

Electrosyntheses, Characterizations and Electrochromic Properties of a Novel Copolymer of 4,4'-di(N-Carbazoyl)Biphenyl with 4H-Cyclopenta[2,1-b:3,4-b']Dithiophene

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P(CBP-co-CPDT), a novel copolymer, was successfully achieved by electrochemical oxidation of the monomer mixtures of 4,4'-di(N-carbazoyl)biphenyl (CBP) and 4H-cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) in acetonitrile/ dichloromethane (1:1, by volume) solution containing 0.2 M NaClO₄ as a supporting electrolyte. Characterizations of the resulting polymer P(CBP-co-CPDT) were performed by cyclic voltammetry (CV), UV-vis spectroscopy, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The P(CBP-co-CPDT) film had distinct electrochromic properties and exhibited four different colors (reddish brown, blue, sap green and greenish blue) under various potentials. Maximum contrast ($\Delta T\%$) and response time of the copolymer film were measured as 26.2% and 0.32 s at 430 nm. An electrochromic device (ECD) based on P(CBP-co-CPDT) and poly(3,4-ethylenedioxythiophene) (PEDOT) was also constructed and characterized. The optical contrast ($\Delta T\%$) was found to be 39.8% with a response time of 0.36 s at 628 nm. The coloration efficiency (CE) of the device was calculated to be 319.98 cm² C⁻¹ at 628 nm.

Keywords: π -conjugated polymers; 4,4'-di(N-carbazoyl)biphenyl; Cyclopenta[2,1-b:3,4-b']dithiophene; Spectroelectrochemistry; Electrochromic devices

1. INTRODUCTION

Electrochromism is defined as the property inherent in some materials which enable them to electrochemically switch between different colored states as a result of oxidation-reduction reaction

[1]. Recently, Electrochromic (EC) polymers have drawn a lot of attentions due to their outstanding coloration efficiency, fast switching times, multiple colorations with the same material, fine-tunability of the band gap (and the color), high stability, thin film flexibility and cost effectiveness [2-7]. These polymers have various application areas such as polymer light-emitting diodes (LEDs) [8], sensors [9], actuators [10], solar cells [11], electrochromic devices [12-15], and so on.

Copolymerization is an easy, facile method to control the electrochromic properties of conducting polymers. This procedure allows one to obtain materials with controlled properties without suffering the experimental disadvantages associated to the preparation of new homopolymers, i.e. complex synthetic routes to develop sophisticated monomers [16]. Thus, copolymerization of distinct monomers or homopolymerization of hybrid monomers containing several distinct units can lead to interesting combination of the properties observed in the corresponding homopolymers [17].

Among conjugated polymers, carbazole-containing polymers deserve a great attention owing to high thermal and photochemical stability, easily forming stable polarons (radical cations), photoconductivity and electrochromic properties [18-21]. Recently, the electrochromic properties of poly(4,4'-di(N-carbazoyl)biphenyl) (PCBP) are studied by Sermet Koyuncu et al. [22]. PCBP films exhibit reasonable electrochromic characters, but the electropolymerization of the monomer come into being oligomer films and the stability of the electrochromic devices are not very well. Meanwhile, 4H-cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) and its derivatives, which have strong electron donating properties as kinds of the fused aromatic rings, have attracted great attention owing to the possibility of forming homopolymers, copolymers with narrower band gaps [23-26]. Therefore, it is expected that the introduction of 4H-cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) units into the main chain of PCBP might achieve a tunable band-gap polymer, which may be greatly helpful in preparing high quality electronic materials.

According to above considerations, we successfully synthesized copolymers based on 4,4'-di(N-carbazoyl)biphenyl (CBP) and 4H-cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) via the electrochemical oxidation of CBP/CPDT mixtures. The obtained copolymers were investigated by cyclic voltammetry (CV) and characterized by FT-IR and UV-vis. The electrochromic, spectroelectrochemical properties and morphology of the copolymer were also investigated. The copolymer had four different colors (reddish brown, blue, sap green and greenish blue). In addition, we constructed and characterized dual type electrochromic devices based on P(CBP-co-CPDT) and PEDOT in details.

2. EXPERIMENTAL

2.1. Materials

4,4'-di(N-carbazoyl)biphenyl (CBP, Tokyo Chemical Industry CO., LTD, Japan), 4H-cyclopenta[2,1-b:3,4-b']dithiophene (CPDT, Trademax Pharmaceuticals & Chemicals Co., Shanghai, China, 98%), commercial high-performance liquid chromatography grade acetonitrile (ACN, Tedia Company, INC., USA), dichloromethane (DCM, Sinopharm Chemical Reagent CO., LTD, China) and

3,4-ethylenedioxythiophene (EDOT, Aldrich, 98%), were all used as received without further treatment. poly(methyl methacrylate) (PMMA), propylene carbonate (PC), Lithium perchlorate (LiClO_4) and Sodium perchlorate (NaClO_4) were all obtained from Shanghai Chemical Reagent Company, China. LiClO_4 and NaClO_4 were dried in vacuum at 60 °C for 24 h before use. Indium-tin-oxide-coated (ITO) glass (Sheet resistance : $< 10 \Omega \square^{-1}$, purchased from Shenzhen CSG Display Technologies, China) was washed with ethanol, acetone and deionized water successively under ultrasonic, and then dried by N_2 flow.

2.2. Electrochemistry

Electrochemical syntheses and experiments were performed in a one-compartment cell with a CHI 760 C Electrochemical Analyzer (Shanghai ChenHua Instrument Co. China) under computer control, employing a platinum wires with a diameter of 0.5 mm as working electrode, a platinum ring as counter electrode, and a silver wire as pseudo reference electrode. The working and counter electrodes for cyclic voltammetric experiments were placed 0.5 cm apart during the experiments. All of the electrochemical experiments were carried out at room temperature under nitrogen atmosphere. All electrochemical polymerization and CV tests were taken in ACN/DCM (1:1, by volume) containing 0.2 M NaClO_4 as a supporting electrolyte. The pseudo reference electrode was calibrated externally using a 5 mM solution of ferrocene (Fc/Fc^+) in the electrolyte ($E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.25 \text{ V vs. Ag wire}$ in ACN/DCM (1:1, by volume) solution containing 0.2 M NaClO_4 and all the potentials mentioned follow were vs. the Ag wire electrode. The half-wave potential ($E_{1/2}$) of Fc/Fc^+ measured in ACN/DCM (1:1, by volume) solution containing 0.2 M NaClO_4 was 0.28 V vs. SCE. Thus, the potential of Ag wire was assumed to be 0.03 V vs. SCE. All of the electrochemical experiments were carried out at room temperature under nitrogen atmosphere.

2.3. Characterizations

The obtained copolymer films were studied by cyclic voltammetry. UV–vis spectra were carried out on a Perkin-Elmer Lambda 900 UV–vis–near-infrared spectrophotometer. FT-IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer, where the samples were dispersed in KBr pellets. Scanning electron microscopy (SEM) measurements were taken by using a Hitachi SU-70 thermionic field emission SEM. Digital photographs of the polymer films were taken by a Canon Power Shot A3000 IS digital camera.

2.4. Spectroelectrochemistry

Spectroelectrochemical data was recorded on Perkin-Elmer Lambda 900 UV–vis–near-infrared spectrophotometer connected to a computer. A three-electrode cell assembly was used where the working electrode is an ITO glass, the counter electrode was a stainless steel wire, and an Ag wire was used as pseudo-reference electrode. The copolymer films for spectroelectrochemistry were prepared by

potentiostatically deposition on ITO electrode (the active area: $0.9 \text{ cm} \times 2.0 \text{ cm}$). The measurements were carried out in ACN/DCM (1:1, by volume) solution containing 0.2 M NaClO_4 .

2.5. Preparation of the gel electrolyte

A gel electrolyte based on PMMA (MW: 350.000) and LiClO_4 was plasticized with PC to form a highly transparent and conductive gel. ACN was also included as a high vapor pressure solvent to allow an easy mixing of the gel components. The composition of the casting solution by weight ratio of ACN: PC: PMMA: LiClO_4 is 70:20:7:3. The gel electrolyte was used for construction of the polymer electrochromic device cell [2].

2.6. Construction of electrochromic devices

Electrochromic devices (ECDs) were constructed using two complementary polymers, namely P(CBP-co-CPDT) as the anodically coloring material and PEDOT as the cathodically coloring material. The P(CBP-co-CPDT) and PEDOT films were electrodeposited on two ITO glasses (the active area: $1.8 \text{ cm} \times 2.0 \text{ cm}$) at 1.3 and 1.4 V, respectively. Electrochromic device was built by arranging the two polymer films (one oxidized, the other reduced) facing each other separated by a gel electrolyte.

3. RESULTS AND DISCUSSION

3.1 Electrochemical polymerization and characterizations

3.1.1. Electrochemical polymerization

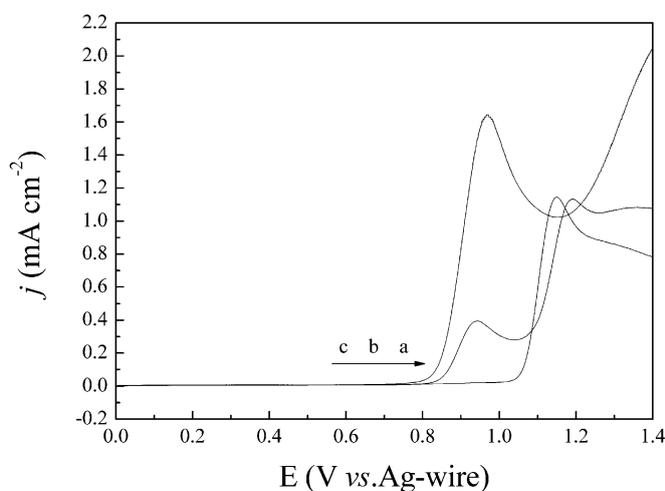
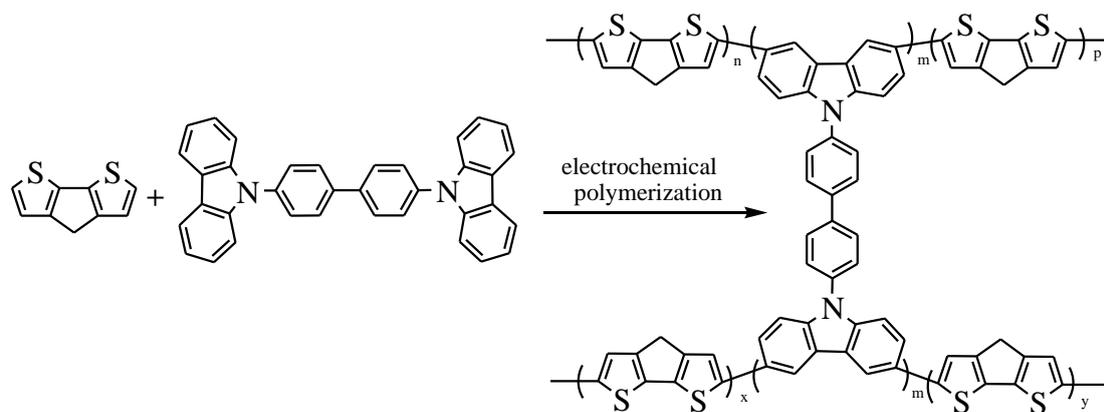


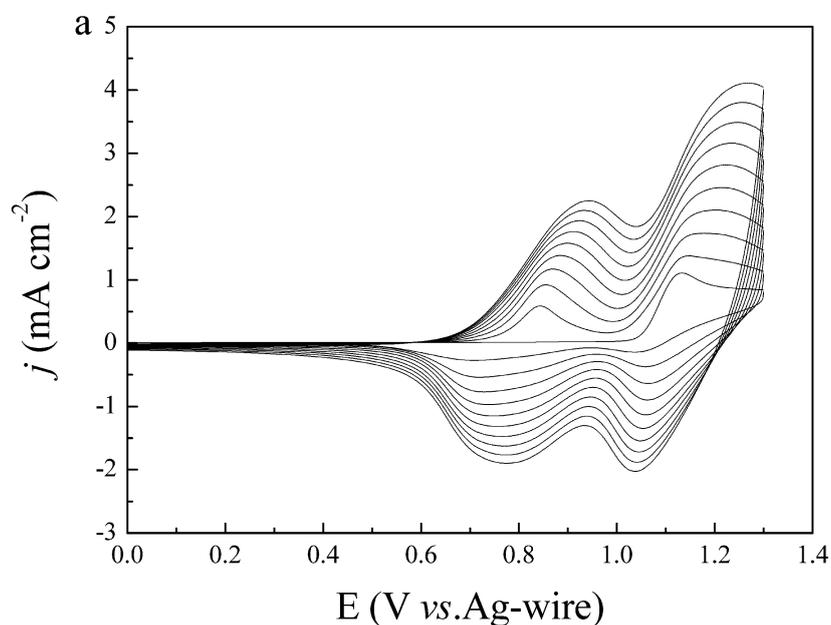
Figure 1. Anodic polarization curves of (a) 0.002 M CBP , (b) 0.002 M CBP and 0.002 M CPDT , (c) 0.002 M CPDT in in ACN/DCM containing 0.2 M NaClO_4 at a scan rates of 100 mV s^{-1} . j denotes the current density, E denotes the potential.



Scheme 1. Synthetic route of the copolymer of CBP and CPDT.

The anodic polarization curves of 0.002 M CBP and 0.002 M CPDT in ACN/DCM (1:1, by volume) solution containing 0.2 M NaClO₄ are shown in Fig. 1. The onset oxidation potential (E_{onset}) of CBP and CPDT in the solution are approximately +1.05 V (Fig. 1a) and +0.82 V (Fig. 1c), respectively. As can be seen from Fig. 1b, the E_{onset} of the CBP/CPDT at 1:1 mixture is +0.85 V, which is intervenient between that of CBP and CPDT, indicating the existence of the interaction between two monomers in ACN/DCM (1:1, by volume) solution containing 0.2 M NaClO₄. The synthetic route of the copolymer of CBP and CPDT is illustrated in Scheme 1.

Fig. 2 displays the successive cyclic voltammogram (CV) curves of 0.002 M CBP, 0.002 M CPDT and the CBP/CPDT mixture at 1:1 (0.002 M CBP and 0.002 M CPDT) in ACN/DCM (1:1, by volume) containing 0.2 M NaClO₄ at a potential scan rate of 100 mV s⁻¹. As the CV scan continued, polymer films are formed on the working electrode surface. The increase in the redox wave current densities implies that the amount of conducting polymers deposited on the electrode is increasing [27].



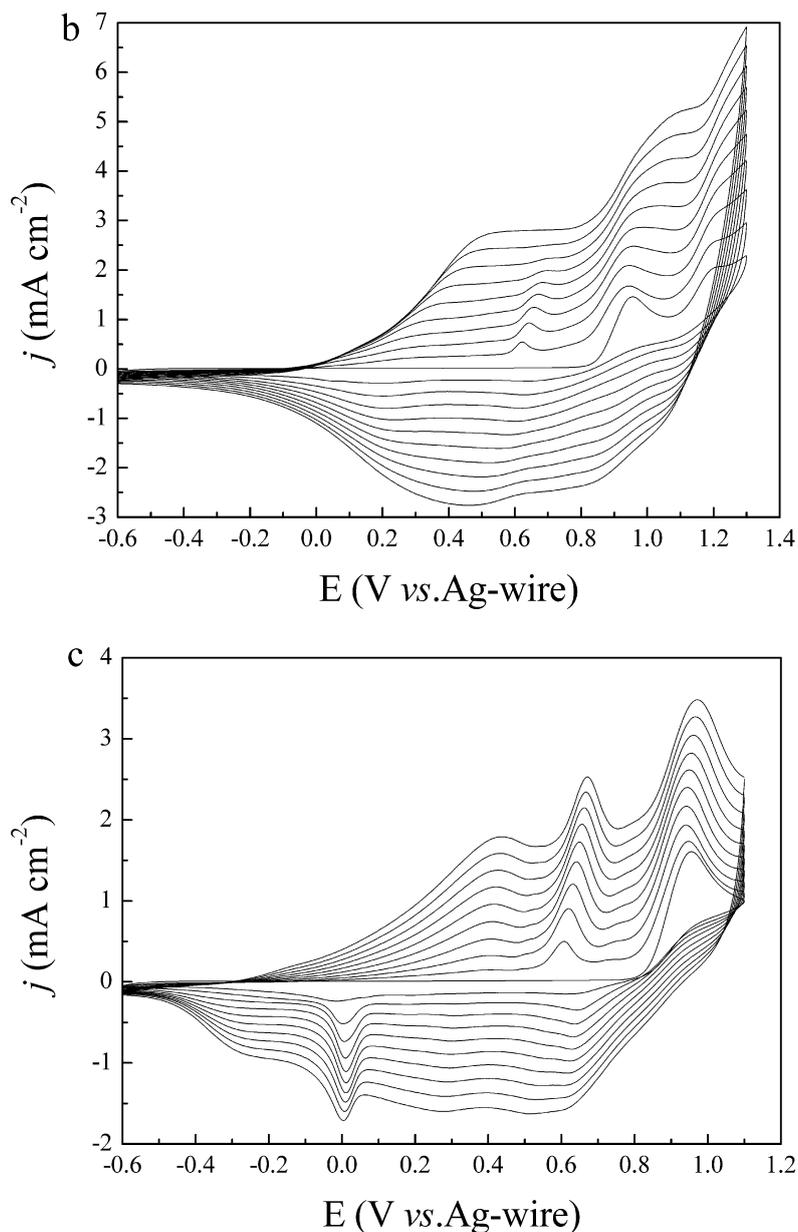


Figure 2. Successive CV curves of (a) 0.002 M CBP, (b) the mixture of 0.002 M CBP and 0.002 M CPDT, (c) 0.002 M CPDT in ACN/DCM containing 0.2 M NaClO₄. Scanning rates: 100 mV s⁻¹. j denotes the current density.

As shown in Fig. 2(a), the polymerization of CBP shows two reversible redox processes, the oxidation and reduction peaks of the first redox process appears at +0.94 V and +0.77 V, respectively. The reduction peak of the second redox process is located at +1.04 V, and the corresponding oxidation peak is overlapped with the oxidation waves of the CBP monomer [28]. The CV curves of CPDT show two oxidation peak at +0.67 V and +0.97 V, respectively. And a reduction peak is observed at +0 V (Fig. 2(c)). However, the CV curves of the CBP/CPDT mixture at 1:1 exhibit an anodic peak and a cathodic peak approximately at +1.1 V and +0.47 V, respectively (Fig. 2(b)), which is different from those of CBP and CPDT, indicating the formation of a new polymer consisting of both CBP and CPDT units.

3.1.2. Electrochemistry of the P(CBP-co-CPDT) film

Fig. 3(a) shows the CV curves of the copolymer (prepared with the feed ratio of CBP/CPDT at 1:1 on platinum wire by sweeping the potentials from -0.6 V and $+1.3$ V) at different scanning rates between 25 and 300 mV s^{-1} in a monomer-free solution of ACN/DCM (1:1, by volume) containing 0.2 M NaClO_4 . The copolymer film exhibits two reversible redox processes. The peak current densities (j) are proportional to the potential scan rates (Fig. 3(b)), indicating that the copolymer film is electroactive and adheres well to the electrode [29]. This also demonstrates that the electrochemical processes of the copolymer are reversible and not diffusion limited [30].

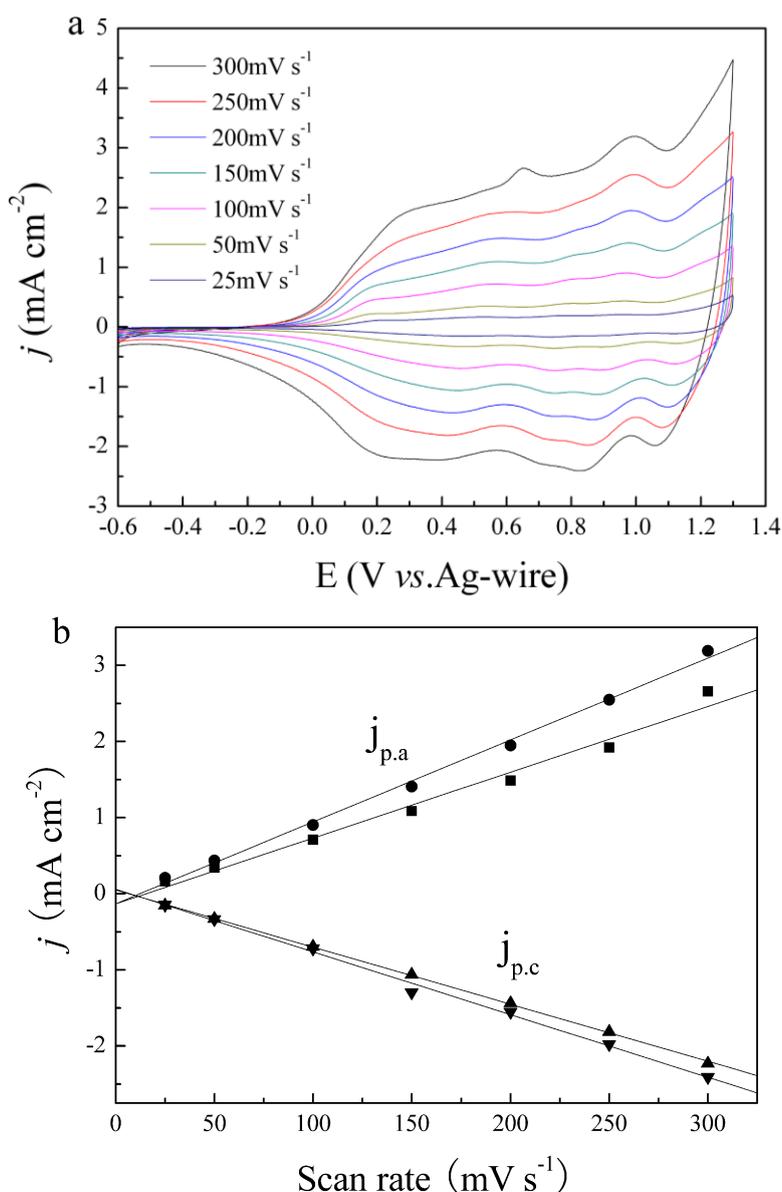


Figure 3. (a) CV curves of the copolymer at different scan rates in the monomer-free solution of ACN/DCM containing 0.2 M NaClO_4 . (b) scan rate dependence of the anodic and cathodic peak current densities graph. $j_{p.a}$ and $j_{p.c}$ denote the anodic and cathodic peak current densities, respectively.

3.1.3. FT-IR spectra of polymers

PCBP, PCPDT and P(CBP-co-CPDT) prepared potentiostatically were analyzed by FT-IR spectra, as shown in Fig. 4. In the spectrum of PCBP (Fig. 4a), the peak at 1228 cm^{-1} indicates the existence of C–N signals in PCBP [28]. According to the spectrum of PCPDT (Fig. 4c), the peak at 1633 cm^{-1} was due to C=C stretching vibration of thiophene ring and the 810 cm^{-1} band reflects the stretching mode of C–S. And, the absorption bands at 989 and 943 cm^{-1} can be assigned to the pentadiene groups [31]. The FT-IR spectrum of P(CBP-co-CPDT) (Fig. 4b) contains the characteristic peaks of both PCBP and PCPDT. Compared with corresponding homopolymers, the band at 1633 cm^{-1} in the spectrum of the copolymer originates from C=C stretching vibration of thiophene ring of PCPDT, indicating the presence of CPDT units in the copolymer. Meanwhile, the band at 1228 cm^{-1} can also be found, which is ascribed to the C–N bonds in the PCBP. All the above features indicate that copolymer contains both CBP and CPDT units.

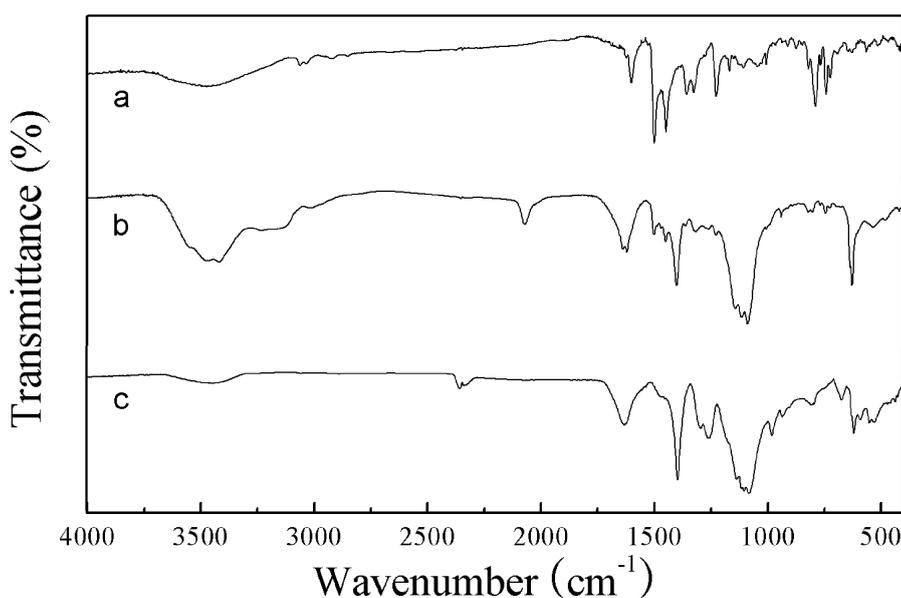


Figure 4. FT-IR spectra of (a) PCBP, (b) copolymer and (c) PCPDT in ACN/DCM solution containing 0.2 M NaClO_4 , respectively.

3.1.4. Morphology

The morphologies of polymer films were investigated by scanning electron microscopy (SEM). Fig. 5 gives the SEM images of PCBP, P(CBP-co-CPDT) and PCPDT, which were prepared on ITO electrodes potentiostatically and dedoped before characterization. As shown in Fig. 5a, PCBP shows a cohesive structure with clusters of granules. PCPDT has granular particle clusters with more porous structure. (Fig. 5c). However, the morphology of P(CBP-co-CPDT) film is circular filamentous structure like a straw mat (Fig. 5b). The difference of morphology between copolymer and homopolymers also confirms the occurrence of copolymerization between CBP and CPDT units.

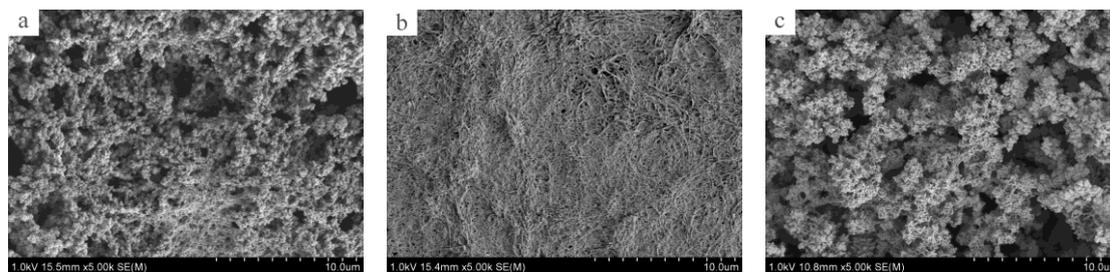


Figure 5. SEM images of (a) PCBP, (b) P(CBP-co-CPDT) and (c) PCPDT deposited potentiostatically on ITO electrode.

3.1.5. UV-vis spectra of polymers

Fig. 6 depicts the UV-vis spectra of dedoped (a) PCBP, (b) P(CBP-co-CPDT) and (c) PCPDT deposited on ITO electrode (the active area: $0.9 \text{ cm} \times 2.0 \text{ cm}$) with the same polymerization charge ($3.2 \times 10^{-2} \text{ C}$). As can be seen from Fig. 6, the UV-vis spectrum of PCBP film shows the π - π^* electron transition peak at about 339 nm (Fig. 7a), while the PCPDT film exhibits a much broader absorption at around 550 nm and a weak shoulder at 377 nm (Fig. 6c). On the other hand, the spectrum of the P(CBP-co-CPDT) shows both the characteristic absorptions of PCBP and PCPDT, which are located at 355 and 428 nm, respectively (Fig. 6b). The former has a slight red-shift about 16 nm of the main absorption of copolymer film in contrast to that of pure PCBP due to the incorporation unit of CPDT, further confirming the occurrence of copolymerization [32].

It has been well known that conjugated polymers are promising materials for electrochromic applications, the colors of polymers films on ITO at dedoped and doped states were also recorded, as shown in the insets of Fig. 6. As can be seen from Fig. 6, PCBP is a light yellow color in dedoped state at +0 V and light green color in the doped state at +1.3 V (Fig. 6A and Fig. 6A'). PCPDT displays a purple in its dedoped state at -0.6 V and gray polymer in its doped state at +1.1 V (Fig. 6C and Fig. 6C'), respectively. However, P(CBP-co-CPDT) changes color from reddish brown in the dedoped state (Fig. 6B) at -0.6 V to greenish blue in the doped state (Fig. 6B') at +1.3 V. The electrochromism phenomenon of the P(CBP-co-CPDT) is significantly different from those of two individual homopolymers, further confirming the formation of copolymer consisting of both CBP and CPDT units.

Besides, the optical band gap (E_g) of polymer was deduced from the absorption band edges (λ_{onset}). The E_g of the P(CBP-co-CPDT) film was calculated as 1.91 eV, which was lower than that of PCBP (3.22 eV) and higher than that of PCPDT (1.68 eV). The effect of copolymerization between CBP and CPDT leads to an obvious decrease in the E_g comparing with that of PCBP, which implied that the introduction of CBP units into PCPDT can tune the E_g of the copolymer.

Table 1 summarizes the onset oxidation potential (E_{onset}), maximum absorption wavelength (λ_{max}), low energy absorption edges (λ_{onset}), HOMO and LUMO energy levels and the optical band gaps (E_g) values of PCBP, PCPDT and the copolymers (prepared with the feed ratio of PCBP/PCPDT at 1:1) quite clearly. HOMO energy levels of them are calculated by using the formula $E_{\text{HOMO}} =$

$-e(E_{onset} + 4.43)$ (vs. SCE) and LUMO energy levels (E_{LUMO}) of them are calculated by the subtraction of the optical band gap (E_g) from the HOMO levels.

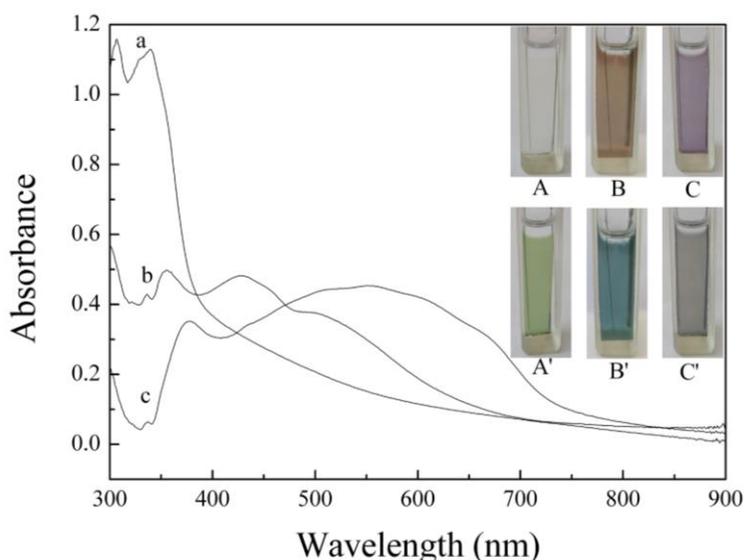


Figure 6. UV-vis spectra of dedoped (a) PCBP, (b) P(CBP-co-CPDT) and (c) PCPDT deposited on ITO at the neutral state. Insets: (A) light yellow color, (B) reddish brown, (C) purple, and (A') light green color, (B') greenish blue, (C') gray of PCBP, P(CBP-co-CPDT) and PCPDT, respectively.

Table 1. The onset oxidation potential (E_{onset}), maximum absorption wavelength (λ_{max}), low energy absorption edges (λ_{onset}), HOMO and LUMO energy levels and optical band gap (E_g) values of PCBP, PCPDT, and the copolymers (prepared with the feed ratio of CBP/CPDT at 1:1).

Compounds	E_{onset} , vs. (Ag-wire) (V)	λ_{max} (nm)/ λ_{onset} (nm)	E_g (eV)	HOMO (eV)	LUMOb (eV)
PCBP	0.74	339/385	3.22	-5.17	-1.95
P(CBP-co-CPDT)	0.05	355/649	1.91	-4.48	-2.57
PCPDT	-0.08	550/740	1.68	-4.35	-2.67

^aCalculated from the low energy absorption edges (λ_{onset}).

^bCalculated by the subtraction of the optical band gap (E_g) from the HOMO level.

3.2. Electrochromic properties of P(CBP-co-CPDT) film

3.2.1 Spectroelectrochemical properties of P(CBP-co-CPDT) 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 [33]. The P(CBP-co-CPDT) film coated ITO (prepared potentiostatically at +1.3 V) was switched between -0.6 V and +1.3 V in ACN/DCM (1:1, by volume) solution containing 0.2 M

NaClO₄ in order to obtain the in situ UV–vis spectra (Fig. 7). At the neutral state, the copolymer film exhibits two absorption bands at 353 and 429 nm due to the π - π^* transition. As shown in Fig. 7, the intensity of the P(CBP-co-CPDT) π - π^* electron transition absorption decreases while two charge carrier absorption bands located at around 700 nm and more than 900 nm increase dramatically upon oxidation. The appearance of charge carrier bands can be attributed to the evolution of polaron and bipolaron bands [28].

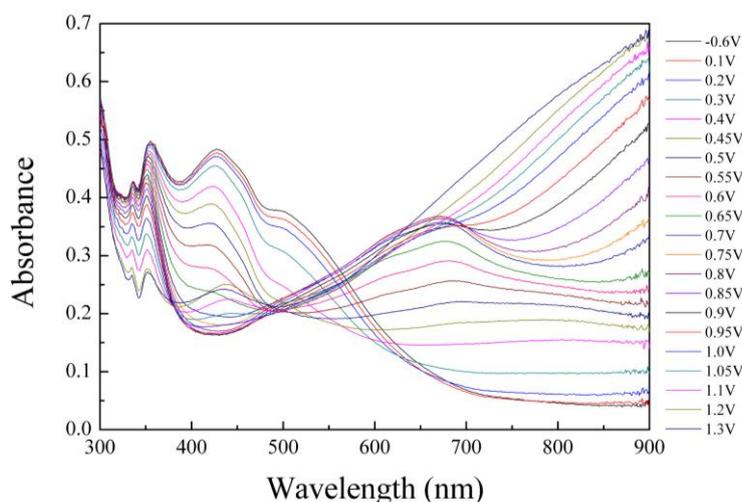


Figure 7. Spectroelectrochemical spectra of P(CBP-co-CPDT) films on ITO electrode as applied potentials in ACN/DCM solution containing 0.2 M NaClO₄

While there are many methods to quantify and represent color, one of the most widely applicable to measuring color of materials illuminated by a standard light source is the 1976 CIE LAB (or L*a*b*) with the value of L* representing how light versus dark the measured material is, the value a* representing how red versus green, and b* representing how yellow versus blue the material is [33]. The P(CBP-co-BT) has distinct electrochromic properties.

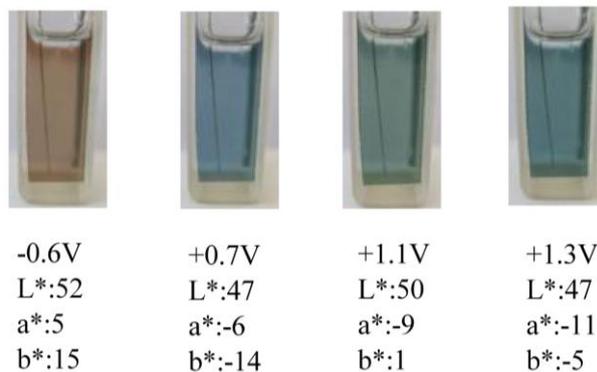


Figure 8. Colors and corresponding L*, a*, b* values of the P(CBP-co-CPDT) film at different applied potentials.

The P(CBP-co-CPDT) has distinct electrochromic properties. It shows four different colors in neutral and oxidized states. The reddish brown color of the film at neutral state (-0.6 V) turns into blue color (+0.7 V) and sap green (+1.1 V) at intermedia doped state, and then into greenish blue color at full doped state (+1.3 V). These colors and corresponding L, a, b values are given in Fig. 8.

3.2.2 Electrochromic switching of P(CBP-co-CPDT) film in solution

It is important that polymers can switch rapidly and exhibit a noteworthy color change for electrochromic applications [34]. For this purpose, double potential step chronoamperometry technique is used to investigate the switching ability of P(CBP-co-CPDT) film between its neutral and full doped state (Fig. 8) [35]. The dynamic electrochromic experiment for P(CBP-co-CPDT) film was carried out at 430 nm. The potential was interchanged between - 0.6 V (the neutral state) and + 1.2 V (the oxidized state) at regular intervals of 5 s. One important characteristic of electrochromic materials is the optical contrast ($\Delta T\%$), which can be defined as the transmittance difference between the redox states. The $\Delta T\%$ of the P(CBP-co-BT) is found to be 26.2% at 430 nm, as shown in Fig.9.

The coloration efficiency (CE) is also an important characteristic for the electrochromic materials. CE can be calculated by using the equations and given below [36]:

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

where T_b and T_c are the transmittances before and after coloration, respectively. ΔOD is the change of the optical density, which is proportional to the amount of created color centers. η denotes the coloration efficiency (CE). ΔQ is the amount of injected charge per unit sample area. CE of P(CBP-co-CPDT) film is measured as $96.73 \text{ cm}^2 \text{ C}^{-1}$ (at 430 nm) at full doped state, respectively.

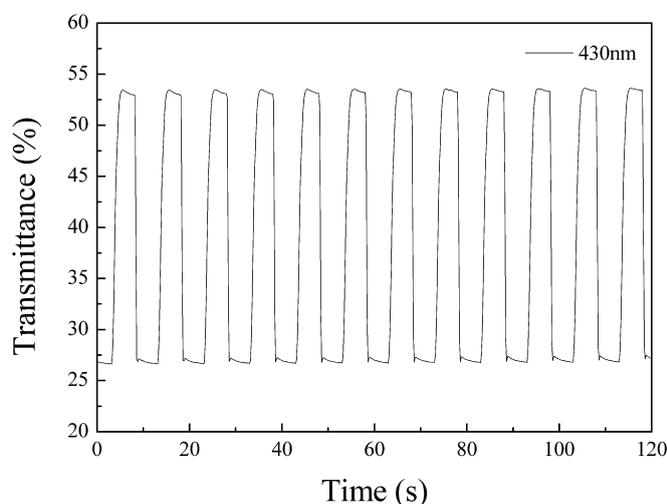


Figure 9. Electrochromic switching, optical response for P(CBP-co-CPDT) at 430 nm by applying potentials between -0.6 V and +1.30 V with a residence time of 5 s.

Response time, one of the most important characteristics of electrochromic materials, is the time needed to perform a switching between the neutral state and oxidized state of the materials [37]. The response required to attain 95% of total transmittance difference is found to be 1.4 s from the reduced to the oxidized state and 0.32 s from the oxidized to the reduced state. Compared to PCBP homopolymer film reported by Sermet Koyuncu et al. [22], the copolymer P(CBP-co-CPDT) film has high optical contrast and fast response time which might be attributed to the introduction of CPDT units into the polymer backbone.

3.3. Spectroelectrochemistry of electrochromic devices (ECDs)

3.3.1 Spectroelectrochemical properties of ECD

A dual type ECD consisting of P(CBP-co-CPDT) and PEDOT constructed and its spectroelectrochemical behaviors were also studied. Before composing the ECD, the anodically coloring polymer film (P(CBP-co-CPDT)) was fully reduced and the cathodically coloring polymer (PEDOT) was fully oxidized. The P(CBP-co-CPDT)/PEDOT device was switched between -0.8 V and $+1.7$ V. As the applied potential increased, the P(CBP-co-CPDT) layer started to be oxidized while PEDOT layer was reduced, which led to a new absorption at 628 nm (Fig.10).

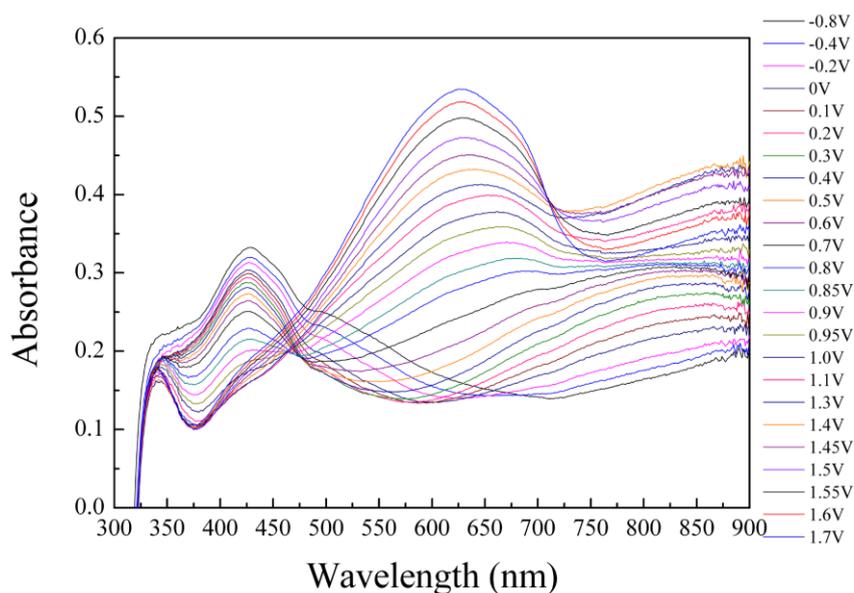


Figure 10. Spectroelectrochemical spectra and the colors of P(CBP-co-CPDT)/PEDOT device at various applied potentials

3.3.2. Switching of ECD

Kinetic studies were also done to test the response time of P(CBP-co-BT)/PEDOT ECD. Under a potential input of 0 and $+1.6$ V at regular intervals of 4 s, the optical response at 628nm, as illustrated

in Fig. 11. The response time is found to be 0.58 s at 95% of the maximum transmittance difference from the neutral state to oxidized state and 0.36 s from the oxidized state to the neutral state, and optical contrast ($\Delta T\%$) is calculated to be 39.8%. The P(CBP-co-CPDT)/PEDOT device has higher optical contrast and faster response time compared with those of PCBP/PEDOT device [22]. The CE of the device (the active of area: $1.8 \text{ cm} \times 2.5 \text{ cm}$) is calculated to be $319.98 \text{ cm}^2 \text{ C}^{-1}$ at 628 nm.

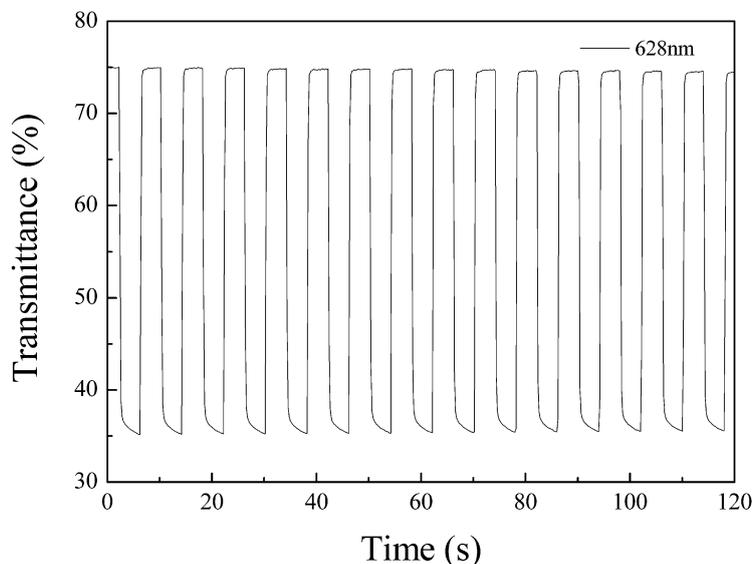


Figure 11. Electrochromic switching, optical response for P(CBP-co-CPDT)/PEDOT device at 628 nm (visible region) by applying potentials between 0 V (the neutral state) and +1.3 V (the oxidized state) with a residence time of 4 s.

3.3.3 Open circuit memory of ECD

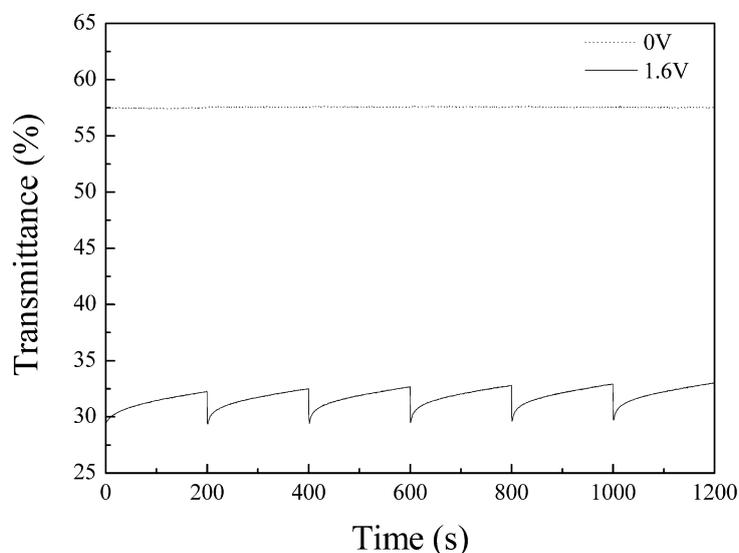


Figure 12. Open circuit stability of the (PCBP-co-PCPDT)/PEDOT device monitored at 628 nm.

The optical memory in the electrochromic devices is an important parameter because it is directly related to its application and energy consumption during the use of ECDs [37]. The optical spectrum for P (CBP-co-CPDT)/PEDOT device was monitored at 700 nm as a function of time at 0 V and +1.6 V by applying the potential for 1 s for each 200 s time interval. As shown in Fig. 12, it shows a true permanent memory effect since there is almost no transmittance change under applied potential or open circuit conditions at 0 V. It is rather less stable in terms of color persistence at +1.6 V, however this matter can be overcome by application of current pulses to freshen the fully colored states.

3.3.4 Stability of the 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 [37]. For this reason, the P(CBP-co-CPDT)/PEDOT device was tested by cyclic voltammetry of the applied potential between -0.8 V and $+1.6$ V with 500 mV s^{-1} to evaluate the stability of the device (Fig. 13). After 500 cycles, 89.55% of its electroactivity is retained and there is no obvious decrease of activity between 500 cycles and 1000 cycles. These results show that this device has good redox stability.

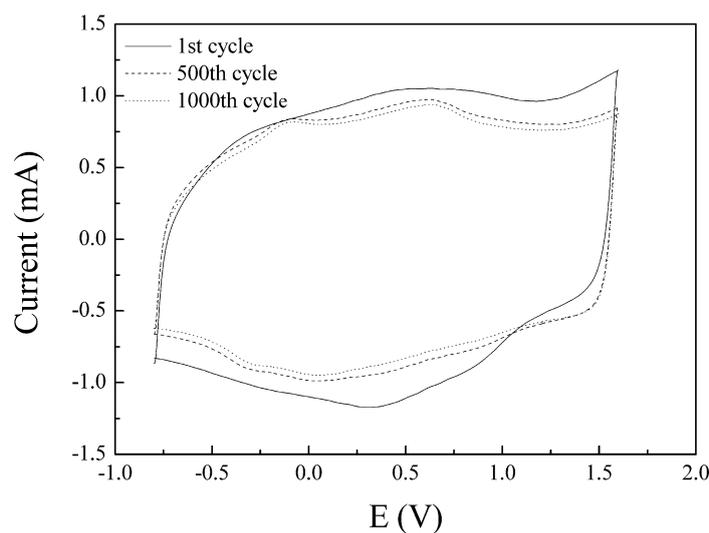


Figure 13. Cyclic voltammogram of P(CBP-co-CPDT)/PEDOT device as a function of repeated with a scan rate of 500 mV s^{-1} .

4. CONCLUSION

A new copolymer based on CBP and CPDT was successfully synthesized by electrochemical oxidation of the monomers mixture in ACN/DCM (1:1, by volume) solution containing 0.2 M NaClO_4 .

Cyclic voltammetry, UV–vis, FT-IR analyses and scanning electron microscopy confirmed that the resulting polymer was a copolymer rather than a blend or a composite of the respective homopolymers. According to the spectroelectrochemical analyses, the copolymer film had distinct electrochromic properties and showed four different colors (reddish brown, blue, sap green and greenish blue) under various potentials. Maximum contrast ($\Delta T\%$) was found to be 26.2% and response time was measured 0.32 s at 430 nm. The dual type electrochromic device (ECD) based on P(CBP-co-CPDT) and PEDOT was constructed and its electrochromic properties were also studied. The studies showed that the optical contrast ($\Delta T\%$) and response time were 39.8% and 0.36 s at 628 nm. The coloration efficiency (CE) of the device was calculated to be $319.98 \text{ cm}^2 \text{ C}^{-1}$ at 628 nm. This ECD also shows good optical memories and redox stability. Considering these results, this device is a promising candidate for commercial applications.

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References

1. H. Seol, H. Jeong, S. Jeon, *J. Electroanal. Chem.* 636 (2009) 107–112.
2. G. Sonmez, H. Meng, F. Wudl, *Chem. Mater.* 16 (2004) 574-580.
3. G. Sonmez, C. K. F. Shen, Y. Rubin, F. Wudl, *Angew. Chem. Int. Ed.* 43 (2004) 1498-1502.
4. A. Yildirim, S. Tarkuc, M. Ak, L. Toppare, *Electrochim. Acta.* 53 (2008) 4875-4882.
5. G. Sönmez, I. Schwendeman, P. Schottland, K. Zong, J.R. Reynolds, *Macromolecules.* 36 (2003) 639–647.
6. M. Li, A. Patra, Y. Sheynin, M. Bendikov, *Adv. Mater.* 21 (2009) 1707-1711
7. C. Ma, M. Taya, C.Y. Xu, *Electrochim. Acta.* 54 (2008) 598-605.
8. A. Kraft, A.C. Grimsdale, A.B. Holmes, *Angew. Chem. Int. Ed.* 37 (1998) 402-428.
9. H. Zhang, J. Zhao, H. Liu, H. Wang, R. Liu, J. Liu, *Int. J. Electrochem. Sci.* 5 (2010) 295-301.
10. E. Smela, *Adv. Mater.* 15 (2003) 481-494.
11. S. Gunes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.* 107 (2007) 1324–1338.
12. M. Ak, E. Sahmetlioglu, L. Toppare, *J. Electroanal. Chem.* 621 (2008) 55-61.
13. A. Yildirim, S. Tarkuc, M. Ak, L. Toppare, *Electrochim. Acta.* 53 (2008) 4875–4882.
14. G.M. Nie, L.J. Zhou, Q.F. Guo, S.S Zhang, *Electrochem. Commun.* 12 (2010)160-163.
15. J.H. Kang, Z.C. Xu, S.M. Paek, F. Wang, S.J. Hwang, J. Yoon, J.H. Choy, *Chem. Asian J.* 6 (2011) 2123–2129.
16. C. Ocampo, C. Alemán, R. Oliver, M.L. Arnedillo, O. Ruiz, F. Estrany, *Polym. Int.* 56 (2007) 803–809.
17. J.R. Reynolds, J.P. Ruiz, A.D. Child, K. Nayak, D.S. Marynick, *Macromolecules.* 24 (1991) 678–687.
18. A. Kimoto, J.S. Cho, K. Ito, D. Aoki, T. Miyake, K. Yamamoto, *Macromol. Rapid Commun.* 26 (2005) 597–601.
19. S. Walkim, B.-R. Aich, Y. Tao, M. Leclerc, *Polym. Rev.* 48 (2008) 432.
20. A. Oral, S. Koyuncu, _I. Kaya, *Synth. Met.* 159 (2009) 1620–1627.

21. Fatma Baycan Koyuncu, Sermet Koyuncu, Eyup Ozdemir, *Electrochim. Acta.* 55 (2010) 4935–4941.
22. S. Koyuncu, B. Gultekin, C. Zafer, H. Bilgili, M. Can, S. Demic, İ. Kaya, S. Icli, *Electrochim. Acta.* 54 (2009) 5694–5702.
23. J. Hou, S. Zhang, T.L. Chen, Y. Yang, *Chem. Commun.* 49 (2008) 6034–6036.
24. C.-G. Wu, M.-I. Lu, S.-J. Chang, C.-S. Wei, *Adv. Funct. Mater.*, 17 (2007) 1063–1070.
25. Y.J. Cheng, L.C. Hung, F.Y. Cao, W.S. Kao, C.Y. Chang, C.S. Hsu, *J. Polym. Sci.: Part A: Polym. Chem.* 49 (2011) 1791–1801.
26. P. Coppo, D.C. Cupertino, S.G. Yeates, M.L. Turner, *Macromolecules.* 36 (2003) 2705–2711.
27. C. Zhang, Y. Xu, N.C. Wang, Y. Xu, W.Q. Xiang, M. Ouyang, C.A. Ma, *Electrochim. Acta.* 55 (2009) 13–18.
28. Bin Wang, Jinsheng Zhao, Renmin Liu, Jifeng Liu, Qingpeng He, *Solar Energy Materials & Solar Cells.* 95 (2011) 1867–1874
29. G. W. Lu, G. Q. Shi, *J. Electroanal. Chem.* 586 (2006) 154–160.
30. B. Yigitsoy, S. Varis, C. Tanyeli, I.M. Akhmedov, L. Toppare, *Electrochim. Acta.* 52 (2007) 6561–6568.
31. U.R. Lee, T.W. Lee, M.H. Hoang, N.S. Kang, J.W. Yu, K.H. Kim, K.-G. Lim, T.-W. Lee, J.-I. Jin, D.H. Choi, *Org. Electron.* 12 (2011) 269–278.
32. G.M. Nie, L.Y. Qu, J.K. Xu, S.S. Zhang, *Electrochim. Acta.* 53 (2008) 8351–8358.
33. J. Hwang, J.I. Son, Y.-B. Shim, *Sol. Energy Mater. Sol. Cells.* 94 (2010) 1286–1292.
34. E. Yildiz, P. Camurlu, C. Tanyeli, I. Akhmedov, L. Toppare, *J. Electroanal. Chem.* 612 (2008) 247–256.
35. E. Sefer, F.B. Koyuncu, E. Oguzhan, S. Koyuncu, *J. Polym. Sci.: Part A: Polym. Chem.* 48 (2010) 4419–4427.
36. S.J. Yoo, J.H. Cho, J.W. Lim, S.H. Park, J. Jang, Y.-E. Sung, *Electrochem. Commun.* 12 (2010) 164–167.
37. G.M. Nie, L.J. Zhou, Q.F. Guo, S.S. Zhang, *Electrochem. Commun.* 12 (2010) 160–163.