An Efficient Electroluminescence Copolymer Based on Vinyl-Linked Donor–Acceptor System

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ABSTRACT: Using copolymerization functionalization, poly[3,4-dioctyloxythiophene-alt-2,5-bis(4-vinylphenyl)-1,3,4-oxadiazole] (P3,4DOOTV-OXD) combining electrochemical properties of poly(3,4-dioctyloxythiophene) (P3,4DOOT, donor) and 1,3,4-oxadiazole (OXD, acceptor) was synthesized through Heck reaction and evaluated with ¹H-NMR, FTIR, gel permeation chromatography (GPC), UV-vis spectroscopy, photoluminescence (PL), and electroluminescence (EL) spectra. This D/A alternating copolymer, with regiosymmetrical 3,4-dioctyloxythiophene, has good solubility in common organic solvents. The optical properties investigations showed that the band-gap energy of P3,4DOOTV-OXD is 10% higher than that of P3,4DOOT (2.27 eV) at 2.52 eV in solid film. However, the photoluminescence (PL) quantum yield is as high as 57.4%, > two times more than that of homopolymer P3,4DOOT in CHCl3 solution, and displays bright green-yellow luminescence (518 nm) in solu-

INTRODUCTION

Later years, conjugated polymers have been developed into useful materials for a variety of applications in electronic and electrochemical devices,¹ such as organic field-effect transistors (OFETs),² organic light-emitting diodes (OLEDs),^{3–5} and sensors.⁶ Thiophene and 1,3,4-oxadizole derivatives are of considerable interest due to their promising optical and electronic properties in the field of OLEDs.^{7–12} However, thiophene units are electron donator in nature and hence have greater tendency to transport holes than transporting electrons, which always results in low efficiency of the OLED devices. While 1,3,4-oxadizole units are electron acceptor, which show greater tendency to transport electrons than holes.¹³ One of the require-

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 21075015. tion and yellow (542 nm) in solid film. Cyclic voltammogram indicated that the copolymer has bipolar properties, and the band gap energy (E_g) calculated based on the cyclic voltammogram is consistent with that deduced from the absorption spectra at 2.40 eV. By using indium-tin oxide (ITO) as the anode, poly(ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS) as the hole-injection layer, P3,4DOOTV-OXD as the emitter and aluminum (Al) as the cathode, double-layer device with the structure of [ITO/PEDOT: PSS (50 nm)/polymer/Al (130 nm)] shows typical diode characters and exhibit bright yellow electroluminescence (562–552 nm) under the forward bias. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 50–54, 2011

Key words: copolymer; thiophene; oxadiazole; photoluminescence; electroluminescence; organic light-emitting diode

ments for efficient OLEDs is balanced charge injection from the two electrodes and efficient transport of both holes and electrons within the luminescent layer in the device structure. Many investigations have proven that conjugated D-A type polymers played an important role on their balanced charge transporting property and showed an unique electrochemical and optical properties.^{14–16} This study is motivated by the above background and succeed in designing and synthesizing a novel D-A-type conjugated polymer P3,4DOOTV-OXD, which contains 3,4-dioctyloxythiophene as electron-donating segment and 1,3,4-oxadizole unit as electron acceptor. Introduction of long alkoxy pendants at 3 and 4-positions of the thiophene ring improves the solvent processibility and hole carrying ability of the corresponding polymer.¹⁷ On the other hand, inserting of 1,3,4-oxadizole unit in system enhances the electron transporting property. Further, incorporation of vinylene linkages facilitates to planarize the polymer back-bone by overcoming torsional interactions between rings that could help to alter the band gap.¹⁸ Electroluminescent (EL) performance of the polymer as the luminescent material was investigated based on double-layers OLED architecture.

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EXPERIMENTAL

Materials and instrumental measurements

All reagents were purchased from Aldrich Chemical, Acros Organics, Merck, and Fluka. Reagent grade solvents were dried when necessary and were purified by distillation.

¹H-nuclear magnetic resonance (NMR) measurement was carried out with a Bruker Avance 300 MHz using tetramethylsilane (TMS)/ deuterated solvent signal as internal reference. FTIR spectra were recorded on a Nicolet 700 FTIR spectrometer. Elemental analysis was performed with Elementar Vario III. Gel permeation chromatography (GPC) was performed with a Perkin-Elmer series 200 apparatus. UV-vis spectra were recorded on a UV-4100 spectrophotometer, and photoluminescence spectra were recorded on a Spex FL-2T2 spectrofluorometer. The electrochemical study was carried out using a CHI660B CV electrochemical analyzer. Cyclic voltammogram was recorded using a three electrode cell system with a Pt disc working electrode, a Pt wire as the counter electrode and a Ag/ AgCl electrode as the reference electrode at a scan rate of 25 mV s⁻¹. The current/voltage was measured by a current/voltage source (Keithley 2400), and electroluminescence spectra was measured with a Minolta CS-1000.

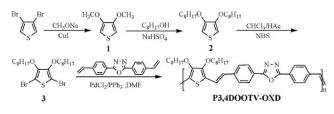
Synthesis

Preparation of monomers

General procedure for the synthesis of 3,4-dimethoxythiophene $(1)^{19}$. To a mixture of N-methyl-2-pyrrolidone (NMP, 130 mL) and methanol (50 mL) was added small pieces of sodium (15 g, 650 mmol) and stirred. After the sodium disappeared, 3,4-dibromothiophene (24.2 g, 100.0 mmol) and CuI (4.8 g, 25.0 mmol) were added and the reaction solution was heated slowly to 115°C for 3.5 h. After cooling and filtered, the filtrate was poured into 500 mL saturated NaCl solution, and the sloution was extracted by diethyl ether (100 mL) for three times. The organic phase was dried over anhydrous MgSO4 and evaporated. The product was purified by vacuum distillation to give 1 as a colorless oil in 66% yield, bp 100–102°C (10–11 mmHg). ¹H-NMR (CHCl₃-d), δ (ppm): 3.85 (s, 6H), 6.18 (s, 2H). IR (KBr), v (cm⁻¹): 3118, 3000, 2957, 2826, 1567, 1504, 1447, 1412, 1135.

General procedure for the synthesis of 3,4-dioctyloxythiophene (2). Under a nitrogen atmosphere, a solution of **1** (7.2 g, 50.0 mmol), octyl alcohol (26 g, 200 mmol), and NaHSO₄ (0.60 g, 5.00 mmol) in dry toluene (25 mL) was heated to 112° C and stirred for 5 h. After the reaction, the catalyst of NaHSO₄ was filtered off and the product was purified by column





Scheme 1 Synthetic procedure of the polymer.

chromatography (silicagel; eluent: petroleum ether/ ethyl acetate (99 : 1 v/v)) to get colorless oil in 62% yield. ¹H-NMR (CHCl₃-*d*), δ (ppm): 0.91 (t, 6H, *J* = 7.5 Hz), 1.29–1.87 (m, 24H), 3.98 (t, 4H, *J* = 6 Hz), and 6.18 (s, 2H). IR (KBr), v (cm⁻¹): 3115, 2954, 2929, 2862, 1560, 1498, 1460, 1375, 1155.

General procedure for the synthesis of 2,5-dibromo-3,4dioctyloxythiophene (3)²⁰. A solution of **2** (4.98 g, 10.0 mmol) in chloroform (CHCl₃, 8 mL) and acetic acid (4 mL) was shielded from light and brought under argon atmosphere. Then, *N*-bromosuccinimide (3.92 g, 22.0 mmol) was added in small portions at 0°C. After 3 h, the reaction mixture was poured into NaOH (40 mL, 1*M*), and the crude compound was extracted with dichloromethane. After purification by column chromatography, a yellow oil of **3** was obtained in 67% yield. ¹H-NMR (CHCl₃-*d*), δ (ppm): 0.85 (t, 6H, *J* = 6.9 Hz), 1.28–1.79 (m, 24H), 4.06 (t, 4H, *J* = 6.6 Hz). IR (KBr), v (cm⁻¹): 2964, 2934, 2848, 1561, 1488, 1466, 1341, 1038.

Preparation of the polymer

Poly[*3*,*4-dioctyloxythiophene*-alt-2,*5-bis*(*4-vinylphenyl*)-*1*,*3*,*4-oxadiazole*]. P3,4DOOTV-OXD was synthesized through Heck reaction, according to a procedure similar to that described in the literature,^{21,22} as shown in Scheme 1. 2,5-bis(4-vinylphenyl)-1,3,4-oxadiazole was synthesized according to the references.²³

The solution of 3 (0.996 g, 2.0 mmol), 2,5-bis(4vinylphenyl)-1,3,4-oxadiazole (0.55 g, 2.0 mmol), triphenylphosphine (0.13 g, 0.5 mmol), and PdCl₂ (0.01 g, 0.056 mmol) in the mixture of 1.4 mL triethylamine and 14 mL N,N-dimethylformamide (DMF) was added to a Schlenk flask purged with N₂. The solution was stirred at 120°C for 12 h and 140°C for 2 h. By filtration, Soxhlet extraction and crystalization, P3,4DOOTV-OXD with brown solid was obtained in yield of 53%. ¹H-NMR (CHCl₃-d), δ (ppm): 0.88 (t, 6H, J = 6.3 Hz), 1.30–1.84 (m, 24H), 3.95-4.15 (m, 4H), 6.83 (d, 1H, J = 16.2 Hz), 7.37(d, 1H, J = 16.2 Hz), 7.60 (d, 4H, J = 8.2 Hz), and8.10 (d, 4H, J = 7.6 Hz). IR (KBr), v (cm⁻¹): 2961, 2926, 2846, 1602, 1553, 1488, 1419, 1379, 1065. Element. Anal. Calcd. for C38H46N2O3S: C, 74.75; H, 7.54; N, 4.59; S, 5.25. Found: C, 74.12; H, 7.41; N, 4.83; S, 5.36.

Fabrication of organic light-emitting device

The EL device had the structure of a [ITO/PEDOT: PSS (50 nm)/polymer/Al(130 nm)] device as it used indium-tin oxide (ITO) as the anode, poly(ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS) as the hole-injection layer, P3,4DOOTV-OXD as the emitter and aluminum as the cathode. The ITO glass was cleaned as described in other literature.²⁴ PEDOT was spin coated on the top of ITO substrate from a 0.7 wt % dispersion in water and then dried in vacuum, then the polymer (10 mg) was dissolved in 1 mL CHCl₃ and the solution was spin coated at a speed of 1800 rpm onto PEDOT film to form the polymer thin film. Finally, aluminum as cathode was thermally evaporated onto the polymer film under 10^{-6} Torr, and the deposition rate was about 0.1 nm/s.

RESULTS AND DISCUSSION

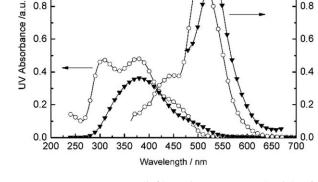
Characterization of polymer

The chemical structure of the polymer was confirmed by NMR spectra and FTIR. The singlet peak around δ 6.18, due to =C—H protons on thiophene ring, is not found in the ¹H-NMR spectra of P3,4DOOTV-OXD, which reflects the high degree of polymerization of the corresponding polymer. A broad peak around δ 3.95–4.15 belongs to $-OCH_2$ protons of the alkoxy group appending on thiophene ring. In addition, multiple peaks were obtained in the range of δ 1.30–1.84, due to $-(CH_2)_n$ — protons of the alkoxy groups, and a triplet peak around δ 0.88 belongs to $-CH_3$ protons of the alkoxy groups. Two duple peaks of δ 6.83 and δ 7.37 belong to =C—H protons of ethylene and δ 7.60–8.10 are aromatic protons of OXD.

The elemental analysis result for the polymer is in agreement with their expected empirical formula. The polymer show excellent solubility, and they can be soluble in many common organic solvents, such as CHCl₃, THF, DMF, and so on. P3,4DOOTV-OXD was measured by means of gel permeation chromatography (GPC) using THF as eluant against polystyrene standards. The average molecular weight of the polymer was measured as $M_w = 30,116$, $M_n = 13,111$, and PDI = 2.29.

Optical properties

The UV–visible absorption and photoluminescence (PL) spectra of the polymer were recorded both in dilute CHCl₃ solution (10^{-5} mol L⁻¹) and in thin film. As shown in the left of Figure 1, the absorption spectra of the polymer displayed an absorption maximum at 374 nm, typical of the $\pi \rightarrow \pi^*$ transition of the conjugated backbone and the absorption band



- Solution

- Film

1.0

Figure 1 UV spectra (left) and PL spectra (right) of the polymer in $CHCl_3$ solution and thin film.

at 307 nm belongs to the oxadiazole units,¹³ in $CHCl_3$ solution. The absorption maxima of the polymer thin film is 381 nm, which is shifted to longer wavelength with respect to that in solution, and this phenomenon can be accounted for by the fact that the polymer in solution can be in the form of a coil with a small effective conjugation length, and the solid state can be a more extended structure with more extensive electronic delocalization.^{25,26}

The optical band gaps (E_g) of the polymer are calculated according to the formula: $\alpha hv = B (hv - E_g)^n$, where α is the absorbance coefficient, h is the Planck constant, and n (the value is 0.5) is the transition type, respectively.²⁷ By drawing the $(hvA)^2 - hv$ curves and extending the linearity edge of absorbance to intersect with energy axis, then the band gap is obtained to be 2.52 eV, about 10% higher than that of P3,4DOOT (2.27 eV²⁸) in solid film.

The right of Figure 1 shows that the emissive maxima (excited at 350 nm) of the polymer in $CHCl_3$ solution is 518 nm, and the polymer thin film emits intense yellow light with emission peak at 542 nm. Consequently, the PL emission spectra of the polymer thin film exhibits a red shift in comparison to that obtained from its solution. This can be attributed to the interchain and/or intrachain mobility of the excitons and excimers generated in the polymer in the solid-state phase. The PL quantum yield of the polymer in $CHCl_3$ solution was determined using quinine sulfate as a standard.²⁹ The relative quantum yield of the polymer is as high as 57.4%, > two times more than that of 3,4-dioctyloxythiophene homopolymer.²⁸

Electrochemical properties

The cyclic voltammogram of a P3,4-DOOTV-OXD coated Pt disc was measured in a one-compartment three-electrode cell with a Pt wire counter electrode

1.0

PL Intensity / a.u.

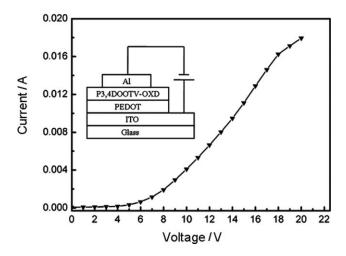


Figure 2 I-V characteristics of the double-layer device [ITO/PEDOT/P3,4DOOTV-OXD/Al]. Inset: configurations of the device.

and a Ag/AgCl reference at a scan rate of 25 mV s⁻¹. The electrolyte was 0.1*M* tetrabutyl-ammoniumperchlorate (TBAP) in acetonitrile, and the cell purified with argon.

When the polymer was swept cathodically, it showed onset reduction potential at around -1.55 V. While sweeping anodically, the polymer showed onset oxidation potential at around 0.85 V. These values indicate that the polymer has good hole and electron charge carrier properties.³⁰ According to the equations reported in the references,²¹ i.e., $E_{\text{HOMO}} = -[E_{\text{oxd onset}} + 4.68 \text{ eV}]$ and $E_{\text{LUMO}} = -[E_{\text{red onset}} + 4.68 \text{ eV}];$ where E_{oxd} onset and $E_{\rm red oxd}$ are the onset potentials for the oxidation and reduction processes of a polymer, respectively. The HOMO energy level of the polymer was estimated to be -5.53 eV, and the LUMO energy level of the polymer was estimated to be -3.13 eV, respectively. The band gap of the polymer was estimated to be 2.40 eV. The value is quite close to that obtained by the optical method. Consequently, the ionization potential $(I_p = |E_{HOMO}|)$ of P3,4-DOOTV-OXD at 5.53 eV is appropriated to donor. The electron affinity $(I_a = |E_{LUMO}|)$ is 3.13 eV, which is quite high and is benefit to the electrons injecting from the cathode.

Electroluminescence property

To study the electroluminescence property of P3,4DOOTV-OXD, double-layer diode with the configuration of [ITO/PEDOT: PSS (50 nm)/polymer/ Al (130 nm)] was fabricated. Under a bias in the forward direction from 7 to 19 V, this double-layer diode could emit visible yellow light. The currentvoltage (I-V) curve (Fig. 2) of the device presents a typical diode character which current increasing with the forward bias adding, the turn-on voltage is at 7 V. The EL spectrum shows a small blueshift in maximum value (562-552 nm) with 1-2 nm step length according to the applied voltage ranging from 7 to 19 V [Fig. 3(a)]. In addition, the EL intensity is increased with the enhancing of bias and the top intensity is at 18 V with a bright yellow electroluminescence [Fig. 3(b)]. This can be contributed to the enhanced energy of charge carries and more excimers generated along with the applied voltage. Consequently, the luminescence chance of excitons is larger at high energy level than that of low energy level relatively. However, crossing the top, the emission intensity of device is decreased and quenched finally because of breakdown.

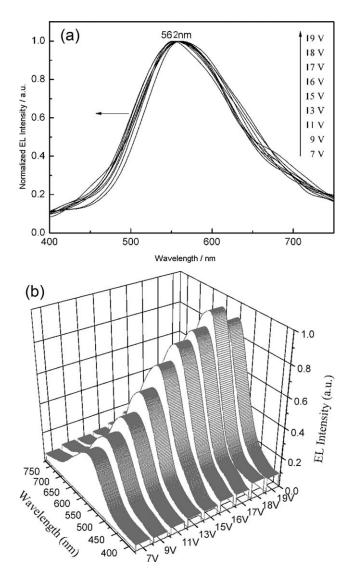


Figure 3 EL spectra of the double-layer device [ITO/ PEDOT/P3,4DOOTV-OXD/Al] under different applied voltage. (a) Normalized EL spectra; (b) EL spectra of relative intensity.

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CONCLUSIONS

A novel organic light-emitting D-A type alternating copolymer poly[3,4-dioctyloxy- thiophene-alt-2,5-bis(4vinylphenyl)-1,3,4-oxadiazole] (P3,4DOOTV-OXD) was synthesized and characterized. Optical properties indicates that P3,4DOOTV-OXD possesses 57.4% luminescence quantum yield, > two times more than that of P3,4DOOT, with optical band gap energy at 2.52 eV. The cyclic voltammogram investigation shows that the ionization potential of P3,4-DOOTV-OXD at 5.53 eV is appropriated to donor. The high electron affinity of 3.13 eV make the electrons inject from the cathode more easily. The band gap of the polymer is estimated to be 2.40 eV, which is quite close to that obtained by the optical method. The double-layer device with the structure of [ITO/PEDOT:PSS (50 nm)/P3,4DOOTV-OXD/Al (130 nm)] is fabricated, which exhibits bright yellow electroluminescence (562-552 nm) and typical diode character.

All the results confirmed that P3,4DOOTV-OXD is a promising yellow light-emitting material for EL devices, and the work for improving the performance of the double- or multiple-layer device based on the polymer is under taking.

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