Synthesis and Characterization of Conjugated Polymers Based on Benzoselenadiazole

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A multistep synthesis of the electron-poor 4,7-di(thiophen-2-yl)benzo[c][1,2,5]selenadiazole are presented. The new deficient acceptor has good solubility in organic solvents to permit an appropriate coating process. P1 was synthesized by direct oxidative polymerization under the reaction condition with $FeCl_3$ and CH_3NO_2. The spectra of polymers P1 to P2 show homogenous absorptions across most of the visible spectrum (450-650 nm). Solutions of P1 show a dark purple-black colour due to the lack of absorption in the far blue and red regions. And the solution of P2 exhibits a bright orange-red colour due to the increased reflection/transmission of red light. Both of the polymers were characterized by IR, UV-visible and cyclic voltammetry.

Keywords: π-Conjugated polymers, Donor-acceptor, [2,1,3]-Benzoselenadiazole, Dual-band-absorbing polymers.

INTRODUCTION

Conjugated polymer semiconductors are finding growing applications in electronics and optoelectronics, including light-emitting diodes, photovoltaic cells, thin film transistors and electro chromic cells[1]. Their molecular structures contain electron rich and electron deficient moieties linked *via* a π-conjugated bridge. In recent years, a number of narrow-band gap π-conjugated polymers absorbing at longer wavelengths than wide-band gap all-donor parents (*e.g.*, P3HT, MEHPPV and MDMO-PPV) have been synthesized[2-4]. With the concept of band gap-engineering, the idea that various colours can subsequently be accessed and taken advantage of. For example, in recent years, the DA approach has proven particularly useful in the synthesis of non emissive polymer electro chromes, extending the palette of colours available for electro chromic display technologies[5]. In excitonic solar cells, excit on dissociation occurs almost exclusively at the interface between two materials of differing electron affinities *i.e.*, the electron donor and electron acceptor[6]. To generate an effective photocurrent in these organic solar cells, an appropriate donor-acceptor pair and device architecture must be selected.

One of the most widely applied strategies to make narrow band gap donor polymers is the synthesis of an alternating copolymer from electron-rich (donor) and electron-deficient (acceptor) units in their backbone. For the incorporation of conjugated heterocyclic units can greatly influence the properties of conjugated polymers[7]. Quinoxaline, thiophene,

thieno-[3,4-b]pyrazine and silole have emerged as useful heterocycles units for conducting a variety of conjugated polymers for photovoltaic application[8]. A wide range of conjugated polymers and related oligomers contain hetero atoms with available lone pairs of electrons. DA type polymers generally show two distinct optical absorption bands, which can be modulated as a function of the composition of donor and acceptor moieties in the main chain[9]. The tuning of the dual-band absorption character of DA type polymers provides an elegant method of modifying spectral characteristics to achieve desired colours.

With the perspective of solution-processed conjugated heterocyclic unit based 2,1,3-benzothiadiazole, we report the new synthesis of poly(4,7-di(thiophen-2-yl)benzol[c][1,2,5,]-selenadiazole).

EXPERIMENTAL

Chemical reagents were purchased from Acros Corp and used without further purification. All solvents used were spectroscopic grade and were purified by distillation before use.

Synthesis of dibromobenzo[c][1,2,5]thiadiazole (M1): Bromine was added drop wise over a period of 5 min to a vigorously stirred suspension of benzo[c][1,2,5]thiadiazole in hydrobromic acid (30 mL) at 120 °C. The reaction was left to stir for 36 h during which a canary yellow precipitate formed. Water (100 mL) was added, the suspension left to stir for 10 min, then filtered and washed with a little water. The yellow

solid was dried *in vacuo* for 24 h to give the pure product. (25 g, 91.3 %) ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ-aromatic H, 7.73 (s, 2H)

Synthesis of 3,6-dibromobenzene-1,2-diamine: Dibromobenzo[c][1,2,5]thiadiazole (2.29 g, 10 mmol) and sodium borohydride (5.7 g, 150 mmol) were added to ethanol at 0 °C and stirred at room temperature for 36 h. The solution was added water and ethyl acetate then was separated by separatory funnel. The organic layer was dried over MgSO$_4$ then concentrated under reduced pressure and purified by chromatography on a silica column eluting with petroleum ether/ethyl acetate (5:1, v/v) to afford a yellow solid (1.9 g, 71 % yield). ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ-aromatic H, 6.86 (d, 2H), 3.92 (s, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 133.73,123.27, 109.70.

Synthesis of dibromobenzo[c][1,2,5]selenadiazole: To a solution of 3,6-dibromobenzene-1,2-diamine (1.33 g, 5 mmol) in ethanol and the solution of selenium dioxide (0.67 g, 6 mmol) was added at 60 °C for 24 h. The solution was extracted by ethyl acetate and the organic layer was dried over MgSO$_4$ then concentrated under reduced pressure to a yellow solid (1.6 g, 96 % yield). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ-aromatic H, 7.51 (s, 2H).

Synthesis of 4,7-di(thiophen-2-yl)benzo[c][1,2,5]-selenadiazole (M$_2$): Under the protection of the adjacent in Ar$_2$ bromine thiophene (6 g, 6.1 mmol) dropped to the magnesium (1.8 g, 12 mmol), with constant stirring for 0.5 h. Then trimethylborate (4.6 g, 7.32 mmol) was dropped to the mixture slowly and the solution was stirred at -78 °C. The hydrochloric acid (2 mol/L) was added to the solution, stirred for 0.5 h. The solution was extracted with ethyl acetate. The organic layer was dried over MgSO$_4$ then filtrated to afford a white solid. To a solution of dibromobenzo[c][2,1,3]selendiazole (0.68 g, 2 mmol) in freshly distilled THF was added Pd(PPh$_3$)$_4$(0.1 g, 0.08 mmol) and thiophene boric acid (0.75 g, 5.8 mmol) and the mixture was stirred at room temperature for 0.5 h under argon environment. Then the mixture was stirred at 80 °C for 32 h. The solvent was evaporated and purified by column chromatography (silica gel, petroleum ether as eluent) to a red solid (0.54 g, 81 % yield). ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ-aromatic H, 8.02 (d, 2H), 7.80 (s, 2H), 7.45 (d, 2H), 7.20 (t, 2H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 126.1, 127.2, 127.5, 127.7, 139.6, 158.2.

Synthesis of polymer: To a suspension of eight equivalent of anhydrous FeCl$_3$ (4 mmol) in 5 mL CH$_3$NO$_2$ was added drop wise a solution of one equivalent of the monomer (0.5 mmol) dissolved in 3 mL of CHCl$_3$. After stirring the mixture at room temperature for 3 h, 100 mL of methanol was added to precipitate the polymer. The mixture was put in the freezer overnight. After filtration, the polymer was washed with CH$_2$Cl$_2$ and methanol, respectively and dried under vacuum for 24 h. Polymer 1; dark purple powder with 46 % yield.

Reactions were monitored by thin-layer chromatography on plates coated with 0.25 mm silica gel 60 F254. NMR spectra were obtained with a Bruker AV-400 spectrometer with teramethylsilane (TMS) as internal reference and CDCl$_3$ as solvent. Absorption spectra were obtained with an Agilent 8453 UV/visible spectrometer. The number-average molecular weight (Mn) and molecular weight distribution (Mw/Mn) of the resulting polymers were determined by using a waters 1515 gel permeation chromatograph (GPC) which was performed on an HP 1100 HPLC, equipped with a refractive-index detector (Waters 2414), using three Styragel HR 2, HR 4, HR 5 of 300 × 7.5 mm columns (packed with 5 mm particles of different pore sizes). Electrochemical measurements of these polymers were performed with a Model 263 potentiostat-galvanost at (EG&G Princeton Applied research) electrochemical workstation under computer control at room temperature.

RESULTS AND DISCUSSION

To prepare black-to-transmissive electrochromic polymers *via* direct oxidative polymerization, we demonstrate a facile synthetic route as shown in Fig. 1. The deficient acceptor monomer of M1 was prepared in good yields over four steps starting from the readily commercially available material. The
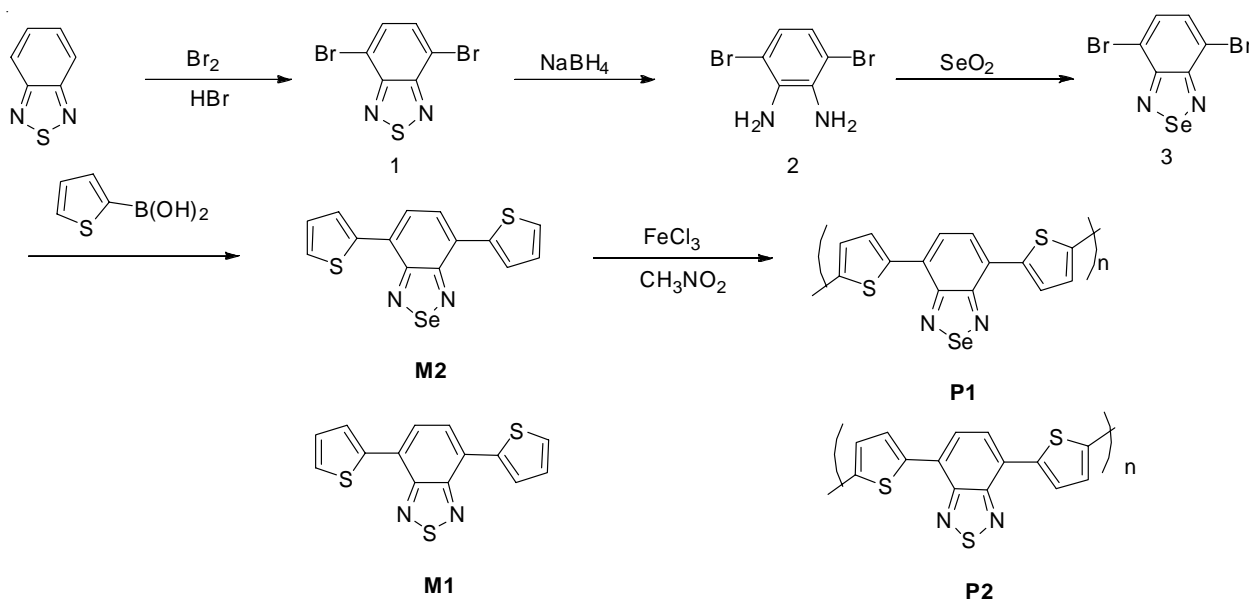

Fig. 1. Synthesis of poly(4,7-di(thiophen-2-yl)benzol[c][1,2,5,]selenadizole)

first step, benzo[c][1,2,5]thiadiazole was brominized in HBr. This reaction, was filtrated, washed and dried, the yield was above 90 %. Here, the acceptor dibromobenzo[c][1,2,5]thiadiazole was first reacted with $NaBH_4$, the product was extracted with ethyl acetate and dried. Then the 3,6-dibromobenzene-1,2-diamine was added in ethanol solution containing two oxidation of selenium to produce the final compound with high yield (96 %). The monomer M1 was synthesized as bright red solid by palladium-catalyzed Suzuki coupling reaction by dibromobenzo[c][2,1,3]selendiazole and two electron-rich thiophene boric acid. Finally, P1 was synthesized by direct oxidative polymerization under the reaction condition with $FeCl_3$ and CH_3NO_2.

IR spectra of P1: IR spectrum of the polymer shows a $\nu(C\text{-}C)$ peak of disubstituted thiophe neat 1045 cm^{-1}. $\nu(C=C)$ and $\nu(C\text{-}H)$ absorption peaks of terminal thiophene at about 1741 cm^{-1} and about 1029 cm^{-1}, 1093 cm^{-1}, respectively, are not observable.

Optical properties: The photophysical characteristics of the monomers have been investigated by UV-visible absorption in dilute chloroform solution. The absorption spectra for monomer 1, monomer 2, polymer 1 and 2 were measured in $CHCl_3$ (1.0×10^{-5} mol l^{-1}) at room temperature and showed on Fig. 2.
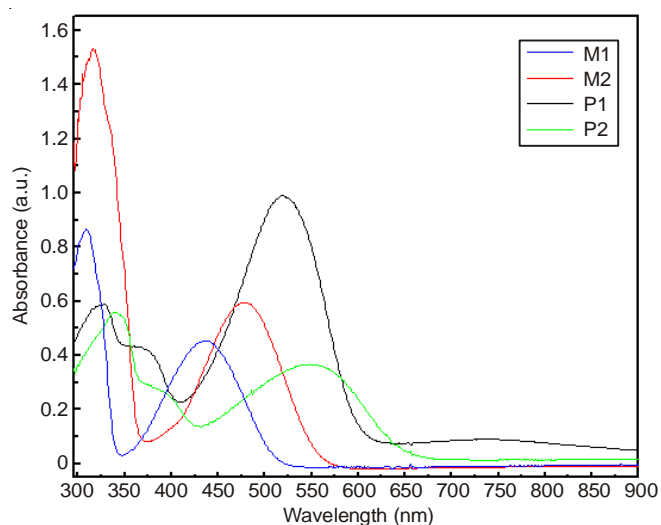

Fig. 2.   UV-visible absorption spectra of M1, M2, P1 and P2 in $CHCl_3$ solution

In solution, the λ_{max} absorption of the monomer 1 and 2 observed at 300 nm due to π-π* transition. The absorption band centered at 440 nm due to the formation of charge transfer from thiophene unit to benzothiadiazole unit. The difference in absorption maxima was relatively small but M1 exhibits a weak absorption peak at 478 nm and was red-shifted to 31 nm compared to M2 which shows a weak absorption peak at 447 nm. A broad spectral absorption is evident ranging from approximately 400 nm to greater than 650 nm for two polymers. Unlike the spectra of typical donor-acceptor polymers, which generally have two distinct absorption bands, the spectra of polymers P1 to P2 show homogenous absorptions across most of the visible spectrum (450-650 nm). The solutions of P1 show a dark purple-black colour due to the lack of absorption in the far blue and red regions. And the solution of

P2 exhibits a bright orange-red colour due to the increased reflection/transmission of red light.

Electrochemical properties of polymers: The electrochemical behaviour of the copolymers was investigated by cyclic voltammetry. Cyclic voltammograms of the polymers in degassed anhydrous dichloromethane containing 0.1 mol/L Bu_4NBF_4 and a potential scan rate of 100 mV/s. We could record only one p-doping and one n-doping process of the copolymers. The onsets of oxidation processes of the random copolymers were 0.75 V for P1 and 0.91 V for P2, respectively. These results indicated that the oxidation process of the polymer P1 occurred at a lower potential, as compared with that of the P2. As is stated above, the onsets of the n-doping processes of the two polymers are -0.89 V for P2 and -0.08 V for P1, which are the reductions of the benzothiadiazole and benzoselenadizole moieties (Fig. 3).
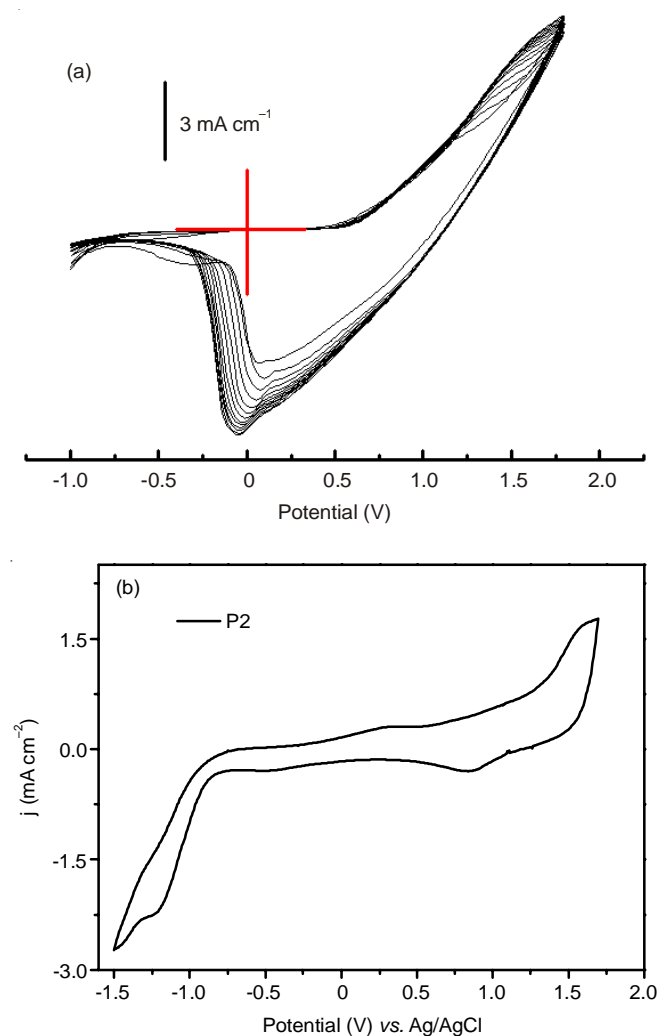

Fig. 3. Cyclic voltammograms of the polymers (a) P1 and (b) P2

According to the reported method, the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) energy levels could be estimated by using the energy level of ferrocene as a reference. HOMO and LUMO levels calculated according to an empirical formula (HOMO) = $-e(E_{ox} + 4.8)$ eV and LUMO = $-e(E_{red} + 4.8)$ eV[10] are also listed in Table-1. Based on the HOMO and LUMO

TABLE-1 HOMO AND LUMO ENERGY LEVEL VALUES DETERMINED BY DFT CALCULATIONS					
Polymer	E_{ox}^{on} (V)	E_{red}^{on} (V)	HOMO (eV)	LUMO (eV)	E_g^{ec} (ev)
P1	0.75	-0.08	-5.55	-4.72	0.83
P2	0.91	-0.89	-5.71	-3.91	1.80

energy level, the band gaps (E_g) of the two polymers were 1.80 eV for P2 and 0.83 eV for P1 (Table-1).

Conclusion

In conclusion, we have demonstrated a new short and relatively efficient synthesis of 4,7-di(thiophen-2-yl)benzo[c]-[1,2,5]selenadizole which makes these classes of molecules much more readily available for use as components in new materials for organic electronics applications. The synthesis of a series conjugated copolymers of thiophene and benzothiadiazole and benzoselendiazole was shown on the paper. However, the effect is more pronounced for the LUMO, which resides predominantly near the acceptor fragment. This differential influence over the HOMO and the LUMO is responsible for the observed decrease in band gap energy

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