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Synthesis and characterization of efficient orange-red emitting poly(*p*-phenylenevinylene) derivatives with 1,3,4-oxadiazole unit

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Abstract

A series of the statistical copolymers of tetradecyloxy-3,5-bis-{2-(4-bromo-phenyl)-[1,3,4]oxadiazole}-benzene (**4**), 1,4-didecyloxy-2,5-diiodobenzene (**5**) and 1,4-dodecyloxy-2,5-divinylbenzene (**6**), for efficient light emitting diode were synthesized. As the feed ratio of compound **4** decreased, the absorption band at 320–360 nm decreased in the UV–vis spectra. In addition, as the composition of compound **4** decreased, the absorption intensity ratio at 1541 cm^{-1} decreased in the FT-IR spectra. The photoluminescence and electroluminescence emission color of **P** showed green-yellow color ($\lambda_{max} = 552$ nm). However, the maximum wavelength of photoluminescence and electroluminescence of **P1** and **P2** were 581 and 583 nm, respectively, which were dramatically red-shifted than that of **P**. Moreover, these values were almost the same as the values of **P3** (580 nm). It is concluded that the energy transfer from high energy oxadiazole segments to low energy alkoxy-PPV segments occurred completely. The efficiency of ITO/**P2**/Al was 0.0181%, which is the best efficiency among the device based on the copolymers. This is presumably due to that **P2** has the best balanced hole- and electron-injection/transporting properties among the copolymers.

Keywords: Poly(*p*-phenylenevinylene); Conjugated 1,3,4-oxadiazole; Electroluminescence; Energy transfer

1. Introduction

Polymer light emitting diodes (PLEDs) have been widely studied owing to its easy processibility and cost effectiveness. A pioneering achievement was made by Cavendish Laboratory, using poly(*p*-phenylenevinylene) (PPV) [1]. Many researches have been done for improving the device efficiency and for tuning the emission color. One of the strategies to improve efficiency of PLED is to synthesize new efficient polymers with hole or electron transporting materials. It has been continuously reported that the π-conjugated polymers containing aromatic 1,3,4-oxadiazole (OXD) [2–11], 1,2,4-triazole (TAZ) [11–14] in the main chain or in the side chains show improved device efficiency.

In this article, we have synthesized a series of PPV copolymers in which tetradecyloxy-3,5-bis-{2-(4-bromo-phenyl)-[1,3,4]oxadiazole}-benzene (**4**) were incorporated as a comonomer in the PPV backbone. The structural design of the polymer is basically aimed at improving the efficiency by introducing conjugated 1,3,4-oxadiazole, which is expected to be an electron transporter. In general, the band gap energy of the polymers containing OXD derivatives is lager than dialkoxy-PPV [2,6–9,11]. From the structures of the copolymers (Scheme 2), we can expect that the energy transfer from the OXD segments with large band gap to the alkoxy-PPV segments with small band gap will occur completely. We investigated the fundamental optical properties and electroluminescent (EL) properties as well as the role of OXD in the improvement of EL efficiency of the polymers.

2. Experimental

2.1. Measurements

The synthesized compounds were characterized by ^{1}H NMR spectra that were obtained using Varian Unity spectrometer (INOVA 300 or 500 MHz). The elemental analysis was performed with Carlo Erba elemental analyzer (CarloErba 1108).

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FT-IR spectra were recorded by Nicolet 205 FT-IR spectrometer. Thermogravimetric analysis (TGA) of the polymers was performed under nitrogen atmosphere at a heating rate of 20 °C/min with Thermogravimetric Analyzer (Thermal Analysis 2050). The UV–vis spectra of the polymer were measured using a spectrophotometer (Hewlett-Packard HP8453) with a photodiode array detector. The photoluminescence (PL) and electroluminescence (EL) spectra of the polymers were obtained using a Photon Technology Spectroflourophotometer. The current–voltage (*I*–*V*) and EL intensity–voltage (EL–*V*) characteristics were measured using a current/voltage source and a calibrated photodiode (Newport 818UV/CM) and a power meter (Newport 1830-C). UV–vis and PL measurements and evaluation of EL devices were performed under ambient conditions.

2.2. Materials

Tetrahydrofuran (THF) and diethyl ether were distilled over sodium/benzophenone. Tributylamine were distilled over calcium hydride. All other chemicals were purchased from Aldrich Chemical Co. and were used as received unless otherwise stated. 1,4-Didecyloxy-2,5-diiodobenzene (**5**) and 1,4-didodecyloxy-2,5-divinyl-benzene (**6**) were synthesized according to the literature procedure [5,15].

2.3. Monomer and polymer synthesis

2.3.1. 5-Tetradecyloxy-isophthalic acid dimethyl ester (*1*)

A mixture of 27.73 g (0.10 mol) of 1-bromotetradecane, 13.82 g (0.10 mol) of potassium carbonate and 21.02 g (0.10 mol) of 5-hydroxy-isophthalic acid dimethyl ester was dissolved in 100 mL of acetone and was refluxed for 24 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature. The solid particles were filtered and washed with chloroform. After removal of the solvent from combined filtrate, the crude product was dissolved in chloroform, washed with several times with aqueous NaOH and brine, and then dried over anhydrous magnesium sulfate. After removing the solvent in a rotary evaporator, the crude solid product was purified by recrystallization from chloroform/methanol. The product yield was 30.65 g (75.4%). ^{1}H NMR (CDCl$_3$, ppm): δ 8.23 (s, 1H), 7.71 (s, 2H), 4.02–3.99 (t, $J = 6.8$, 2H), 3.91 (s, 6H), 1.81–1.75 (m, 2H), 1.47–1.42 (m, 2H), 1.33–1.24 (m, 20H), 0.87–0.84 (t, $J = 6.8$, 3H). Anal. Calcd. for $C_{24}H_{38}O_5$: C, 70.90; H, 9.42. Found: C, 70.94; H, 9.49.

2.3.2. 5-Tetradecyloxy-isophthalic acid dihydrazine (*2*)

A mixture of 28.45 g (0.070 mol) of compound **1** and excess of hydrazine hydrate dissolved in 150 mL of methanol was refluxed for 24 h. The precipitate was filtered and washed with water then dried under vacuum. The yield of the white solid product was 26.81 g (94.2%). ^{1}H NMR (CDCl$_3$/DMSO-d_6, ppm): δ 9.10 (s, 2H), 7.55 (s, 1H), 7.16 (s, 2H), 3.84 (br, 4H), 3.66–3.63 (t, $J = 6.6$, 2H), 1.43–1.37 (m, 2H), 1.10–1.04 (m, 2H), 0.96–0.88 (m, 20H), 0.51–0.48 (t, $J = 6.8$, 3H). Anal. Calcd. for $C_{22}H_{38}N_4O_3$: C, 64.99; H, 9.42; N, 13.78. Found: C, 64.95; H, 9.48; N, 13.69.

2.3.3. N,N′-Bis-(4-bromophenyl)-5-tetradecyloxy isophthalic acid dihydrazide (*3*)

A solution of 8.78 g (0.040 mol) of *p*-bromobenzoyl chlororide in 10 mL of *N*,*N*-dimethyacetamide (DMAc) was slowly added into a solution of 8.13 g (0.020 mol) of compound **2** and 4.04 g (0.040 mol) of triethylamine in 20 mL of DMAc at 4 °C. After completion of addition of *p*-bromobenzoyl chlororide, the reaction mixture was stirred at room temperature for 4 h and then the reaction mixture was poured into 300 mL of water. The precipitate was filtered and washed with water. The filtered solid product purified by recrystallization from methanol. The white solid product yield was 12.74 g (82.5%). ^{1}H NMR (CDCl$_3$, ppm): δ 8.21 (s, 1H), 8.12–8.10 (d, $J = 8.5$, 2H), 7.90 (s, 2H), 7.65–7.63 (d, $J = 8.5$, 2H), 4.14–4.12 (t, $J = 6.3$, 2H), 1.89–1.84 (m, 2H), 1.55–1.49 (m, 2H), 1.39–1.26 (m, 20H), 0.89–0.86 (t, $J = 6.7$, 3H). Anal. Calcd. for $C_{36}H_{44}Br_2N_4O_5$: C, 55.97; H, 5.74; N, 7.25. Found: C, 55.85; H, 5.67; N, 7.59.

2.3.4. Tetradecyloxy-3,5-bis-{2-(4-bromo-phenyl)-[1,3,4]oxadiazole}-benzene (*4*)

A solution of 7.73 g (0.010 mmol) of compound **3** in 20.0 mL of freshly distilled POCl$_3$ was refluxed for 6 h. Excess of POCl$_3$ was distilled off the reaction mixture, and then the residue was poured into iced water. The precipitate was filtered and washed with water. The filtered cake was dissolved in chloroform and wash with aqueous sodium bicarbonate. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed using a rotary evaporator. The crude product purified by recrystallization from chloroform/methanol. The white solid product yield was 6.92 g (94.0%). ^{1}H NMR (CDCl$_3$, ppm): δ 8.36 (s, 1H), 8.04–8.02 (d, $J = 8.5$, 2H), 7.80 (s, 2H), 7.71–7.69 (d, $J = 8.5$, 2H), 4.14–4.12 (t, $J = 6.3$, 2H), 1.89–1.84 (m, 2H), 1.55–1.49 (m, 2H), 1.39–1.26 (m, 20H), 0.89–0.86 (t, $J = 6.7$, 3H). Anal. Calcd. for $C_{36}H_{40}Br_2N_4O_3$: C, 58.71; H, 5.47; N, 7.61. Found: C, 58.75; H, 5.45; N, 7.51.

2.3.5. Polymerization

The feed ratio of each monomer was shown in Scheme 2. The monomers, 2.0 mol.% of Pd(OAc)$_2$, 1.0 mol.% of tri-*o*-tolyl-phosphine and 0.31 mL of tributylamine in 10 mL of *N*,*N*-dimethylformamide (DMF) was stirred for 24 h at 120 °C. The hot reaction mixture was poured into methanol then the red precipitate was collected by filtration. The filtered polymer precipitate was redissolved in 100 mL of chloroform then washed with 400 mL of deionized water. The water layer was decanted carefully. The black catalyst particles in the polymer solution were removed by filtration then the solvent was removed using a rotary evaporator. The polymer was dissolved in small amount of THF then poured into methanol. The red polymer precipitate was collected by filtration and dried under vacuum.

3. Results and discussion

3.1. Monomer and polymer synthesis

Schemes 1 and 2 shows synthetic procedures for the monomers and polymers. Compound **4**, **5** and **6** are the key