



Phosphine Oxide-Functionalized Polyfluorene Derivatives: Synthesis, Photophysics, Electrochemical Properties, and Electroluminescence Performance

Zhang-Lin Zhou, Lihua Zhao, Sity Lam, Gary Gibson, James Brug, Zeng-Shan Guo, Deang Liu, Cheng Wang, Jian Pei, Samuel S. Mao

HP Laboratories
HPL-2010-150

Keyword(s):

conjugated polymers; polyfluorenes; photophysical properties; electrochemical properties; electroluminescence

Abstract:

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 ^1H and ^{13}C NMR, UV-vis and photoluminescent spectroscopy, gel permeation chromatography, and TGA/DSC. Their photoluminescent emission spectra showed single broad peaks at about 445 nm in thin films, as compared to 419 and 440 nm in dilute solutions. The difference 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 characterized in devices with a configuration of ITO/PEDOT: PSS/Polymer/Alq₃/LiF/Al. The best device result was obtained using polymer **P1**, which provided an efficiency of 4.2 Cd/A at 6V.

External Posting Date: October 6, 2010 [Fulltext]

Approved for External Publication

Internal Posting Date: October 6, 2010 [Fulltext]

Phosphine Oxide-Functionalized Polyfluorene Derivatives: Synthesis, Photophysics, Electrochemical Properties, and Electroluminescence Performance

Zhang-Lin Zhou^{a,}, Lihua Zhao^a, Sity Lam^a, Gary Gibson^a, James Brug^a, Zeng-Shan Guo^b,
Deang Liu^c, Cheng Wang^b, Jian Pei^{b,*}, and Samuel S. Mao^{c,*}*

^a Information Surfaces Lab, Hewlett Packard Labs, Hewlett Packard Company, 1501 Page Mill Road, Palo Alto, CA 94304, U. S. A.

^b The Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

^c Lawrence Berkeley National Laboratory and Department of Mechanical Engineering, University of California, Berkeley, CA, USA

* Corresponding authors. Emails: zhang-lin.zhou@hp.com; jianpei@pku.edu.cn; ssmao@newton.berkeley.edu

Abstract: 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 ¹H and ¹³C NMR, UV-vis and photoluminescent spectroscopy, gel permeation chromatography, and TGA/DSC. Their photoluminescent emission spectra showed single broad peaks at about 445 nm in thin films, as compared to 419 and 440 nm in dilute solutions. The difference 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 characterized in devices with a configuration of

ITO/PEDOT: PSS/Polymer/Alq₃/LiF/Al. The best device result was obtained using polymer **P1**, which provided an efficiency of 4.2 Cd/A at 6V.

Keywords: conjugated polymers; polyfluorenes; photophysical properties; electrochemical properties; electroluminescence;

Introduction

π -conjugated polymers with electronically rigid backbones have attracted considerable interest due to their electronic and optoelectronic applications, such as in 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 and chemical stability, good solubility in common organic solvents, and amenability to facile modification of the side chains without affecting the conjugation of the main chain^[4]. To date, 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], 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 nanocrystals to 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 showed both high sensitivity and selectivity towards Fe³⁺ ions^[5]. Herein, we design and synthesize a series of PFs incorporating phosphine groups in order to endow these polymers with multifunctional properties, particularly for use in electroluminescent devices. Our PF derivatives reported herein possess good thermal stability, large band gaps, and good film-forming properties. The electroluminescence (EL) properties of these polymers were

investigated in an organic light-emitting diode (OLED) device configuration of ITO/PEDOT:PSS/Polymer/Alq₃/LiF/Al. The best device result was obtained using polymer **P1**, which provided an efficiency of 4.2 Cd/A at 6V. The superior efficiency of this device may result from the formation of smaller energy barriers for holes and electrons when employing polymer **P1**.

Experiment

General method

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. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 300 MHz or Mercury plus 400 MHz using CDCl₃ as solvent unless otherwise noted. All chemical shifts were reported in parts per million (ppm). ¹H NMR chemical shifts were referenced to TMS (0 ppm) or CHCl₃ (7.26 ppm), and ¹³C NMR chemical shifts were referenced to CDCl₃ (77.23 ppm). Absorption spectra were recorded on a 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 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° 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 in acetonitrile containing 0.1 M *n*Bu₄NPF₆ as a supporting electrolyte using a BASI Epsilon workstation. Carbon 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 spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer.

Synthesis

Diocetylphosphine Oxide (2). A solution of di-*n*-butylphosphite (3.92 mL, 20 mmol) in THF (50 mL) was added to a solution of *n*-C₈H₁₇MgBr in Et₂O (2.0 M, 30 mL) under N₂ at room temperature. The mixture was refluxed for 4 hours. H₂SO₄ aqueous solution (25%, 40 mL) was added over a period of 30 minutes at room temperature. The mixture was then extracted with EtOAc three times. The organic layers were combined, washed with brine, and then dried over Na₂SO₄. 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%). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 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-diocetylphosphine oxide hexyl)-9H-fluorene (4). A solution of **2** (1.32 g, 4.8 mmol) in THF (40 mL) was added dropwise to a suspension of NaH (8 mmol) in anhydrous THF (10 mL). The mixture was refluxed for 1 hour, and then transferred dropwise to a solution of 2,7-dibromo-9,9-bis(6-bromohexyl)-9*H*-fluorene (1.3 g, 2 mmol) in anhydrous THF. The mixture was refluxed for 6 hours. After removal of the solvents under reduced pressure, the residue was purified by column chromatography using a PE-EtOAc-CH₃OH mixture (5:1:0 to 0:100:5) as eluent to give **4** as a light yellow oil (1.49 g, 72%). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 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). ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 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)Cl₂ (1.8 g, 0.22 mmol) in 1,4-dioxane (150 mL) was stirred for 12 hours at 80 °C. After cooling to room temperature, water and chloroform were added into the mixture. The resulting organic layer was washed with brine and then dried over anhydrous Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified using silica gel column chromatography with petroleum as the eluent to give **6** as a white solid (13.4 g, 75%). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 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(PPh₃)₄ (24 mg, 0.02 mmol), 2-3 drops of aliquat 336, and 1.66 g of K₂CO₃ were added into a two-neck flask and degassed by N₂, 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 hours. 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 Na₂SO₄. After removal of the solvent under reduced pressure, the residue was added to stirred methanol to yield a precipitate. The precipitate was dissolved in chloroform and re-precipitated from methanol. The resulting precipitate was placed in a Soxhlet apparatus and extracted with refluxed acetone for 48 hours to remove small molecules and catalyst residue, and then dried at 60 °C in a vacuum oven to give **P1** as a light yellow solid (675 mg, 86%). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.68-7.86 (m, 8H), 2.11-2.12 (m, 4H), 0.88-1.26 (m, 17H), 0.77-0.87 (m, 10H). ¹³C NMR (50 MHz, CDCl₃, ppm): δ 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 procedures similar to those used to prepare polymer **P1** as a light yellow solid (674 mg, 83%). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.68-7.86 (m, 8H), 1.76-2.12 (m, 5H), 1.15-1.26 (m, 18H), 0.80-0.88 (m, 10H). ¹³C NMR (50 MHz, CDCl₃, ppm): δ = 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 procedures similar to those used to prepare polymer **P1** as a light yellow solid (733 mg, 85%). ^1H NMR (300 MHz, CDCl_3 , ppm): δ = 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): δ = 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 procedures similar to those used to prepare polymer **P1** as a light yellow solid (778 mg, 64%). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.67-7.87 (m, 16H), 2.13 (m, 8H), 0.78-1.56 (m, 128H). ^{13}C NMR (50 MHz, CDCl_3 , ppm): δ 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} .

Results and Discussion

Scheme 1 illustrates a synthetic approach to monomers **4** and **6**. The reaction of di-*n*-butylphosphite (**1**) with $\text{C}_8\text{H}_{17}\text{MgBr}$ afforded ioctylphosphine Oxide (**2**) with a 69% yield, which was followed by the $\text{S}_{\text{N}}2$ reaction with 2,7-dibromo-9,9-bis(6-bromohexyl)-9H-fluorene (**3**) to give 2,7-dibromo-9,9-bis(6-dioctylphosphine oxide hexyl)-9H-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.

at 60 °C in vacuum oven. These polymers were readily soluble in common organic solvents, such as THF, CHCl₃, and toluene. Therefore, their basic chemical structures were clearly determined by ¹H and ¹³C NMR, and FT-IR. An FT-IR feature at 1633~1637 cm⁻¹ 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, 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.

Table 1. Molecular Weight of the Polymers

Polymer	<i>M_n</i>	<i>M_w</i>	PDI
P1	12215	24166	1.9
P2	12224	23614	1.9
P3	10134	18364	1.8
P4	3960	5148	1.3

The thermal stability of each polymer 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 behavior 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 measurements of **P1-P3** did not show phase transitions 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 its low molecular weight or an excess of alkyl chains.

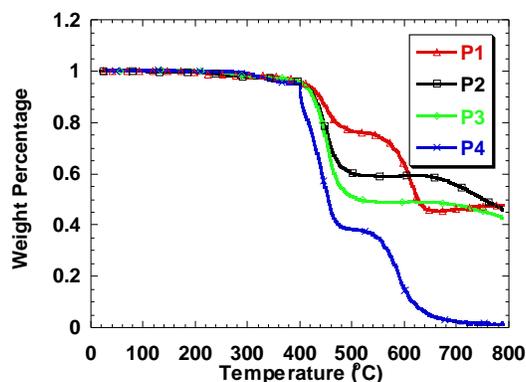


Figure 1. Thermal gravimetric analysis of **P1-P4** in nitrogen atmosphere.

Figure 2a shows normalized UV-vis absorption and photoluminescence (PL) spectra for polymers **P1**, **P2**, **P3**, and **P4** in dilute THF solutions in a concentration of 1×10^{-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 2**. As illustrated in **Figure 2a**, polymers **P1-P4** exhibited similar absorption maxima λ_{max} (383 nm for **P1**, 390 nm for **P2**, 389 nm for **P3**, 387 nm for **P4**), indicating they are not affected by the ratio of P=O groups in these polymers. The PL spectra of **P1**, **P2**, **P3**, and **P4** in dilute THF solutions, excited at the absorption maximum wavelength, were almost identical. Their emission features peaked at about 418 nm with a clear vibronic shoulder at 441 nm, which indicated that these polymers have 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 transitions of absorption and emission, indicating little structural reorganization in the excited state [11].

We also measured their absorption and emission properties in thin solid films (as shown in **Figure 2b**). 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 were broadened relative

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

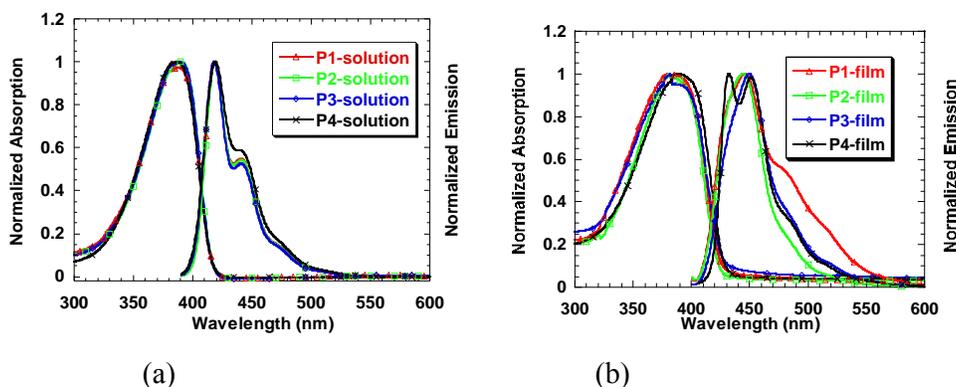


Figure 2. Normalized UV-vis absorption and PL spectra of **P1-P4**, in dilute solutions (1×10^{-6} M based on the polymer repeat unit) and in thin film. (a): UV-vis absorption spectra and PL spectra in dilute solutions; (b): UV-vis absorption spectra and PL spectra in thin film.

Table 2. UV-visible and photoluminescence spectra of **P1-P4**, in dilute solutions (1.0×10^{-6} M) and in thin films at room temperature.

polymer	UV-vis λ_{\max}^a (nm)	PL λ_{\max}^a (nm)	UV-vis λ_{\max}^b (nm)	PL λ_{\max}^b (nm)
P1	383	418, 441	379	445
P2	389	419, 441	381	444
P3	390	418, 441	381	449
P4	387	419, 440	389	450

^a in dilute THF solutions (1.0×10^{-6} M) at room temperature. ^b in thin films.

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*-Bu₄NPF₆ (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, $E_{HOMO} = -e(E_{ox} + 4.4)$ (eV), and $E_{LUMO} = -e(E_{red} + 4.4)$ (eV) [12], are listed in **Table 3**. 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**.

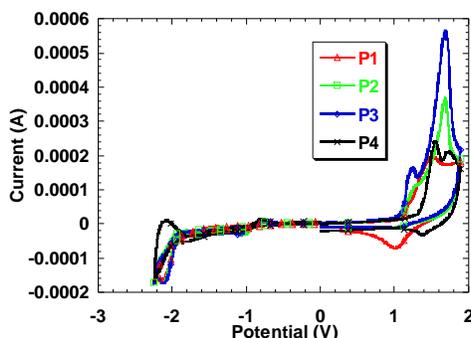
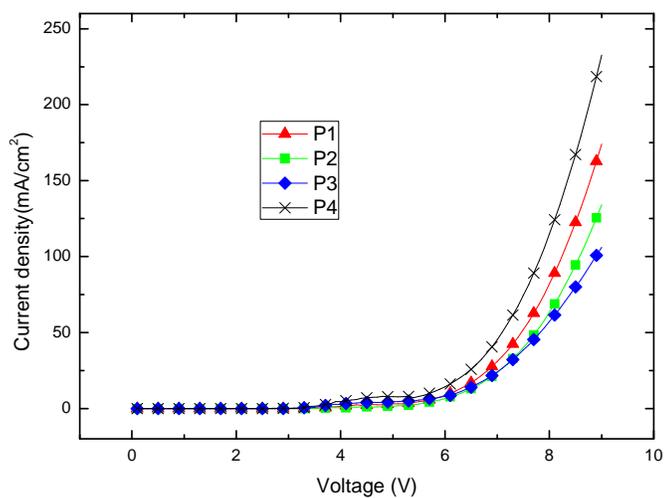


Figure 3. Cyclic voltammograms of **P1-P4** in thin film coated on carbon electrodes in 0.1 mol/L Bu_4NPF_6 , CH_3CN solution.

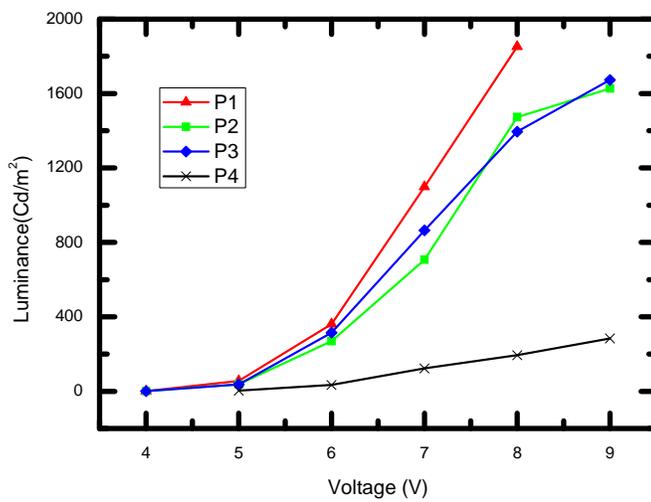
The electroluminescence (EL) properties of these polymers were recorded using an organic light-emitting diode (OLED) device configuration of ITO/PEDOT: PSS/Polymer/ Alq_3 /LiF/Al. Alq_3 served as an electron-transport-layer in the devices. The ITO-coated glass substrate (200nm, $20\Omega/\square$) was cleaned ultrasonically in acetone, ethanol and purified water. PEDOT: PSS was coated by spin casting and dried at 150 °C for 30 minutes. The polymers **P1-P4** were coated by spin casting from a chloroform solution with a concentration of 5 mg/ml. Then Alq_3 (10 nm), LiF (1.5nm) and Al (100 nm) as cathode were thermally evaporated in a vacuum chamber under a pressure of $\sim 8 \times 10^{-7}$ 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 efficiency, which was 4.2 Cd/A at 6V, was obtained from Polymer **P1**. The OLED devices with polymer

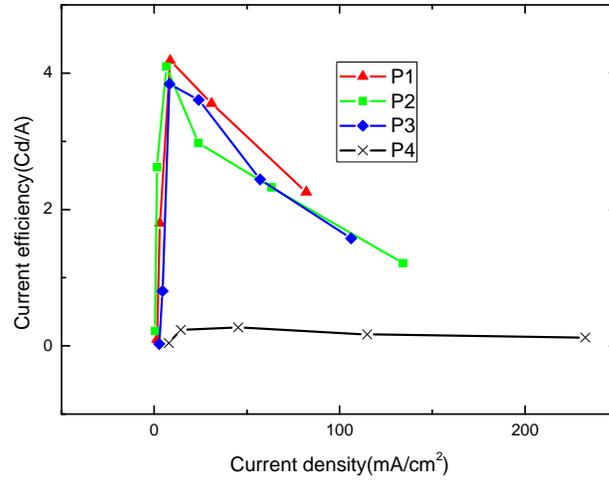
P1 showed the best performance because it provided the smallest energy barriers for holes and electrons (as shown in **Fig. 5**), as indicated by the electrochemical properties shown in **Table 3**.



(a)



(b)



(c)

Figure 4. The characteristics of the OLED devices. (a) Current density-Voltage characteristics. (b) Luminance-Voltage characteristics. (c) Current efficiency- Current density characteristics.

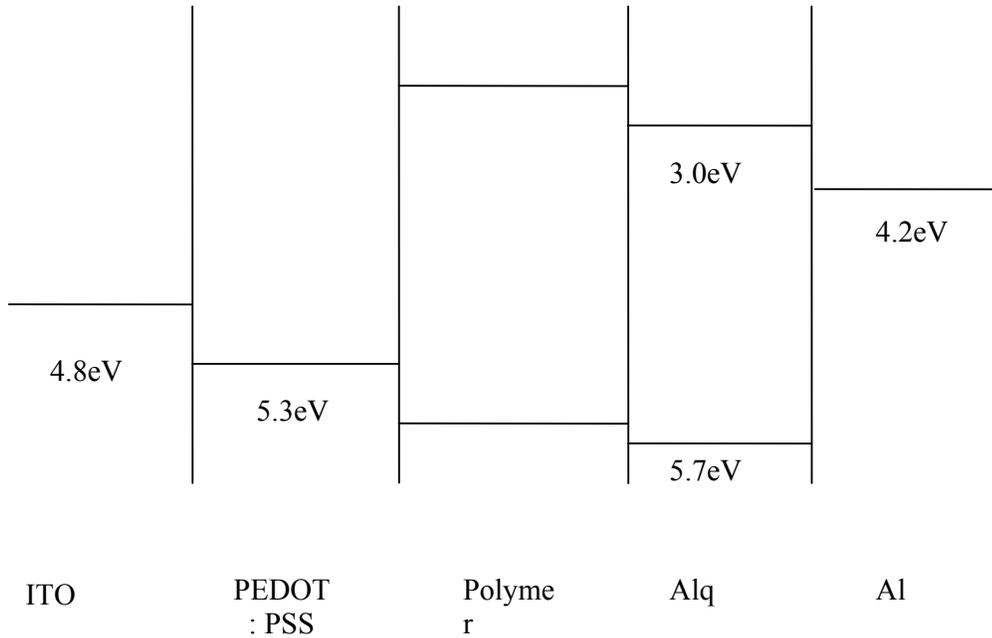


Figure 5. Energy level of the OLED devices.

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

Conclusion

In conclusion, we synthesized four new PFH derivatives **P1**, **P2**, **P3** and **P4** via Suzuki polymerization. These polymers are the first examples of synthesis 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 photoluminescent emission features in thin film form showed broadened peaks (at about 445 nm) relative to 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 using an organic light-emitting diode (OLED) device configuration of ITO/PEDOT: PSS/Polymer/Alq₃/LiF/Al. The best device efficiency (4.2 Cd/A at 6V) was obtained using polymer **P1**, which provided the smallest energy barriers to holes and electrons. More detailed work on optimizing devices and device performance are in progress.

References

- [1] [1a] D. Braun, A. J. Heeger, *Appl. Phys. Lett.* **1991**, 58, 1982; [1b] P. L. Burns, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend, R. W. Gymer, *Nature* **1992**, 356, 47; [1c] Q. Pei, G. Yu, C. Zhang, Y. Yang, A. J. Heeger, *Science* **1995**, 269, 1086; [1d]

C. D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becker, K. Meerhotz, *Nature* **2003**, *421*, 829.

[2] [2a] A. J. Lovinger, L. J. Rothverg, *J. Mater. Res.* **1996**, *11*, 1581; [2b] Z. Bao, A. J. Lovinger, J. Brown, *J. Am. Chem. Soc.* **1998**, *120*, 207; [2c] Z. Bao, A. Dodabalapur, A. J. Lovinger, *Appl. Phys. Lett.* **1996**, *69*, 4108-4110; [2d] H. Sirringhaus, N. Tessler, R. H. Friend, *Science* **1998**, *280*, 1741-1744; [2e] A. Babel, S.A. Jenekhe, *Adv. Mater.* **2002**, *14*, 371-374.

[3] [3a] C. W. Tang, *Appl. Phys. Lett.* **1986**, *48*, 183; [3b] D. Wohrle, D. Meissner, *Adv. Mater.* **1991**, *3*, 129; [3c] G. Yu, A. J. Heeger, *J. Appl. Phys.* **1995**, *78*, 4510-4515; [3d] A. C. Arias, J. D. MacKenzie, R. Stevenson, J. J. M. Halls, M. Inbasekaran, E. P. Woo, D. Richards, R. H. Friend, *Macromolecules* **2001**, *34*, 6005; [3e] S. A. Jenekhe, S. Yi, *Appl. Phys. Lett.* **2000**, *77*, 2635.

[4] [4a] M. T. Bernius, M. Inbasekaran, J. O'Brien, W. S. Wu, *Adv. Mater.* **2000**, *12*, 1737; [4b] D. Neher, *Macromol. Rapid. Commun.* **2001**, *22*, 1366; [4c] U. Scherf, E. J. W. List, *Adv. Mater.* **2002**, *14*, 477; (d) G. Klärner, J. K. Lee, M. H. Davey, R. D. Miller, *Adv. Mater.* **1999**, *11*, 115; [4e] W. L. Yu, J. Pei, W. Huang, A. J. Heeger, *Adv. Mater.* **2000**, *12*, 828; [4f] T. Virgili, D. G. Lidzey, D. D. C. Bradley, *Adv. Mater.* **2000**, *12*, 58; [4g] K. S. Whitehead, M. Grell, D. D. C. Bradley, M. Jandke, P. Strohriegel, *Appl. Phys. Lett.* **2000**, *76*, 2946; [4h] M. Grell, W. Knoll, D. Lupo, A. Meisel, T. Miteva, D. Neher, H. G. Nothofer, U. Scherf, A. Yasuda, *Adv. Mater.* **1999**, *11*, 671.

[5] [5a] B. Liu, G. C. Bazan, *J. Am. Chem. Soc.* **2006**, *128*, 1188; [5b] S. Wang, B. S. Gaylord, G. C. Bazan, *J. Am. Chem. Soc.* **2004**, *126*, 5446; [5c] B. Liu, S. Wang, G. C. Bazan, A. Mikhailovsky, *J. Am. Chem. Soc.* **2003**, *125*, 13306; [5d] C. Fan, K. W. Plaxco, A. J. Heeger, *J. Am. Chem. Soc.* **2002**, *124*, 5642; [5e] G. Zhou, Y. X. Cheng, L. X. Wang, X. B. Jing, F. S. Wang, *Macromolecules* **2005**, *38*, 2148; [5f] X. Zhou, J. Yan, J. Pei, *Macromolecules* **2004**, *37*, 7078; [5g] G. Zhou, G. Qian, L. Ma, Y. X. Cheng, Z. Y. Xie, L. X. Wang, X. B. Jing, F. S. Wang, *Macromolecules* **2005**, *38*, 5416; [5h] C. J. Qin, Y. X. Cheng, L. X. Wang, X. B. Jing,

- F. S. Wang, *Macromolecules* **2008**, *41*, 7798; [5i] C. J. Qin, X. F. Wu, B. X. Gao, H. Tong, L. X. Wang, *Macromolecules* **2009**, *42*, 5427.
- [6] [6a] F. Huang, L. Hou, H. Wu, X. Wang, H. Shen, W. Cao, *J. Am. Chem. Soc.* **2004**, *126*, 9845; [6b] H. Wu, F. Huang, Y. Mo, W. Yang, D. Wang, J. Peng, *Adv. Mater.* **2004**, *6*, 1826, [6c] R. Yang, H. Wu, Y. Cao, G. C. Bazan, *J. Am. Chem. Soc.* **2006**, *128*, 14422.
- [7] X. G. Peng, M. C. Schlamp, A. V. Kadavanich, A. P. Alivisatos, *J. Am. Chem. Soc.* **1997**, *119*, 7019.
- [8] H. Skaff, K. Sill, T. Emrick, *J. Am. Chem. Soc.* **2004**, *126*, 11322.
- [9] [9a] U. Scherf, E. J. W. List, *Adv. Mater.* **2002**, *14*, 477; [9b] X. Gong, P. K. Iyer, D. Moses, G. C. Bazan, A. J. Heeger, S. S. Xiao, *Adv. Funct. Mater.* **2003**, *13*, 325; [9c] X. Gong, D. Moses, A. J. Heeger, *J. Phys. Chem. B* **2004**, *108*, 8601.
- [10] [10a] K. Y. Pu, Z. Fang, B. Liu, *Adv. Funct. Mater.* **2008**, *18*, 1321; [10b] B. Chu, *Laser Light Scattering: Basic Principles and Practice*, 2nd ed, Academic Press, San Diego, CA **1991**; [10c] J. Hall, J. M. Lehn, A. DeCian, J. Fischer, *Helv. Chim. Acta* **1991**, *74*, 1.
- [11] J. C. Yan, X. Chen, Q. L. Zhou, J. Pei, *Macromolecules* **2007**, *40*, 832.
- [12] D. M. Leeuw, M. M. J. Simenon, A. R. Brown, R. E. F. Einerhand, *Synth. Met.* **1997**, *87*, 53.