33]. Moreover, it can be seen from Fig. 3b that the absorption edges of the films are almost identical for all copolymers. As estimated from the band edges of absorption spectra (in film), the optical band gaps varied slightly from 2.93 to 2.97 eV.

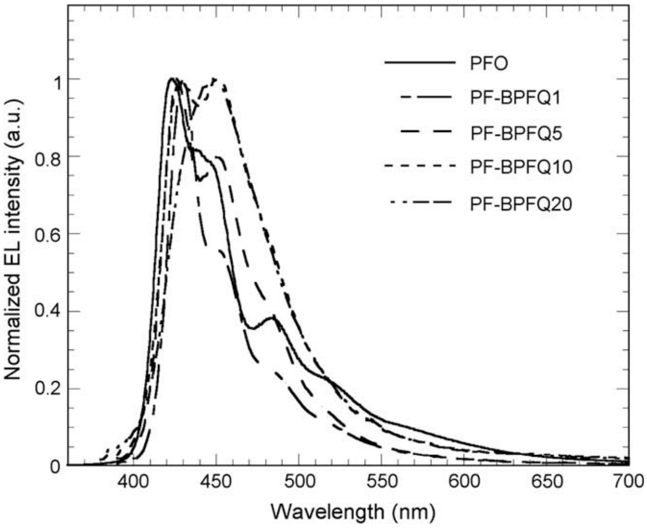

Fig. 5. EL spectra of polymers.

The photoluminescence (PL) spectra of copolymers in dilute toluene solution (10^{-5} mol L^{-1}) (a) and in film (b) are shown in Fig. 3. The PL spectra in film were quite similar to that of in toluene solution, and all of which did not show unexpected low-energy band emission. As can be seen from Fig. 4a, with the increasing content of BPFQ, the peak- and shoulder-emission were dominated at 417 nm and about 440 nm, respectively. However, the shoulder emission disappeared for copolymer PF–BPFQ20, and only emission at 425 nm was observed. The photophysical properties of copolymers are summarized in Table 2. All of fluorescence quantum yields of the copolymers decreased gradually with increasing the content of BPFQ in copolymer, from 79% for PF–BPFQ1 to 36% for PF–BPFQ20. The probable reason might be the greater intramolecular charge transfer with the increasing BPFQ content [33].

In order to study thermal stabilities of PL emission of the copolymer film, we first spin-coated PEDOT onto the ITO substrate followed by drying in a vacuum oven, and a thin film of copolymer (taking PF–BPQF5 as the example) was spin-coated subsequently, and then annealed at different temperatures from 80 °C to 200 °C for 2 h, respectively in nitrogen atmosphere. As shown in Fig. 4, the PL spectra after thermal treatment have no distinct change compared to the pristine PF–BPQF5 even when the film was annealed at temperatures much higher than its T_g for 2 h. Further experiments based on the other copolymers exhibit similar results. This fact indicated that the incorporation of fluorinated quinoxaline unit into polyfluorene main chain was an effective approach to achieve stable blue emission in PL procedure.

Table 3
Electroluminescent properties of polymers.

Polymer	Cathode buffer	V_{th} (V)	EQE$_{max}$ (%)	LE$_{max}$ (cd A^{-1})	L_{max} (cd m^{-2})	CIE (x, y)
PFO	–	5.7	0.52	0.42	501	(0.17, 0.10)
PF–BPFQ1	–	7.6	0.53	0.43	788	(0.16, 0.07)
PF–BPFQ5	–	4.5	1.17	0.94	1407	(0.16, 0.08)
PF–BPFQ10	–	6.3	0.10	0.08	181	(0.18, 0.12)
PF–BPFQ20	–	6.3	0.07	0.05	135	(0.19, 0.15)
PFO	TPBI	6.2	0.64	0.52	631	(0.19, 0.12)
PF–BPFQ1	TPBI	7.2	2.30	1.90	1156	(0.17, 0.10)
PF–BPFQ5	TPBI	8.6	2.99	2.39	2776	(0.16, 0.10)
PF–BPFQ10	TPBI	8.4	0.77	0.62	483	(0.17, 0.12)
PF–BPFQ20	TPBI	6.8	0.92	0.74	468	(0.17, 0.12)

Device configuration: ITO/PEDOT/polymer/cathode buffer/Ba/Al.

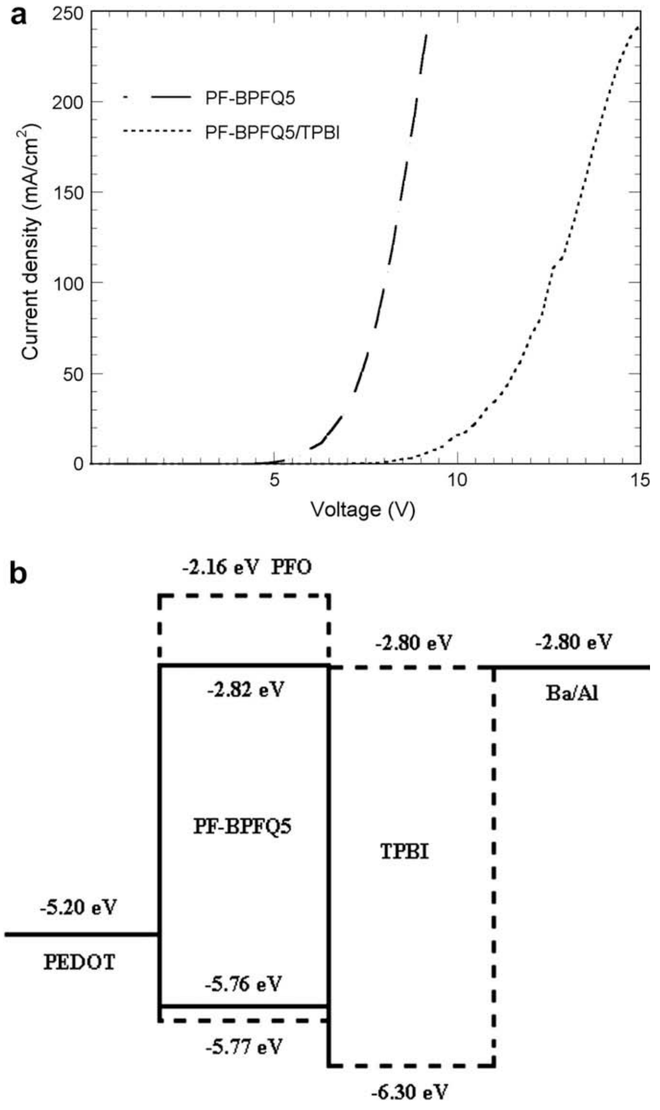

Fig. 7. *J*–*V* characteristics based on PF–BPFQ5 (a) and the energy level diagram of devices (b).

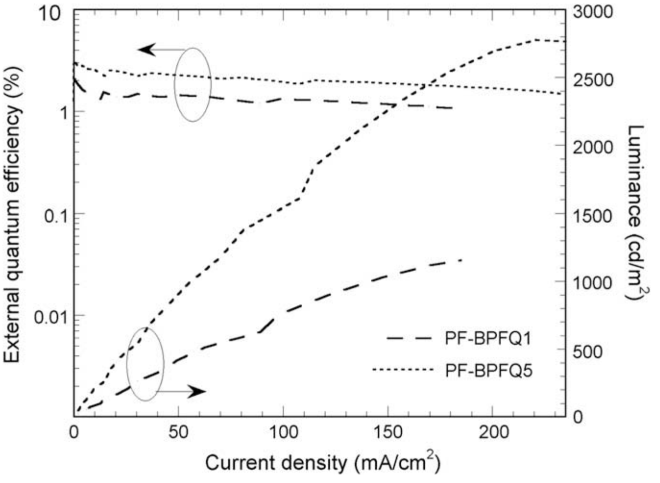

Fig. 8. QE–*J*–*L* characteristics of polymers PF–BPFQ1 and PF–BPFQ5.

3.5. Electroluminescent properties

As can be seen from the EL spectra in Fig. 5, no low-energy band emission was found in the EL spectra. The spectra remained blue with all of the contents of BPFQ in copolymers except a slight red-shift with the increasing content of BPFQ from 1 to 20 mol%, wherein the CIE coordinates change from (0.16, 0.07) to (0.19, 0.15). Since the electron deficient BPFQ moiety could act as charge trap unit, then the electron density of the fluorene segments were reduced and the charge delocalization in such donor–acceptor system was improved with the increasing content of BPFQ [27] followed by giving rise to a slight bathochromic shift in EL spectra.

To further investigate the electroluminescent stabilities of the copolymers, the EL spectra (taking PF–BPFQ5 as the example) in different current densities were recorded. As shown in Fig. 6, the profiles of the EL spectra only had a slight deviation with the current densities increased from 5 to 200 mA/cm^2 (corresponding applied voltages increase from 8.8 to 15.4 V, respectively), which meant the good spectra stabilities of these copolymers in EL procedure. Actually, further experiments based on the other copolymers showed similar results. The spectra stabilities might be attributed to that the electron-deficiency BPFQ moiety could withdraw the electrons from the fluorene segments, thereby even if there were a small amount of defects, the EL spectra based on these copolymers would still not be significantly influenced.

With the device configuration of ITO/PEDOT/polymer/Ba/Al based on the resulted copolymers, the best device performances were attained by copolymer PF–BPFQ5 containing 5 mol% of BPFQ unit. The peak external quantum efficiency (EQE_{max}) and luminous efficiency (LE_{max}) achieved 1.17% and 0.94 cd A^{-1}, respectively, with CIE coordinate of (0.16, 0.08), which were very close to NTSC standard blue luminescence of (0.14, 0.08). Noted, these results were entirely based on the single layer device configuration. However unfortunately, for copolymers with BPFQ fraction exceeded 10 mol%, the comprehensive performances otherwise lowered. Taking PF–BPFQ20 as an example, the EQE_{max} and LE_{max} were only 0.07% and 0.05 cd A^{-1}, respectively. The comprehensive electroluminescent properties are summarized in Table 3. These results clearly illustrated that there might be an optimum content for the incorporated heterocyclic BPFQ moiety.

The device configuration was an important factor for device efficiency [34–36]. In considering that the LUMO energy levels of copolymers were lowered with increasing the content of BPFQ unit, it would be expected that the incorporation of BPFQ unit into polymer backbone could improve electron-accepting ability of the copolymers compared to PFO. However, given the hole transport ability of polyfluorene were almost three orders of that of electrons [19,20], it was quite probable that only 5 mol% of BPFQ moiety in copolymer backbone was not efficient enough to transport enough electrons so as to balance the charge injection, whilst the device performances turned to inferior if extra BPFQ were incorporated. Thus, it was suspected that the charge balances of hole and electron in the emissive layer would be enhanced and the device performances would be dramatically improved if an additional hole block layer (HBL) was inserted between the emissive layer and the cathode [34]. Here, a layer of 1,3,5-tri(phenyl-2-benzimidazole)-benzene (TPBI), which has comparatively deep HOMO (−6.30 eV) and favorable LUMO (−2.80 eV) energy level [37] was inserted to block the holes not being quenched in the cathode. Given the LUMO energy level of TPBI (−2.80 eV) was the same as the Ba/Al cathode (−2.80 eV) and very close to the LUMO energy level of PF–BPFQ5 (−2.82 eV) (Fig. 7b), the electron injection from the cathode would not be influenced by the additional layer of TPBI. However, since there was a barrier of 0.64 eV between the HOMO of PF–BPFQ5 (−5.76 eV) and TPBI (−6.30 eV), the injected hole would be strictly confined in the emissive layer. The current density–voltage (*J*–*V*) characteristics and the device energy diagram (Fig. 7a) provided further insight into the roles played by the TPBI in the device. As can be seen from Fig. 7a and Table 3, the *J*–*V* characteristic shifted to a higher voltage and the device performances were obviously enhanced by insertion of a TPBI layer. The device based on PF–BPFQ5 showed an EQE_{max} of 2.99%, and a LE_{max} of 2.39 cd A^{-1}, with CIE coordinates of (0.16, 0.10). The enhanced efficiencies of the resulted devices with a TPBI layer illustrates that a more balanced hole and electron currents were achieved.

Fig. 8 showed the external quantum efficiency–current density–luminance (QE–*J*–*L*) characteristics of the devices based on PF–BPFQ1 and PF–BPFQ5, respectively. It was clearly seen that the QEs decline slightly with the increased current density, indicating that the materials and devices have a good stability.

4. Conclusion

A series of novel blue light-emitting polyfluorenes were prepared via incorporating fluorinated quinoxaline unit (BPFQ) into poly(9,9-dioctyl-2,7-diyl)fluorene (PFO) backbone. The incorporated BPFQ moiety could impart copolymers good electron affinity which followed by facilitate electron injection. No green emission was observed in both PL and EL spectra of all copolymers. The devices' performances were obviously improved when TPBI was used as a hole block layer.

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References

[1] Huang F, Zhang Y, Liu MS, Cheng YJ, Jen AKY. High-efficiency and color stable blue-light-emitting polymers and devices. Adv Funct Mater 2007;17:3808–15.

[2] Tang S, Liu MR, Lu P, Xia H, Li M, Xie ZQ, et al. A molecular glass for deep-blue organic light-emitting diodes comprising a 9,9′-spirobifluorene core and peripheral carbazole groups. Adv Funct Mater 2007;17:2869–77.

[3] Wu HB, Zou JH, Liu F, Wang L, Mikhailovsky A, Bazan GC, et al. Efficient single active layer electrophosphorescent white polymer light-emitting diodes. Adv Mater 2008;20:696–702.

[4] Gong X, Iyer PK, Moses D, Bazan GC, Heeger AJ, Xiao SS. Stabilized blue emission from polyfluorene-based light-emitting diodes: elimination of fluorenone defects. Adv Funct Mater 2003;13(4):325–30.

[5] Liu J, Cao JX, Shao SY, Xie ZY, Cheng YX, Geng YH, et al. Blue electroluminescent polymers with dopant–host systems and molecular dispersion features: polyfluorene as the deep blue host and 1,8-naphthalimide derivative units as the light blue dopants. J Mater Chem 2008;18:1659–66.

[6] Lim SF, Friend RH, Rees ID, Li J, Ma YG, Robinson K, et al. Suppression of green emission in a new class of blue-emitting polyfluorene copolymers with twisted biphenyl moieties. Adv Funct Mater 2005;15:981–8.

[7] Zhu R, Lai WY, Wang HY, Yu N, Wei W, Peng B, et al. Monodisperse star-shaped compound and its blend in uncapped polyfluorene matrices as the active materials for high-performance pure blue light-emitting devices. Appl Phys Lett 2007;90(14):141909.

[8] Zhan X, Liu Y, Wu X, Wang S, Zhu DB. New series of blue-emitting and electron-transporting copolymers based on fluorene. Macromolecules 2002;35:2529–37.

[9] Ego C, Grimsdale AC, Uckert F, Yu G, Srdanov G, Mullen K. Triphenylamine-substituted polyfluorene – a stable blue-emitter with improved charge injection for light-emitting diodes. Adv Mater 2002;14(11):809–11.

[10] Wu FI, Reddy DS, Shu CF, Liu MS, Jen AKY. Novel oxadiazole-containing polyfluorene with efficient blue electroluminescence. Chem Mater 2003; 15(1):269–74.

[11] Craig MR, de Kok MM, Hofstraat JW, Schenning APHJ, Meijer EW. Improving color purity and stability in a blue emitting polyfluorene by monomer purification. J Mater Chem 2003;13(12):2861–2.

[12] Yang W, Huang J, Liu C, Niu YH, Hou Q, Yang RQ, et al. Enhancement of color purity in blue-emitting fluorene-pyridine-based copolymers by controlling the chain rigidity and effective conjugation length. Polymer 2004;45: 865–72.

[13] Wu FI, Dodda R, Jakka K, Huang JH, Hsu CS, Shu CF. Enhancing the thermal and spectral stabilities of polyfluorene-based blue-light-emitting materials by incorporating pendent spiro-cycloalkyl groups. Polymer 2004;45(12): 4257–63.

[14] Lee J, Cho HJ, Jung BJ, Cho NS, Shim HK. Stabilized blue luminescent polyfluorenes: introducing polyhedral oligomeric silsesquioxane. Macromolecules 2004;37(23):8523–9.

[15] Li JY, Ziegler A, Wegner G. Substituent effect to prevent autoxidation and improve spectral stability in blue light-emitting polyfluorenes. Chem Eur J 2005;11(15):4450–7.

[16] Yang W, Hou Q, Liu CZ, Niu YH, Huang J, Yang RQ, et al. Improvement of color purity in blue-emitting polyfluorene by copolymerization with dibenzothiophene. J Mater Chem 2003;13:1351–455.

[17] Zhu Y, Gibbons KM, Kulkarni AP, Jenekhe SA. Polyfluorenes containing dibenzo[*a*,*c*]phenazine segments synthesis and efficient blue electroluminescence from intramolecular charge transfer states. Macromolecules 2007;40(4):804–13.

[18] Huang JS, Li G, Wu E, Xu QF, Yang Y. Achieving high-efficiency polymer white-light-emitting devices. Adv Mater 2006;18:114–7.

[19] Redecker M, Bradley DDC, Inbasekaran M, Woo EP. Nondispersive hole transport in an electroluminescent polyfluorene. Appl Phys Lett 1998;73:1565–7.

[20] Babel A, Jenekhe SA. Charge carrier mobility in blends of poly(9,9-dioctylfluorene) and poly(3-hexylthiophene). Macromolecules 2003;36:7759–64.

[21] Fukuda T, Kanbara T, Yamamoto T, Ishikawa K, Takezoe H, Fukuda A. Polyquinoxaline as an electron injecting material for electroluminescent device. Synth Met 1997;85:1195–6.

[22] Huo LJ, Tan ZA, Zhou Y, Zhou EJ, Han MF, Li YF. Poly(quinoxaline vinylene) with conjugated phenylenevinylene side chain: a potential polymer acceptor with broad absorption band. Macromol Chem Phys 2007;208(12):1294–300.

[23] Yamamoto T, Lee BL, Kokubo H, Kishida H, Hirota K, Wakabayashi T, et al. Synthesis of a new thiophene/quinoxaline CT-type copolymer with high solubility and its basic optical properties. Macromol Rapid Commun 2003;24(7):440–3.

[24] Jung SH, Kim DY, Cho HN, Suh DH. Synthesis and properties of new fluorene-based polyquinoxalines with an ether linkage in the main chain for light-emitting diodes. J Polym Sci Part A Polym Chem 2006;44(3):1189–98.

[25] Champion RD, Cheng KF, Pai CL, Chen WC, Jenekhe SA. Electronic properties and field-effect transistors of thiophene-based donor–acceptor conjugated copolymers. Macromol Rapid Commun 2005;26(23):1835–40.

[26] Fukuda T, Kanbara T, Yamamoto T, Ishikawa K, Takezoe H, Fukuda A. Polyquinoxaline as an excellent electron injecting material for electroluminescent device. Appl Phys Lett 1996;68(17):2346–8.

[27] Kulkarni AP, Zhu Y, Jenekhe SA. Quinoxaline-containing polyfluorenes: synthesis, photophysics, and stable blue electroluminescence. Macromolecules 2005;38(5):1553–63.

[28] Sakamoto Y, Suzuki T, Miura A, Fujikawa H, Tokito S, Taga Y. Synthesis, characterization, and electron-transport property of perfluorinated phenylene dendrimers. J Am Chem Soc 2000;122:1832–3.

[29] Heidenhain SB, Sakamoto Y, Suzuki T, Miura A, Fujikawa H, Mori T, et al. Perfluorinated oligo(*p*-phenylene)s. Efficient n-type semiconductors for organic light-emitting diodes. J Am Chem Soc 2000;122:10240–1.

[30] Dimitrakopoulos CD, Malenfant PRL. Organic thin film transistors for large area electronics. Adv Mater 2002;14:99–117.

[31] Ying L, Yang XL, Feng J, Wang CY, Cheng L. Synthesis and properties of poly(phthalazinone ether ketone ketone)s containing pendent methyl groups. Mater Sci Eng 2006;B132:20–3.

[32] Bredas JL, Silbey R, Boudreaux DS, Chance RR. Chain-length dependence of electronic and electrochemical properties of conjugated systems: polyacetylene, polyphenylene, polythiophene, and polypyrrole. J Am Chem Soc 1983;105:6555–9.

[33] Jenekhe SA, Lu L, Alam MM. New conjugated polymers with donor–acceptor architectures. Macromolecules 2001;34:7315–24.

[34] Du B, Wang L, Wu HB, Yang W, Zhang Y, Liu RS, et al. High-efficiency electrophosphorescent copolymers containing charged iridium complexes in the side chains. Chem Eur J 2007;13:7432–42.

[35] Wu HB, Huang F, Mo YQ, Yang W, Wang DL, Peng JB, et al. Efficient electron injection from a bilayer cathode consisting of aluminum and alcohol/water-soluble conjugated polymers. Adv Mater 2004;16:1826–30.

[36] Zeng WJ, Wu HB, Zhang C, Huang F, Peng JB, Yang W, et al. Polymer light-emitting diodes with cathodes printed from conducting Ag paste. Adv Mater 2007;19:810–4.

[37] D'Andrade BW, Holmes RJ, Forrest SR. Efficient organic electrophosphorescent white-light-emitting device with a triple doped emissive layer. Adv Mater 2004;16:624–8.