

Electrosynthesis and Characterization of an Electrochromic Material from Poly(1,6-bis(2-thienyl)pyrene) and Its Application in Electrochromic Device

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ABSTRACT: Electrochemical polymerization of 1,6-bis(2-thienyl)pyrene (BTP) could be achieved in acetonitrile/dichloromethane (ACN/DCM) (1:1, by volume) solution containing sodium perchlorate (NaClO₄) as a supporting electrolyte. The resulting polymer poly(1,6-bis(2-thienyl)pyrene) (PBTP) were characterized by cyclic voltammetry, UV-vis spectroscopy, and scanning electron microscopy. The resulting polymeric film has distinct electrochromic properties and exhibits three different colors under various potentials. Moreover, the PBTP film showed reasonable optical contrast (DT %) at 700 nm is found to be 29% and satisfactory response time is measured as 1.3 s. An electrochromic device (ECD) based on PBTP and poly(3,4-ethylenedioxythiophene) was also constructed and characterized. This ECD has these qualities: quick switching time, reasonable contrast, and good optical memories and redox stability. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39770.

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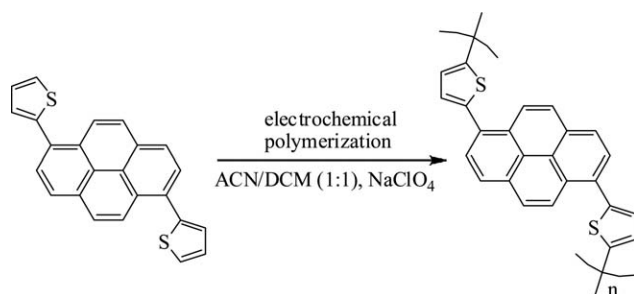
INTRODUCTION

Electrochromic materials and devices have been studied for years because of their scientific and technological interest.^{1,2} The electrochromism with electroactive materials present a reversible change in optical properties when the material is electrochemically oxidized or reduced.³ Even though electrochromism was first observed in inorganic materials such as tungsten trioxide (WO₃) and iridium dioxide (IrO₂), the limitations of these compounds motivated researchers towards the utilization of organic materials.⁴ Electrochromic conjugated polymers have potential applications due to their better stability, faster switching times, and excellent processability rather than inorganic electrochromic materials, but the most exciting properties are that the same material can display multiple colors while switching between their different redox states,⁵ and fine-tuning of the color transition through chemical structure modification of the conjugated backbone.^{6,7} The design and synthesis of new monomers and improvement in the ability of switching properties are current issues being investigated by researchers.

As a kind of electrochromic materials, polythiophene was reported to display a red to blue and a red to black-green switches on p- and n-dopings, respectively,^{8,9} and the energy

gaps fall into 2.0–2.2 eV, depending on the molecular weights of the polymers.¹⁰ A great deal of effort has been devoted to develop new thiophene based polymers for improving optoelectronic properties by modifying the monomer repeat unit or substitution of functional groups onto the polymer backbone. For instance, substitution of thiophenes with aromatic rings has shown to be an attractive way to obtain electrochromically superior polymers, such as poly(1,4-bis(2-thienyl)benzene)¹¹ (yellow in neutral state and green on oxidation), poly(1,4-di(thiophen-3-yl)benzene)¹² (yellow in neutral state and blue on oxidation), poly(1,5-bis(2-thienyl)naphthalene) and poly(2,6-bis(2-thienyl)naphthalene),¹³ (transparent pale yellow in neutral form and opaque dark blue on oxidation), having with optical band gaps of 2.31, 2.14, 2.7, and 2.5 eV, respectively. The introduction of aromatic units into the backbone of polythiophene stabilizes the conjugated π -bonds system effectively, allowing the fine tuning of the optical band gap and retaining the easy connectivity and good optics of thiophenes.¹⁴

Recently, a series of pyrene derivatives containing thienyl groups, such as 1,6-bis(2-thienyl)pyrene (BTP), have been synthesized and the field-effect characteristics of these molecules were studied by Ashizawa et al.¹⁵ To further study the properties



Scheme 1. The electrochemical polymerization of BTP monomer.

of their polymers, our group has synthesized and electropolymerized a series of asymmetrical monothiénylpyrenes and symmetrical dithienylpyrenes.¹⁶ The design of symmetrical position substitutions (thiophene) of the pyrene ring can lead to polymers with minimal side reactions upon electropolymerization.¹³ Because of the conjugated structures of the corresponding monomers, poly(1,6-bis(2-thienyl)pyrene) (PBTP) can be easily achieved by electrochemical polymerization of BTP monomer in common organic solution with a much lower oxidation potentials than that of thiophene.¹⁷ Preliminary study showed that the monomer BTP and its polymer PBTP presented good electrochemical and optical properties. In light of these distinct properties of the polymer PBTP, it is more interesting to further study its electrochromic properties and its application in electrochromic devices (ECDs).

In this study, BTP monomer was electrochemically polymerized to form the polymer PBTP. The spectroelectrochemical and electrochromic properties of the PBTP film were studied in detail. It is interesting to find that the PBTP film presents multichromic properties. Its dual type polymer ECDs constructed with PEDOT were also investigated in detail. The ECD has fast response time, satisfactory optical contrast and good cyclic voltammetry (CV) stability. Some of the preliminary results obtained in this research program have already been reported earlier,¹⁶ but some of the data will be used here for comparative purposes where appropriate.

EXPERIMENTAL

Materials

The BTP monomer was synthesized as reported previously by our group.¹⁵ 3,4-Ethylenedioxythiophene (EDOT, 98%) was purchased from Aldrich Chemical and used as received. Commercial high-performance liquid chromatography grade acetonitrile (ACN, Tedia Company, USA), poly(methyl methacrylate) (PMMA, Shanghai Chemical Reagent Company), dichloromethane (DCM, Shanghai Chemical Reagent Company), propylene carbonate (PC, Shanghai Chemical Reagent Company), and lithium perchlorate (LiClO_4 , Shanghai Chemical Reagent Company, 99.9%) were used directly without further purification. Sodium perchlorate (NaClO_4 , Shanghai Chemical Reagent Company, 98%) was dried in a vacuum at 60°C for 24 h before use. Other reagents were all used as received without further treatment. Indium-tin-oxide-coated (ITO) glass (sheet resistance: $< 10 \Omega \text{ sq}^{-1}$, was purchased from Shenzhen CSG Display Technologies, China), which was successively washed with ethanol,

acetone, and deionized water in an ultrasonic bath and then dried by a constant stream of N_2 .

Equipments

Scanning electron microscopy (SEM) measurements were taken by using a Hitachi SU-70 thermionic field emission SEM. CV was carried out on CHI 760 C electrochemical workstation using three-electrode system. UV-vis spectra were measured on a Perkin-Elmer Lambda 900 UV-vis-near-infrared spectrophotometer. Digital photographs were taken by a Canon Power Shot A3000 IS digital camera.

Electrochemistry and Spectroelectrochemistry

Electrochemical synthesis and experiments were performed in a three-electrode cell consisting of platinum wire or indium tin oxide (ITO) coated glass as the working electrode (WE), platinum ring as the counter electrode (CE), and Ag wire (0.03 V vs. SCE¹⁸) as the pseudo reference electrode (RE). All electrochemical polymerization and CV tests are taken in an ACN/DCM (1 : 1, by volume) solution containing 0.2M NaClO_4 as a supporting electrolyte. All of the electrochemical experiments are carried out at room temperature under nitrogen atmosphere.

Spectroelectrochemical measurements were carried out in a homemade cell, which consists of a quartz cell, an Ag wire (RE), a Pt wire (CE), and an ITO-coated glass (WE). The cell was placed in the optical path of the sample light beam in a Perkin-Elmer Lambda 900 spectrophotometer. All measurements were carried out in ACN/DCM (1 : 1, v : v) solution containing 0.2M NaClO_4 as a supporting electrolyte. The polymeric films that were used for spectroelectrochemistry were prepared by potentiostatically depositing the polymer onto the ITO electrode (the active area: $0.9 \times 2.1 \text{ cm}^2$). Their thickness was controlled by the total charge passed through the cell.

Preparation of the Gel Electrolyte

A gel electrolyte was prepared using ACN:PC:PMMA: LiClO_4 in the ratio of 70 : 20 : 7 : 3 by weight, which was first dissolving LiClO_4 in ACN. PMMA was then added into the solution under vigorous stirring and heat to dissolve PMMA. Finally, PC, as a plasticizer, was introduced to the reaction medium. The mixture was stirred for 24 h to form a homogeneous gel.

Assembly of ECDs

The ECDs were assembled by using two complementary polymers, namely, PBTP as the anodically coloring material and PEDOT as the cathodically coloring material. Both PBTP and PEDOT films were electrodeposited onto ITO glass electrodes (the active area: $1.8 \times 2.3 \text{ cm}^2$) with the same polymerization charge ($2.8 \times 10^{-2} \text{ C}$). The ECDs were built by arranging the two polymer films (one oxidized, the other reduced), facing each other, separated by a gel electrolyte.

RESULTS AND DISCUSSION

Electrochemical Polymerization and Characterization of PBTP Films

Electrochemical Polymerization. The electrochemical polymerization of monomer BTP was carried out in a mixture of DCM/CAN (1 : 1, by volume) solution containing 0.2M NaClO_4 as a

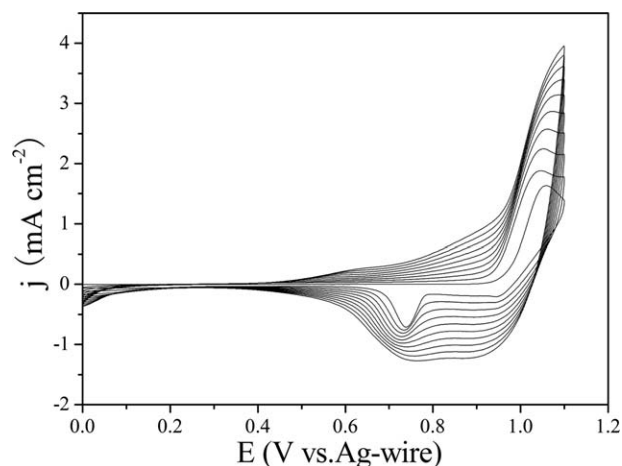


Figure 1. Cyclic voltammogram curves of 0.005M BTP in 0.2M NaClO₄/ACN/DCM solution at a scan rate of 100 mV s⁻¹. *j* denotes the current density.

supporting electrolyte (Scheme 1). The consecutive potential scanning, which reveal the electroactivities of monomer BTP and the corresponding polymer are given in Figure 1. The voltammogram of BTP exhibits an irreversible oxidation wave at 1.05 V due to the monomer oxidation. With the monomer oxidation, two reduction waves of the oligomer appeared at 0.74 and 0.86 V, while the corresponding oxidation waves were overlapped with the oxidation waves of the BTP monomer and cannot be observed clearly.¹⁹ As the CV scan continued, polymeric films were formed on the WE surface. The increase in the redoxwave current densities indicated that the thickness of polymeric film on the electrode was increasing. Moreover, the onset oxidation potential (E_{onset}) of the monomer was $\sim 0.92\text{V}$, which was determined from the intersection of the two tangents drawn at the rising oxidation current and background current in the cyclic voltammogram.²⁰ This value is lower than that of 2,2'-bithiophene (BT) monomer (1.11V)²¹ and of 1,4-bis(2-

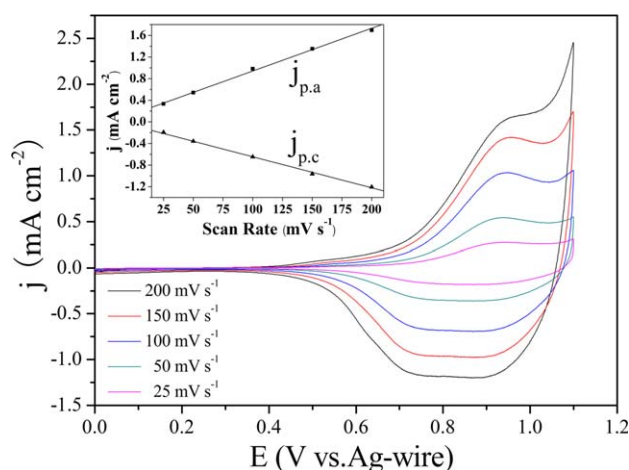


Figure 2. CV curves of the PBTP film at different scan rates between 25 and 200 mV s⁻¹ in the monomer-free 0.2M NaClO₄/ACN/DCM solution. Inset: graph of the scan rate dependence of the anodic ($j_{p,a}$) and cathodic ($j_{p,c}$) peak current densities. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

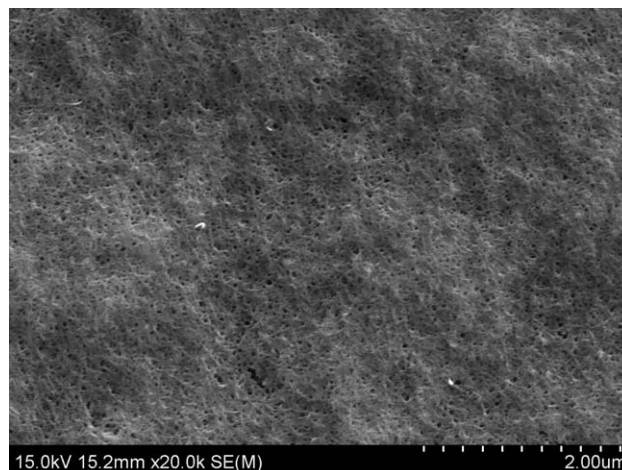


Figure 3. SEM image of PBTP deposited on ITO electrode at 1.1 V potentiostatically.

thienyl)-benzene (BTB) monomer (1.05 V)¹¹ indicating an extended π -conjugation along the bithiophene molecule by the introduction of pyrene as the π -center.

Electrochemistry of the PBTP Film. The CVs of the polymeric film were recorded in the potential range between 0 and 1.1 V at different scan rates between 25 and 200 mV s⁻¹ in a monomer-free electrolyte solution of an ACN/DCM (1 : 1, by volume) containing 0.2M NaClO₄ (Figure 2). As presented in Figure 2, a well defined redox couple appears at around 0.95 and 0.83 V, respectively. Also, as seen from inset of Figure 2, a linear increase in the peak current densities as a function of the scan rates confirmed a tightly bounded electroactive polymeric film on the electrode surface as well as nondiffusional redox process.²²

Morphology. The morphology of PBTP film was investigated by SEM. The PBTP film was prepared by constant potential electrolysis from the solution of 0.2M NaClO₄/ACN/DCM containing 0.005M monomer on ITO electrode and dedoped before characterization. As shown in Figure 3, the PBTP film displays a straw mat-like structure with small holes, which may facilitate the doping/dedoping movement of anions in the polymeric film.

Optical Properties of BTP Monomer and PBTP Film. The UV-vis spectra of BTP monomer in DCM and PBTP film deposited on ITO electrode are shown in Figure 4. The absorption maximum (λ_{max}) of the monomer BTP (Figure 4, Curve a) and the neutral state PBTP (Figure 4, Curve b) are centered at 371 and 416 nm, respectively. The difference between the λ_{max} corresponding to the monomer and the corresponding polymer for BTP, which is about 45 nm, is owing to the increased conjugation length in the polymer.²³

The UV-vis absorption data of the present monomer BTP and its polymer PBTP are summarized in Table I together with the corresponding data for the structurally related monomers (e.g., bithiophene (BT),²¹ 1,4-bis(2-thienyl)-benzene (BTB),¹¹ 2,6-bis(2-thienyl)naphthalene (2,6-BTN),¹³ and 1,3,6,8-tetrakis(2-thienyl)pyrene (TTP)²⁴) or their polymers (e.g., PBT, PBTB,

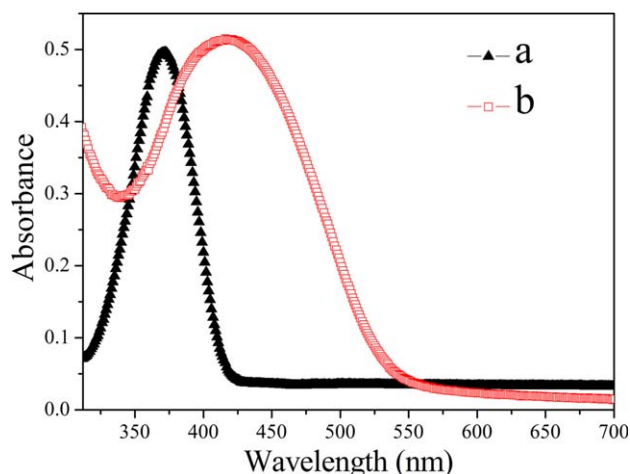


Figure 4. UV-vis spectrum: (a) BTP monomer dissolved in DCM; (b) PBTP film deposited on ITO electrode at the dedoped state. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and P(2,6-BTN)) for comparison. Monomer BTP shows red-shifted wavelength absorption maxima (λ_{max}) by 69–31 nm in comparison with monomer BT, BTB, and 2,6-BTN ($\lambda_{\text{max}} = 302$, 324, and 340 nm, respectively) due to its slightly more extended conjugation lengths. While, compared to molecule TTP (abs $\lambda_{\text{max}} = 406$ nm), monomer BTP demonstrated absorption maxima value that is significantly blue-shifted by 35 nm. In the corresponding polymers absorption, polymers PBTB and P(2,6-BTN) ($\lambda_{\text{max}} = 411$ and 400 nm, respectively) show slightly blue-shifts of 5–16 nm, whereas PBT shows red-shift by 30 nm as compared to PBTP. The PBT's red-shift relative to PBTP might be caused by the lower degree of conjugation of PBTP than that of PBT due to the incorporation of the rigid pyrene moieties into polymer main chains. The increase in the main-chain rigidity of PBTP than that of PBT would decrease the degree of polymerization and then the length of the conjugated chain (i.e., conjugation degree). Moreover, the optical band gaps (E_g) obtained from the absorption onsets (λ_{onset})²⁵ of the BTP and

PBTP were found to be 2.99 and 2.33 eV, respectively, which follow a same trend as λ_{max} discussed above when compared with the structurally related BT, BTB, 2,6-BTN and their polymers.

Finally, the onset oxidation potential (E_{onset}) of the aforementioned monomers and polymers as well as their respective HOMO/LUMO energy levels are also collected in Table I. It is also worth noting that monomer BTP reveals a lower E_{onset} (0.92 V) as compared to BT (1.11 V) and BTB (1.05 V) due to its extended conjugation length. HOMO energy levels of them were estimated by using the formula $E_{\text{HOMO}} = -e(E_{\text{onset}} + 4.4)$ (E_{onset} vs. SCE).²⁰ As shown in Table I, the HOMO level of the PBT, PBTB, and PBTP were calculated as -5.07 , -5.20 and -5.13 eV, respectively. The higher HOMO level could suggest an easier hole injection into films from ITO electrodes in electronic device applications. The LUMO energy levels of the PBT, PBTB, and PBTP were calculated from the values of the band gaps and HOMO energy levels to provide -3.09 , -2.89 , and -2.80 eV, respectively. The decrease of the LUMO energy levels from PBTP to PBT is attributed to the lower optical band gaps.

Electrochromic Properties of PBTP Film

Spectroelectrochemical Properties of PBTP Film. Spectroelectrochemistry is a useful method for studying the changes in the absorption spectra and the information about the electronic structures of conjugated polymers as a function of the applied voltage. The PBTP film coated ITO (prepared potentiostatically at +1.1 V, the active area was $0.9 \times 2.1 \text{ cm}^2$) is switched between 0 and +1.1 V in ACN/DCM (1 : 1, by volume) solution containing 0.2M NaClO₄ in order to obtain the *in situ* UV-vis spectra (Figure 5). At the neutral state, the polymeric film revealed an absorption peak at 416 nm due to the $\pi-\pi^*$ transition. Upon increase of the applied potential, the intensity of the PBTP $\pi-\pi^*$ electron transition absorption decreased while two charge carrier absorption bands located at around 705 nm and longer than 900 nm increased dramatically. The appearance of charge carrier bands could be attributed to the evolution of polaron and bipolaron bands.²⁶ Furthermore, the PBTP film

Table I. The Onset Oxidation Potential (E_{onset}), Maximum Absorption Wavelength (λ_{max}), HOMO, and LUMO Energy Levels and Optical Band Gap (E_g) of Monomer Bithiophene (BT), 1,4-Bis(2-thienyl)-benzene (BTB), 2,6-Bis(2-thienyl)naphthalene (2,6-BTN), 1,3,6,8-Tetrakis(2-thienyl)pyrene (TTP) and 1,6-Bis(2-thienyl)pyrene (BTP), and Their Corresponding Polymers, i.e. PBT, PBTB, and P(2,6-BTN) and PBTP

Compounds	E_{onset} , vs. (Ag-wire) (V)	λ_{max} (nm)	E_g^a (eV)	HOMO (eV)	LUMO ^b (eV)
BT ^{11,21}	1.11	302	3.63	-5.59	-1.96
BTB ¹¹	1.05	324	3.41	-5.53	-2.12
2,6-BTN ¹³	-	340	-	-	-
BTP	0.92	371	2.99	-5.35	-2.36
TTP ²⁴	-	406	2.58	-	-
PBT ^{11,21}	0.64	446	1.98	-5.07	-3.09
PBTB ¹¹	0.72	411	2.31	-5.20	-2.89
P(2,6-BTN) ¹³	-	400	2.5	-	-
PBTP	0.70	416	2.33	-5.13	-2.80

^a Calculated from the low energy absorption edge: $E_g = 1240/\lambda_{\text{onset}}$.

^b Calculated by the subtraction of the optical band gap from the HOMO level.

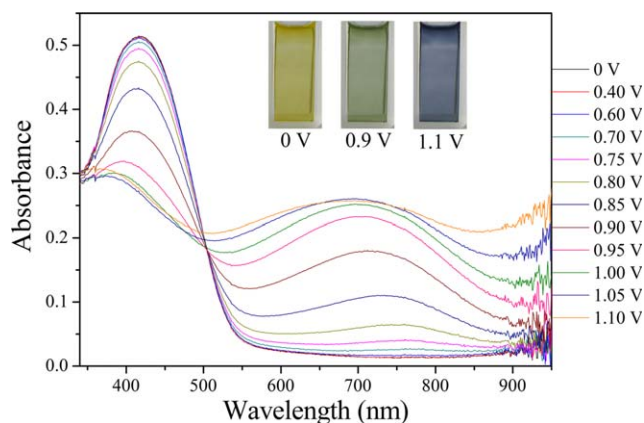


Figure 5. Spectroelectrochemical spectra of the PBTP film on ITO electrode as applied potentials between 0 and 1.1 V in monomer-free 0.2M NaClO₄/ACN/DCM solution. Inset: colors of polymeric film at different applied potentials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

showed three colors under various potentials. As shown in the insets of Figure 5, the film showed yellow to blue color change with an intermediate green color during the dedoping–doping process. This multicolor property makes PBTP a promising material for applications in smart windows or displays.

Electrochromic Switching of PBTP Film in Solution. The dynamic electrochromic experiment for PBTP film, which coated on ITO electrode (the active area was $0.9 \times 2.1 \text{ cm}^2$) with the polymerization charge of $2.8 \times 10^{-2} \text{ C}$ was carried out at visible region (700 nm) in ACN/DCM (1 : 1, by volume) solution containing 0.2M NaClO₄. The potential was interchanged between 0 V (the neutral state) and 1.1 V (the oxidized state) at regular intervals of 3 s. The electrochromic switching data of PBTP film are tabulated in Table II together with PBTB¹¹ and poly(1,4-bis(2-thienyl)naphthalene) (P(1,4-BTN))²⁷ films for comparison. One important characteristic of electrochromic materials is the optical contrast ($\Delta T\%$), which can be defined as the transmittance difference between the redox states. As depicted in Figure 6, the PBTP film reveals a stable color change between the redox states (yellow to blue) with an optical contrast ($\Delta T\%$) is calculated to be 29% at 700 nm, which is lower than that of PBTB film (yellow to green, 44.8% at 610 nm)¹¹ and higher with respect to P(1,4-BTN) (yellowish green to blue, 24% at 700 nm).²⁷ Response time, one of the most

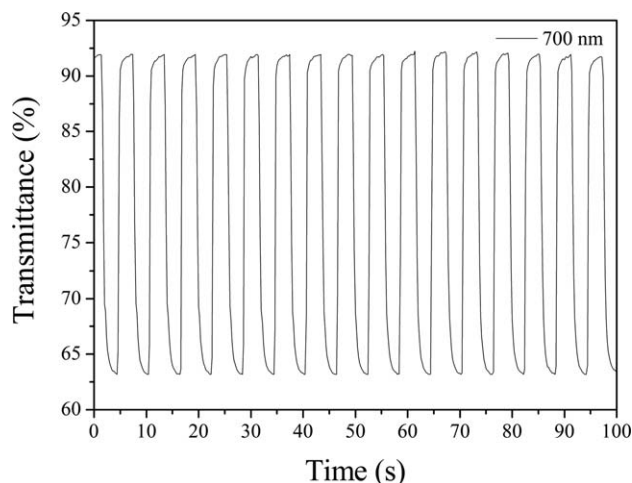


Figure 6. Electrochromic switching response for the PBTP film monitored at different wavelengths in 0.2M NaClO₄/ACN/DCM solution between 0 and 1.1 V with residence time of 3 s at 700 nm.

important characteristics of electrochromic materials, is the necessary time for 95% of the full optical switch (after which the naked eye could not sense the color change).²⁸ The optical response time of PBTP film was found to be 0.41 s for bleaching process and 1.30 s for coloring process, indicating its ease of charge transport from the dedoped to the doped state. The PBTP film exhibits a faster response time in comparison with that of the structurally similar polymer PBTB (1.6 s) and P(1,4-BTN) (1.78 s).

The coloration efficiency (CE) is also an important characteristic for the electrochromic materials. It is defined as the change in the optical density (ΔOD) for the charge consumed per unit electrode area (ΔQ).²⁹ The corresponding equations are given below:

$$\Delta OD = \lg\left(\frac{T_b}{T_c}\right) \text{ and } \eta = \frac{\Delta OD}{\Delta Q}$$

where T_b and T_c are the transmittances before and after coloration, respectively, and η denotes the CE. CE of PBTP film was measured as $100 \text{ cm}^2 \text{ C}^{-1}$ (at 700 nm) at full doped state, comparable to that obtained in conducting poly(bisthienyl-arylene) derivatives. Taking together these results suggest that PBTP films exhibit enough promising electrochromic characteristic under open conditions.

Table II. Electrochromic Switching Properties of PBTB, P(1,4-BTN), P(2,6-BTN), and PBTP

Materials	Optical contrast ($\Delta T\%$)	Response time (s)	Color efficiency ($\text{cm}^2 \text{ C}^{-1}$)	Color
PBTB	44.8% (610 nm)	1.6 (610 nm)	162	Yellow (r) Green (o)
P(1,4-BTN) ²⁷	48.4% (504 nm)	0.88 (504 nm)	-	Yellowish green (r)
	45.2% (770 nm)	0.84 (770 nm)	-	Blue (o)
P(2,6-BTN) ¹³	-	-	-	Transparent pale yellow (r)
				Opaque dark blue (o)
PBTP	29% (700 nm)	1.3 (700 nm)	100	Yellow (r) Blue (o)

r, reduced state; o, oxidized state.

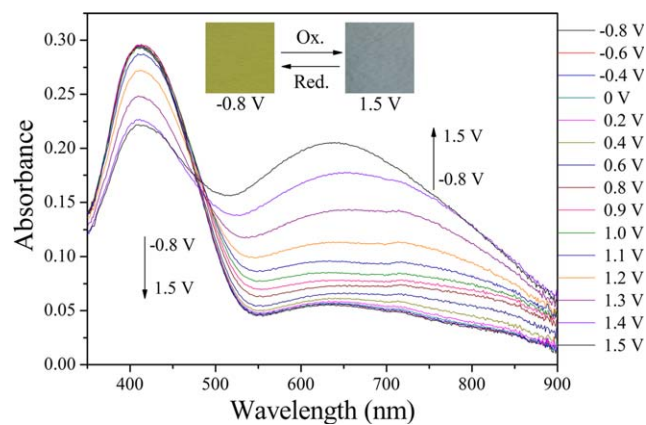


Figure 7. Spectroelectrochemical spectra of the PBTP/PEDOT device at various applied potentials from -0.8 to 1.5 V. Inset: the colors of the device at -0.8 V (the neutral state) and 1.5 V (the oxidized state). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Spectroelectrochemistry of Electrochromic Devices

Spectroelectrochemical Properties of ECDs. To investigate the electrochromic performance of BTP based polymers (PBTP) in ECDs, dual type complementary colored ECDs in glass/ITO/PBTP/PEDOT/ITO/glass configuration were constructed. The optoelectronic behaviors of the ECDs were investigated by the UV-vis spectrophotometer, while incrementally increasing the applied potential. Figure 7 shows the spectroelectrochemistry study of PBTP/PEDOT ECD between -0.8 and 1.5 V bias to anodically coloring layer. At -0.8 V, ECD revealed a well defined transition at 412 nm, which is in accordance with the spectral behavior of PBTP in neutral state. Since, this is a dual type device, at this point PEDOT layer is expected to be in its oxidized state showing no significant transition in visible region and hence the color of the ECD was yellowish green (Figure 7, inset). Upon stepwise increase of the applied potential to 1.5 V, a new band appeared at 634 nm due to the π - π^* transition of PEDOT in its reduced state, while the peak at 412 nm started to decrease, and thus, at this voltage, the color of the ECD was blue (Figure 7, inset).

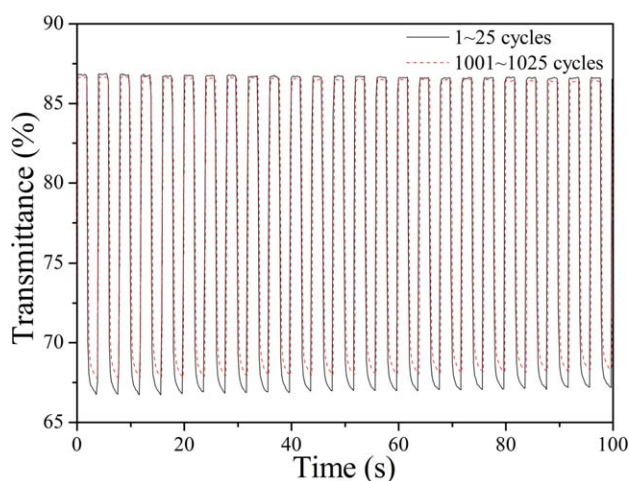


Figure 8. Electrochromic switching, optical transmittance change monitored at 625 nm for the PBTP/PEDOT device between -0.8 and 1.5 V with a residence time of 3 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

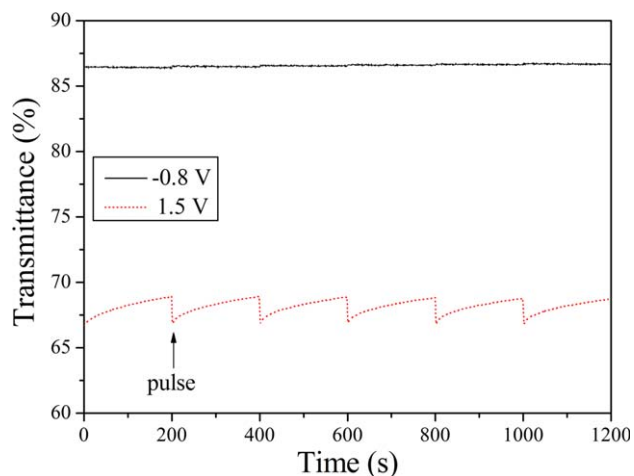


Figure 9. Open circuit stability of the PBTP/PEDOT device monitored at 625 nm.

Switching of ECD. Kinetic studies were also performed to test the percent transmittance changes and the response time of the PBTP/PEDOT ECD. Under a potential input of -0.8 and 1.5 V at regular intervals of 3 s, the optical response at 625 nm was illustrated in Figure 8. The optical contrast ($\Delta T\%$) was calculated to be 20% . The response time was found to be 0.62 s at 95% of the maximum transmittance difference from the neutral state to oxidized state and 0.38 s from the oxidized state to the neutral state. The PBTP/PEDOT device displays a higher optical contrast as compared to the P(1,4-BTN)/PEDOT device (10% and 0.57 s at 640 nm).²⁷ Moreover, the device has a reasonable CE, which was calculated to be 283 cm^2 C^{-1} at 625 nm. After 1000 cycles switching, the device kept working without significant loss in its performance. It was shown that the redox stability of device is quite high, retaining about 93% of its optical activity after 1000 th switch.

Open Circuit Memory of ECD. The optical memory in the ECDs is an important parameter, because it is directly related to its application and energy consumption during the use of ECDs.³⁰ The optical spectrum for the PBTP/PEDOT device was monitored at 600 nm as a function of time at -0.8 and 1.5 V

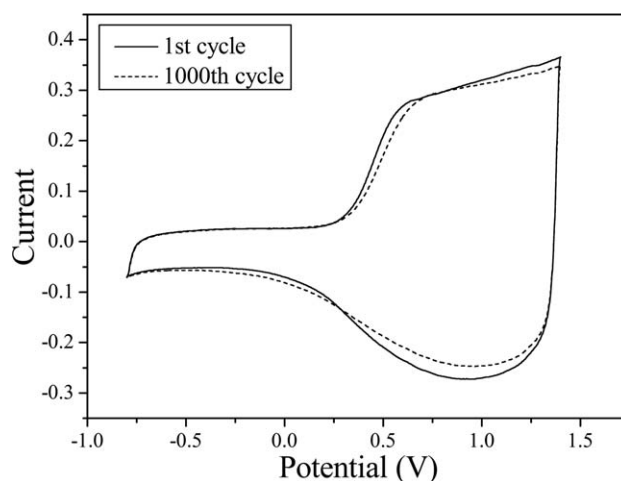


Figure 10. Cyclic voltammogram of the PBTP/PEDOT device as a function of repeated scans with 500 mV s^{-1} .

by applying the potential for 1 s for each 200 s time interval. As shown in Figure 9, in yellowish green colored state, the device showed a true permanent memory effect since there was not almost transmittance change under the applied potential or open circuit conditions. In blue colored state, the device was rather less stable in terms of color persistence; however, this matter can be overcome by applying current pulses to freshen the fully colored states.

Stability of ECD. The stability of the devices toward multiple redox switching usually limits the utility of electrochromic materials in ECD applications. Therefore, redox stability is another important parameter for ECD.³¹ For this reason, the PBTP/PEDOT device was tested by CV of the applied potential between -0.2 and 1.3 V with 500 mV s⁻¹ to evaluate the stability of the device (Figure 10). After 1000 cycles, 95.5% of its original electroactivity was retained accompanied by unperturbed color change from yellowish green to blue, which indicates that this device has good redox stability.

CONCLUSIONS

On the basis of CBP and BT is successfully synthesized by electrochemical oxidation of the monomers. A new copolymer PBTP was successfully synthesized by electrochemical oxidation of the monomer in mixture of ACN/DCM (1 : 1, by volume) solution containing 0.2 M. The obtained polymeric film was studied by CV, UV-vis spectra, and SEM. According to the spectroelectrochemical analyses, the PBTP film has distinct electrochromic properties and presents three different colors (yellow, green, and blue) under different voltages. Maximum contrast ($\Delta T\%$) and response time of the PBTP film were measured as 29% and 1.3 s at 700 nm. The dual type ECD based on PBTP and PEDOT was also constructed and characterized. Electrochromic switching study results show that optical contrast ($\Delta T\%$) and response time are 20% and 0.62 s at 625 nm, respectively. The CE of the ECD was calculated to be 283 cm² C⁻¹. This ECD also shows reasonable redox stability with unperturbed color change from yellowish green to blue. In light of the excellent features above, the PBTP could be a good candidate as an anodic electrochromic material.

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