Polymer 55 (2014) 1698-1706

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Improved electroluminescence efficiency of polyfluorenes by simultaneously incorporating dibenzothiophene-*S*,*S*-dioxide unit in main chain and oxadiazole moiety in side chain

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ARTICLE INFO

Article history: Received 26 October 2013 Received in revised form 19 January 2014 Accepted 8 February 2014 Available online 18 February 2014

Keywords: Polyfluorenes 3,7-Dibenzothiophene-*S*,*S*-dioxide Oxadiazole

ABSTRACT

A series of efficient and spectrally stable blue light-emitting polyfluorene derivatives containing 3,7dibenzothiophene-*S*,*S*-dioxide (**SO**) unit in main chain and oxadiazole (**OXD**) moiety in the side chain were synthesized via Suzuki copolymerization. It was realized that the glass transition temperatures of the resulted copolymers **PFSO-OXD** increased gradually with the content of **OXD**, while the UV-vis absorption, photoluminescence spectra, as well as electrochemical properties were not significantly influenced by the molar ratio of **OXD** unit. Apparent solvatochromism of copolymers **PFSO-OXD** can be realized by varying polarity of solvents from toluene to dichloromethane. Light-emitting devices based on **PFSO-OXD** exhibited superior performances to those of **PFSO** and **PF-OXD20** due to the more balanced charge carrier mobility of the devices. The electroluminescence spectra of all copolymers are independent with the current densities and thermal annealing. The best device performance was achieved based on **PFSO-OXD20** with a maximal luminous efficiency of 4.9 cd A⁻¹ with the Commission Internationale de L'Eclairage (CIE) coordinates of (0.16, 0.12). The results indicated that the strategy of concurrently incorporating **SO** and **OXD** unit into the main chain and side chain of polyfluorenes, respectively has great potential to achieve efficient blue light-emitting polymers.

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1. Introduction

Polymer light-emitting diodes (PLEDs) have attracted considerable attention in recent years due to their great potential for the fabrication of large-area and flexible displays on the basis of cost-effective solution-processing techniques [1-4]. In order to achieve high performance full-color displays, light-emitting polymers with three primary color of red, green and blue emission are principally needed [5-7]. While the green and red-emitting polymers have been attained by various systems, efficient and spectrally stable blue light-emitting polymers with the Commission Internationale de L'Eclairage (CIE) coordinates of x + y < 0.3 remain great challenge because of the trade-off between luminous efficiency and color purity [8,9]. To address this point, extensive efforts have been devoted to the development of blue light-emitting

polymers with stable electroluminescence. Representative approaches include incorporating various electron-deficient moieties [10–12], using star-burst or hyperbranched framework to get rid of annihilation of excitons [8,13,14], relying on the next-generation thermal assisted delayed fluorescent emission [15] or hybridized local and charge transfer state [16] and so forth.

Among the currently available blue light-emitting polymer systems, recently emerged conjugated copolymers containing electron-deficient dibenzothiophene-*S*,*S*-dioxide (**SO**) moiety are of particular interests on account of their high efficiency and excellent spectral stability [17–23]. **SO** unit is quite similar to the fluorene moiety in shape, wherein the C-9 position of fluorene is replaced by electron-deficient *S*,*S*-dioxide in **SO** moiety [24]. The incorporation of **SO** unit into the backbone of conjugated polymers can lead to decreased lowest unoccupied molecular orbital (E_{LUMO}) energy levels, which is favorable for electron injection [25]. On the basis of this strategy, a series of conjugated copolymers based on fluorene or carbazole as electron-rich moiety, and **SO** unit which was 2,8-







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linked or 3,7-linked positions as electron-deficient moiety have been reported [17–23,25]. Highly efficient copolymers are therefore accessible based on this strategy with the luminous efficiency as high as 6.0 cd A^{-1} [17]. Even though the incorporation of more **SO** unit into the backbone of copolymers may lead to increased device performance, further improving the molar ratio of **SO** unit will lead to broadened emitting spectra due to the gradually dominated intramolecular charge transfer emission located at ca. 490 nm [26,27], which is unfavorable for the achievement of pureblue light-emitting polymers.

It is well-known that the oxadiazole (OXD) unit has high electron-affinity of ca. 2.16 eV [28,29], and its derivatives of 2-(4biphenylyl)5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) and related copolymers has been widely used as electron-injection/ transport materials in organic light emitting diodes [30–33]. Bipolar conjugated copolymers bearing **OXD** pendant chain as electron-deficient unit demonstrated improved electron-injection along with balanced charge transportation [34]. In this contribution, we introduced an alternative approach of incorporating an additional electron-deficient OXD moiety as the side chain to construct efficient blue light-emitting fluorene-co-SO-OXD based copolymers. We surmise that the resulted copolymers that simultaneously containing electron-deficient moieties of SO and OXD moiety in the main chain and side chain, respectively may have specific advantages including enhanced electron transport properties that is favorable for the balance of charge carriers in the active layer, along with the improved solubility of copolymers.

2. Experimental

All commercially available reagents were distilled according to standard procedure prior to use. 2,7-Dibromo-9,9-bis-(4-hydroxyphenyl)fluorene (1) [35], 2,7-dibromo-9,9-dioctylfluorene (4), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (5) and 3,7-dibenzothiophene-*S*,*S*-dioxide (6) were synthesized according to the previously reported procedures [17,36].

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 300 spectrometer (operating at 300 MHz for ¹H NMR, and 75 MHz for ¹³C NMR) in deuterated chloroform solution with tetramethylsilane as a reference. Gel permeation chromatography (GPC) measurements were performed in tetrahydrofuran (THF) with a Waters 2410 refractive index detector. Cyclic voltammetry (CV) measurement was carried out at a scan rate of 50 mV/s at room temperature under argon using a CHI660A electrochemical workstation with tetra(n-butyl)ammonium hexafluorophosphate (n-Bu₄NPF₆, 0.1 M) in acetonitrile as the electrolyte. Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209 at a heating rate of 20 °C min⁻¹. The differential scanning calorimetry (DSC) was measured on a Netzsch DSC 204 under nitrogen flow at a heating rate of 10 °C min⁻¹. UV-vis absorption spectra were recorded with a HP 8453 spectrophotometer. Photoluminescence (PL) spectra were recorded with a spectrofluorometer (Spex Fluorolog-3). PL quantum yields were measured using an ISO80 LabSphere integrating sphere with excitation by a 325 nm HeCd laser (Melles Griot).

2.1. 2-(4-Fluorobenzoyl)-5-[4-tert-butylphenyl]-[1,3,4]oxadiazole(2)

A mixture of 4-*t*-butylbenzhydrazide (7.68 g, 40 mmol), triethylamine (4.04 g, 40 mmol) and chloroform (200 mL) was stirred at about 0 °C in a 250 mL three-neck flask. Then 4-fluorobenzoyl chloride (6.32 g, 40 mmol) dissolved in chloroform (20 mL) was added to the mixture dropwise. After 2 h, the reaction mixture was concentrated and washed with petroleum ether for three times to afford crude product as white power. Then the resulting product was dissolved in SOCl₂ (15 mL) and was heated for 16 h under 70 °C. After cooling to room temperature, the reaction mixture was dropped into water, filtered and recrystallized from ethanol to give the target compound (9.00 g) as white needles. Yield: 76%. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.14 (m, 2H), 8.06 (d, *J* = 8.52 Hz, 2H), 7.56(d, *J* = 8.52 Hz, 2H), 7.23 (t, *J* = 8.73 Hz, 2H), 1.35(s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 166.42, 164.71, 163.56, 163.06, 155.46, 129.23, 129.11, 126.76, 126.09, 120.96, 120.40, 120.36, 116.55, 116.26, 35.11, 31.12.

2.2. 2,7-Dibromo-9,9-bis(4-(4-(5-(4-tert-butylphenyl)-2-oxadiazolyl)phenyloxy)phenyl)fluorene (**3**)

A mixture of compound **1** (5.08 g, 10 mmol), **2** (7.4 g, 25 mmol) and sodiumhydride (0.96 g, 40 mmol) was dissolved in N,N-dimethylformide (DMF, 300 mL) and stirred at 150 °C under argon for 20 h. The reaction mixture was poured in water. The organic layer was then extracted by dichloromethane, dried over magnesium sulfate (MgSO₄) and concentrated. The crude product was purified by chromatography on silica gel using petroleum ether/dichloromethane/ethyl acetate (8/1/1, v/v/v) as the eluent followed by recrystallization from ethanol to give the target compound (7.4 g)as white needles. Yield: 70%. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.10 (d, J = 8.85 Hz, 4H), 8.05 (d, J = 8.55 Hz, 4H), 7.63 (d, J = 8.55 Hz, 2H), 7.54 (m, 8H), 7.20 (d, *J* = 8.82 Hz, 4H), 7.15 (d, *J* = 8.85 Hz, 4H), 7.03 (d, I = 8.79 Hz, 4H), 1.37 (s, 18H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 164.61, 164.07, 160.14, 155.42, 155.36, 152.97, 140.20, 138.09, 131.36, 129.68, 129.38, 128.94, 126.84, 126.17, 122.16, 121.93, 121.23, 119.70, 119.03, 118.93, 64.74, 35.21, 31.25.

2.3. General procedures of Suzuki copolymerization, taking PFSO as an example

Compound 4 (642.6 mg, 1.0 mmol), 5 (438.7 mg, 0.8 mmol), and 3,7-dibromo-dibenzothiophene-S,S-dioxide **(6)** (74.8 mg, 0.2 mmol), tetrakis(triphenylphosphine)palladium, $(Pd(PPh_3)_4,$ 3 mg), tetraethylammonium hydroxide aqueous solution (Et₄NOH, 20 wt/v%, 2 mL) and toluene (15 mL) was stirred under argon and heated to 100 °C. The solution was kept at 100 °C with vigorous stirring under argon for 24 h. Then phenylboronic acid (20.0 mg) was added and the reaction was allowed to stirring for 6 h. And then bromobenzene (0.2 mL) was added and the reaction was allowed to stirring for another 6 h. After cooling to room temperature, the solution was precipitated into methanol (200 mL) and filtered. The solids were re-dissolved in dichloromethane and washed with water for three times. After removal of the volatile under reduced pressure, the concentrated solution was precipitation in methanol to give target copolymer. The resultant polymers were washed by using Soxhlet extraction by using acetone and dried under vacuum to give the 663 mg of yellowish fibers with yields of 90%. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.20 (br, Ar H), 7.86-7.61 (br, Ar H), 1.15 (m, CH₂), 0.84-0.79 (m, CH₃). Anal. Calcd. (%) for [(C₂₉H₄₀)₉₀(C₁₂H₆O₂S)₁₀]_n: C 88.40; H 9.88; S 0.86. Found: C 87.85; H 10.05; S 1.05.

2.4. PF-**OXD**20

Monomer **3** (424.4 mg, 0.4 mmol), **4** (642.6 mg, 1.0 mmol), **5** (329.0 mg, 0.6 mmol), yield: 76%. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.11–8.02 (br, Ar H), 7.78–7.43 (br, Ar H), 7.18–7.04 (br, Ar H), 1.36–1.13 (m, CH₂), 0.84–0.74 (m, CH₃). Anal. Calcd. (%) for [(C₂₉H₄₀)₈₀(C₆₁H₄₈O₄N₄)₂₀]_n: C 86.63; H 8.48; N 2.28. Found: C 86.08; H 9.08; N 2.26.



Scheme 1. Synthesis of monomer and copolymers.

2.5. PFSO-OXD10

Monomer **3** (212.2 mg, 0.2 mmol), **4** (642.6 mg, 1.0 mmol), **5** (329.0 mg, 0.6 mmol), **6** (74.8 mg, 0.2 mmol), yield: 57%. ¹H NMR (300 MHz, CDCl₃) δ (ppm), 8.20–8.02 (br, Ar H), 7.84–7.43 (br, Ar H), 7.19–7.04 (br, Ar H), 1.43–1.14 (m, CH₂), 0.88–0.80 (m, CH₃). Anal. Calcd. (%) for [(C₂₉H₄₀)₈₀(C₁₂H₆O₂S)₁₀(C₆₁H₄₈O₄N₄)₁₀]_n: C 86.76; H 8.87; N 1.33; S 0.76. Found: C 86.30; H 8.87; N 1.34; S 1.05.

2.6. PFSO-OXD20

Monomer **3** (424.4 mg, 0.4 mmol), **4** (642.6 mg, 1.0 mmol), **5** (219.4 mg, 0.4 mmol), **6** (74.8 mg, 0.2 mmol), yield: 46%. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.20–8.02 (br, Ar H), 7.78–7.42 (br, Ar H), 7.19–7.04 (br, Ar H), 1.43–1.13 (m, CH₂), 0.88–0.80 (m, CH₃). Anal. Calcd (%) for [(C₂₉H₄₀)₇₀(C₁₂H₆O₂S)₁₀(C₆₁H₄₈O₄N₄)₂₀]_n: C 85.49; H 8.08; N 2.37; S 0.68. Found: C 85.05, H 8.45, N 2.26, S 1.07.

2.7. PFSO-OXD30

Monomer **3** (636.5 mg, 0.6 mmol), **4** (642.6 mg, 1.0 mmol), **5** (109.7 mg, 0.2 mmol) and **6** (74.8 mg, 0.2 mmol), yield: 48%. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.20–8.02 (br, Ar H), 7.78–7.42 (br, Ar H), 7.18–7.04 (br, Ar H), 1.43–1.12 (m, CH₂), 0.83–0.75 (m, CH₃).

2.8. PFSO-OXD40

Monomer **3** (848 mg, 0.8 mmol), **4** (642.6 mg, 1.0 mmol), **6** (74.8 mg, 0.2 mmol), yield: 51%. ¹H NMR (300 MHz, CDCl₃) δ (ppm):

8.20–8.02 (br, Ar H), 7.77–7.43 (br, Ar H), 7.18–7.04 (br, Ar H), 1.43–1.14 (m, CH₂), 0.83–0.75 (m, CH₃).

2.9. Device fabrication and characterization

Polymers were dissolved in p-xylene. Patterned ITO coated glass substrates were cleaned with acetone, detergent, deionized water and 2-propanol followed by an ultrasonic bath. After treating with oxygen plasma, 40 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 12 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). Finally, 1.5 nm of CsF followed by 120 nm of aluminum (thickness monitored with a STM-100/MF-Sycon guartz crystal) were subsequently evaporated on the top of an EL polymer layer in a vacuum of 3 \times 10⁻⁴ Pa. Current-voltage (I-V) characteristics were recorded in the nitrogen dry-box using a Keithley 236 source-measurement unit and a calibrated silicon photodiode. EL spectra and CIE color coordinates were measured by a PR 705 photometer (Photo Research).

The hole- and electron-only devices were used as ITO/ PEDOT:PSS(40 nm)/copolymer (169 nm)/MoO₃(10 nm)/Al and ITO/ Al(30 nm)/polymer (169 nm)/Ca (3 nm)/Al, respectively. To fabricate the hole-only device, a layer of MoO₃ (10 nm) instead of cesium fluoride was thermally deposited on top of the emission layer with a protective aluminum layer, with the remaining steps the same as those for the bipolar device. For the electron-only device, ITO glass was deposited with a layer of aluminum (30 nm) to replace the



Fig. 1. DSC (a) and TGA (b) curves of copolymers.

PEDOT:PSS film, then a thick copolymer layer (141 nm for **PFSO**, 209 nm for **PF-OXD20** and 169 nm for **PFSO-OXD20**) was spin-cast from *p*-xylene solution on top of the aluminum layer and annealed at 100 °C for 20 min. Profilometry (Tencor Alfa-Step 500) was used to determine the thickness of the films. Finally, 1.5 nm of CsF followed by 100 nm of aluminum (thickness monitored with a STM-100/MF Sycon quartz crystal) were thermally evaporated through a shadow mask at a base pressure of 3.0×10^{-4} Pa to form the cathode.

3. Results and discussion

3.1. Synthesis of monomer and copolymers

The detailed procedure for the synthesis of monomer and copolymers are illustrated in Scheme 1. Monomer 2,7-dibromo-9,9bis(4-(4-(5-(4-*tert*-butylphenyl)-2-oxadiazolyl)phenyloxy)phenyl) fluorene (3) was prepared based on the aromatic nucleophilic substitution reaction of compounds 2,7-dibromo-9,9-bis-(4hydroxyphenyl)fluorene (1) and 2-(4-fluorobenzoyl)-5-[4-tertbutylphenyl]-[1,3,4]oxadiazole (2), since the electron-withdrawing **OXD** group can effectively stabilize the negative charge developed through a stabilized transition state (Meisenheimer complex) to lower the activation energy for the displacement reaction of the arvl fluorides group [37], which accordingly lead to relatively high yield of 70%. Suzuki copolymerization was carried out with molar feed ratio of monomer 3, 2,7-bis(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)-9,9-dioctylfluorene (4), 2,7-dibromo-9,9dioctylfluorene (5) and 3,7-dibenzothiophene-S,S-dioxide (6) of 0:50:40:10, 20:50:30:0, 10:50:30:10, 20:50:20:10, 30:50:10:10 and 40:50:0:10, and the resulted copolymers were referred as **PFSO**, PF-OXD20, PFSO-OXD10, PFSO-OXD20, PFSO-OXD30 and PFSO-OXD40, respectively. The copolymers were end-capped with phenylboronic acid and bromobenzene to remove active end-groups of polymer main chain.

All copolymers can be readily dissolved in common organic solvents including toluene, chloroform, tetrahydrofuran (THF), chlorobenzene, etc, illustrating great potential for solution processing procedures. The number average molecular weight (M_n) and polydispersity indices (PDI) of copolymers were evaluated by gel permeation chromatography (GPC) with THF as eluent and linear polystyrene as standard, which were in the range of 7.9–12.2 kDa and 1.7–2.3, respectively.

3.2. Thermal properties

Thermal properties of copolymers were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) with corresponding characteristics shown in Fig. 1. One can realize that copolymer **PFSO**, which do not contain **OXD** moiety in the backbone, exhibited typical liquid crystal (LC) like transition at about ca. 156 °C, which is quite close to that of poly(9,9dioctylfluorene) (PF) of ca. 160 °C [38]. In contrast, all the other copolymers containing **OXD** in side chains did not show distinct LC transition, as the bulky **OXD** side chain may obstruct the formation of ordered structures. From Fig. 1a one can obviously recognize that the glass transition temperature (T_g) of copolymers gradually increased from 113 to 160 °C with the molar ratio of the incorporated **OXD** moiety increased from 10 to 40 mol%, indicating that the incorporated **OXD** moiety in side chain is favorable for thermal stability of copolymers. It is also worth pointing out that copolymer PFSO-OXD20, which simultaneously comprising SO and OXD moieties in main chain and side chain, respectively, exhibited higher T_g of 140 °C than that of 103 °C and 125 °C for its counterparts of **PFSO** and **PF-OXD20**, respectively. The fact demonstrated that the combination of both SO and OXD moiety are favorable for the thermal property of copolymers. Further TGA measurements illustrated that all copolymers exhibit good thermal stability, with onset decomposition temperatures (T_d) in the range of 417–435 °C under a nitrogen atmosphere, as can be referred in Fig. 1b. The outstanding thermal stability of copolymers is essentially positive for the long-term stability of fabricated device. The corresponding thermal properties data are summarized in Table 1.

3.3. Photophysical properties

Fig. 2 showed the UV-vis absorption spectra of all copolymers in toluene solution with concentration of 1×10^{-5} mol L⁻¹ and in thin films. The strong peak at ca. 390 nm can be attributed to the $\pi - \pi^*$ transitions of **PF** backbone, while the additional absorption peaked at ca. 300 nm arised with the incorporation of **OXD** unit. It was also found that the intensity of the peak located at ca. 300 nm increases with increasing **OXD** unit content. Moreover, the absorption profiles of all copolymers that containing **SO** unit in main

Table 1	
Molecular weights and thermal properties of copolymers.	

Copolymer	<i>M</i> _n /kDa	PDI	$T_{\rm g}/^{\circ}{\rm C}$	$T_{\rm d}/^{\circ}{\rm C}$
PFSO	9.3	1.7	103	428
PF-OXD20	11.8	2.1	125	431
PFSO-OXD10	10.4	1.7	113	426
PFSO-OXD20	12.2	2.3	140	417
PFSO-OXD30	12.0	2.2	158	435
PFSO-OXD40	7.9	2.3	160	433



Fig. 2. UV-vis absorption of copolymers in toluene solution (a) and in film (b).

chain exhibited nearly identical absorption profiles in the range of 335–440 nm, along with a slightly broadened absorption profiles with respect to copolymer **PF-OXD20** in both toluene solution and thin films. This observation might be attributed to the effects of intramolecular charge transfer (ICT) due to the incorporation of the electron-deficient **SO** unit in the backbone of polyfluorene, which agrees with previously reported **SO** based copolymer systems [17,27]. The UV-vis absorption profiles of copolymers in chloroform and chlorobenzene solution (Figure S1 in the Supporting Information) are quite comparable to those of in toluene solution.

By comparing the absorption profiles of copolymers in toluene solution (Fig. 2a) with a concentration of ca. 1×10^{-5} mol mL⁻¹ and in film (Fig. 2b), one can realize that the full width at half maximum (FWHM) increased from 50 to 57 nm for **PF-OXD20**, and from 53 to 68 nm for other copolymers containing **SO** unit. The broadened absorption profiles revealed stronger aggregation as can be attributed to the increased molecular interaction due to the incorporated **SO** unit. It was also recognized that the intensity of the peak at ca. 300 nm increases with the molar ratio of **OXD** unit, which was consistent with that of in toluene solution. The optical band gap (E_{g}^{opt}) as estimated from the onset of absorption as thin films are in the range of 2.83–2.94 eV as summarized in Table 2.

Fig. 3a shows the photoluminescence (PL) spectra of copolymers in toluene solution with concentration of 1×10^{-5} mol L⁻¹. It was found that copolymer **PF-OXD20** exhibited the maximum photoluminescence (PL) emission at 419 nm along with a shoulder peak at 438 nm, which was quite comparable to that of typical emission

Table 2					
Optical and	electrochemical	characterization	of the	copolyn	ners

Polymer	E _{ox} a /V	E _{red} ^b /V	E _{HOMO} ^c /eV	E _{LUMO} ^d /eV	E ^{cv e} /eV	E ^{opt f} /eV	QE _{PL} g /%
PFO	1.46	-2.14	-5.86	-2.26	3.61	_	_
PFSO	1.54	-1.84	-5.94	-2.56	3.30	2.85	61
PF-OXD20	1.45	-2.06	-5.85	-2.34	3.51	2.94	20
PFSO-OXD10	1.48	-1.77	-5.88	-2.63	3.24	2.87	39
PFSO-OXD20	1.52	-1.75	-5.92	-2.65	3.27	2.85	56
PFSO-OXD30	1.50	-1.75	-5.90	-2.65	3.25	2.85	51
PFSO-OXD40	1.51	-1.72	-5.93	-2.68	2.23	2.83	51

^a Onset of oxidation potential.

Table 2

^b Onset of reduction potential.

^c Calculated from the oxidation potential.

^d Calculated from the reduction potential.

 e Calculated from the E_{HOMO} and E_{LUMO} energy levels.

^f Calculated from the onset of the absorption as thin films.

^g Measured as thin films.

of poly(9,9-dialkylfluorene) in toluene solution [39]. In contrast, copolymers PFSO-OXD that contained SO and OXD unit in the main chain and side chain, respectively, exhibited nearly indistinguishable PL spectra with peak emission located at ca. 429 nm, which has a bathochromic shift of ca. 10 nm with respect to that of PF-OXD20 as can be attributed to the ICT effects. Additionally, distinct solvatochromism of PL spectra was realized by using different solvents of toluene, chlorobenzene, THF, chloroform as well as dichloromethane, which have various parameters of polarity (Table S1 in the Supporting Information). Taking **PFSO-OXD20** as an example, the well-resolved emission can be realized in non-polar solvent of toluene and became featureless in polar solvent of dichloromethane, while the emission maximum bathochromic shifted from 429 nm in toluene to that of ca. 450 nm in dichloromethane, as demonstrated in Fig. 3b. It is also worth pointing out that copolymer PF-OXD20 exhibited slightly higher PL quantum efficiency in toluene, THF as well as dichloromethane solution than the other copolymers, but much lower PL quantum efficiency than the other copolymers in chloroform (Figure S2 in the Supporting Information). However, the PL quantum efficiency in all kinds of solutions for copolymers containing SO and OXD unit in the main chain and side chain, respectively, were slightly higher than that of PFSO, indicating the superiority of the incorporated OXD moiety as the side chain.

The PL emission of copolymers as thin films was demonstrated in Fig. 4a. It was realized that the PL emission of copolymers containing **SO** moiety in the backbone showed nearly indistinguishable profiles with the maximum emission located at ca. 450 nm, which has a bathochromic shift of ca. 20 nm relative to that of ca. 427 nm for **PF-OXD20**, as can be attributed to the lack of ICT effects in **PF-OXD20**. We note that there is ca. 10 nm bathochromic shift of the PL emission as thin films of all copolymers with respect to those of in toluene solutions, which is understandable due to the aggregation of the molecular main chain in solid state. Additionally, as illustrated in Table 2, even though copolymers **PFSO-OXD** showed slightly lower PL quantum efficiency (QE_{PL}) in thin films, their QE_{PL} are much higher than copolymer **PF-OXD20**.

Investigation of thermal stabilities of PL emission of copolymer films was carried out by spin-coating copolymer films atop prefabricated ITO/PEDOT:PSS, which were then drying under vacuum followed by annealing at various temperatures from 80 to 160 °C for 2 h in the inert atmosphere. Representative spectra based on copolymer **PFSO-OXD20** were shown in Fig. 4b. No discernable change was found with respect to that of the pristine film even when the annealing was performed at the temperature higher than its T_g for 2 h, illustrating the excellent thermal stability of the resulted copolymers.



Fig. 3. PL spectra of copolymers in toluene solution (a), and in different solvents of PFSO-OXD20 (b) with a concentration of ca. 1×10^{-5} mol mL⁻¹.



Fig. 4. PL spectra of PFSO-OXD20 thermal annealed at various temperature.

3.4. Electrochemical properties

The electrochemical properties of the copolymers were examined by cyclic voltammetry (CV) under inert atmosphere with the graphite, platinum wire and Ag/AgCl as the working electrode, counter electrode and reference electrode, respectively. All measurements were carried out in tetrabutyl ammonium hexa-fluorophosphate (Bu₄NPF₆) solution (0.1 M in acetonitrile) at a scan rate of 50 mV s⁻¹ with corresponding curve shown in Fig. 5.

The oxidation potential of polymers were calibrated to the ferrocene/ferrocenium redox couple (F_c/F_c^+) , which was determined to be 0.40 V under the same experimental conditions. It is assumed that the redox potential of F_c/F_c^+ has an absolute energy level of -4.8 eV to vacuum [40,41]. Therefore, the highest occupied molecular orbital energy levels (E_{HOMO}) and LUMO energy levels (E_{LUMO}) of polymers were calculated according to the equation of $E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.40) \text{ (eV)}$ and $E_{\text{LUMO}} = -e(E_{\text{red}} + 4.40) \text{ (eV)}$, where the E_{ox} and E_{red} is the onset of the oxidation and reduction potential relative to Ag/Ag⁺, respectively [40,41]. It was found that all copolymers exhibited analogous E_{HOMO}, which located in the range of $-5.85 \sim -5.94$ eV and was quite comparable with that of poly(9,9-dioctylfluorene) (**PFO**), indicating that the incorporation of the electron-deficient SO and OXD moieties did not significantly disturb the E_{HOMO} . The comparatively deep E_{HOMO} of copolymers would provide superb stability. On the other hand, copolymers containing **SO** moiety in the backbone exhibited analogous E_{LUMO} ranged from -2.63 to -2.68 eV, which were distinctly lower than those of -2.26 eV and -2.34 eV for PFO and PF-OXD20, respectively. The decreased E_{LUMO} can be attributed to the incorporated electron-deficient SO in the backbone of copolymers, whilst the **OXD** in the side chain of copolymer would not influence the molecular frontier orbitals of the resulted copolymers since the **OXD** moiety is linked to polymer backbone through a nonconjugated linkage. Detailed parameters of CV measurement are summarized in Table 2.



Fig. 5. Cyclic voltammograms of polymer thin films in an acetonitrile electrolyte solution of *n*-Bu₄NPF₆ (0.1 M).



Fig. 6. EL spectra of copolymers.

3.5. Electroluminescence properties

Light-emitting diodes with the configuration of ITO/PEDOT:PSS/ copolymers/CsF/Al were fabricated to investigate the electroluminescence (EL) performances of the resulted copolymers. Fig. 6 demonstrates the electroluminescence spectra of devices based on these copolymers at current density of 10 mA cm⁻². It was realized that the EL profiles of all copolymers are quite similar to their PL spectra, and all copolymers exhibited blue emission without unexpected emission of low-energy band at ca. 530 nm corresponding to the fluorenone defects [42]. The EL emission of all copolymers containing **SO** unit in the main chain of copolymers located at ca. 450 nm, which exhibited a distinctly bathochromic shift relative to that of 425 nm for **PF-OXD20**. The fact can be attributed to the ICT effects between the electron-rich fluorene and electron-deficient **SO** moiety [17], while the non-conjugated linked **OXD** in side chain has little effect on the EL emission profiles.

Investigation of the EL spectral stability was performed by varying the applied current density during devices operation as well as thermally annealed the specific device at various temperatures for 2 h. Representative EL spectra based on copolymer **PFSO-OXD20** as an example were summarized in Fig. 7. It was recognized that the EL spectra remain almost unchanged with respect to the pristine device by varying the applied current densities from 6 to 240 mA cm⁻² (Fig. 7a), as well as performing thermal annealing at different temperature of 80, 100, 120 and 160 °C (Fig. 7b). We also noted that the unexpected low-energy emission band corresponding to the excimers or fluorenone-defects cannot be discerned even at comparatively high current density of 240 mA cm⁻² as well as when the film were thermally annealed at the temperature higher than the glass transition temperature, indicating the superb EL stability of devices based on the resulted copolymers.

As can be seen in Fig. 8a, devices based on copolymer PFSO and **PFSO-OXD20** exhibited lowest threshold voltage (*V*_{th}) of ca. 3.1 V, which was slightly lower than that of ca. 3.6 V for copolymer PF-OXD20 that without SO unit in the backbone. The maximum luminance (L_{max}) of devices based copolymers **PFSO-OXD** are much higher than that of **PFSO** and **PF-OXD20**, which may be attributed to the more balanced charge carrier transportation in the emissive layer. Fig. 8b summarized the characteristics of luminous efficiency (LE) as a function of current density (J). One can clearly observe that, devices based on copolymer PFSO and PF-OXD20 exhibited moderate performance, which has the maximum LE (LE_{max}) of 1.8 and 0.9 cd A^{-1} , respectively. On the contrary, devices based on copolymers **PFSO-OXD** exhibited superior performances to those of based on **PFSO** and **PF-OXD20**, especially when the current density higher than 10 mA cm⁻². Best device performance was achieved based on copolymer **PFSO-OXD20**, which has LE_{max} of 4.9 cd A⁻¹ and L_{max} of 8450 cd m⁻² with CIE coordinates of (0.16, 0.12). Detailed device performances are summarized in Table 3. It is worth noting that these device performances were achieved based on standard device structures, further optimization of device structures may lead to improved performances. Nevertheless, when comparing to the reported blue light-emitting copolymers that containing heterocyclic groups such as oxadiazole [43–45], quinoxaline [10], silafluorene [46,47] and dibenzothiophene [36], the resulted polymers exhibited obviously improved device performance in terms of relatively high luminous efficiency due to the incorporated electron-deficient **SO** moiety. On the other hand, with respect to the **SO** based copolymers [17,20,23,25], the advantage of the resulted polymers involves the achievement of efficient blue emission at low SO ratio, which can effectively avoid gradually broadened emitting spectra with increased content of SO unit. The fact demonstrated that the current strategy can be an effectual approach to achieve highly efficient blue light emitting polymer with good color purity as well as excellent spectra stability.

Insight into the impact of the incorporated **SO** and **OXD** on the charge carrier transport properties of copolymers came from the measurement of space charge limited current (SCLC). Single charge carrier devices were fabricated with configuration of ITO/



Fig. 7. EL spectra of PFSO-OXD20 under different applied current densities (a) and varied thermal annealing temperatures (b).



Fig. 8. B - V (a) and L - J (b) characteristics of devices with architecture of ITO/PEDOT:PSS/copolymer/CsF/Al.

Table 3

Device performances with structure of ITO/PEDOT:PSS/copolymer/CsF/Al.

Copolymer	V _{on} ^a (V)	LE_{max} (cd A ⁻¹)	$L_{\rm max}$ (cd m ⁻²)	CIE ^b (x, y)
PFSO	3.7	1.8	6548	(0.15, 0.15)
PF-OXD20	3.6	0.9	2209	(0.18, 0.15)
PFSO-OXD10	3.5	2.6	7842	(0.15,0.14)
PFSO-OXD20	3.2	4.9	8450	(0.16, 0.12)
PFSO-OXD30	3.8	3.8	9617	(0.15, 0.13)
PFSO-OXD40	3.3	3.4	6450	(0.15, 0.12)

^a Corresponding to luminance of 1 cd m⁻².

^b Measured at current density of 10 mA m⁻².

PEDOT:PSS/copolymer/MoO₃/Al and ITO/Al/copolymer/Ca/Al for hole-only and electron-only devices, respectively. These so-called hole-only devices are fabricated by replacing common cathode of CsF/Al with high work function MoO₃/Al. The increasing offset between the Fermi energy of the cathode and the ELUMO of MoO3 (2.3 eV) reduces the number of injected electrons to levels at which the injected holes significantly dominate. A similar analysis can be carried out for the electron-only devices by replacing the ITO (4.7 eV) with a lower work function metal Al (4.2 eV), which can make sure that the carriers are almost exclusively electrons as a result of increasing offset between the Fermi level of the anode and the HOMO energy level of blue light-emitting polymers (about 5.9 eV) [48]. The resulted current density – voltage (I - V) characteristics based on copolymers PFSO, PF-OXD20 and PFSO-OXD20 as active layer were demonstrated in Fig. 9. It was realized that the copolymer PFSO that containing SO in the main chain, and PF-OXD20 that containing OXD in the side chain, exhibited imbalanced hole and electron fluxes, as the hole mobility is distinctly higher than that of electron mobility in a range of the applied electric field intensity. The imbalanced charge carrier transportation may lead to inferior device performances at high current, which is consistent with the fast efficiency roll-off as shown in Fig. 8b. In contrast, well-balanced hole and electron fluxes can be realized for copolymer **PFSO-OXD20** which simultaneously bearing **SO** and **OXD** unit in the main chain and side chain, respectively. The fact indicated that our strategy of incorporating **OXD** moiety into the backbone of fluorene–*co*–**SO** copolymer can effectively improve the electron transportation and resulted in balanced charge carrier across the emissive layer, which can in turn lead to the improved device performances.

4. Conclusion

In summary, a series of efficient and spectrally stable blue lightemitting polyfluorenes were synthesized by simultaneously incorporating **SO** and **OXD** moiety into the backbone and the side chain, respectively. The resulted copolymers exhibited superb electroluminescence stability, as no low-energy emission can be observed by varying the applied current densities or thermally annealed devices at different temperatures. It was also realized that the efficiencies of all copolymers that simultaneously containing **SO** and **OXD** unit are superior to copolymers that only bearing **SO** or **OXD** unit, which can be attributed to the improved electron transportation that can in turn lead to well-balanced charge carrier transportation. Best device performance with the maximum luminous efficiency of 4.9 cd A^{-1} and CIE coordinates of (0.16, 0.12) were achieved based copolymer **PFSO-OXD20** as emissive layer. The results indicated that our strategy by concurrently



Fig. 9. J - V characteristics of single carrier devices of PFSO (a), PF-OXD20 (b) and PFSO-OXD20 (c).

incorporating electron-deficient **SO** and **OXD** moieties can be promising approach to realize efficient blue light-emitting copolymers.

Acknowledgments

The authors are grateful for financial support from the National Natural Science Foundation of China (grant Nos. 51303056, 21074038, 21303256 and 51273069), the Research Fund for the Doctoral Program of Higher Education of China (20130172110005) and the Fundamental Research Funds for the Central Universities, South China University of Technology (No. 2014ZM0005).

Appendix A. Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.polymer.2014.02.032.

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