

# Chemosynthesis, characterizations and electrochromic properties of a novel solution-processable donor-acceptor type copolymer

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**Abstract.** Chemical copolymerization of 4, 7-bis (4-hexyl-5-trimethylstannyl-2-thienyl) -2,1,3-benzothiadiazole and 2, 5-didecyloxy-1,4-dibromobenzene was carried out in refluxed toluene with bis (triphenylphosphine) palladium(II) chloride (Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>) as catalyst to give donor-acceptor type poly (4, 7 -bis (4-hexyl-2-thienyl) -2,1,3-benzothiadiazole-co-p-didecyloxybenzene) (PTBTB) via Stille-coupling reaction. Spectroelectrochemical and electrochromic properties of the resulting copolymer were characterized by cyclic voltammetry (CV) and UV-Vis-NIR spectroscopy. Cyclic voltammetry showed a definite electrochemical redox behavior of PTBTB polymer during the p-doping progress and an explicit reduction peak at about -1.4 V at the n-doped state. And spectroelectrochemical studies demonstrated that the hybrid polymer film had distinct electrochromic properties with color changing from red in the reduced form (0 V) to light gray upon step-wise oxidation (1.03 V) and tile blue at the fully oxidized state (1.4 V). Further kinetic studies results indicated that the hybrid polymer had decent optical contrast ratios (34.3% for 517 nm and 65.2% for 1600 nm), favorable coloration efficiency (238 cm<sup>2</sup>/C) and fast response time (0.6 s). The material hold promise for electrochromic applications.

## 1. Introduction

In recent years, electrochromic technique, especially due to broad application prospects of electrochromic devices, such as the smart windows, color sunglasses, glare-free mirror, color display, electronic paper and military camouflage and other fields, have caused widespread concern at home and abroad [1]. A reversible optical/color change observed in a material because of the electrochemical redox reaction at different applied external voltages is defined as electrochromism. Organic conjugated conductive polymers as an important class of electrochromic materials have received much more attention because of its unique advantages including lower cost, better toughness, easier processing, richer color change and easier molecular structure modification to improve the electrochromic properties than the inorganic materials. In the family of conducting polymers, donor-acceptor type materials, which are composed of alternating electron-donating groups and electron-withdrawing groups, have been documented to be with high hole mobility capability and can optimize the spectral absorption range and the energy band-gap, thus presenting distinguished optical and electronic properties [2].

Benzothiadiazole (BTD) with electron-withdrawing imine nitrogens (C=N) has only recently been established as a good acceptor-type unit for D-A conjugated systems. Previously reported benzothiadiazole based D-A type polymers are usually obtained by coupling with electron donating thiophene or its derivatives as donor units. Well defined extension of the conjugated length in its structure between benzothiadiazole and thiophene groups are often associated with low band-gap [3], which can lead to specific optoelectronic properties [4,5]. However, if we want to achieve the electrochromic films by large-scale production, the need for high solubility of the polymers is of greatest importance.

Taking into consideration the demand for both low energy band-gap and improved solubility, we have succeeded in preparation of a new donor-acceptor copolymer with high molecular weights, excellent solubility and low optical band-gap at about 1.98 eV. In addition, the spectroelectrochemical and electrochromic properties of the resulting PTBTB copolymer film are detailedly described in this article. The polymer exhibits multichromic properties with three distinctive colors and significant changing in UV-Vis-NIR absorption spectra at different applied potentials.

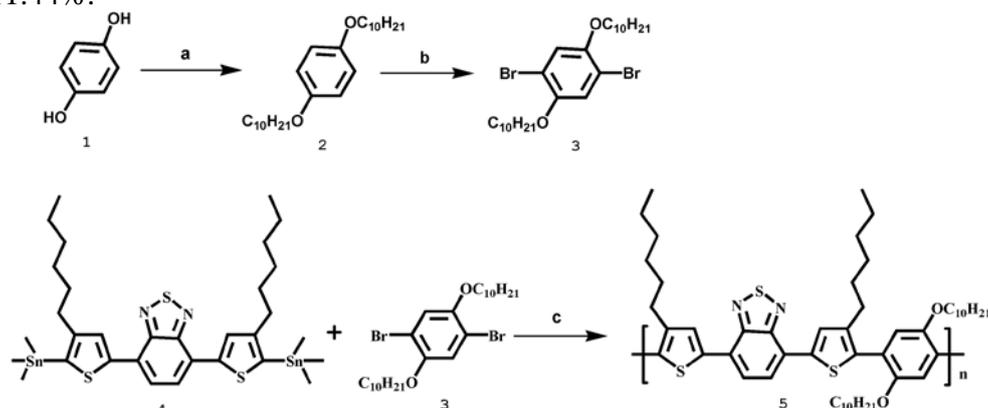
## 2. Experimental

### 2.1 General.

All chemicals were obtained from Aldrich Chemical and directly used without any other purification. Polymer thin films were prepared by spray-coated onto ITO/glass working electrode for electrochemical measurements and optical studies. Cyclic voltammetry (CV) was performed using a CHI 760 C workstation in 0.1 M TBAHF<sub>6</sub>/ACN at a scan rate of 100 mV/s with platinum wire as the counter electrode, and Ag wire as the pseudo-reference electrode (-0.03 V vs. SCE). UV-Vis-NIR spectra of the polymer film were recorded on a Varian Cary 5000 spectrophotometer at a scan rate of 600 nm/min. Elemental analyses were performed on a Carlo-Erba 1160 elemental analyzer. Waters 1515-2414 gel permeation chromatography (GPC) was used to determine the molecular weight of the polymer. Photographs of the polymer film were taken by using a Canon (Power Shot A3000) digital camera.

### 2.2 Synthesis.

1,4-Didecyloxybenzene (2) was prepared in high yield through alkylation of hydroquinone (1) in the presence of 1-bromine decane in DMF solution (yields, 91%) and subsequent bromination of the obtained alkoxy benzene (2) with HBr in glacial acetic acid under reflux heat treatment for 8 h (yields, 82%). The Stille coupling reaction of 2,5-didecyloxy-1,4-dibromobenzene with 4,7-bis(4-hexyl-5-trimethylstannyl-2-thienyl)-2,1,3-benzothiadiazole in the presence of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> as catalyst, gave the crude polymer production, which was then purified by Soxhlet extraction with methanol and acetone to afford poly(4,7-bis(4-hexyl-2-thienyl)-2,1,3-benzothiadiazole-co-p-didecyloxybenzene) as red solid in 83% yield. GPC for C<sub>52</sub>H<sub>76</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub>: M<sub>n</sub>: 20.3 kDa, PDI: 1.91. Elem. Anal. Calcd. for C<sub>52</sub>H<sub>76</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub>: C, 72.85%; H, 8.93%; N, 3.27%; O, 3.73%; S, 11.22%. Found: C, 72.41%; H, 9.03%; N, 3.32%; O, 3.80%; S, 11.44%.



Scheme 1. Synthesis of the polymer.

## 3. Results and discussion

### 3.1 Cyclic voltammetry.

In order to investigate the electrochemical redox behavior of PTBTB, cyclic voltammetry (CV) studies were performed in 0.1 M TBAHF<sub>6</sub>/ACN solution. CV curve (figure 1) showed the distinct anodic redox behavior and cathodic reduction process. In addition, the ionization potentials ( $E_{\text{HOMO}}$ ) and the electron affinity ( $E_{\text{LUMO}}$ ) of were calculated according to the following empirical equations:

HOMO =  $-(E_{\text{ox,onset}} + 4.4)$  and LUMO =  $-(E_{\text{red,onset}} + 4.4)$ , where the  $E_{\text{ox,onset}}$  and  $E_{\text{red,onset}}$  are the onset oxidation potential and the onset reduction potential versus standard calomel electrode (SCE), respectively. And the electrochemical band-gap were calculated to be 1.86 eV by the subtraction of the HOMO level from the LUMO level. Other electrochemical data were all listed in Table 1 in detail.

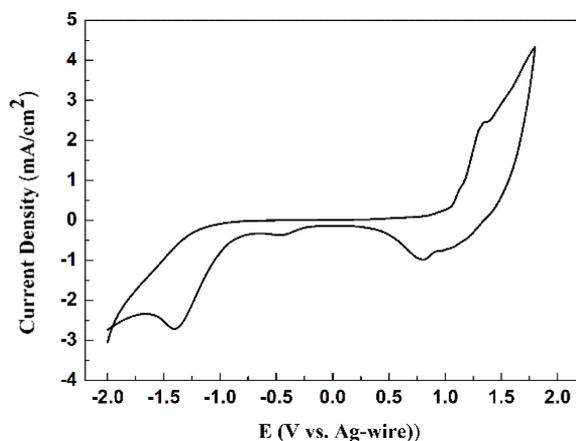


Figure 1. Cyclic voltammogram of PTBTB film casted on ITO/glass electrode in 0.1 TBAHF6/ACN at 100 mV/s

Table 1 electrochemical and optical data of PTBTB

Polymer	$E_{\text{ox,onset}}$ , vs.Ag (V)	$E_{\text{red,onset}}$ , vs.Ag (V)	$E_{\text{g,ec}}$ (eV)	$\lambda_{\text{onset}}$ (nm)	$E_{\text{g,op}}$ (eV)	HOMO (eV)	LUMO(eV)
PTBTB	1.02	-0.84	1.86	627	1.98	-5.39	-3.53

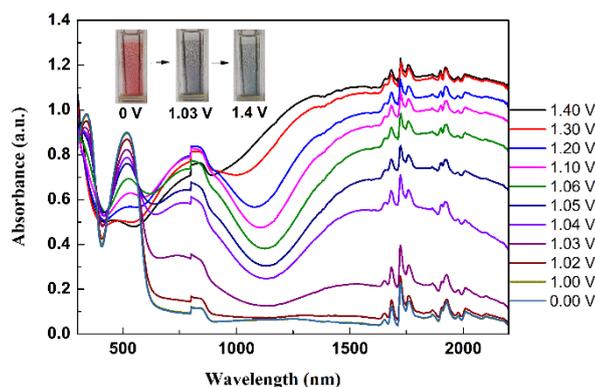


Figure 2. UV-Vis-NIR absorption spectra of PTBTB film on ITO electrode at various applied potentials between 0 V and 1.40 V.

### 3.2 Spectroelectrochemistry.

The absorption spectra of PTBTB in thin film at various applied potentials are performed and distinct absorption changes could be observed in Fig. 2. At the neutral state, PTBTB film exhibits two major characteristic absorption bands centered at 344 and 517 nm, which can be assigned to the strong  $\pi-\pi^*$  transition and the internal charge transfer (ICT) between the thiophene donor and benzothiadiazole acceptor moiety, respectively. Optical band-gap for this polymer in the film state was estimated from the lowest-energy band edge of the UV-Vis-NIR absorption spectra. Optical band gap of PTBTB was calculated to be 1.98 eV, which is significantly larger than the electrochemical band-gap. When the applied potential reached +1.03 V, the intensities of CT transition bands decreased and new absorption band at about 800 nm were detected due to the formation of charge

carriers (polarons). Meanwhile, red color of the film at neutral state (0 V) turned into light gray at intermedia doped state (+1.03 V). At fully oxidized state (+1.4 V), low-energy bipolaronic band at over 1200 nm in the near-infrared (NIR) region significantly increased. And the color of the film turned into tile blue finally. In addition, the changes in percentage transmittance ( $\Delta T\%$ ) between the neutral (0 V) and oxidized states (1.4 V) were found as 34.3% for 517 nm with a response time of 0.6 s. The coloration efficiency (CE) was calculated to be  $238 \text{ cm}^2/\text{C}$ . It is worth noting that optical contrast can reach up to 65.2% in the NIR region for PTBTB film make this electrochromic material good candidate to be used in NIR applications [6].

#### 4. Conclusions

A novel benzothiadiazole-based donor-acceptor type conjugated polymer has been designed and successfully synthesized via Stille-coupling reaction. The resulting copolymer has high solubility in some common organic solvents due to the incorporation of long alkoxy side chain. It is noted that PTBTB has red color in the neutral state and switches to light gray/tile blue upon oxidation. The electrochemical and optical band gaps of the polymer film are found to be 1.86 eV and 1.98 eV, respectively. Moreover, good redox behavior, high CE and contrast ratio, and fast response time of this novel material make it excellent candidate for electrochromic application.

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