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# Phosphine oxide-functionalized polyfluorene derivatives: Synthesis, photophysics, electrochemical properties, and electroluminescence performance

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A series of phosphine oxide-functionalized polyfluorene derivatives, PFH-PO-40-1 (**P1**), PFH-PO-20-1 (**P2**), PFH-PO-10-1 (**P3**), and PFH-PO-1-1 (**P4**), were prepared via a palladium-mediated Suzuki cross-coupling reaction. The structures and purities of all polymers were fully characterized by $^{1}H$ and $^{13}C$ NMR, UV-vis and photoluminescent spectroscopy, gel permeation chromatography, and TGA/DSC. Their emission features showed single broad peaks at about 445 nm in film, compared with those in dilute solutions, which might be caused by some degree of aggregation in the excited states of the backbones. The best electroluminescence (EL) performance of these polymers with configuration of ITO/PEDOT:PSS/Polymer/$Alq_3$/LiF/Al was obtained from **P1** (current efficiency was 4.2 Cd/A at 6V).

**organic light-emitting diodes, polyfluorene derivatives, electroluminescence**

## 1 Introduction

π-Conjugated polymers with electronically rigid backbones have attracted considerable interest due to their electronic and optoelectronic applications, such as organic light-emitting diodes (OLEDs) [1], organic field effect transistors (OFETs) [2], and photovoltaics [3], as well as other organic semiconducting devices. Polyfluorene derivatives (PFs) have emerged as a class of promising optoelectronic materials, due to their strong blue electroluminescence (EL), high thermal/chemical stability, good solubility in common organic solvents, and facile modification of the side chains without affecting the conjugation of the main chain [4]. Up to now, PFs with a variety of functional groups in the side chains such as ionic groups or special receptors have been used in several fields such as chemo/biosensors [5] and PLEDs [6].

Phosphine oxide groups have been widely used in the preparation of quantum dots due to their strong affinity for inorganic nanocrystals [7]. In addition, phosphine oxide groups were embedded into conjugated polymers to form hybrid nanocomposites between polymers and nanocrystal and realize efficient Förster energy transfer from the polymer to nanocrystal [8]. Wang's group previously reported PFs with phosphonate/phosphonic acid groups in the side chains which both showed high sensitivity and selectivity towards $Fe^{3+}$ ion [5j]. Herein, we design and synthesize a series of PFs via the introduction of phosphine groups into PFs in order to endow these polymers multifunctional properties, especially in electroluminescence. Our PF derivatives reported herein possesses good thermal stability, large band

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gap, and good film-forming properties. The electroluminescence (EL) properties of these polymers are recorded on an organic light-emitting diode (OLED) device configuration of ITO/PEDOT:PSS/Polymer/$Alq_3$/LiF/Al. The best device result (Current efficiency was 4.2 Cd/A at 6V) is obtained from polymer **P1**, which might bedue to that the hole and electron in this device had the smallest energy barrier.

## 2 Experimental

### 2.1 General experimental

Chemicals were purchased and used as received. All air and water sensitive reactions were performed under nitrogen atmosphere. Toluene and THF were distilled from sodium. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury 300 MHz or Mercury plus 400 MHz using $CDCl_3$ as solvent unless otherwise noted. All chemical shifts were reported in parts per million (ppm). $^1$H NMR chemical shifts were referenced to TMS (0 ppm) or $CHCl_3$ (7.26 ppm), and $^{13}$C NMR chemical shifts were referenced to $CDCl_3$ (77.23 ppm). Absorption spectra were recorded on PerkinElmer Lambda 35 UV-vis Spectrometer. PL spectra were carried out on a PerkinElmer LS55 Luminescence Spectrometer. MALDI-TOF mass spectra were recorded on a Bruker BIFLEX III or AUTOFLEX III time-of-flight (TOF) mass spectrometer (Bruker Daltonics, Billerica, MA, USA) using a 337 nm nitrogen laser with dithranol as the matrix. Elemental analyses were performed using a German Vario EL III elemental analyzer. Differential scanning calorimetry analyses were performed on a METTLER TOLEDO Instrument DSC822$^e$ calorimeter. GPC was obtained through a Waters GPC 2410 with a refractive index detector in THF using a calibration curve of polystyrene standards. Thermal gravimetric analyses (TGA) were measured on Thermal Analysis SDT2960. Cyclic voltammetry was performed using BASI Epsilon workstation and measurements were carried out in acetonitrile containing 0.1 M $n$Bu$_4$NPF$_6$ as a supporting electrolyte. The carbon electrode was used as a working electrode and a platinum wire as a counter electrode, all potentials were recorded versus Ag/AgCl (saturated) as a reference electrode. The scan rate was 100 mV s$^{-1}$. EL spectrum was recorded on a Hitachi F-7000 fluorescence spectrophotometer.

### 2.2 Synthesis

*Dioctylphosphine oxide (**2**)*

To a solution of $n$-$C_8H_{17}MgBr$ in $Et_2O$ (2.0 M, 30 mL) was added a solution of di-$n$-butylphosphite (3.92 mL, 20 mmol) in THF (50 mL) under $N_2$ at room temperature. The mixture was refluxed for 4 h. $H_2SO_4$ aqueous solution (25%, 40 mL) was added during the period of 30 min at room temperature. The mixture was then extracted with EtOAc three times. The organic layers were combined, washed with brine, and then dried over $Na_2SO_4$. After removal of the solvents under reduced pressure, the residue was purified by recrystallization in hexane to give **2** as a white solid (3.8 g, 69%). $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 1.88–1.96 (m, 4H), 1.58–1.84 (m, 8H), 1.28–1.42 (m, 20H), 0.86–0.90 (t, $J$ = 6.6 Hz, 6H). EI-MS: $m/z$ 274 ($M^+$).

*2,7-dibromo-9,9-bis(6-dioctylphosphine oxide hexyl)-9H-fluorene (**4**)*

To a suspension of NaH (8 mmol) in anhydrous THF (10 mL) was added a solution of **2** (1.32 g, 4.8 mmol) in THF (40 mL) dropwise. The mixture was refluxed for 1 h, and then was transferred to a solution of 2,7-dibromo-9,9-bis (6-bromohexyl)-9*H*-fluorene (1.3 g, 2 mmol) in anhydrous THF dropwise. The mixture was refluxed for 6 h. After removal of the solvents under reduced pressure, the residue was purified by column chromatography using petroleum ether-EtOAc-$CH_3OH$ mixture (5:1:0 to 0:100:5) as eluents to give **4** as a light yellow oil (1.49 g, 72%). $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ = 7.42–7.54 (m, 6H), 1.89–1.94 (t, $J$ = 8.1 Hz, 4H), 1.88–1.63 (m, 72H), 0.85–0.90 (t, $J$ = 6.6 Hz, 12H), 0.56 (m, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$= 151.6, 138.5, 129.8, 125.5, 121.0, 120.8, 55.0, 39.5, 31.3, 30.7, 30.5, 30.3, 30.1, 28.8, 28.6, 27.8, 26.9, 22.9, 22.1, 21.1, 13.6. ESI MS: $m/z$ = 1035.5 $[M + H]^+$.

*2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (**6**)*

A mixture of 2,7-dibromo-9,9-dihexylfluorene (15 g, 30.5 mmol), KOAc (18 g, 183 mmol), bis(pinacolato)diborane (16.4 g, 64 mmol), and Pd(dppf)$Cl_2$ (1.8 g, 0.22 mmol) in 1,4-dioxane (150 mL) was stirred for 12 h at 80 °C. After being cooled to room temperature, water and chloroform were added into the mixture, the organic layer was washed with brine, and then dried over anhydrous $Na_2SO_4$. After removal of the solvent under reduced pressure, the residue was purified over silica gel column chromatography with petroleum as the eluent to give **6** as a white solid (13.4 g, 75%). $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$= 7.70–7.81 (m, 6H), 1.39 (s, 24H), 1.01–1.11 (m, 12H), 0.72–0.76 (t, $J$ = 6.9 Hz, 6H).

*PFH-PO-40-1 (**P1**)*

Compounds **4** (40 mg, 0.049 mmol), **5** (468 mg, 0.951 mmol), **6** (586 mg, 1 mmol), Pd($PPh_3$)$_4$ (24 mg, 0.02 mmol), 2-3 drops of aliquat 336, and 1.66 g of $K_2CO_3$ was added into a two-neck flask and degassed by $N_2$, then degassed toluene (11 mL) and deionized water (6 mL) were injected by syringe. The mixture was stirred under nitrogen purge at 95 °C for 48 h. After cooling to room temperature, water and chloroform were added, the separated organic layer was washed with brine and water, and then dried over anhydrous $Na_2SO_4$. After removal of the solvent under reduced pressure, the residue was added to stirred methanol to give a

precipitate. The precipitate was dissolved in chloroform and reprecipitated from methanol. The resulting precipitate was placed in a Soxhlet apparatus and extracted with refluxed acetone for 48 h to remove small molecules and catalyst residue, and then was dried at 60 °C in a vacuum oven to give **P1** as a light yellow solid (675 mg, 86%). $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$= 7.68–7.86 (m, 8H), 2.11–2.12 (m, 4H), 0.88–1.26 (m, 17H), 0.77–0.87 (m, 10H). $^{13}$C NMR (50 MHz, $CDCl_3$, ppm): $\delta$ = 152.0, 140.8, 140.2, 132.3, 129.0, 128.8, 128.6, 127.4, 126.4, 121.8, 120.2, 55.6, 40.6, 31.7, 29.9, 29.2, 24.1, 22.8, 21.8, 14.2. FT-IR (KBr): 2926, 2853, 1636, 1457, 1250, 1117, 885, 813 cm$^{-1}$.

*PFH-PO-20-1 (**P2**)*

This polymer was prepared following the similar procedures used to prepare polymer **P1** as a light yellow solid (674 mg, 83%). $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$= 7.68–7.86 (m, 8H), 1.76–2.12 (m, 5H), 1.15–1.26 (m, 18H), 0.80–0.88 (m, 10H). $^{13}$C NMR (50 MHz, $CDCl_3$, ppm): $\delta$= 152.0, 140.8, 140.2, 132.5, 132.3, 129.0, 128.8, 128.6, 127.4, 126.4, 121.8, 120.2, 55.6, 40.6, 32.0, 31.6, 31.0, 29.9, 29.2, 27.2, 25.9, 24.1, 22.8, 21.6, 14.2. FT-IR (KBr): 2925, 2851, 1633, 1457, 1249, 884, 813 cm$^{-1}$.

*PFH-PO-10-1 (**P3**)*

This polymer was prepared following the similar procedures used to prepare polymer **P1** as a light yellow solid (733 mg, 85%). $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$= 7.68–7.86 (m, 8H), 2.11–2.13 (m, 4H), 1.26–1.52 (m, 20H), 0.77–0.88 (m, 11H). $^{13}$C NMR (50 MHz, $CDCl_3$, ppm): $\delta$= 152.0, 151.7, 140.8, 140.2, 132.5, 132.3, 129.0, 128.8, 128.5, 127.4, 126.4, 121.8, 120.2, 55.5, 40.6, 32.0, 31.7, 31.4, 31.1, 29.9, 29.6, 29.2, 27.8, 26.5, 24.1, 22.8, 21.7, 14.2. FT-IR (KBr): 2924, 2851, 1637, 1457, 1249, 998, 884, 813 cm$^{-1}$.

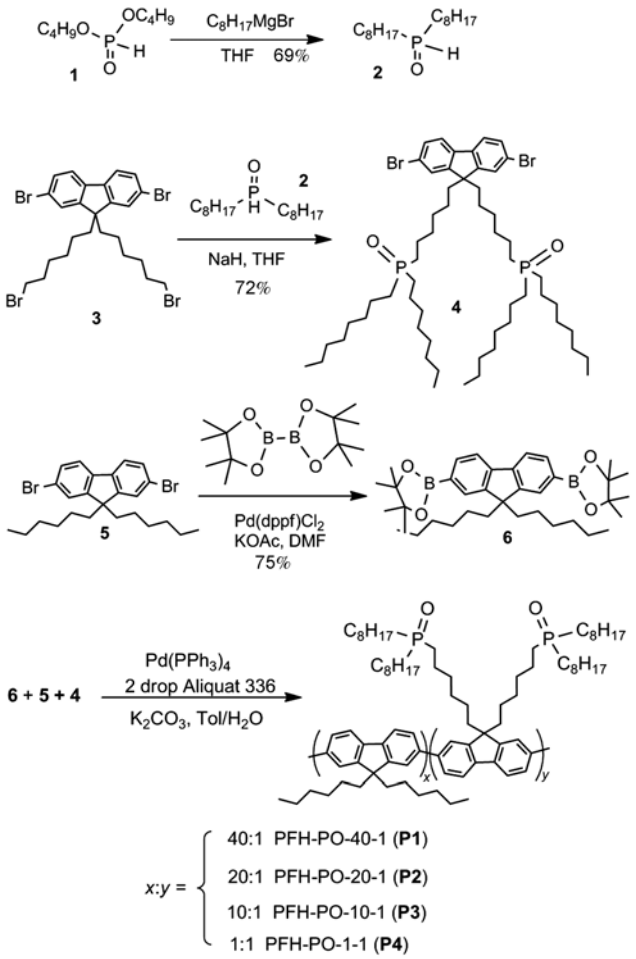
*PFH-PO-1-1 (**P4**)*

This polymer was prepared following the similar procedures used to prepare polymer **P1** as a light yellow solid (778 mg, 64%). $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 7.67–7.87 (m, 16H), 2.13 (m, 8H), 0.78–1.56 (m, 128H). $^{13}$C NMR (50 MHz, $CDCl_3$, ppm): $\delta$ 152.0, 151.6, 140.7, 140.5, 140.2, 126.4, 121.5, 120.2, 55.6, 55.4, 40.5, 31.9, 31.6, 31.4, 31.1, 29.8, 29.6, 29.2, 26.9, 24.0, 22.8, 21.8, 14.2. FT-IR (KBr): 2925, 2852, 1636, 1452, 1147, 813 cm$^{-1}$.

## 3 Results and discussion

### 3.1 Synthesis of polymers P1–P4 and characterization

Scheme 1 illustrates a synthetic approach to monomers **4** and **6**. The reaction of di-*n*-butylphosphite (**1**) with $C_8H_{17}MgBr$ afforded dioctylphosphine oxide (**2**) with a 69% yield, which was followed by the $S_N2$ reaction with 2,7-dibromo-9,9-bis(6-bromohexyl)-9*H*-fluorene (**3**) to give 2,7-dibromo-9,9-bis(6-dioctylphosphine oxide hexyl)-9*H*-fluorene (**4**) with a 72% yield. 2,7-Dibromo-9,9-dihexylfluorene (**5**) reacted with 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi(1,3,2-dioxaborolane) to afford 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (**6**) with a 75% yield.




**Scheme 1** The synthetic route to these polymers.

Monomers **4** and **5** with different ratios were polymerized with monomer **6** via a palladium-mediated Suzuki cross-coupling reaction to afford four corresponding phosphonic-functionalized polymers **P1**, **P2**, **P3**, and **P4**, respectively, as shown in Scheme 1. The crude polymers were washed with methanol, water, and methanol again, successively, and were placed in a Soxhlet apparatus and extracted with refluxed acetone for 48 h, and then were dried at 60 °C in a vacuum oven. These polymers were readily soluble in common organic solvents, such as THF, $CHCl_3$, and toluene. Therefore, their basic chemical structures were clearly determined by $^1$H and $^{13}$C NMR, and FT-IR. The FT-IR feature with characteristics of 1633–1637 cm$^{-1}$ was proved the existence of P=O groups in these polymers. The molecular weights of these polymers were determined by gel permeation chromatography (GPC) with THF as the eluent, calibrated against polystyrene standards. As shown in Table 1,

**Table 1** Molecular weight and absorption and photoluminescence properties of **P1–P4** in dilute solutions ($1.0 \times 10^{-6}$ M) and in thin films at room temperature

| Polymer | $M_n$ | $M_w$ | PDI | UV-vis $\lambda_{max}$ [a)] (nm) | PL $\lambda_{max}$ [a)] (nm) | UV-vis $\lambda_{max}$ [b)] (nm) | PL $\lambda_{max}$ [b)] (nm) |
|---|---|---|---|---|---|---|---|
| **P1** | 12215 | 24166 | 1.9 | 383 | 418, 441 | 379 | 445 |
| **P2** | 12224 | 23614 | 1.9 | 389 | 419, 441 | 381 | 444 |
| **P3** | 10134 | 18364 | 1.8 | 390 | 418, 441 | 381 | 449 |
| **P4** | 3960 | 5148 | 1.3 | 387 | 419, 440 | 389 | 450 |

a) In dilute THF solutions ($1.0 \times 10^{-6}$ M) at room temperature. b) In thin films.

the GPC analysis indicated that the number-average molecular weight ($M_n$) and polydispersity index (PDI) of these polymers were in the ranges from 3960 to 24166 and from 1.3 to 1.9, respectively.

The thermal stability of polymers was investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere. As shown in Figure 1, the onset degradation temperature of **P1–P4** was about 300 °C under nitrogen atmosphere. Differential scanning calorimetry (DSC) was used to determine the thermally induced phase transition behaviors of **P1–P4** under nitrogen atmosphere at a heating rate of 10 °C $min^{-1}$. However, unlike typical poly(9,9-dialkylfluorene)s (**PAFs**), DSC measurement of **P1–P3** did not show any phase transition in the temperature range from 0 to 300 °C, except that **P4** showed a low $T_g$ at about 80 °C which might be due to low molecular weight or too many alkyl chains in the polymer.

### 3.2 Photophysical and electrochemical properties

Figure 2(a) shows normalized UV-vis absorption and photoluminescence (PL) spectra of polymers **P1**, **P2**, **P3**, and **P4** in dilute THF solutions at a concentration of $1 \times 10^{-6}$ M based on the polymer repeat unit. These polymers showed the same absorption and emission features in dilute solution as homopolymer poly(9,9-dihexylfluorene) [9]. The photophysical properties of these polymers in dilute solutions are summarized in Table 1. As illustrated in Figure 2(a), polymers **P1–P4** exhibited similar absorption maximum $\lambda_{max}$ (383 nm for **P1**, 390 nm for **P2**, 389 nm for **P3**, 387 nm for **P4**), which was not affected by the ratio of P=O groups in

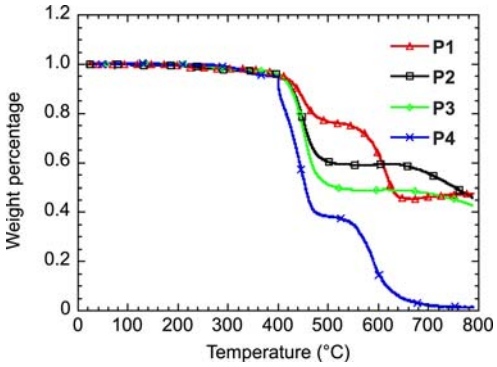



**Figure 1** Thermal gravimetric analysis of **P1–P4** in nitrogen atmosphere.

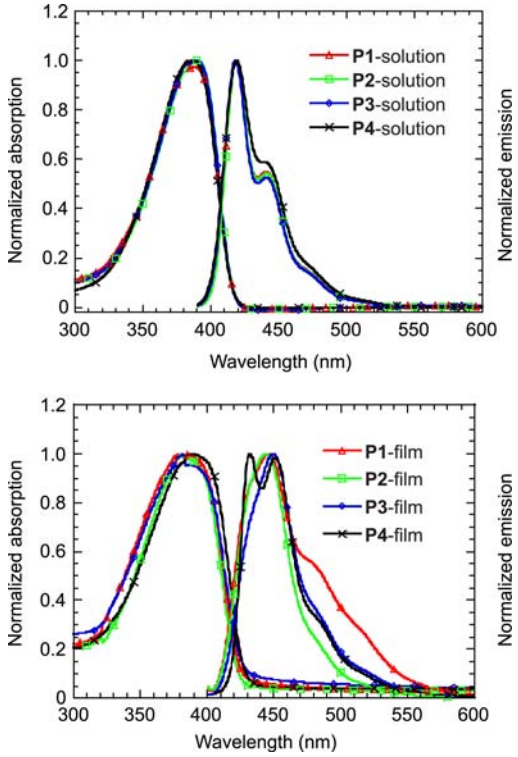



**Figure 2** Normalized UV-vis absorption and PL spectra of **P1–P4**, in dilute solutions ($1 \times 10^{-6}$ M based on the polymer repeat unit) and in thin film. UV-vis absorption spectra and PL spectra in dilute solutions (top); (b): UV-vis absorption spectra and PL spectra in thin film (down).

these polymers. The PL spectra of **P1**, **P2**, **P3**, and **P4** in dilute THF solutions, excited at the absorption maximum wavelength, showed almost identical PL behaviors. Their emission features peaked at about 418 nm with a clear vibronic shoulder at 441 nm, which indicated that these polymers exhibited well-extended chain conformation due to their good solubility in THF [10]. These five polymers also showed very small Stokes shifts (about 30 nm) between the 0–0 transition of absorption and emission, indicating a little structural reorganization in the excited state [11].

We also measured their absorption and emission properties in thin solid films (as shown in Figure 2(b)). The photophysical properties of these polymers in thin films are summarized in Table 2 as well. The absorption features of polymers **P1–P4** in thin films were almost identical to those in dilute solutions. Their emission features showed single broad peaks at about 445 nm except **P4**, compared with

**Table 2** Electrochemical properties of **P1–P4** in thin film

| Polymer | $E_{ox}$ (V) | $E_{red}$ (V) | HOMO (eV) | LUMO (eV) | $E_{gap}$ (eV) |
|---|---|---|---|---|---|
| **P1** | 1.17 | –1.85 | –5.57 | –2.55 | 3.02 |
| **P2** | 1.19 | –1.90 | –5.59 | –2.50 | 3.09 |
| **P3** | 1.20 | –1.92 | –5.60 | –2.48 | 3.12 |
| **P4** | 1.30 | –2.00 | –5.70 | –2.40 | 3.30 |

those in dilute solutions, which might be caused by some degree of aggregation in the excited states of the polymers' main chains.

The electrochemical behavior of these polymers, as shown in Figure 3, was investigated by cyclic voltammetry (CV). The CV was performed in a solution of *n*-$Bu_4NPF_6$ (0.1 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under the protection of nitrogen. A carbon electrode coated with a thin polymer film was used as the working electrode. A platinum wire was used as the counter electrode, and all potentials were recorded versus Ag/AgCl (saturated) as a reference electrode. The oxidation and reduction peaks appeared at 1.2 to 1.5 V and –2.1 to –2.2 V, respectively, which were attributed to the oxidation and reduction potentials for the polymers' main chains. The HOMO and LUMO levels calculated according to an empirical formula [12],

$$E_{HOMO} = -e\left(E_{ox} + 4.4\right)(\text{eV}), \text{ and } E_{LUMO} = -e\left(E_{red} + 4.4\right)(\text{eV}),$$

Table 2 illustrates the electrochemical properties of **P1–P4**. From the electrochemical data, it was estimated that the band gap of these functionalized polymers was around 3.02–3.30 eV for **P1–P4**.

### 3.3 Electroluminescence properties

The electroluminescence (EL) properties of these polymers were recorded on an organic light-emitting diode (OLED) device configuration of ITO/PEDOT:PSS/polymer/$Alq_3$/LiF/Al. $Alq_3$ worked as an electron-transport-layer in the devices. The ITO-coated glass substrate (200 nm, 20Ω/γ) was cleaned with the ultrasonic wave in acetone, ethanol and purified water. PEDOT:PSS was coated by spin casting and dried at 150 °C for 30 min. These polymers were coated by spin casting from a chloroform solution with a concentration of 5 mg/mL. Then $Alq_3$ (10 nm), LiF (1.5 nm), and Al

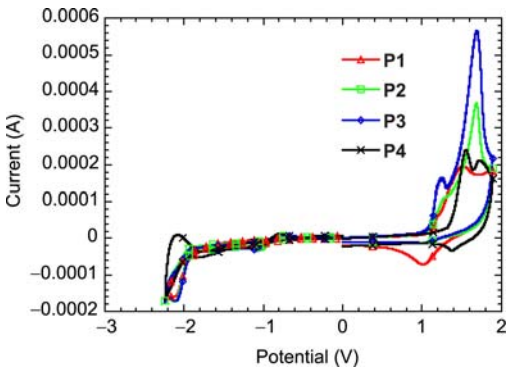



**Figure 3** Cyclic voltammograms of **P1–P4** in thin film coated on carbon electrodes in 0.1 mol/L $Bu_4NPF_6$, $CH_3CN$ solution.

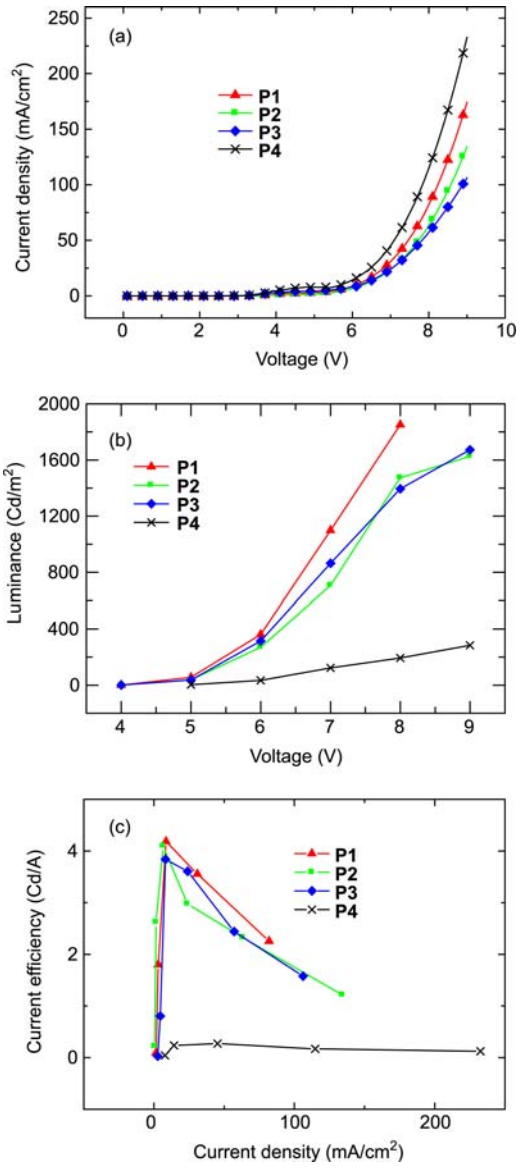



**Figure 4** The characteristics of the OLED devices. Current density-Voltage characteristics (a), luminance-voltage characteristics (b), current efficiency-current density characteristics (c).

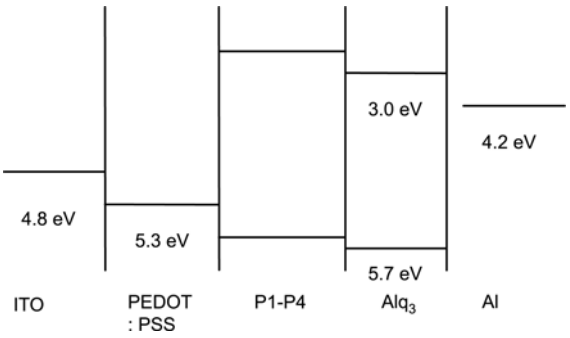



**Figure 5** Energy level of the OLED devices.

**Table 3** Electrochemical properties of **P1**–**P4** in thin film

| Polymer | $E_{ox}$ (V) | $E_{red}$ (V) | HOMO (eV) | LUMO (eV) | $E_{gap}$ (eV) |
|---|---|---|---|---|---|
| **P1** | 1.17 | –1.85 | –5.57 | –2.55 | 3.02 |
| **P2** | 1.19 | –1.90 | –5.59 | –2.50 | 3.09 |
| **P3** | 1.20 | –1.92 | –5.60 | –2.48 | 3.12 |
| **P4** | 1.30 | –2.00 | –5.70 | –2.40 | 3.30 |

(100 nm) as cathode were thermally evaporated in a vacuum chamber under a pressure of ~$8 \times 10^{-7}$ Torr. The current density-voltage characteristics of the OLEDs were determined with a Keithley source meter (model 2420). The luminance values were measured with a Minolta luminance meter (model LS-110).

Figure 4 shows the characterizations of the OLED devices. The best device result (Current efficiency was 4.2 Cd/A at 6V) was got from Polymer **P1**. Since the device performance of OLED was influenced by the energy barriers for charge carriers, the OLED devices with polymer **P1** showed the best performance because holes and electrons had the smallest energy barrier in the devices (as shown in Figure 5) according to the electrochemical properties(as shown in Table 3).

## 4 Conclusions

In conclusion, we synthesized four new polyfluorene derivatives **P1**, **P2**, **P3** and **P4** via a Suzuki polymerization. These polymers are the first examples of PF copolymer derivatives with phosphine oxide groups in the side chains. These polymers possess good thermal stability, large band gap, and good film-forming properties. Their emission features showed single broad peaks at about 445 nm except **P4**, compared with those in dilute solutions, which might be caused by some degree of aggregation in the excited states of the polymers' main chains. The electroluminescence (EL) properties of these polymers were recorded on an organic light-emitting diode (OLED) device configuration of ITO/PEDOT:PSS/Polymer/$Alq_3$/LiF/Al. The best device result (Current efficiency was 4.2 Cd/A at 6 V) was got from Polymer **P1**, which might be due to that the hole and electron in this device had the smallest energy barrier. More detailed work on optimizing devices and device performance is in progress.

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