A new conjugated polymer with donor-acceptor architectures based on alternating 1,4-divinyl-2,5-dioctyloxybenzene and 5,8-(2,3-dipyridyl)-quinoxaline: Synthesis, characterization, and photoinduced charge transfer

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Received 25 October 2011; accepted in revised form 26 December 2011

Abstract. A new conjugated polymer with donor-acceptor architectures poly[1,4-dioctyloxyphenylene-2,5-diethenylene-(2,3-dipyridine-2-ylquinoxaline-5,8-diyl)ethylene] (PPV-BD) was synthesized successfully, in which the electron-donating unit was alkoxy substituted phenyl ring, and the electron-accepting unit was a quinoxaline. The resulting polymer had a lower band-gap (1.98 eV) compared to poly[2-methoxy-5-(2-ethyl)hexoxy-phenylenevinylene] (MEH-PPV, 2.12 eV), and was characterized by infrared spectroscopy (IR), nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), gel permeation chromatography (GPC), ultraviolet-visible (UV-vis) spectroscopy, photoluminescence (PL) spectroscopy and X-ray diffraction (XRD). Its photoinduced charge transfer applications in polymer solar cell (PSC) and trinitrotoluene (TNT) detection were studied respectively, and the results indicated that this polymer might be a good candidate material for PSC or detecting TNT in solution.

Keywords: polymer synthesis, characterization, chemosensor material, photoinduced charge transfer, photovoltaic material

1. Introduction

Conjugated polymers have attracted considerable attention due to their versatile applications in the fields of polymer light-emitting diodes (PLED) [1–3], polymer field-effect transistors (PFETs) [4, 5], chemical sensors [6], photodetectors [7], polymer solar cells (PSCs) [8], etc. In recent years, several polymers based on poly(phenylenevinylene)s (PPVs) have been synthesized and used as the active layer in photovoltaic devices [9–13]. A major drawback of most conjugated polymers for their application in PSCs is the rather poor match of the absorbance spectrum with the solar spectrum. The wavelength of maximum absorbance for most PPV derivatives

lies below 500 nm ($E_g = 2.0\sim 2.2$ eV), which is on the far blue side of the spectrum [14, 15]. By using low band-gap materials, an improved overlap with the solar spectrum would allow an increase in photovoltaic energy conversion. The band-gap of π -conjugated polymers can be controlled through the chemical structure of the system [16]. π -conjugated polymers with donor-acceptor architectures are currently of interest because the intramolecular charge transfer can facilitate ready manipulation of the electronic structure (HOMO/LUMO levels), leading to small band-gap semiconducting polymers [17–20]. In addition, conjugated polymers have been proven quite useful in creating highly sensi-

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tive fluorescent chemical sensors [21–23]. The conjugated polymer backbone allows efficient electron delocalization and exciton migration over large distances, thereby creating amplified sensory responses compared with small-molecule-based sensors. An additional advantage of using polymers as sensor materials emerges from that the sensory devices can easily be fabricated from these materials on electrodes either by spin coating and/or drop casting from solution or anodic electrochemical polymerization from an electrolyte solution.

In this paper, a new conjugated polymer with donor-acceptor architectures poly[1,4-dioctyloxyphenylene-2,5-diethenylene-(2,3-dipyridine-2-ylquinoxaline-5,8-diyl)ethylene] (PPV-BD) was synthesized successfully, in which the electron-donating unit was alkoxy substituted phenyl rings, and the electron-accepting unit was a quinoxaline. The quinoxaline is a good electron-accepting unit, and it has been designed in donor-acceptor fluorine-based or thiophene-based copolymers [24]. The resulting polymer had a lower band-gap (1.98 eV) compared

to poly[2-methoxy-5-(2-ethyl)hexoxy-phenylenevinylene] (MEH-PPV, 2.12 eV [25]), and was characterized by infrared spectroscopy (IR), nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), gel permeation chromatography (GPC), ultraviolet-visible (UV-vis) and photoluminescence (PL) spectroscopy. Additionally, its photoinduced charge transfer (PCT) applications in PSCs and trinitrotoluene (TNT) detection were studied respectively, and the results indicated that this polymer might be a good candidate material for PSCs or detecting TNT in solution. The molecular structure of PPV-BD is shown in Figure 1.

2. Experimental

2.1. Materials

The main reagents such as p-hydroquinone (AR, Analytical Reagent), palladium (II) acetate (AR), 2,2'-bipyridyl (AR), [Bu(4N)]BF₄ (AR) were purchased from J&K Scientific Ltd., China, used as received. All the solvents used in this study were purified according to standard methods prior to use.

Figure 1. Molecular structure of polymer PPV-BD

1,4-divinyl-2,5-dioctyloxybenzene (monomers 1) and 5,8-dibromo-2,3-dipyridylquinoxaline (monomer 2) were synthesized according to the published literatures [26–28].

2.2. Measurements

The target compounds were characterized by NMR spectra using Bruker AVANCE 400 spectrometer (Bruker Corporation, Karlsruhe, Germany) with chloroform-*d* as the solvent and tetramethylsilane as the internal standard. Polymer molecular weight was determined by size-exclusion chromatography with multi-angle laser light-scattering detection (SEC-MALLS). SEC was performed using a high-performance liquid chromatography (HPLC) pump (Waters 515, Waters Corporation, USA) and a column (200 mm × 0.8 mm, MZ-Gel SDplus 500 Å 5 μm). Column effluent was monitored sequentially with a miniDawn light-scattering detector (Wyatt technology Corporation, Santa, Barbara, CA, USA) and an Optical rEX differential refractometer (Wyatt Technology Corporation, Santa, Barbara, CA, USA). Two 25 mm high-pressure filter with 0.22 and 0.1 μm pores (Millipore Corporation, Bedford, Massachusetts, USA) were used for on-line filtration of the mobile phase. UV-vis spectra were recorded on a Shimadzu UV-2501PC/2550 (Shimadzu Corporation, Kyoto, Japan). Photoluminescence spectra were measured in a HITACHI F-4600 fluorescence spectrometer (Hitachi Corporation, Tokyo, Japan). FT-IR spectra were taken on a Bruker Tensor 27FT-IR spectrophotometer (Bruker Corporation, Karlsruhe, Germany) with KBr pellets. Thermogravimetric analysis (TGA) of the synthesized polymer was performed on a HENVEN HCT-1 (Beijing Scientific Instrument Factory, Beijing, China) thermal analysis system at a heating rate of 10°C/min up to 500°C in a nitrogen flow rate of 80 mL/min. Ele-

mental C, H, N was performed on a Flash EA 1112 elemental analyzer (Thermo Electron Corporation, Waltham, USA). Cyclic voltammetry was carried out using thin films of polymer prepared from chloroform with PARSTAT-2273 (Princeton Applied Research, AMETEK, Inc., Oak Ridge, USA) in a solution of [Bu(4)N]BF(4) (0.1M) in acetonitrile at a scan rate 50 mV/s. Scanning electron microscope (SEM) images were performed in Shimadzu SSX-550 (Shimadzu Corporation, Kyoto, Japan). X-ray diffraction (XRD) data were collected using a Siemens Bruker D500 X-ray diffractometer (Bruker Corporation, Karlsruhe, Germany) at a scanning rate of 4°/min in the 2θ range from 0 to 80°, with graphite monochromatized Cu Kα radiation.

2.3. Syntheses of monomers and polymer

PPV-BD was synthesized via the Heck reaction polycondensation between monomer 1 and monomer 2 in presence of palladium (II) acetate catalyst. The synthetic routes of polymer PPV-BD are shown in Figure 2.

The syntheses of the monomer 1, monomer 2 and polymer PPV-BD are described as follows:

Synthesis of monomer 1 [26, 27]

Monomer 1 was synthesized according to the literatures [26, 27]. 18.06 g (17.3 mmol) of 1,4-bis(bromide-triphenylphosphine methyl)-2,5-dioctyloxybenzene was dissolved in a co-solvent of 230 mL dichloromethane and 70 mL (40%) formaldehyde solution. Then, 140 mL (20%) NaOH solution was added dropwise, the mixture was stirred for 15 h at 0°C under inert atmosphere. Finally, 30 mL water and 60 mL dichloromethane were added into the reactive solution. The organic layer was separated and washed by water, then dried with anhydrous Na₂SO₄. The crude product was formed after sol-

Figure 2. Synthetic routes of polymer PPV-BD

Figure 3. ^1H NMR spectrum of 1,4-bis(octyloxy)-2,5-divinylbenzene

vents evaporating, and recrystallized with ethanol several times to get 3.68 g of monomer 1 as white crystals. Yield 55%, mp: 45–46°C.

^1H NMR (CDCl_3 ; δ/ppm): 0.87–1.82 (m, 30H, H2–H8), 3.93–3.98 (t, 4H, H1), 5.69–5.71 (d, 4H, H9), 6.98 (s, 2H, H10), 7.03–7.08 (t, 2H, H11) (details in Figure 3). FT-IR (KBr, cm^{-1}): 3082 ($\nu(\text{Ar-H})$), $\nu(=\text{CH}_2)$), 3019 ($\nu(=\text{CH})$), 2943, 2919 ($\nu_{\text{as}}(-\text{CH}_3, -\text{CH}_2-)$), 2850 ($\nu_{\text{s}}(-\text{CH}_3, -\text{CH}_2-)$), 1212 ($\nu(\text{C-O})$), 1618, 1500, 1466 ($\text{Ar}(\text{C}=\text{C})$, vinyl- $\nu(\text{C}=\text{C})$), 993, 893 ($\gamma(\text{CH}=\text{CH}_2)$). Anal. Calcd. (%) for $\text{C}_{26}\text{H}_{42}\text{O}_2$ (386.61): C, 80.77; H, 10.95. Found (%): C, 80.71; H, 12.27.

Synthesis of monomer 2 [28]

A solution of 2,3-diamino-1,4-dibromobenzene (1.03 g, 3.8 mmol) and 2,2'-bipyridil (0.806 g, 3.8 mmol) in 25 mL ethanol was heated to reflux for 3 h, then cooled to 0°C. The formed precipitate was isolated by filtration and washed with ethanol to afford 1.16 g of monomer 2 as yellow solid. Yield 70%, mp: 251–253°C.

^1H NMR (CDCl_3 ; δ/ppm): 7.25–7.28 (d, 2H, H4), 7.87–7.98 (d, 2H, H1, H2, H3), 8.26–8.32 (m, 4H, H5) (details in Figure 4). ^{13}C NMR (CDCl_3 ; δ/ppm): 123.4, 123.8, 124.5, 133.6, 136.9, 139.3, 148.2,

Figure 4. ^1H NMR spectrum of 5,8-dibromo-2,3-dipyridylquinoxaline

153.4, 156.5. Anal. Calcd. (%) for $\text{C}_{18}\text{H}_{10}\text{Br}_2\text{N}_4$ (442.11): C, 48.90; H, 2.28; N, 12.67. Found (%): C, 48.01; H, 2.47; N, 11.53.

Synthesis of PPV-BD

250 mg (0.65 mmol) of monomer 1, 240 mg (0.65 mmol) of monomer 2, 14.6 mg (0.065 mmol) of palladium acetate and 248 mg (0.81 mmol) of tris(2-methylphenyl)phosphine were added into a

Figure 5. ^1H NMR spectrum in CDCl_3 of PPV-BD

co-solvent of 4 mL triethylamine and 10 mL N,N-dimethylformamide. The mixed solution was heated to reflux for 24 h under inert atmosphere. After cooling to room temperature, the reactant was added into 300 mL methanol slowly. The resulting precipitate was centrifuged to collect 150 mg of polymer PPV-BD as a deep-red powder. Yield 36%.

^1H NMR (CDCl_3 ; δ/ppm): 0.77–1.85 (m, 30H, H2–H8), 3.93–4.14 (d, 4H, H1), 6.98–7.19 (m, 4H, H9–H12), 7.33–8.52 (m, 12H, Ha–Hh) (details in Figure 5). FT-IR(KBr, cm^{-1}): 3060 ($\nu(\text{Ar-H, or vinyl-H})$), 2930 ($\nu_{\text{as}}(-\text{CH}_3, -\text{CH}_2-)$), 2850 ($\nu_{\text{s}}(-\text{CH}_3, -\text{CH}_2-)$), 1672 ($\nu(\text{C=N})$), 1595, 1466 ($\nu(\text{Ar(C=C)})$), 1384 ($\delta(-\text{CH}_3)$), 1278 ($\nu(\text{C-C})$), 1203 ($\nu(\text{C-O})$), 751 ($\gamma(\text{Ar(=CH)})$). GPC(polystyrene standards): $M_n = 11\,010$, $M_w = 15\,050$, $\text{PDI} = 1.37$. Anal. Calcd. (%) for $(\text{C}_{44}\text{H}_{50}\text{N}_4\text{O}_2)_n$ (666.92) $_n$: C, 79.05; H, 7.78; N, 8.38. Found (%): C, 80.74; H, 6.88; N, 7.48.

3. Results and discussion

3.1. Solubility and thermal stability

Since introducing the flexible long-chain alkyl into the benzene ring, polymer PPV-BD has a good solubility in polar solvents such as chloroform, tetrahy-

Figure 6. TGA curve of PPV-BD

drofuran and 1,2-dichlorobenzene, and the maximum solubility in chloroform is about 27 mg/mL. Figure 6 shows the TGA traces of polymer PPV-BD. The polymer showed almost no mass loss at a low temperature, but exhibited a weight loss of approximately 5% at 228°C. Hence, it can be concluded that the polymer PPV-BD has good thermal stability in a nitrogen atmosphere, which is suitable for application in optoelectronic devices.

3.2. Absorption and fluorescence properties

In order to investigate the relationships between the thickness and fluorescent performance, different thickness of polymer films were chosen to test their fluorescence properties by photoluminescence spectroscopy. The different thickness of polymer films were prepared by dissolving a certain mass of PPV-BD in chloroform to get different concentration samples (a: 5 mg/mL, b: 10 mg/mL, c: 15 mg/mL, d: 20 mg/mL, e: 27 mg/mL). Different thickness of polymer thin-films were deposited on quartz with a KW-4A spin coater (Institute of Microelectronics of Chinese Academy of Science, China) at a spin rate of 800 rpm using the above solutions, and placed under vacuum overnight before test. Figure 7 is the PL emission spectra of different thickness of PPV-BD films. It can be seen from the Figure 7, with the concentration of PPV-BD increasing, the maximum PL wavelength is red-shifting gradually. The maximum PL wavelength of PPV-BD film (625 nm) pre-

Figure 7. PL emission spectra of different thickness of PPV-BD films (a: 5 mg/mL, b: 10 mg/mL, c: 15 mg/mL, d: 20 mg/mL, e: 27 mg/mL)

Table 1. Optical data of polymers PPV-BD and MEH-PPV

Polymer	UV-vis [nm]				PL-em [nm]		E_g^{opt} [eV]	
	$\lambda_{\text{max}}(\text{CHCl}_3)$	$\lambda_{\text{max}}(\text{film})$	$\lambda_{\text{onset}}(\text{CHCl}_3)$	$\lambda_{\text{onset}}(\text{film})$	$\lambda_{\text{max}}(\text{CHCl}_3)$	$\lambda_{\text{max}}(\text{film})$	CHCl_3	film
PPV-BD	505	534	609	625	609	625	2.03	1.98
MEH-PPV[25]	490	503	565	590	—	—	2.20	2.12

Figure 8. UV-vis spectra and PL-emission spectra (Ex: 350 nm) of PPV-BD in CHCl_3 and in film

pared from the maximum concentration (27 mg/mL) shows the largest red-shifting which red shift about 10 nm compared to that of PPV-BD film (615 nm) prepared from minimum concentration (5 mg/mL). Perhaps, with the solution concentration increasing, the thickness of film is increased accordingly, the thicker film will lead to a better π - π^* stacking, therefore, presenting a larger red-shifting.

The photophysical characteristic of PPV-BD was investigated by UV-vis spectroscopy and photoluminescence spectroscopy in dilute chloroform solution (0.035 mg/mL) and in film (prepared from 27 mg/mL solution) on quartz, respectively. The UV-vis absorption spectra and photoluminescence emission spectra of polymer PPV-BD in CHCl₃ and film are shown in Figure 8. Optical data of the polymer PPV-BD and MEH-PPV are summarized in Table 1. Figure 9 shows the molecular structure of MEH-PPV.

Figure 9. Molecular structure of MEH-PPV

It can be seen from Figure 8 that polymer PPV-BD presents a slight red-shifting in their principal absorption and fluorescence bands in thin films relative to in solution. It may be attribute to conformational preferences in thin films that the interpolymer interactions is increased, forming a π -stacking of polymer chains [29, 30].

Table 1 shows the maxima of absorption at long wavelength of polymers PPV-BD and MEH-PPV in chloroform at 505 and 490 nm respectively, and 534 and 503 nm in film respectively. The results show that the absorption maximum of PPV-BD exhibits a 29 nm red-shifting in CHCl_3 and 31 nm red-shifting in film compared to MEH-PPV, respectively. Furthermore, the absorption spectrum onset of PPV-BD in chloroform is at about 609 nm, shifting to a longer wavelength compared to MEH-PPV ($\lambda_{\text{onset}} = 565$ nm, $E_g^{\text{opt}} = 2.20$ eV), corresponding to an optical band-gap (E_g^{opt}) of 2.03 eV. As anticipated, the alternation of electron-rich alkoxy substituted aromatic and electron-deficient quinoxaline units along conjugated backbone results in a decrease of the band-gap. The results show that PPV copolymers containing electron-acceptor unit quinoxaline can lower the band-gap.

As described above, the red-shifting of the UV-vis peak in film (Figure 8) suggests that PPV-BD assumes a self-assembled stacked structure in the solid state [31]. The XRD pattern of PPV-BD shown in Figure 10 supports this view. According to the Bragg equation (Equation (1)):

$$2d \sin \theta = n \lambda \quad (1)$$

Figure 10. XRD pattern of PPV-BD. The inset is a diagrammatic drawing of PPV-BD film

The peak with a d value of 15.8 Å is considered to correspond to the distance between the main chains separated by the octyloxy group (d_1); the peak with a d value of 4.0 Å is considered to correspond to the face-to-face distance between coplanar polymer chains (d_2).

3.3. Photoinduced Charge Transfer studies

3.3.1. PCT in polymer solar cell

Polymer PPV-BD and fullerene C_{60} (PPV-BD/ C_{60} ~approximately 1/4, w/w) were dissolved in 1, 2-dichlorobenzene. Polymer thin films were deposited on quartz with a KW-4A spin coater at a spin rate of 1000 rpm by using the above solution. The PL-emission spectra are shown in Figure 11. It shows that when the polymer PPV-BD is blended with fullerene C_{60} , the fluorescence of PPV-BD almost completely quenched. According to the quenching rate formula (Equation (2)):

$$Q\% = \frac{f_a - f_b}{f_a} \cdot 100 \quad (2)$$

where, $Q\%$ denotes quenching rate, f_a denotes fluorescence intensity when the quencher mass is zero, f_b denotes the fluorescence intensity when a certain mass of quencher is added to the polymer. Thus, we can get the final fluorescence quenching rate of PPV-BD is 99.8% (PPV-BD/ C_{60} ~ 1/4, w/w). Because energy (exciton) transfer from the polymer to C_{60} is highly endergonic. We attribute the fluorescence quenching to electron transfer, although a contribution from increased nonradiative decay (e.g., intersystem crossing) cannot be ruled out. From these results, it can be referred that the polymer PPV-BD may be a good candidate photovoltaic material for PSCs.

Figure 11. PL-emission spectra of PPV-BD and PPV-BD/ C_{60} (approximately 1/4, w/w) in films

3.3.2. PCT application in TNT Detection

A mixed solution was prepared by dissolving 1.4 mg PPV-BD in 14 mL chloroform, then dividing it into seven parts to get samples (0.1 mg/mL). Each part of the PPV-BD solution was mixed with a chloroform solution of TNT (0, 5, 50, 300, 500, 1000, 4000 ppm), respectively. The fluorescent properties of the mixtures were recorded immediately by fluorescence spectra at excitation wavelengths of 350 nm.

Figure 12 shows the PL-emission spectra of PPV-BD in chloroform solution upon successively adding different concentrations of TNT solution. The intensity of the fluorescence decreased gradually as the concentration of TNT increased, which may be attributed to the destruction of the polymer conjugation upon interacting with TNT molecules. As we know, one property of nitroaromatics which may be exploited in detection schemes is the electron accepting capability. Substitution of the electron-withdrawing nitro groups on the aromatic ring lowers

Figure 12. PL-emission spectra of PPV-BD with different TNT concentration solutions

the energy of the empty π^* orbitals, thereby making these compounds good electron acceptors. Conjugated polymers are electron donors. Donor ability is further enhanced in their delocalized π^* excited states. Excited state delocalization is important because exciton migration increases the frequency of interaction with a bound quencher, which contributes to enhanced detection sensitivity. Fluorescent conjugated polymers have therefore been applied to the detection of nitroaromatic explosives. As it can be seen from Figure 12, when the concentration of TNT was only 5 ppm, the fluorescence quenching rate of PPV-BD was 10.66%. When the concentration of TNT was 50 ppm, and the fluorescence quenching rate of PPV-BD was 37.77%. When the concentration of TNT was 4000 ppm, the fluorescence quenching rate of PPV-BD was nearly 100%. Thus, it can be concluded that the polymer PPV-BD may also be suitable for using as a TNT chemosensor material. In short, whether conjugated polymer PPV-BD blending with C_{60} or TNT, fluorescence quenching is often achieved through an electron-transfer donor-acceptor mechanism, as depicted in Figure 13.

3.4. Electrochemical properties

Thin film of polymer was drop cast from chloroform (10 mg/mL). The CV of PPV-BD was carried out in acetonitrile at a potential scan rate of 50 mV/s. Saturated calomel electrode (SCE) served as the reference electrode. It was calibrated with ferrocene ($E_{Fc/Fc^+} = 0.5$ V vs. SCE). HOMO and LUMO energy levels were estimated here on the basis of the reference energy level of ferrocene (4.4 eV below the vacuum) [33] according the Equation (3):

Figure 13. Electron-transfer fluorescence quenching [32]

Figure 14. Cyclic voltammograms of PPV-BD

$$E_{\text{HOMO/LUMO}} = [- (E_{\text{onset(vs.SCE)}} - E_{\text{onset(Fc/Fc}^+\text{vs.SCE)}})] - 4.4 \text{ eV} \quad (3)$$

Figure 14 shows the cyclic voltammograms (CV) of polymer PPV-BD. It shows that polymer PPV-BD reduction and oxidation are irreversible. The oxidations was observed with an onset potential at about 1.18 V versus SCE and the reductions was observed with an onset potential at about -1.22 V versus SCE. The HOMO and LUMO energy levels were estimated to be -5.08 and -2.68 eV. There is an obvious difference between LUMO of polymer PPV-BD and C₆₀ (-4.5 eV) or TNT (-3.74 eV) which makes an effective charge transfer possible between polymer PPV-BD and C₆₀ or TNT. The CV band-gap of polymer PPV-BD is 2.40 eV is slightly larger than its optical band. The discrepancy of values lies within the range of errors, and this discrepancy is probably due to interface barrier for charge injection [34, 35].

4. Conclusions

A new conjugated polymer with donor-accepter architectures based on alternating 1,4-divinyl-2,5-dioctyloxybenzene and 5,8-(2,3-dipyridyl)-quinoxaline was synthesized successfully. The polymer is thermostable, and it has common film-forming ability. The band-gap of PPV-BD was estimated to 1.98 eV (E_g^{opt}), which exhibited a reduction compared to MEH-PPV. Similarly, it showed a red-shifted UV-vis absorption peak in comparison to MEH-PPV. The results show that introduction of quinoxaline units leads to a reduction of the band-gap of poly(p-phenylenevinylene)s (PPVs) copolymers.

Its PCT applications in PSCs and TNT detection were studied respectively, and the results indicated that this polymer might be a good candidate material for PSCs or detecting TNT in solution.

Acknowledgements

Financial supported by the ‘Doctorate Foundation of Northwestern Polytechnical University (Grant No.: CX201118), National Program on Key Basic Research Project (973 Program) (Grant No.: 2010CB635111)’ is acknowledged.

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