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Synthesis and Characterization of Fluorene Based Electron Transporting Materials for Polymer Light-Emitting Diodes

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We synthesized fluorene based alternating copolymers comprised of several electron withdrawing groups via Suzuki coupling polymerization. Physical properties were characterized using the UV-vis spectroscopy, photoluminescence (PL) spectroscopy. The absorption peaks of copolymers were red-shifted compared to that of corresponding fluorene homopolymer.

Keywords Electron withdrawing group; PLEDs; polyfluorene

1. Introduction

During the past decade, polymer light-emitting diodes (PLEDs) have attracted continuous attention because of their low costs, processability, and the possibility of flexible fabrication [1]. To achieve high efficiency, low-work-function metals (such as Ca or Ba) are widely used as a cathode to facilitate electron injection. However, these metals are very sensitive to moisture and oxygen forming detrimental quenching sites at interfacial area between the electronluminescence (EL) layer and the cathode [2,3]. Recently, ammonium-functionalized cationic polyflourenes surfactants and their precursors have been found to exhibit excellent electron-injection (or transport) ability in PLEDs [4,5]. Their good solubility in polar solvents such as alcohol renders them as ideal materials for electron transporting layer in solution processed, multilayered PLEDs. In this work, we designed and synthesized several fluorene based alcohol-soluble copolymers having various electron withdrawing groups as an electron transporting layer. The polymers were synthesized by palladium-catalyzed Suzuki coupling reaction and their electronic properties are compared.

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2. Experimental

2.1. *Materials*

Tetrakis(triphenylphosphine)palladium(0) was purchased from STREM Chemicals Co. All other chemical reagents were purchased from Aldrich Co. and used without further purification. The 2,2′-(9,9-bis(6-bromohexyl)-9H-fluorene-2,7-diyl)-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) was synthesized according to procedures in published paper [6].

2.2. *General Procedure for the Conjugated Polymer Synthsis*

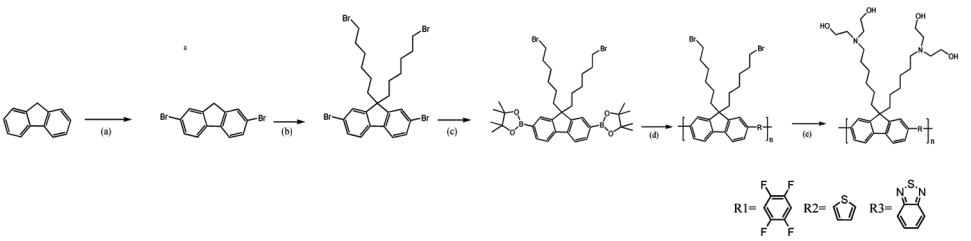
2,2′-(9,9-bis(6-bromohexyl)-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1 g, 1.35 mol), the dibromo monomers (R1, R2, R3) (1.35 mmol), tetrakis(triphenylphospine)palladium (0.0202 mmol) were placed in a 100 mL round bottom flask. A mixture of dried THF (10 mL) and aqueous 2 M potassium carbonate solution (10 mL) were added to the flask. The mixture was violently stirred at 85°C for 36 h and then precipitated into methanol. The polymers were dried under vacuum for 24 h, dissolved in 7 mL THF/DMF (1:1) mixture and then treated with excess diethanolamine while stirring at 85°C for 36 h. The mixture was extracted with chloroform, concentrated, and then precipitated from methanol. Finally, we obtained three types of polymers, referred to as P1, P2 and P3. (yields: 60%, 50% and 62%, respectively). P1: ^{1}H NMR (400 MHz, $CDCl_3$, δ): δ 7.90(m, 2H), 7.47(br, 6H), 3.30(br, 4H), 3.08(br, 4H), 2.03(br, 4H), 1.62(m, 3H), 1.11(br, 10H), 0.77(br, 4H) P2: ^{1}H NMR (400 MHz, $CDCl_3$, δ): δ 7.80(br, 6H), 3.30(br, 4H), 2.19(br, 6H), 1.68(br, 4H), 1.25(br, 6H), 0.84(br, 6H) P3: ^{1}H NMR (400 MHz, $CDCl_3$, δ): δ 7.96(br, 6H), 3.28(br, 4H), 2.18(br, 6H), 1.69(br, 4H), 1.24(br, 4H), 1.15(br, 4H), 0.92(br, 3H), 0.84(br, 2H).

2.3. *Measurements*

^{1}H NMR spectra were recorded on a Varian Mercury 400 NMR spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as a standard. UV-vis spectra were measured by an Optizen 2120UV spectrometer and photoluminescence (PL) spectra were measured by using ISS PC1 photon-counting spectrofluorometer. The electrochemical experiments were carried out using the BAS-100D photoelectron spectrometer.

3. Results and Discussion

The synthetic route is shown in Scheme 1. The physical data of polymers are summarized in Table 1. UV-vis absorption spectra of synthesized polymers are shown in Figure 1. P1 and P2 exhibit absorption maxima at 321 nm and 383 nm, respectively. Two absorption peaks at 309 nm and 425 nm are observed in the absorption spectra of P3. Optical band gaps estimated from the absorption edges of each polymer are in order of P1 (3.42 eV), P2 (2.78 eV), P3 (2.51 eV) [7]. Figure 2 shows the photoluminescence spectra of P1, P2 and P3. Three emission peaks of P1, P2 and P3 are observed at 393 nm, 444 nm and 538 nm, respectively. We were determined HOMO energy levels of P1 (−5.06 eV), P2 (−5.36) and P3 (−5.37) using a BAS-100D photoelectron spectrometer; we estimated the LUMO energy levels P1 (−2.63 eV), P2 (−2.72 eV) and P3 (−1.46 eV) by adding the optical energy gap to the obtained



Scheme 1. Synthetic route of P1, P2 and P3. (a) NaBr, H_2SO_4, EDC, 80°C, 5 h, (b) 1,6-dibromohexane, TBAB, 50% KOH solution, 80°C, 1 h, (c) 1.7 M t-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-[1.3.2]-dioxaborolane −78°C, 3 h, (d) $Pd(PPh_3)_4$, 2 M K_2CO_3, THF 85°C, 36 h, (e) $HN(CH_2CH_2OH)_2$, THF/DMF 1:1, 85°C, 36 h.

Table 1. Summary of the optical properties of the polymers

			Cyclic Volatammetry		Absorption spectroscopic data	
	$\lambda_{PL}{}^{c}$ (nm)	$\lambda_{max}{}^{b}$ (nm)	Oxidation potential[a] (V)	HOMO (eV)	LUMO (eV)	Optical energy gap (eV)
P1	393	321	0.66	−5.06	−2.63	3.42
P2	444	383	0.96	−5.36	−2.72	2.78
P3	538	309	0.97	−5.37	−1.46	2.51

[a]Determined by photoelectron spectrometer (BAS-100D).
[b]Determined by UV-vis absorption spectroscopy using 2120UV spectrometer.
[c]Determined by photoemission spectroscopy using ISS PC1 photon-counting spectrofluorometer.

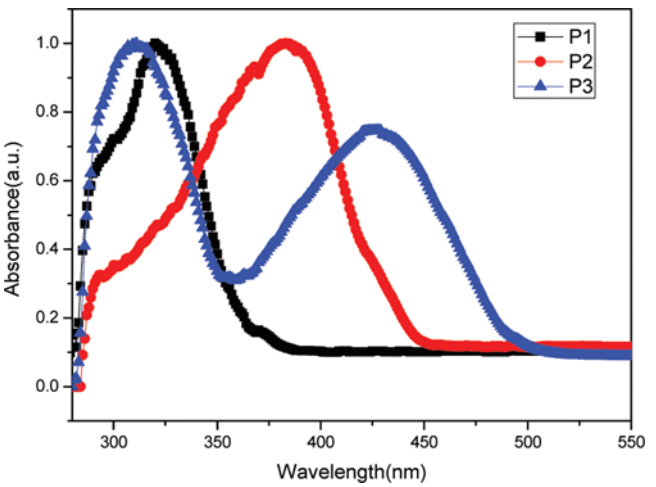


Figure 1. The absorption spectra of P1, P2 and P3 in THF.

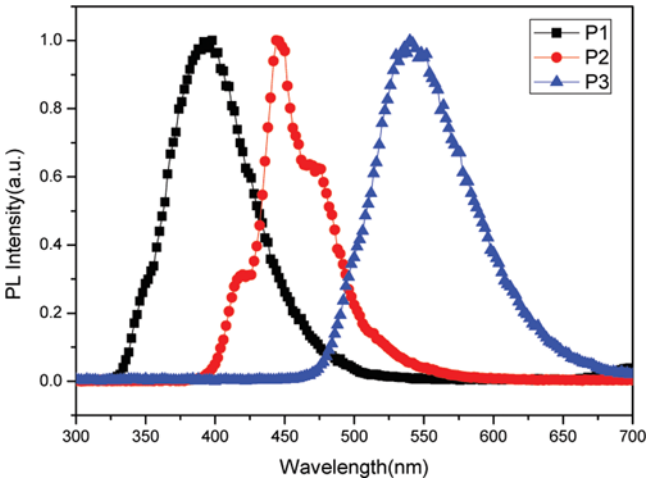


Figure 2. The emission spectra of P1, P2 and P3 in THF.

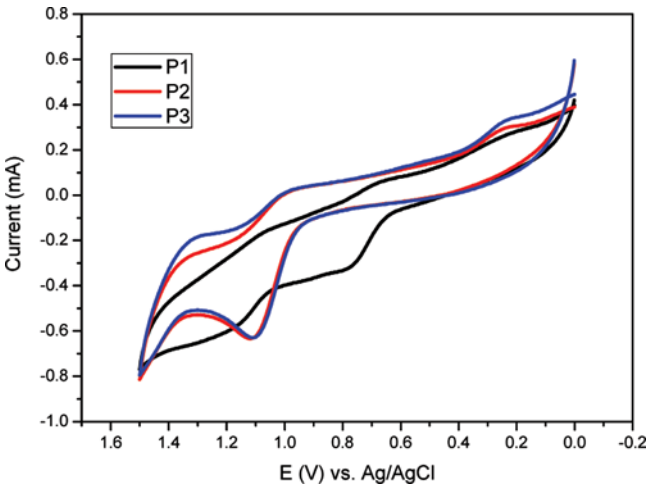


Figure 3. Cyclic voltammograms of the anodic oxidation of P1, P2 and P3.

HOMO energy levels. The cyclic voltammograms of $\sim 10^{-3}$ M CH_3CN solutions of polymers are shown in Figure 3. Cyclic voltammetry (CV) at a scan rate of 100 mVs^{-1} was applied to study the oxidation behavior of polymers. The absorption peaks and emission peaks of copolymers were red-shifted compared to that of corresponding fluorene homopolymer. The band gaps of polymers were controlled by using electron withdrawing group.

4. Conclusion

We successfully synthesized alcohol-soluble alternating copolymers comprising fluorene group and electron withdrawing groups. All these polymers can be processed

from polar solvents such as methanol, which is suitable for multilayer of solution processed PLEDs. Band gap of the polymer can be controlled by introducing proper electron withdrawing monomers, as shown at absorption spectra and emission spectra. These polymers are expected to improve the PLED performance when using as an electron injection/transporting material.

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