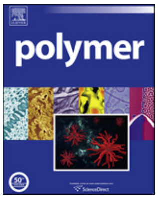
Polymer 50 (2009) 4794–4800

Contents lists available at ScienceDirect

Polymer

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



Amine groups-functionalized alcohol-soluble polyfluorene derivatives: Synthesis, photophysical properties, and self-assembly behaviors

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ARTICLE INFO

Article history:
Received 19 February 2009
Received in revised form
13 August 2009
Accepted 17 August 2009
Available online 22 August 2009

Keywords:
Electroluminescence
Self-assembly
Hydrogen bonding

ABSTRACT

A polyfluorene derivative with primary amine groups on side chains, poly(9,9-bis(6′-aminohexyl)fluorene) (**PF-NH$_2$**), was prepared through de-protection of its analogue polymer poly(9,9-bis(6′-butoxylcarbonylaminohexyl)fluorene) (**PF-BOC**) with hydrochloric acid followed by neutralizing the salt form of poly(6,6′-(9H-fluorene-9,9-diyl)dihexan-1-aminium chloride) (**PF-NION**). **PF-NION** had good solubility in methanol, DMSO, and DMF. Scanning electron microscopic images of **PF-NH$_2$** in thin films revealed that intramolecular/intermolecular hydrogen bonding and π–π stacking interactions probably played an important role in the formation of special surface morphologies, which might be beneficial to the molecular ordering and device fabrication. The electroluminescence property of **PF-NION** was recorded on a simple polymer light-emitting diode (PLED) device configuration of ITO/PEDOT/Polymer/Al. Pure blue electroluminescence is achieved from double-layer PLEDs based on **PF-NION** as the active material with the CIE of (0.16, 0.08).

1. Introduction

π-Conjugated polymers with electronically rigid backbones have attracted considerable interest due to their electronic and optoelectronic applications, such as polymer light-emitting diodes (PLEDs) [1], organic field effect transistors (OFETs) [2], and photovoltaics [3], as well as other organic semiconducting devices. With the introduction of π-conjugated polymers in electronic devices and the development of nanoscience and nanotechnology, the detailed understanding of supramolecular interactions between the individual π-conjugated polymers has become one of the most challenging scientific research areas [4]. Meanwhile, more and more attention has been paid to fabricating optoelectronic devices such as PLEDs [5], OFETs [6], and chemo/biosensors [7] by controlling the nano- and mesoscopic order in conjugated systems to tune the macroscopic properties of the corresponding devices [8]. There are a variety of interactions important in the design of supramolecular materials for π-conjugated polymers, such as π–π stacking [9], hydrogen bonding, metal-ligand, solvatochromism, and so on. Among these interactions, π–π stacking and hydrogen bonding are undoubtedly two of the most important secondary interactions. π–π Stacking usually exists in π-conjugated polymers; while hydrogen bonding is highly selective and directional, and its strength depends largely on the solvent and number of hydrogen bonds [10].

Herein, we present the synthesis of a polyfluorene derivative with primary amine groups in the side chains and its thermal, photophysical, electrochemical, and self-assembly properties. 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 [11]. 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 [12,17b], PLEDs [13]. Primary amine groups have generated more interest in recent years due to their applications in hybrid polymer–nanocrystal composites and self-assembled monolayers (SAMs) [14]. Our PF derivatives, **PF-NION** and **PF-NH$_2$**, reported herein exhibit good thermal stability, a large band gap, and good blue-emitting properties. Scanning electron microscopic (SEM) images of **PF-NH$_2$** in thin films revealed that intramolecular/intermolecular hydrogen bonding and π–π stacking interactions probably play an important role in the formation of special surface morphologies. In addition, **PF-NION** as the salt form has good solubility in methanol, DMF, DMSO, and other polar solvents, which

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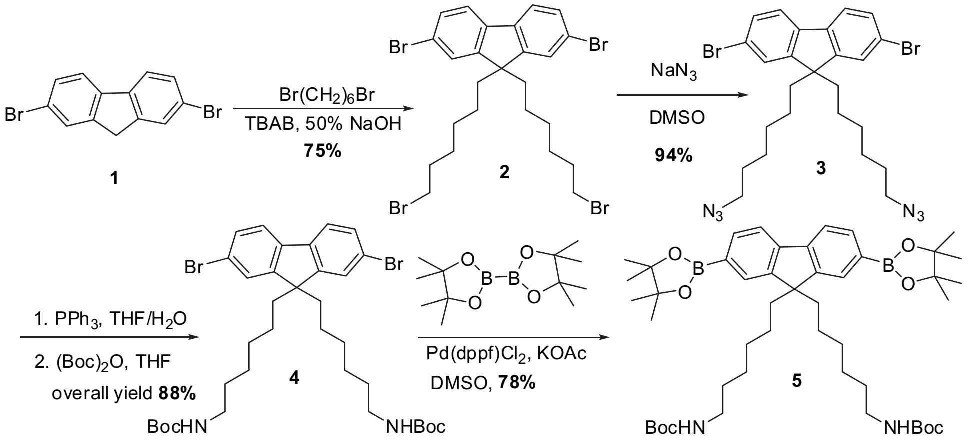
doi:10.1016/j.polymer.2009.08.028



Scheme 1.

are environment-friendly for device fabrication. Double-layer PLEDs using **PF-NION** as emissive layers exhibit pure blue emission, with the CIE (0.1615, 0.0766), and nor excimer or keto-defect was found [15], which make it promising candidate for PLED.

2. Experimental section

2.1. 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. ^{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 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^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 $n\mathrm{Bu_4NPF_6}$ as a supporting electrolyte. 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 JobinYvon Triax 550 Spectrometer.

2.2. Synthesis of monomers and polymers

2.2.1. 2,7-Bibromo-9,9-bis(6′-bromohexyl)fluorene (**2**)

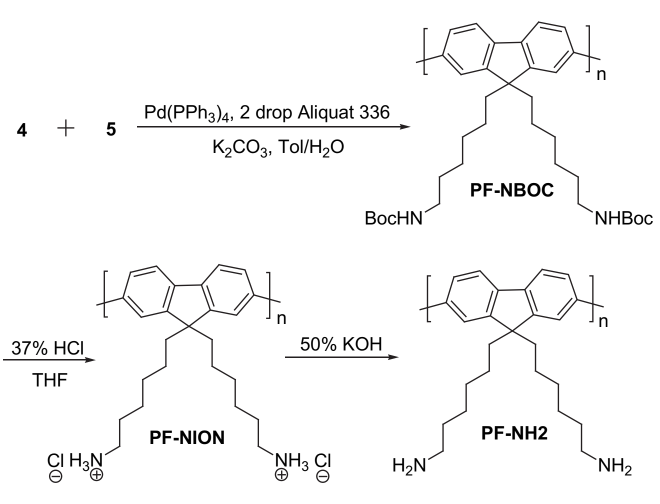
A mixture of 2,7-dibormofluorene (4.86 g, 15 mmol), 1,6-dibromohexane (30 mL), tetrabutylammonium bromine (0.1 g), and aqueous sodium hydroxide solution (30 mL, 50% w/w) was stirred overnight at 70 °C under nitrogen. After diluting the reaction mixture with chloroform, the organic layer was washed with brine and water, and then was dried over anhydrous Na_2SO_4. After removal of excess 1,6-dibromohexane and solvents under reduced pressure, the residue was purified by chromatography with petroleum ether as the eluent to afford 2,7-bibromo-9,9-bis(6′-bromohexyl)fluorene (**2**) (7.3 g, 75%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.43–7.56 (m, 6H), 3.28–3.33 (t, 4H, $J = 6.6$ Hz), 1.89–1.95 (m, 4H), 1.24–1.70 (m, 4H), 1.22–1.25 (m, 8H), 0.53–0.63 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 152.3, 139.2, 130.5, 126.3, 121.7, 121.4, 55.7, 40.2, 34.1, 32.8, 29.1, 27.9, 23.6.

2.2.2. 2,7-Bibromo-9,9-bis(6′-azidohexyl)fluorene (**3**)

A solution of compound **2** (4.87 g, 7.5 mmol) and sodium azide (1.2 g, 18.8 mmol) in 40 mL of DMSO was stirred overnight at 70 °C. The reaction mixture was extracted with Et_2O and H_2O. The combined organic extracts were washed with brine and dried anhydrous Na_2SO_4. After removal of solvents under reduced pressure, the residue was purified by chromatography with petroleum ether to give **3** as a yellow oil (4.04 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.43–7.53 (m, 6H), 3.11–3.16 (t, 4H, $J = 7.2$ Hz), 1.89–1.95 (t, 4H, $J = 8.4$ Hz), 1.38–1.42 (m, 4H), 1.09–1.16 (m, 8H), 0.58–0.60 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 152.3, 139.2, 130.5, 126.3, 121.7, 121.4, 55.7, 51.5, 40.2, 29.5, 28.9, 26.5, 23.7. MS *m*/*z*: 574 (M^+).

2.2.3. 2,7-Bibromo-9,9-bis(6′-butoxylcarbonylaminohexyl)-fluorene (**4**)

To a solution of compound **3** (4.04 g, 7.04 mmol) in THF/H_2O (62 mL/8.4 mL) was added PPh_3 (4.06 g, 15.5 mmol). The reaction



Scheme 2.

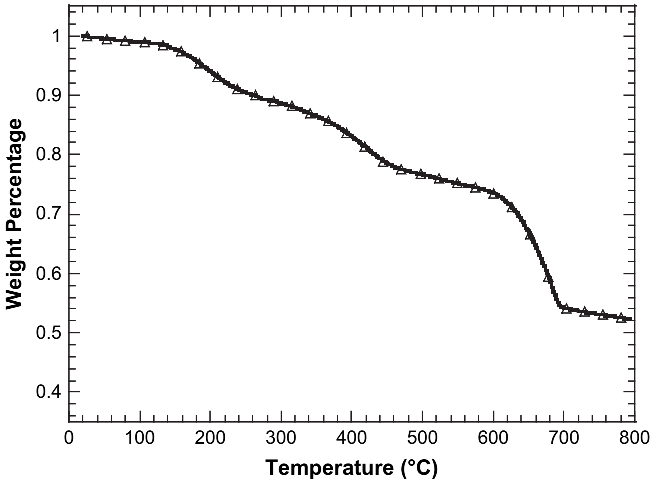


Fig. 1. Thermal gravimetric analysis of **PF-NH$_2$** in nitrogen atmosphere.

mixture was stirred for 12 h at room temperature. After removal of THF and H_2O under reduced pressure, a solution of di-*t*-butyl dicarbonate (4.11 g, 18.87 mmol) in THF was added. The solution was stirred for 4 h at room temperature. After removal of solvents under reduced pressure, the residue was purified over silica gel column chromatography with petroleum ether/ethyl acetate (6:1) as the eluent to give compound **4** as a white solid (4.49 g, 88%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.43–7.53 (m, 6H), 4.50 (s, 2H), 2.97–2.99 (t, 4H, $J = 6.3$ Hz), 1.87–1.93 (t, 4H, $J = 8.4$ Hz), 1.41 (s, 18H), 1.06–1.27 (m, 8H), 0.57 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 156.1, 152.5, 139.2, 130.4, 126.3, 121.7, 121.4, 79.1, 55.8, 40.6, 40.3, 30.1, 29.7, 28.6, 26.6, 23.8. MS *m*/*z*: 722 (M$^+$). Anal. Calcd. for $C_{35}H_{50}Br_2N_2O_4$: C, 58.18; H, 6.97; N, 3.88. Found: C, 58.12; H, 7.12; N, 3.79.

2.2.4. *2,7-Bis(4,4,5,5-tetramethyl–1,3,2-dioxaborolan-2-yl)-9,9-bis(6′-butoxylcarbonylaminohexyl)fluorene (**5**)*

A mixture of 2,7-bibromo-9,9-bis(6′-butoxylcarbonylaminohexyl)fluorene (2 g, 2.77 mmol), KOAc (1.8 g, 18.3 mmol), bis(pinacolato)diborane (1.56 g, 6.1 mmol), Pd(dppf)Cl_2 (0.16 g, 0.22 mmol) in 30 mL of degassed DMSO was stirred at 80 °C for 12 h. After cooled to room temperature, water and chloroform were added into the mixture. The separated organic layer was washed with brine, water and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified over column chromatography with petroleum ether/ethyl acetate (3:1) as the eluent to give **5** as a white solid (1.8 g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.70–7.82 (m, 6H), 4.43 (s, 2H), 2.94–2.96 (t, 4H, $J = 6$ Hz), 1.96–2.01 (t, 4H, $J = 8.4$ Hz), 1.36–1.38(m, 42H), 1.17–1.26 (m, 4H), 1.02 (m, 8H), 0.54 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 156.2, 150.5, 144.1, 133.9, 129.0, 119.7, 83.9, 79.1, 55.3, 40.7, 40.2, 30.1, 29.7, 28.6, 26.5, 25.2, 23.7. MALDI-TOF MS (*m*/*z*): Calcd. for $C_{47}H_{74}Br_2N_2O_8$: 816.6. Found: 816.6 (M$^+$). Anal. Calcd. for $C_{47}H_{74}Br_2N_2O_8$: C, 69.12; H, 9.13; N, 3.43. Found: C, 69.11; H, 9.36; N, 3.29.

2.2.5. *Poly(9,9-bis(6′-butoxylcarbonylaminohexyl)fluorene) (**PF-BOC**)*

To a mixture of **4** (722 mg, 1 mmol), **5** (816 mg, 1 mmol), Pd$(PPh_3)_4$ (24 mg, 0.02 mmol), 2–3 drops of aliquot 336, and 1.66 g K_2CO_3 was added degassed toluene (11 mL) and deionized water (6 mL) by syringe. The reaction mixture was stirred under N_2 at 95 °C for 48 h, and then phenylboronic acid and bromobenzene were added respectively as end-capped agents. The reaction mixture was kept stirring for another day. After cooling to room temperature, water and chloroform was added. The separated organic layer was washed with brine and water, dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was added to petroleum ether to give a precipitate. The precipitate was dissolved in chloroform and purified by passing through a short silica gel to remove Pd and reprecipitated from petroleum ether to give **PF-NHBOC** as a yellow powder, and then placed in a Soxhlet apparatus, extracted with refluxed acetone for 48 h (920 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.60–7.86 (m, 6H), 4.53 (s, 2H), 2.98 (m, 4H), 2.12 (m, 4H), 1.41(s, 18H), 1.25 (m, 4H), 1.14 (m, 8H), 0.82 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 156.2, 151.8, 140.6, 140.3, 126.5, 121.5, 120.3, 79.1, 55.5, 40.7, 40.5, 30.2, 29.9, 28.6, 26.8, 24.2. FT-IR (KBr): 3388, 2931, 1699, 1569, 1407, 1253, 1014, 814, 651 cm^{-1}. Anal. Calcd. for $C_{35}H_{52}N_2O_4$: C, 74.43; H, 9.28; N, 4.96. Found: C, 73.11; H, 9.05; N, 4.60.

2.2.6. *Poly(6,6′-(9H-fluorene-9,9-diyl)dihexan-1-aminium chloride) (**PF-NION**)*

To a solution of **PF-NHBOC** (130 mg, 0.23 mmol) in 20 mL of THF, was added 8 mL of 37% hydrochloric acid. The reaction mixture was stirred for 3 days at room temperature. After removal of the solvent under reduced pressure or under vaccum 50 mL of acetone was added to give a precipitate, and the precipitate was filtered and washed with chloroform to give **PF-NION** as a yellow powder (85 mg, 84%). ^{1}H NMR (300 MHz, CD_3OD, ppm): δ 7.70–7.85 (m, 6H), 2.73–2.76 (m, 4H), 2.18 (m, 4H), 1.44 (m, 4H), 1.13 (m, 8H), 0.70 (m, 4H). ^{13}C NMR (75 MHz, CD_3OD, ppm): δ 152.7, 141.8, 127.9, 127.4, 122.2, 121.3, 56.6, 41.5, 40.7, 40.5, 30.7, 28.4, 27.3, 25.1. FT-IR (KBr): 3430, 2929, 1563, 1406, 1253, 1015, 816, 651 cm^{-1}.

2.2.7. *Poly(9,9-bis(6′-aminohexyl)fluorene) (**PF-NH$_2$**)*

PF-NION (100 mg, 0.23 mmol) was dissolved in minimum methanol, and the solution was added into stirred 50% KOH

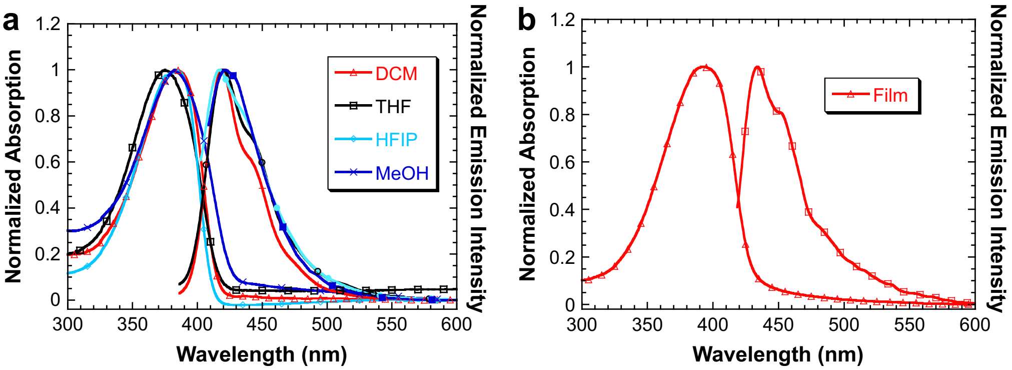


Fig. 2. Normalized UV–vis absorption and PL spectra of **PF-NH$_2$**, in dilute solutions (1×10^{-6} M based on the polymer repeat unit) and in film. (a): UV–vis absorption spectra and PL spectra in different solutions; (b): UV–vis absorption spectra and PL spectra in film.

Table 1
UV–visible and photoluminescence spectra of **PF-NH$_2$**, in dilute solutions (1.0×10^{-6} M) and in thin film at room temperature.

PF-NH$_2$	DCM	THF	HFIP	MeOH	Film
UV–vis(λ_{max})	383	375	384	383	393
PL (nm)	419	420	417	422	434

aqueous solution. After the mixture was stirred at room temperature for 2 h, the precipitate was collected by filtration and purified by dialysis with deionized water for 24 h at room temperature to give **PF-NH$_2$** as a yellow sheet solid (72 mg, 86%). FT-IR (KBr): 3447, 2926, 2856, 1631, 1422, 873, 710 cm^{-1}.

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 illustrates a synthetic approach to monomers **4** and **5**. The reaction of 2,7-dibormofluororene (**1**) with 1,6-dibromohexane in the presence of NaOH aqueous solution afforded 2,7-bibromo-9,9-bis(6′-bromohexyl)fluorene (**2**) in 75% yield, which followed by the reaction with sodium azide to give 2,7-bibromo-9,9-bis(6′-azidohexyl)fluorene (**3**) in 94% yield. Reduction by using PPh$_3$ in THF/H$_2$O, followed by protection of the amine groups with (Boc)$_2$O afforded 2,7-bibromo-9,9-bis(6′-butoxylcarbonylaminohexyl)fluorene (**4**) in 88% overall yield. 2,7-Bis(4,4,5,5-tetramethyl–1,3,2-dioxaborolan-2-yl)-9,9-bis(6′-butoxylcarbonylaminohexyl)fluorene (**5**) was obtained via Suzuki–Miyauri reaction in 78% yield [16].

Finally, a Suzuki cross-coupling reaction between monomers **4** and **5** catalyzed by palladium-mediated afforded a neutral polymer, poly(9,9-bis(6′-butoxylcarbonylaminohexyl)fluorene) (**PF-NBOC**) (as shown in Scheme 2). The crude polymer **PF-NBOC** was washed with methanol, water, and methanol, successively, and then placed in a Soxhlet apparatus, extracted with refluxed acetone for 48 h. Finally, **PF-NBOC** was dried at 60 °C in vacuum oven for 2 days. After such purification, **PF-NBOC** was treated with 37% hydrochloric acid to remove Boc protection groups, and then neutralized by 50% KOH aqueous solution to yield the targeted polymer **PF-NH$_2$**, which was further purified by dialysis with deionized water for 24 h at room temperature.

The chemical structure and purity of the target polymer **PF-NH$_2$** were unequivocally established by full characterizations of its precursor **PF-NBOC**. The Boc-protected neutral polymer **PF-NBOC** was readily soluble in common organic solvents, such as THF, CHCl$_3$, or toluene. The molecular structure and purity of **PF-NBOC** were identified by ^{1}H and ^{13}C NMR, FT-IR, as well as elemental analysis. From the signals of proton NMR (CDCl$_3$, ppm) at chemical shift δ 4.53(s, N*H*Boc, 2H) and δ 1.41(s, NH*Boc*, 18H), the existence of NHBoc groups in the polymer was proved, and was also confirmed by the FT-IR features with characteristics of 3388 and 1699 cm^{-1}. The molecular weight of **PF-NBOC** was determined by gel permeation chromatography (GPC) with THF as the eluent, calibrated against polystyrene standards. The GPC analysis indicated that the number-average molecular weight (M_n) and polydispersity index (PDI) of **PF-NBOC** were 8290 and 1.8, respectively.

Table 2
Electrochemical properties of **PF-NH$_2$** in thin film.

Polymer	E_{ox} (V)	E_{red} (V)	HOMO (eV)	LUMO (eV)	E_{gap} (eV)
PF-NH$_2$	1.06	−1.89	−5.46	−2.51	2.95

3.2. Thermal stability

The thermal stability of polymer **PF-NH$_2$** was investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere. Although the polymer was dried in a vacuum before TGA measurement, there was still some weight loss before 100 °C. This might be due to releasing the associated water. Similar phenomena were observed in other literatures [15a,17]. As shown in Fig. 1, the onset degradation temperature of **PF-NH$_2$** was about 200 °C under nitrogen atmosphere, in which three stages of weight loss of **PF-NH$_2$** were observed. Three stages of decomposition might be attributed to decomposition of amine groups, alkyl chains and main chain of the polymer respectively.[15a]. Differential scanning calorimetry (DSC) was used to determine the thermally induced phase transition behavior of **PF-NH$_2$** under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. However, unlike typical poly(9,9-dialkylfluorenes) (**PAFs**), DSC measurement of **PF-NH$_2$** did not show any phase transition in the temperature range from 0 to 170 °C.

3.3. Photophysical properties

Fig. 2 shows normalized UV–vis absorption and photoluminescent (PL) spectra of **PF-NH$_2$**, in dilute solutions (1.0×10^{-6} M) and in films. As illustrated in Fig. 2a, in dilute solution, **PF-NH$_2$** exhibited almost identical absorption features with λ_{max} at about

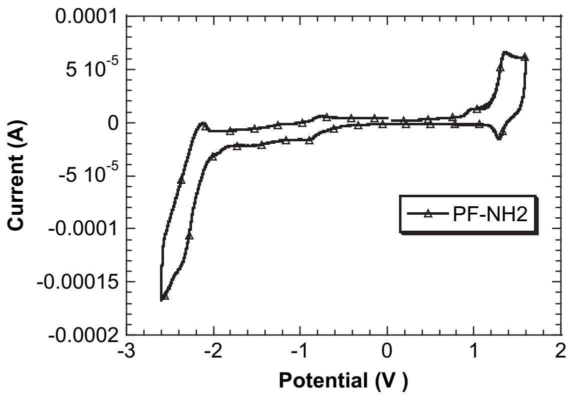


Fig. 3. Cyclic voltammograms of **PF-NH$_2$** film coated on carbon electrode in 0.1 mol/L Bu$_4$NPF$_6$, CH$_3$CN solution.

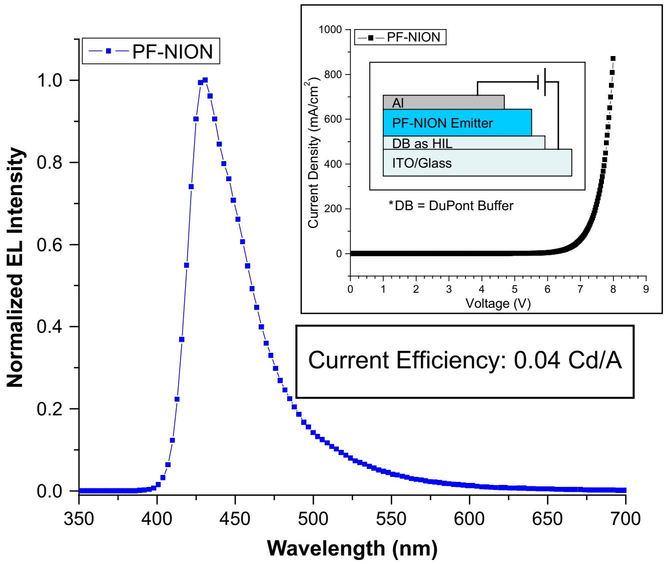


Fig. 4. Electroluminance spectrum of **PF-NION** recorded from an ITO/DB/**PF-NH$_2$**/Al diode (*insert*) operated with a bias of 6 V.

380 nm in different solvents, which also was similar to those of polyfluorene homopolymers. This indicated that **PF-NH$_2$** did not show the strong hydrogen-bonding interactions in dilute solution. The photoluminescent (PL) emission spectra of **PF-NH$_2$**, in different solutions excited at absorption maximum wavelength are illustrated in Fig. 2a. **PF-NH$_2$** showed almost identical behavior in DCM, THF, and HFIP, which were peaked at 417–418 nm with a well-resolved vibronic shoulder at around 440 nm, attributed to the good solubility and well-extended chain conformation of **PF-NH$_2$** in these solvents. In MeOH solution, PL spectrum of **PF-NH$_2$** only showed a broad and structureless peak at 422 nm. In addition, **PF-NH$_2$** also exhibited small Stokes shift (about 30 nm) between 0–0 transition of absorption and emission, indicating a small structural reorganization in the excited state [18].

Normally, as shown in film, the absorption maximum λ_{max} of polyfluorene homopolymers in thin film show blue-shift relative to those in dilute solution due to stronger interchain interaction [19]. However, absorption maximum λ_{max} of **PF-NH$_2$** peaked at 393 nm in film, which was about 17 nm red-shifted in comparison with that in dilute HFIP solution, which might be attributed to aggregation formation due to the strong hydrogen-bonding interactions in film. The PL features of **PF-NH$_2$** with a peak at 434 nm in thin film

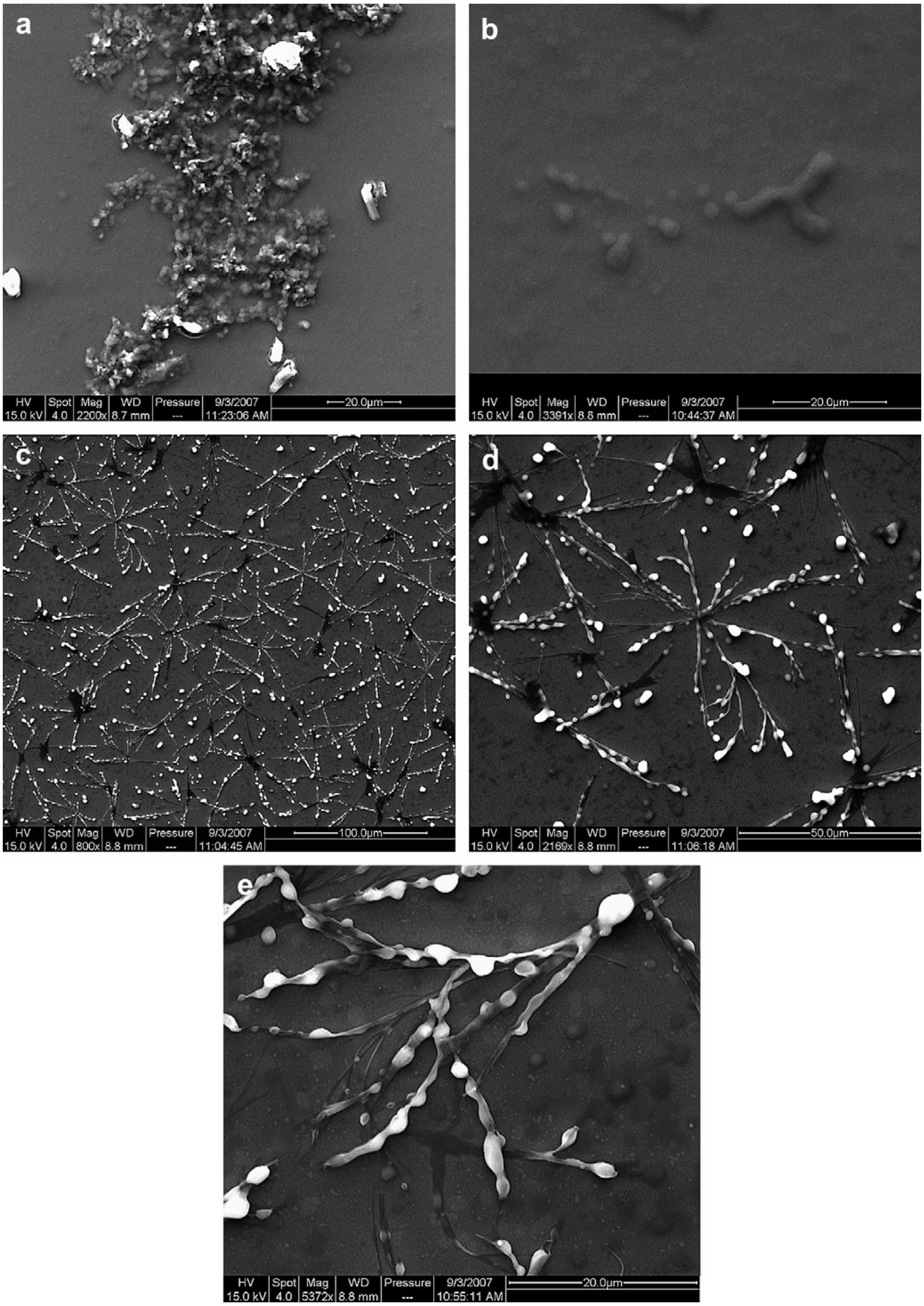


Fig. 5. Scanning electron micrographs (SEM) of the thin film of **PF-NH$_2$**. (a), (b) drop-cast from methanol solution; (c), (d), (e) drop-cast from HFIP solution.

showed the almost identical homopolymers in dilute solution. These results indicated that neither excimer nor exciplex was observed in PL spectra of **PF-NH$_2$** both in solutions and in film, unlike other hydrogen bonding-containing polymers reported in previous papers [8,20], due to different degree of aggregation of polymer backbone. This may indicate that intrachain hydrogen bonding interactions played a key role in our system. The photophysical properties of **PF-NH$_2$** in dilute solutions and in thin film are summarized in Table 1.

3.4. *Electrochemical and electroluminance properties*

The electrochemical behavior of **PF-NH$_2$** was investigated by cyclic voltammetry (CV). The CV was performed in a solution of Bu_4NPF_6 (0.1 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under nitrogen environment. A carbon electrode was coated with a thin polymer film and 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. As shown in Fig. 3, the oxidation and reduction peaks appeared at around 1.3 and 2.1 V, respectively, which were attributed to the oxidation and reduction potentials for the backbone of **PF-NH$_2$**. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **PF-NH$_2$**, calculated according to an empirical formula, $E_{\mathrm{HOMO}} = -e(E_{\mathrm{ox}} + 4.4)$ (eV), and $E_{\mathrm{LUMO}} = -e(E_{\mathrm{red}} + 4.4)$ (eV) [21], are listed in Table 2. From the electrochemical data, it was estimated that the band gap was around 2.95 eV for **PF-NH$_2$**, which was a little larger than the optical band gap of 2.84 eV estimated from absorption onset. A significant difference between gaps determined electrochemically and optically for poly(9,9-dialkylflurenes) were previously reported by Janietz et al. [22], no detailed explanation about the discrepancy between optical and electrochemical gaps was provided in their paper.

A preliminary evaluation of their electroluminance (EL) properties of **PF-NION** was carried out. An OLED device using PF-NION as the emitter was fabricated with a simple configuration with ITO/Dupont Buffer (DB)/**PF-NION**/Al (Fig. 4, insert). A MeOH solution of **PF-NION** was spin-cast onto DB layer. An aluminum cathode was deposited. The device was operated with a bias of 6 V, and EL spectrum was recorded (Fig. 4), No excimer or ketone defect was found, and pure blue light was obtained with CIE (0.16, 0.08). The efficiency of the device was 0.04 Cd/A. An in-depth study of the solid-state behavior of the polymer and optimization of OLED devices utilizing the polymer is currently underway.

3.5. *Self-assembly properties*

Scanning electron microscope (SEM) was used to observe the self-assembly behaviors of **PF-NH$_2$** in thin films, after spontaneous evaporation of methanol or HFIP solution. The corresponding surface morphologies of **PF-NH$_2$** thin films were shown in Fig. 5. When dropped onto the silica substrate from methanol solution, it self-condensed into nanoparticles, while it displayed the morphology similar to the fruit of Sophora japonica after evaporation of HFIP solution. In the salt form, **PF-NION** had good solubility in methanol, DMSO, DMF and other polar solvents, when it turned into neutral form, **PF-NH$_2$** had very poor solubility except HFIP, we postulated that crosslinked network was formed due to hydrogen bonding effect between amine groups. In addition, FT-IR of **PF-NH$_2$** showed the associated hydrogen bonds led to a broad absorption peak at 3447 cm^{-1} of the stretching vibration of N–H bond compared with dissociated N–H bonds which possessed two obvious peaks between 3500 and 3300 cm^{-1}. From the postulation above mentioned, the special morphologies might be mainly attributed to intramolecular/intermolecular hydrogen bonding interaction, π–π stacking or both, further investigation is in progress.

4. Conclusion

In conclusion, we have developed a facile method to prepare an alcohol-soluble polyfluorene derivative (**PF-NH$_2$**) with primary amine groups on side chains. The polymer exhibited good thermal stability, blue-emitting property and a large band gap. The results of SEM images of **PF-NH$_2$** in thin films revealed that intramolecular/intermolecular hydrogen bonding and π–π stacking interactions probably play an important role in the formation of special morphologies. In addition, EL spectra of the **PF-NION** have been recorded on a simple OLED device configuration with ITO/Dupont Buffer (DB)/**PF-NION**/Al, and pure blue light was obtained. The CIE is (0.16, 0.08), and the efficiency is 0.04 Cd/A. An in-depth study of the solid-state behavior of the polymer and optimization of OLED devices utilizing the polymer is currently underway.

Acknowledgment

This work was financially supported by the Major State Basic Research Development Program (Nos. 2006CB921602 and 2009CB623601) and by the National Natural Science Foundation of China (NSFC) and Hewlett Packard Company.

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