

Chemosynthesis and photoelectric characterization of a novel solution-processable electrochromic copolymer based on alternating alkoxybenzene and benzo[1,2-b:4,5-b']dithiophene derivatives

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Abstract. The conjugated polymer poly (4,8 -bis ((2-octyldodecyl) oxy) benzo [1,2-b:4,5-b'] dithiophene-co-p-didecyloxybenzene) (PBTB), was successfully chemically polymerized by reacting (4,8-bis((2-octyldodecyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) with respective 2,5-didecyloxy-1,4-dibromobenzene in favorable yields via Stille cross-coupling reaction. Due to the incorporation of long alkoxy side chain, the resulting copolymer has high solubility in some common organic solvents. Besides, it was characterized by elemental analysis, gel permeation chromatography (GPC), cyclic voltammetry (CV) and UV-Vis-NIR spectroscopy. The electrochemical band-gap and optical band-gap was calculated to be 1.85 eV and 2.03 eV from CV curve and UV-Vis absorption spectrum, respectively. The PBTB film exhibited reversible electrochromic properties and rendered multi-colored display: orange-yellow reduced state (0 V), yellow-gray semi oxidized state (1.15 V) and gray fully oxidized state (1.35 V). In addition, kinetics study of the copolymer film revealed a maximum optical contrast ($\Delta T\%$) of 32%, a fast response time of 0.4 s from the oxidized state to the neutral state and a high coloration efficiency of 267 cm²/C at λ_{max} of 510 nm in the visible region.

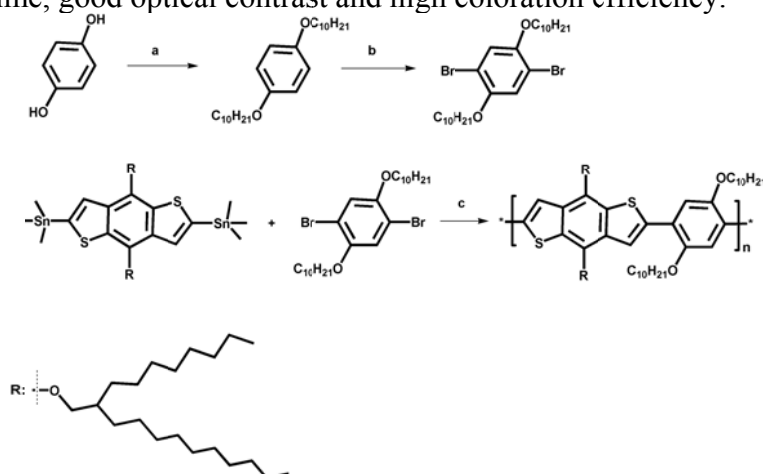
1. Introduction

The electrochromic phenomenon refers to a material or system which can reversibly change the optical properties (transmittance, reflectance, or absorbance) by altering its redox state at an applied external voltage [1]. In appearance, it showed reversible changes in color and transparency due to the formation of polaronic and bipolaronic bands causing a change in the spectral absorption [2]. Electrochromic material is considered to be one of the most promising smart materials since they are potentially useful materials for a broad range of applications such as display devices, smart windows, glare-free mirror, military camouflage, etc.

Even though the inorganic materials are the earlier studied active layers in electrochromic devices and have been utilized over the past few decades, conjugated polymers have received much more attention because of their high optical contrasts, fast response times, easy processing, rich color change, easy molecular design and low cost. In these electrochromic conjugated polymers, polythiophenes aromatic heterocyclic, to be practical, has high degree of stability to oxygen and humidity, making its derivatives are more likely to be synthesized than other aromatic heterocyclic derivatives. At the same time, polythiophene and its derivatives have good redox reversibility and stability in the environmental [3]. Therefore, they displayed broad application prospects in the field of electrochromic.

Recently, a series of thiophene-arylene-thiophene-like conjugated structures of polymers have been synthesized and usually present reasonable electrochromic properties [4,5]. However, their structural composition are usually simple, conjugated effects between the repeated aromatic heterocyclic are weak and because of their low solubility, the vast majority of them are obtained by

the electrochemical polymerization method. Solvent-processable electrochromic polymer with excellent solubility, which can be obtained by chemical polymerization in mass, thus reducing the cost and providing a strong competitive edge for the material commercialization, has become what researchers vigorously pursue.



Scheme 1. Synthetic route of the polymer. (a) DMF, K₂CO₃, 1-bromine decane, TBAB, 120°C, 90 min. (b) HBr, Br₂, 135°C, 5 h. (c) toluene, Pd(PPh₃)₂Cl₂, reflux, 48 h.

2. Experimental section

2.1 Materials and Instrumentation.

All the chemicals and reagents are purchased from Sigma-Aldrich chemical company except that (4,8-bis((2-octyldodecyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) is from Derthon Optoelectronic Materials Science Technology Co LTD. And the reagents adopted in the experiment are all chemical grade and have been directly used without further purification. 1,4-didecyloxybenzene[6] and 2,5-didecyloxy-1,4-dibromobenzene[7] were prepared according to the previously reported literature methods.

Elemental analyses are carried out on a Thermo Finnigan Flash EA 1112, CHNS-O elemental analysis instrument. Molecular weight of the polymer are determined by Waters 1515-2414 gel permeation chromatography (GPC). Electrochemical cyclic voltammetry performance test is performed on a CHI 760 C workstation with ITO/glass as transparent working electrode (WE), platinum wire as the counter electrode, and Ag wire (-0.03 V vs. SCE.) as the pseudo-reference electrode immersed in 0.1 M TBAHF₆/ACN as the supporting electrolyte. Spectroelectrochemical and kinetic measurements are recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer connected with the above electrochemical workstation. Photos of the polymer film are taken with a Canon Power Shot A3000 IS digital camera.

2.2 Synthesis of π -conjugated polymer PBTB.

In turn, (4,8 -bis ((2-octyldodecyl oxy)benzo [1,2-b:4,5-b'] dithiophene-2,6-diyl) bis (trimethylstannane) (0.407 g), 2,5-didecyloxy-1,4-dibromobenzene (0.201 g), Pd(PPh₃)₂Cl₂ (0.015g) and 100 mL toluene were added into 250 mL single-necked flask. The mixture was refluxed under argon atmosphere for 48h. Excess solvent was evaporated, and then a large amount of methanol solvent was added to give the suspension. The polymer obtained by filtration, which was further purified by Soxhlet extraction with MeOH and acetone to remove the catalyst and oligomer, and

then dried under vacuum oven to afford the deep-red solid copolymer (yields, 81.6%). GPC for $C_{76}H_{130}O_4S_2$: M_n : 12.4 kDa, PDI: 1.7. Elem. Anal. Calcd. for $C_{76}H_{130}O_4S_2$: C, 77.89%; H, 11.18%; O, 5.46%; S, 5.47%. Found: C, 77.36%; H, 11.35%; O, 5.58%; S, 5.71%.

2.3 Deposition of π -conjugated polymer PBTB.

The solution of copolymers in chloroform (2 mg/mL) was spray-coated on ITO/glass to form electrochromic layers. The thickness of the polymer film deposited on ITO/glass was controlled by spraying times.

3. Results and discussion

3.1 Electrochemistry.

Cyclic voltammetry (CV) test was used to characterize the electrochemical properties of the polymer. An explicit electrochemical redox behavior of PBTB polymer film can be seen from the CV depicted in Figure 1. Upon p-doping progress, the PBTB film showed an obvious oxidation peak at about 1.75V. Correspondingly, a sharp reduction peak was also found at -1.88 V.

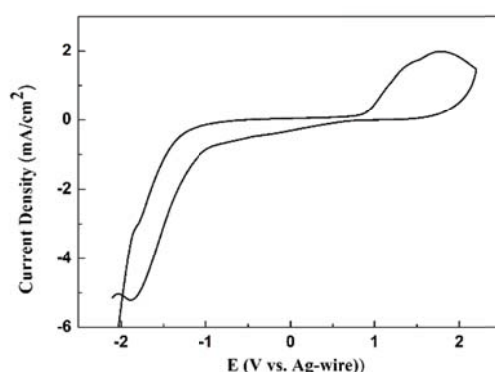


Figure 1. Cyclic voltammetry curve of PBTB film

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated to be -5.32 eV and -3.47 eV, according to the onset oxidation potentials ($E_{ox,onset}$) and the onset reduction potentials ($E_{red,onset}$) of the polymer, respectively. The details about the electrochemical data were listed in Table 1.

Table 1 electrochemical and optical data of PBTB film

Polymer	$E_{ox,onset}$, vs.Ag (V) ^a	$E_{red,onset}$, vs.Ag (V) ^a	$E_{g,ec}$ (eV) ^a	λ_{onset} (nm)	$E_{g,op}$ (eV) ^b	HOMO (eV) ^c	LUMO(eV) ^d
PBTB	0.95	-0.90	1.85	612	2.03	-5.32	-3.47

^a Calculated from CV of the polymer, $E_{g,ec} = E_{ox,onset} - E_{red,onset}$. ^b Calculated from the low energy absorption edges (λ_{onset}), $E_{g,op} = 1241/\lambda_{onset}$. ^c HOMO = $-(E_{ox,onset} + 4.4)$ ($E_{ox,onset}$ vs. SCE). ^d Calculated by the subtraction of the electrochemical band-gap from the HOMO level.

3.2 Spectroelectrochemistry.

The UV-Vis-NIR absorption spectrum of PBTB film at different potentials are shown in Fig. 2. At neutral state, the polymer film showed orange-yellow color with two separated $\pi-\pi^*$ transition absorption peaks located at around 478 nm and 510 nm. And the optical band-gap values of the polymer was calculated to be 2.03 eV from the lowest energy absorption edges. Upon step-wise oxidation, the intensity of $\pi-\pi^*$ electron transition absorption decreased and new absorption band at around 680 nm caused by the formation of charge carriers such as polarons and bipolarons[2] gave rise to a yellow-gray semi oxidized state at 1.15 V. Finally, maximum absorption for the neutral state vanished and another new absorption band emerged at 391 nm. As a result, a gray fully oxidized state was observed at 1.35 V.

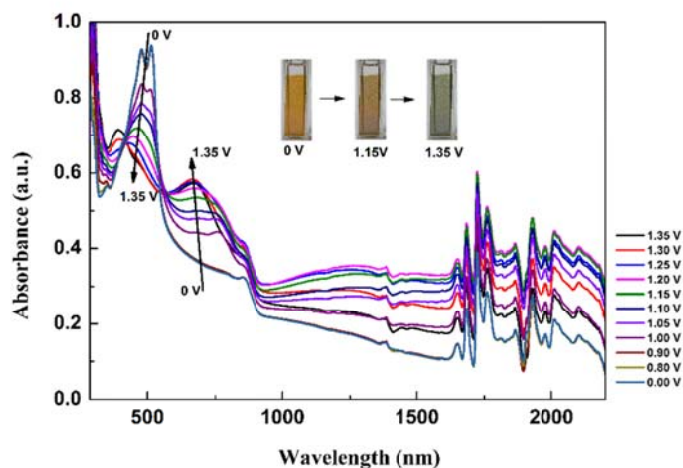


Figure 2. Electronic absorption spectra and the color changes of PBTB film at different potentials

3.3 Electrochromic switching studies.

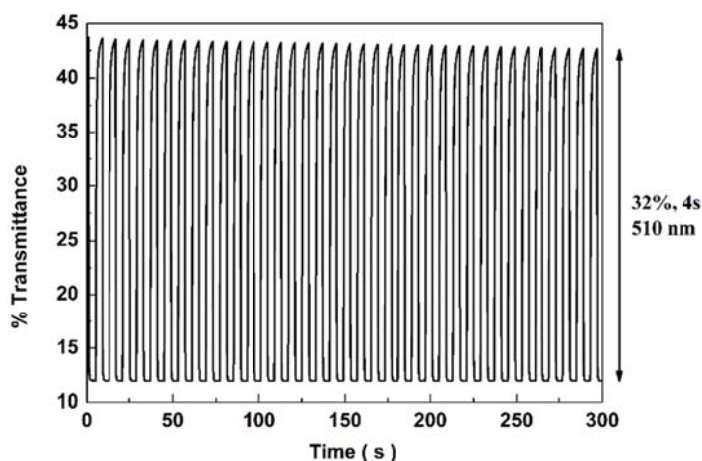


Figure 3. Electrochromic switching, percent transmittance change monitored at 510 nm for PBTB between 0 and 1.35 V

Switching properties of PBTB film were also measured at the maximum absorption in visible regions. As shown in figure 3, it revealed optical contrast value of 32% at 510 nm with a response time of 0.4 s. The coloration efficiency (CE) of PBTB film was calculated to be 267 cm²/C.

4. Summary

In summary, a novel π -conjugated polymers poly (4,8-bis((2-octyldodecyl)oxy) benzo [1,2-b:4,5-b'] dithiophene-co-p-didecyloxybenzene) (PBTB) was synthesized by chemical polymerization. The PBTB film showed three colors (orange-yellow, yellow-gray and gray) at different applied voltages. In addition, the high optical contrast (32%), fast switching time (0.4 s) and satisfactory coloration efficiency (267 cm²/C) make the polymer good candidate for electrochromic display application.

Acknowledgements

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