

Low Band Gap Polymers Synthesized by Electrochemical Polymerization for Electrochromic Devices^{*}

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Abstract Two novel monomers, 10,13-bis(4-octyl-2-thienyl)-dibenzo[a,c]phenazine (OTBP) and 10,13-bis(4-octyl-2-thienyl)-dipyrido[3,2-a:2',3'-c]phenazine (OTPP), were synthesized. Electrochemical polymerization of OTTP and OTBP were carried out in acetonitrile/dichloromethane (ACN/DCM) solvent mixture containing tetra-*n*-butylammoniumhexafluorophosphate (TBAPF₆), and electrochromic properties of POTPP and POTBP are described. Furthermore, the effects of structural difference on electronic properties of electron acceptor units, electrochemical and electrochromic properties of two resulting polymers were examined. The results showed that the OTBP was polymerized at lower potential than OTTP, and this is because OTTP contains two more N atoms in electron acceptor unit and its electron withdrawing ability is stronger than that of OTBP. The UV-Vis-NIR spectra analysis revealed that the POTPP film has three absorption bands centered at 570 nm, 925 nm and 1581 nm, and the POTBP film has two absorptions at 566 nm and 1009 nm, respectively. The electrochromic properties indicated that the two polymer films exhibits reasonable optical contrasts and response time with low band gaps, defined as the onset of the absorption band at 570 nm for POTPP and the absorption band at 566 nm for POTBP, as 1.74 eV for POTPP and as 1.69 eV for POTBP.

Keywords: Low band gap polymer; Donor-acceptor polymer; Electrochemical polymerization; Electrochromic properties.

INTRODUCTION

By definition an electrochromic material has the possibility of changing its color reversibly when they are placed in an applied electric field. Electrochromic materials can be classified in two main types depending on their chemical structure. The first type is an inorganic material which has at least one colored and one bleached state such as WO₃^[1], NiO₂^[2] and TiO₂^[3]. These materials are used in smart windows and optical shutter. The second type are organic materials that including organic dyes and conjugated polymers. The organic dyes are organic small molecules such as the bipyridiniums, which are a class of materials that are transparent in the stable dicationic state and would be highly colored upon one-electron reduction. Conjugated polymers have attracted wide attention due to their ease of process ability, rapid response times, and high optical contrasts and the ability to modify their structure to create multicolor electrochromes^[4–8]. Conducting polymer generation follows a mechanism that is believed to involve either radical-cation/radical-cation coupling or attack of radical-cation on neutral monomer. In their oxidized states, conducting polymers are 'doped' with the counter anions (p-doping) and show a delocalised π -electron band structure. The energy gap between the highest occupied π -electron band

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(valence band) and the lowest unoccupied band (the conduction band) determines the intrinsic optical properties of these materials^[9]. So, conjugated polymers with low-bandgap obtained by electrochemical polymerization of suitable redox active monomers are future materials for electrochromic devices because of their potential ability in visible, IR and microwave electrochromics. This type of polymers can be used in photoelectric devices such as electrochromic displays^[10], vision systems or smart windows^[11].

In recent years, many investigations on the design and synthesis of low-band gap electrochromic polymers have been the major attractive area, and a most successful and flexible strategy to design small band gap polymers involves the alternation of electron-rich and electron deficient units along the polymer chain^[12–19]. In some of this type polymers, quinoxaline units was used as acceptor unit and some works reported that low-bandgap polymers containing quinoxaline units as acceptor unit performed good electrochromic ability^[20–24]. These polymers generally show a variety of excellent properties such as distinct optical changes throughout the visible region, fast switching time, low-voltage electrochromic (the voltage lower than 1.3 V).

In designing low-bandgap conjugated polymers, changing the nature and the position of the heteroatom on the donor or acceptor units is an effective strategy as the heteroatom plays an important role in controlling the electron withdrawing capabilities of electron acceptor unit^[25–30]. So, in this paper we synthesized two monomers, 10,13-bis(4-octyl-2-thienyl)-dipyrido[3,2-*a*:2',3'-*c*]phenazine and 10,13-bis(4-octyl-2-thienyl)-dibenzo[*a,c*]phenazine, to obtain two novel polymers with low-bandgap (Fig. 1). In these monomers, we use 1,10-phenanthroline-5,6-dione and phenanthraquinone to synthesize two electron acceptor units to investigate the influence of imine (C=N) functional groups on electrochemical polymerization and electrochromic properties of these polymers. We investigated electrochromic and switching properties of the polymers synthesized by electrochemical polymerization.

EXPERIMENTAL

Chemicals and Apparatus

Chemicals

All chemicals were purchased from Shanghai Boka Chemical Co. and used as received unless otherwise noted. Dry tetrahydrofuran (THF) was distilled over sodium with addition of benzophenone. 1,10-Phenanthroline-5,6-dione^[31] was synthesized according to the literature procedures. The tetra-*n*-butylammoniumhexafluorophosphate (TBAPF₆) electrolyte dissolved in the solvent mixture of dichloromethane (DCM) and acetonitrile (ACN) (95/5, *V/V*) was used as supporting electrolyte solution in electrochemical polymerization and electrochromic analysis process.

Apparatus

A Zahner-Zennium electrochemical workstation was used for all electrochemical studies. Electrochemical polymerization was performed in a three-electrode cell consisting of an indium tin oxide doped glass slide (ITO) as the working electrode, platinum wire as the counter electrode, and Ag wire as the reference electrode. Electronic absorption spectra and electrochromic switching were taken with a Shimadzu UV-3600 UV-Vis-NIR Spectrophotometer linked with a MCP-1 Potentiostat. ¹H-NMR spectra were recorded in CDCl₃ on a VARIAN INOVA-400 spectrometer (400 MHz). Chemical shifts were given downfield from tetramethylsilane.

Experimental Procedures

Preparation of tributyl(4-octylthiophen-2-yl)stannane (2)

Synthesis of tributyl(4-octylthiophen-2-yl)stannane was carried out by following well-established literature procedures^[32, 33] with slight modifications. 3-Octylthiophene (39.00 g, 200.0 mmol) dissolved in anhydrous THF (150 mL) and butyl-lithium in hexane (2.5 mol/L, 80 mL, 200.0 mmol) was slowly added to the solution at –80 °C. Then the mixture was stirred under nitrogen for 1.5 h, the temperature of the mixture was naturally increased to room temperature in 2 h and stirred for another 3 h. After that the mixture was cooled to –80 °C and

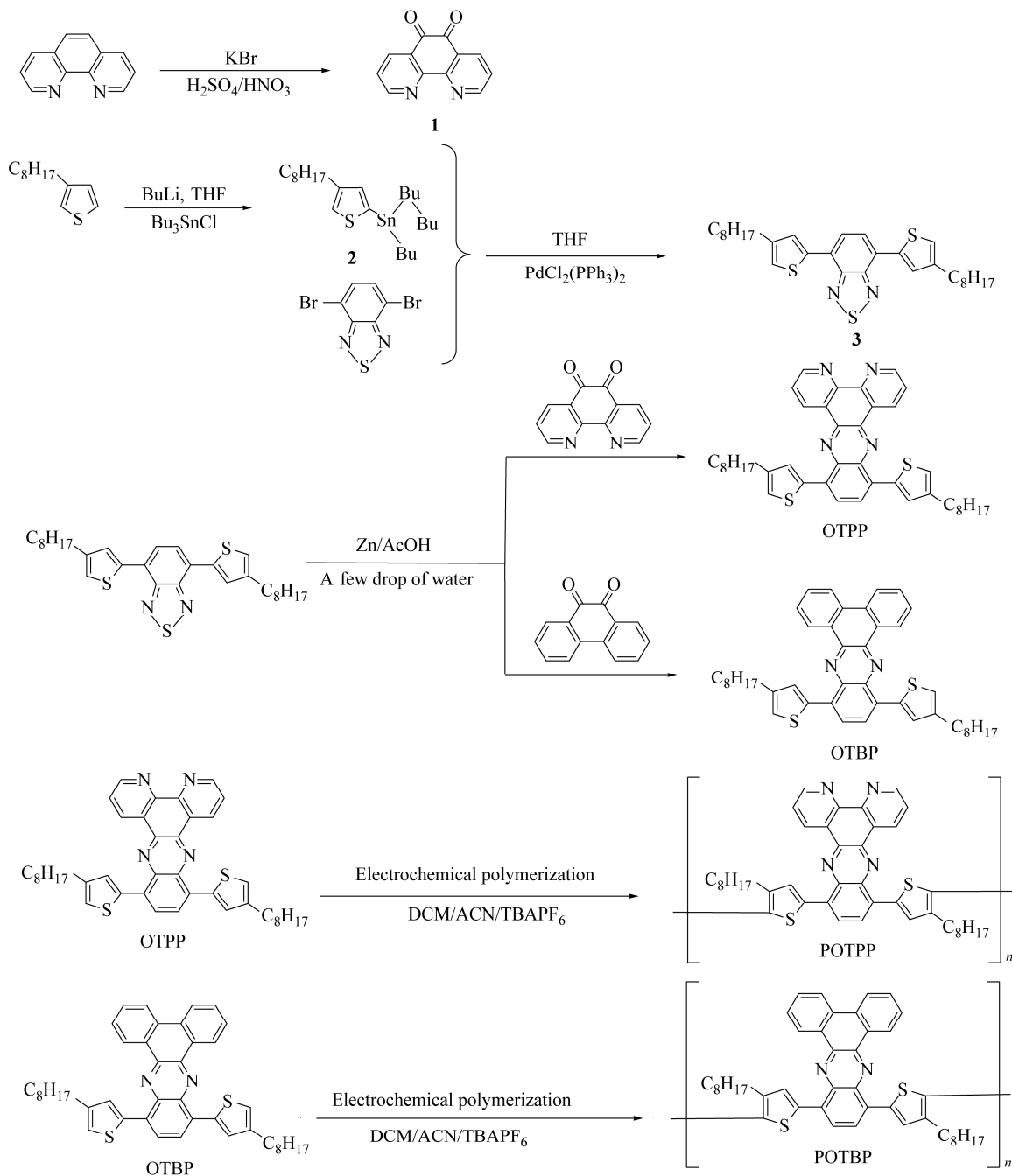


Fig. 1 Schematic route for the synthesis of monomers and polymers

tributylchlorostannane (60 mL, 220.0 mmol) was added dropwise. The mixture was stirred at -80°C for additional 3 h, followed by quenching with 2 mol/L aqueous sodium hydrogen carbonate (200 mL). After that the organic solvent was removed under reduced pressure and the remained solution was extracted with diethyl ether. The diethyl ether solution was washed several times with aqueous sodium carbonate and brine, and dried over MgSO_4 . After removing the solvents, the residue was purified on a column of neutral alumina (hexane as eluent), evaporated and further purified by Kugelrohr distillation to give the desired product as yellow oil

(95.3 g, 98%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 7.18 (d, $J = 2.8$ Hz, 2H); 2.66–2.62 (t, 2H); 1.61–1.52 (m, 8H); 1.42–1.28 (m, 16H); 1.11–1.06 (m, 6H); 0.92–0.86 (m, 12H).

Preparation of 4,7-bis(4-octylthiophene-2-yl)-benzo [1,2,5] thiadiazole (3)

To the solution of 4,7-dibromo-[1,2,5] benzothiadiazole (2.91 g, 10.0 mmol) in anhydrous THF (50 mL) was added compound **2** (14.55 g, 30.0 mmol) and was stirred at room temperature under nitrogen for 30 min. Then $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.14 g, 0.2 mmol) was added to the solution and the mixture was refluxed for 24 h. When the reaction ended the solvent was removed under reduced pressure and the remaining red oil was dissolved in DCM, and 10% HCl solution was added to it and stirred for 1 h. The organic phase was separated and was washed with aqueous sodium carbonate and brine. The organic solvent was removed under reduced pressure after the solution was dried over MgSO_4 . The crude product was recrystallized from ethanol and was purified on a column silica gel using CHCl_3 : petroleum ether (60–90) = 1:1 as the eluent to give the desired product as orange crystal (4.76 g, 91%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 7.97 (d, $J = 1.2$ Hz, 2H); 7.82 (s, 2H); 7.03 (d, $J = 3.2$ Hz, 2H); 2.71–2.67 (t, 2H); 1.72–1.68 (m, 4H); 1.39–1.25 (m, 20H); 0.90–0.86 (m, 6H).

Preparation of 10,13-bis(4-octyl-2-thienyl)-dipyrido[3,2-a:2',3'-c]phenazine (OTPP)

To a solution of **3** (524 mg, 1.0 mmol) in acetic acid (50 mL), zinc dust (1.31 g, 20.0 mmol) and a few drops of water was added to the solution, the reaction mixture was kept at 60 °C overnight and the solution became colorless. The solution was filtered twice and 1,10-phenanthroline-5,6-dione (231 mg, 1.1 mmol) was added to the solution, then was stirred for 48 h at room temperature, after which it was poured into water and extracted by CHCl_3 . The organic phase was separated and was washed with aqueous NaHCO_3 , then the organic solution was dried over MgSO_4 . After removing the organic solvent the crude product was purified on a column silica gel using CHCl_3 : methanol = 20:1 as the eluent to give the desired product as purple powder (582 mg, 89%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 9.29 (s, 2H), 9.12 (s, 2H), 7.79 (s, 2H), 7.56 (s, 2H), 7.43 (s, 2H), 7.09 (s, 2H), 2.69 (s, 4H), 1.74 (s, 4H), 1.40–1.32 (m, 20H), 0.93–0.89 (m, 6H); FTIR (cm^{-1}): 3082, 2957 ν - CH_2 ; 2926–2848 ν Aliphatic C–H; 1627 ν - $\text{C}=\text{N}$ –; 1570, 1404, 730 ν -thiophene.

Preparation of 10,13-bis(4-octyl-2-thienyl)-dibenzo[a,c]phenazine (OTBP)

The monomer was synthesized by the same procedure used for synthesis of OTPP by using compound **3** and phenanthraquinone as raw material. The crude product was purified on a column silica gel using CHCl_3 : petroleum ether (60–90) = 1:1 as the eluent to give the desired product as red orange solid (83%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 9.56 (d, $J = 9.2$ Hz, 2H), 8.57 (d, $J = 9.2$ Hz, 2H), 8.19 (s, 2H), 7.81–7.67 (m, 6H), 7.24 (d, $J = 1.2$ Hz, 2H), 2.77–2.73 (m, 4H), 1.80–1.76 (m, 4H), 1.48–1.25 (m, 20H), 0.91–0.88 (m, 6H); FTIR (cm^{-1}): 3082, 2957 ν - CH_2 ; 2920–2848 ν Aliphatic C–H; 1606 ν - $\text{C}=\text{N}$ –; 1502, 1418, 723 ν -thiophene.

RESULTS AND DISCUSSION

Optical Properties of Monomers

The solution state UV-Vis absorption spectra for the two monomers (OTPP and OTBP) can be seen in Fig. 2. The concentration of the monomers is 1.0×10^{-4} mol/L. All of the monomers showed two distinct absorption bands: the band around 300–500 nm can be assigned to the π - π^* transition. The maximum absorptions of OTPP located at 325 nm and 498 nm, which are red shifted 8 nm and 54 nm in compared with the peaks of OTBP at 317 nm and 444 nm, respectively. The red shift in the π - π^* transition band can be attributed to the nature of electron acceptor units in the two monomers structure. The existence of two more N atoms in OTPP structure leads greater conjugation of OTPP than OTBP. Furthermore, the existence of two more N atoms in OTPP structure than OTBP would lead quinoxaline units to become more electron-deficient. So, the electron withdrawing ability of electron acceptor unit in OTPP is stronger than in OTBP. These changes not only influence the electrochemical properties of monomers, but also affect optical properties of monomers. The stronger electron withdrawing ability, leading to the greater conjugation, contributes to the red shift of OTPP than OTBP.

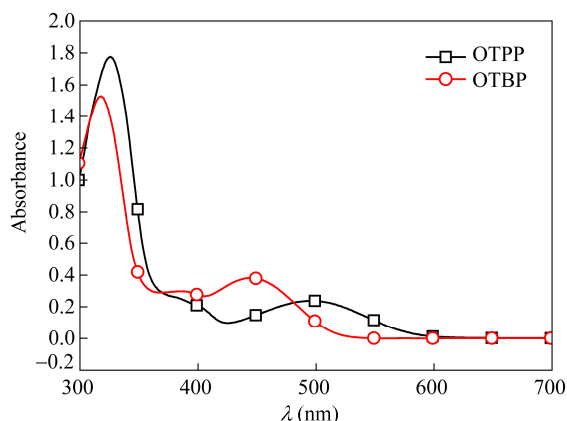


Fig. 2 UV-Vis spectra of OTPP and OTBP in DCM (The concentration of monomers is $c = 1.0 \times 10^{-4}$ mol/L.)

Electrochemistry

We attempted to carry out the electrochemical studies in several different supporting electrolytes such as $\text{NaClO}_4/\text{LiClO}_4$, tetrabutylammoniumtetrafluoroborate (TBABF_4), tetrabutylammonium perchlorate (TBAC) and tetra-*n*-butylammoniumhexafluorophosphate (TBAPF_6). The $\text{LiCO}_4/\text{NaClO}_4$ mixture electrolyte cannot be used to electrochemical experiment due to the electrolyte is soluble in ACN or DCM/ACN solvent mixture when the DCM volume fraction is less than 30%, but the monomers are insoluble in such solvents. Although the monomer and the $\text{LiCO}_4/\text{NaClO}_4$ mixture are soluble in THF, but the electrochemical behavior of the monomer is poor, and it is impossible to obtain good films. The electroactivity of monomers were examined in DCM solution containing 0.1 mol/L TBABF_4 , TBAC and TBAPF_6 , respectively. The results showed that the electrochemical behaviors of monomers were poor by using TBABF_4 and TBAC, but that were well in DCM solution containing TBAPF_6 , and if we use ACN/DCM (5/95, *V/V*) solvent mixture better optical transparent films on ITO glass were formed. So we mainly investigated the electrochemical activity of OTPP and OTBP using TBAPF_6 as supporting electrolyte.

The redox behaviors of OTPP and OTBP were investigated using cyclic voltammetry at room temperature in a conventional three electrode cell. Electrochemical studies were carried out in ACN/DCM (5/95, *V/V*) solvent mixture using 0.1 mol/L TBAPF_6 as supporting electrolyte. The concentration of monomers used for polymerization was 0.01 mol/L for OTPP and 0.005 mol/L for OTBP. During the first anodic scan of OTPP, the onset of oxidation starts at +0.9 V versus an Ag wire pseudo-reference electrode, and a single peak was observed at +1.28 V which corresponds to irreversible oxidation of the monomers (Fig. 3a). Subsequent cycling leads to a new redox couple associated with the oxidation and reduction of the polymers deposited on the ITO electrode surface (Fig. 3c). Upon repeated scanning the increasing current response of the polymer redox process illustrates that electrochemical polymerization is proceeding at the electrode surface to form an electroactive polymer film. On the anodic scans of POTPP, polymer oxidation potential was evolved at +1.02 V and the oxidation potential increased during the repeated scanning. The reduction potential of POTPP was evolved at +1.0 V and the reduction potential decreased to +0.86 V during the repeated scanning.

The cyclic voltammogram of OTBP exhibits two irreversible oxidation wave at +1.03 V and +1.13 V, and an reduction wave at +0.54 V versus Ag wire (Fig. 3b). Subsequent cycling leads to increase the current density of oxidation wave at +1.03 V, and oxidation wave at +1.13 V disappeared. At the same time, the current density at +0.54 was decreased, and a new reduction wave appeared at +0.89 V and the corresponding current density was decreased (Fig. 3d). The increase and decrease of current density corresponding to the oxidation and reduction waves indicate that POTBP polymer film is deposited on the ITO electrode surface. The cyclic voltammogram results showed that the oxidation and reduction potentials of OTBP were lower than those of OTPP measured under the described conditions, this lower potential can be attributed to the HOMO level of OTBP which is higher than that of OTPP^[20], and moreover the quinoxaline unit in OTPP is more electron-

deficient than OTBQ and this can be attributed to the existence of two more N atom in dipyrro of OTTP. So, the electron withdrawing ability of the acceptor unit in OTTP is stronger than that in OTBP which leads to an increase in the redox potential^[21, 34].

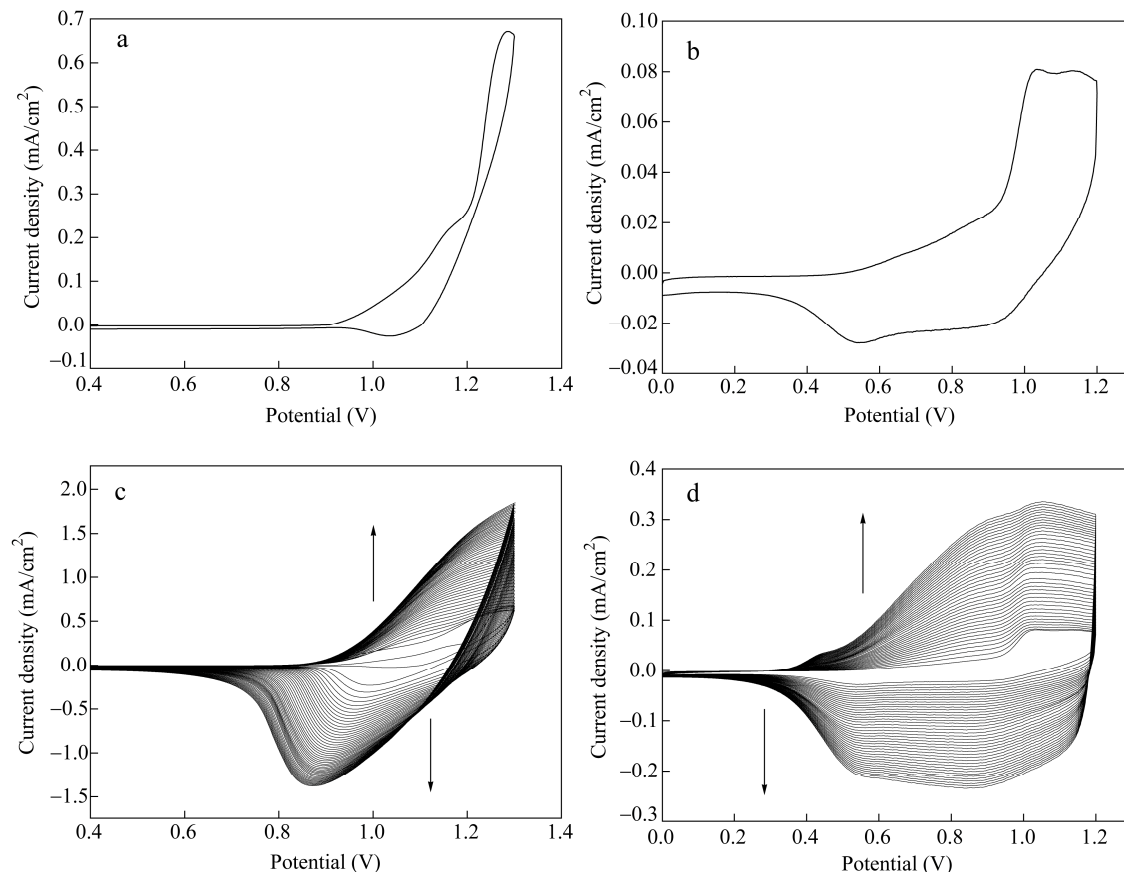


Fig. 3 Single scan cyclic voltammograms of (a) OTTP and (b) OTBP at 100 mV/s in ACN/DCM (5:95) solution containing 0.1 mol/L TBAPF₆ on ITO electrode; Repeated potential scan electrochemical polymerization of (c) OTTP and (d) OTBP in the same solvent-electrolyte system

The scan rate dependences of the anodic and cathodic peak currents of polymer films of POTPP and POTBP were also investigated by CV in a monomer-free electrolyte solution (Fig. 4). A linear relationship between the peak current and scan rate demonstrates that the films were well adhered and maintain reversible redox properties even at high scan rates acquiring rapid charge/discharge process. The anodic current peaks cannot be fully observed at higher scan rates, but can be observed when the scan rate was 50 mV/s and 100 mV/s, so we choose the anodic current density at +1.3 V as anodic peak current.

Figure 5 presents the both p- and n-type doping properties of two polymers. The results show that POTPP has one peak at +1.28 V for p-type doping and one peak at +0.93 V for p-type dedoping and one peak at -0.99 V for n-type doping. The POTBP has one peak at 1.06 V for p-type doping and one peak at +0.78 V for p-type dedoping and one peak at -1.87 V for n-type doping. The HOMO-LUMO values were calculated by the reported method and were summarized in Table 1^[35]. We have known from the Fig. 5 that it was harder for p-doping and easier for n-doping of POTPP films than for those of POTBP films, and it was caused by the difference of electron withdrawing ability of the electron acceptor unit and this differences was discussed above.

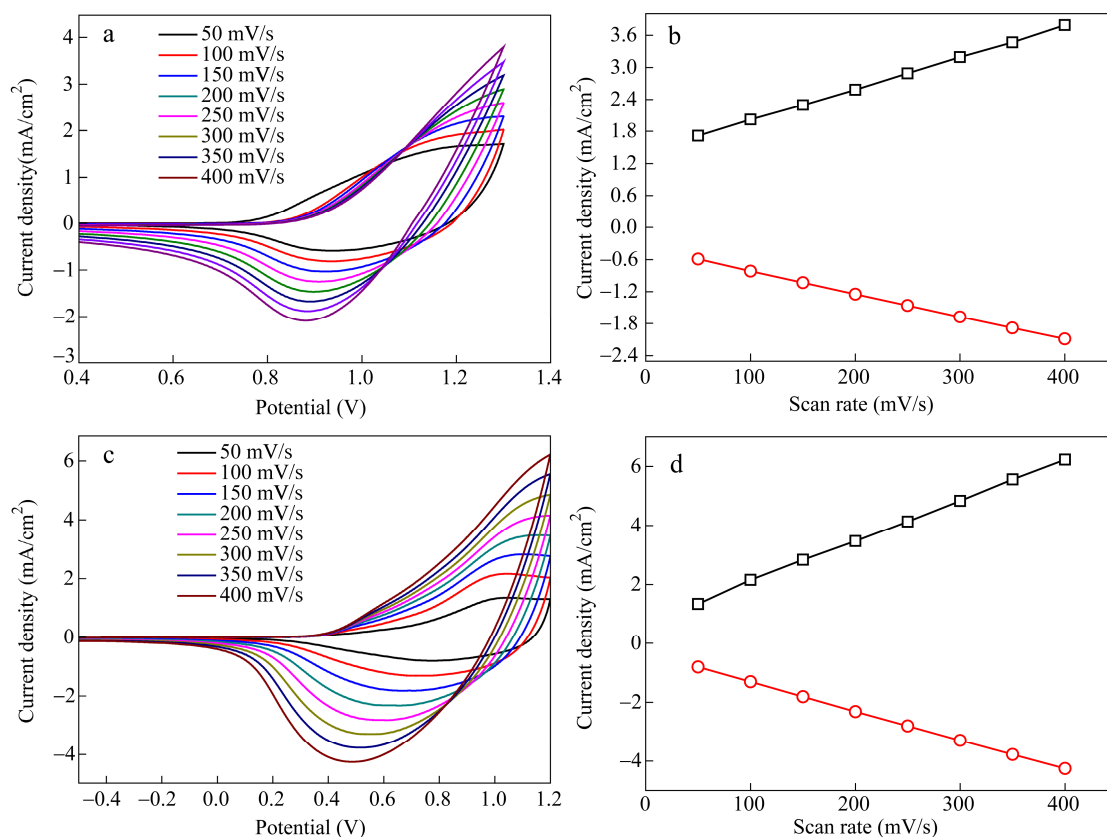


Fig. 4 Scan rate dependence of (a) POTTP film and (c) POTBP in monomer free ACN/DCM (5:95) solution containing 0.1 mol/L TBAPF₆ at scan rates of 50, 100, 150, 200, 250, 300, 350 and 400 mV/s; Relationship of anodic (black square) and cathodic (red circled) current peaks as a function of scan rate for (b) POTTP and (d) POTBP films

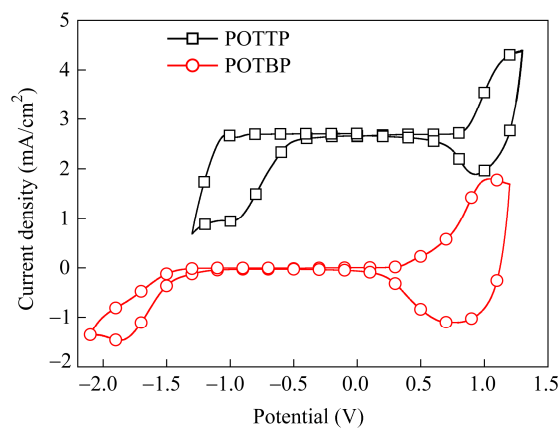


Fig. 5 Cyclic voltammogram of POTTP and POTBP films in 0.1 mol/L TBAPF₆/ACN/DCM (5/95, V/V) at scan rate of 100 mV/s

Table 1. Summary of electrochemical and optical properties of POTTP and POTBP

	$E_{\text{mon}}^{\text{ox}}$ (V)	$E_{\text{p-doping}}$ (V)	$E_{\text{p-dedoping}}$ (V)	$E_{\text{n-doping}}$ (V)	HOMO (eV)	LUMO (eV)	λ_{max} (nm)	E_{g}^{op} (eV)	E_{g}^{ec} (eV)
POTTP	0.5	1.28	0.93	-0.99	-5.57	-4.22	570	1.74	1.34
POTBP	0.88	1.06	0.78	-1.86	-5.09	-3.30	566	1.69	1.79

Electrochromic Studies of Polymers

After electrochemical polymerization of OTPP and OTBP onto ITO surface, we treated the polymer films with phenylhydrazine for 3 h to get the polymers to their neutral states. Electrochromic analysis was performed to evaluate the optical properties of the polymers. Figure 6 shows the electronic absorption series for p-doping of POTPP between + 0.4 V and + 1.4 V, and for p-doping of POTBP between 0 V and + 1.3 V, respectively.

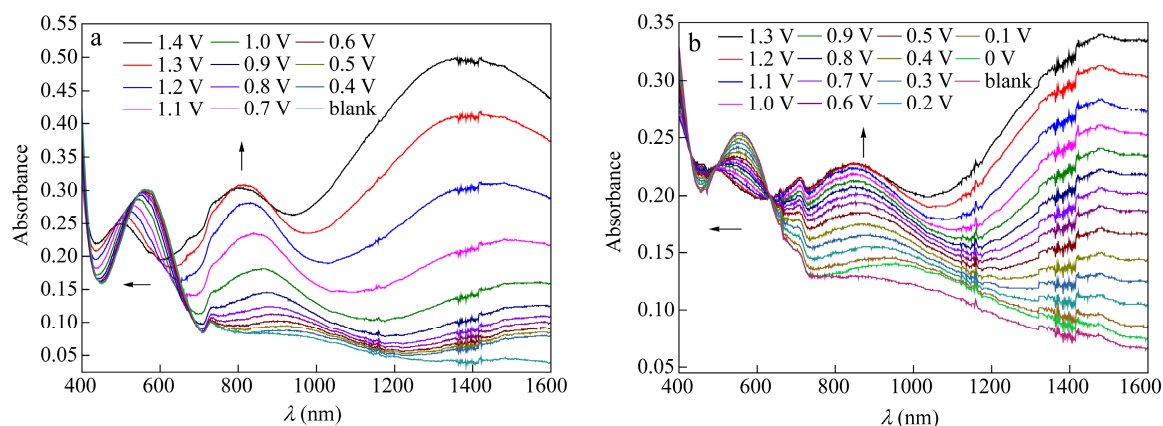


Fig. 6 Electronic absorption spectra of (a) POTPP film and (b) POTBP film on ITO in ACN/DCM (5:95) solution containing 0.1 mol/L TBAPF₆ electrolyte at various applied potentials between + 0.4 V and + 1.4 V for POTPP and between 0 V and + 1.3 V for POTBP

The neutral state of POTPP film is violet blue in color, having one absorption band at 570 nm and one side peak between 700 nm and 1200 nm, and the side peak explains that POTPP film couldn't be fully dedoped to its neutral state (Fig. 6a). Stepwise oxidation of the polymer film shows that the intensity of $\pi-\pi^*$ transition decreases as the color changes from violet blue to violet red. Upon oxidation, the absorption bands intensity at 570 nm decreased and the absorption peaks blue shifted when the potential changes from + 0.4 V to + 1.4 V, finally appear at 500 nm. Two absorption peaks appear at 925 nm and 1581 nm when the applied potential was + 0.4 V. During stepwise oxidation, the absorption intensity of the two bands increased. This is because that during the electrochemical oxidation, the doped extent of the polymer was increased and it leads to increase of intermolecular packing. The absorption peaks at 925 nm and 1581 nm blue shifted while the applied potential was increased and finally appeared at 814 nm and 1380 nm when the applied potential was +1.4 V, blue shifted 111 nm and 201 nm, respectively. The band gap was calculated by onset of the peak at 570 nm as 1.74 eV.

In the neutral state the POTBP film (violet blue in color) exhibits one absorption band with absorption maximum at 566 nm and one side peak between 700 nm and 1300 nm. This side peak is attributed to the polaronic state which indicates the polymer film could not be dedoped to its neutral state^[20]. In the oxidation process, the absorption band intensity at 566 nm decreased and it blue shifted 75 nm, appeared at 491 nm. At the same time there appears two new absorption peaks at 852 nm and 1495 nm and the absorption intensity of the two bands increases with increasing the applied potential. The band gap was calculated by onset of the peak at 566 nm as 1.69 eV.

As shown in Fig. 6, the electronic absorptions of POTPP and POTBP films have one side peak and the all absorption peaks blue shifted during the stepwise oxidation process. This can be attributed to the nature of electron acceptor unit of these two polymers. The electron withdrawing ability of quinoxaline is strong and the charge on the thiophene ring was easily moving to the quinoxaline, and it leads to easy doping of thiophene ring. So, the POTPP film and POTBP film were partially doped during the electrochemical polymerization process and didn't dedoped to their neutral state even treated with phenylhydrazine^[30]. During the oxidation and reduction, injection and ejection of the counter ion become less favorable and the charges are trapped in the polymeric film, and it leads to a side absorption band in the electronic absorption spectra of POTPP film and

POTBP film. Therefore the POTPP and POTBP films could not be dedoped to their neutral state^[20, 29, 30] which was confirmed by CV studies as shown in Fig. 3. It can be seen in Fig. 6(a) that the absorption peaks more blue shifted with increasing the applied potential. This is because during the stepwise oxidation process the electron acceptor unit became more electron deficient and it may increase the molecular orbital energy, so the absorption peaks blue shifted. The absorption peaks in the electronic absorption spectra of POTPP are more blue shifted than those of POTBP. It is due to the existence of two more N atoms in electron acceptor unit of POTPP and its electron withdrawing unit has stronger electron deficient than that of POTBP^[30].

Electrochromic Switching

The stability and the switching ability of electroactive polymer films between the redox states are important factors for development of optical and electrochromic devices. The optical switching ability was examined using a square wave potential step method coupled with optical spectroscopy in a monomer free electrolyte solution. During the experiment, the transmittance at the wavelength of maximum contrast was measured by a UV-Vis spectrophotometer, and the potential was stepwise switched between +0.4 V and +1.4 V for POTPP and between 0 V and +1.3 V for POTBP with a residence time of 10 s. In the optical contrast of POTPP film, the changes in transmittance between neutral (at 0.4 V) and oxidized states (at +1.4 V) were founded to be 28% and 51% for POTPP as in the near-IR regions (814 nm and 1380 nm) (Fig. 7). Furthermore the switching times were calculated as 3 s and 1 s for POTPP film. At the same condition, the optical contrasts were determined for POTBP as 13% and 35% in the near-IR regions (850 nm and 1500 nm), and the switching times determined as 4 s and 1 s for POTBP film. We can summarize from the experimental data of electrochromic switching that the two polymer films exhibit good color switching ability and stability.

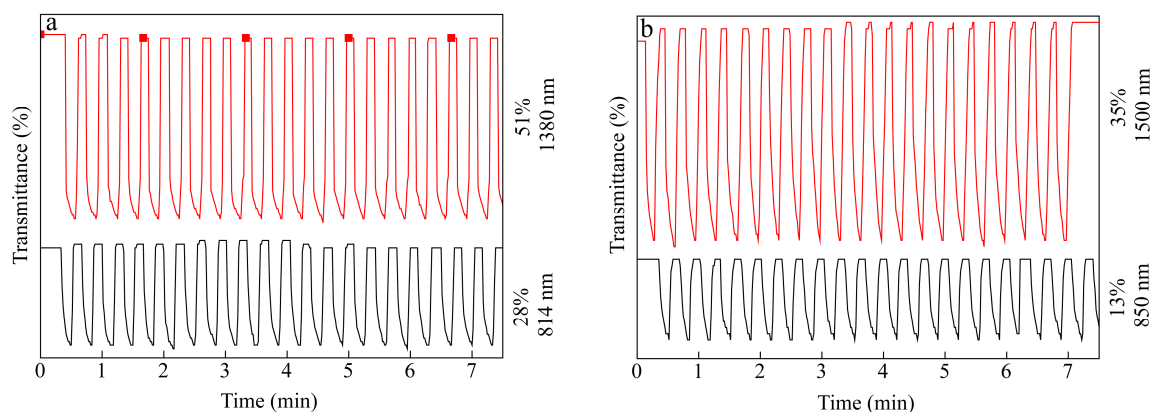


Fig. 7 Electrochromic switching, optical absorbance change monitored of at (a) 814 nm and 1380 nm for POTPP and (b) 850 nm and 1500 nm for POTBP

CONCLUSIONS

In conclusion, two different electroactive donor-acceptor type monomers, consisting of 3-octylthiophene as the donor unit and dipyrdo[3,2-a:2',3'-c]phenazine and dibenzo[a,c]phenazine as the acceptor units, were synthesized *via* a Stille coupling reaction. Two novel donor-acceptor type p-conjugated polymers were synthesized by electrochemical polymerization method, and the influence of the changes of electron acceptor unit's electron withdrawing ability on the optoelectronic properties of the resulting polymers was investigated. The existence of two more N atoms in electron acceptor units increased the electron withdrawing ability of the electron acceptor unit. So, the oxidation potential of OTTP was higher than that of OTBP, and electrochemical polymerization of OTTP was also carried out at higher oxidation potential than that of OTBP. The stronger electron withdrawing ability, leading to the greater conjugation, not only contributes to the red shift in UV-Vis spectra of OTTP compared with OTBP, but also leads to wider absorption bands in electronic absorption spectra

of POTPP than in POTBP. Electrochromic experimental data showed that both polymer films has electrochromic ability in visible and NIR region. POTPP films demonstrate 51% optical contrast in NIR region with 1 s responding time and POTBP films also show 35% optical contrast in NIR region with 1 s responding time.

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