Int. J. Electrochem. Sci., 7 **(2012)** 2764 - 2780

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Synthesis and Characterization of a Novel Electrochromic Copolymer of 4H-cyclopenta[2,1-b:3,4-b’]Dithiophene with Pyrene

Wei Yang[1,2], *Jinsheng Zhao*[2,*], *Ying Kong*[1,*], *Tianyu Kong*[3], *Chuansheng Cui*[2]

[1] State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), QingDao, 266555, P. R. China
[2] Shandong Key laboratory of Chemical Energy Storage and Novel Cell Technology, Liaocheng University, Liaocheng, 252059, P. R. China
[3] State key Laboratory of Electronic Thin Films and Integrated Devices (UESTC)
Corresponding author: Tel: +86-635-8539607; Fax: +86-635-8539607
[*]E-mail: yingkong1967@yahoo.com.cn; j.s.zhao@163.com

Received: 24 February 2012 / *Accepted:* 13 March 2012 / *Published:* 1 April 2012

A copolymer of 4H-cyclopenta[2,1-b:3,4-b’]dithiophene (CPDT) and pyrene was electrochemically synthesized in acetonitrile (ACN) containing sodium perchlorate ($NaClO_4$). Cyclic voltammetry (CV), UV–vis and FT-IR analyses confirmed that the resulting polymer was a copolymer rather than a blend or a composite of the respective homopolymers. Polypyrene has only two colors switched between light yellow in the neutral state and yellowish green in the oxidized state. While poly(CPDT-*co*-pyrene) film exhibited five different colors (reddish brown, brown, purple, indigo and blue). This revealed distinct electrochromic properties from that of the pyrene homopolymer film. Maximum contrast (ΔT %) and response time of the copolymer film were measured as 35.7% and 2.49s at 750 nm. Electrochromic device (ECD) based on poly(CPDT-*co*-pyrene) and poly(3,4-ethylenedioxythiophene) (PEDOT) was also constructed and characterized. This ECD showed a maximum optical contrast (ΔT %) of 28.8% in visible region with a response time of 0.50 s at 666 nm. The coloration efficiency (CE) of the device was calculated to be 920 $cm^2\ C^{-1}$ at 666 nm.

Keywords: Electrochemical polymerization; Conjugated polymer; Pyrene; Electrochromic device; 4H-cyclopenta[2,1-b:3,4-b’]dithiophene.

1. INTRODUCTION

Since the discovery of conducting polymers with high conductivity in 1970s, the conjugated polymers have been considered as promising materials with special electrical and optical properties

[1], and have been widely applied in many fields such as polymer solar cells [2], membranes,[3] electrochromic devices [4, 5], sensors [6], light emitting diodes [7], and so on. These electroactive and photoactive polymers are usually based on thiophene, pyrrole, phenylene, fluorene, or carbazole moieties [8，9]. In recent year, electrochromic polymers have gained a lot of attention due to their several advantages over inorganic compounds, such as low cost, processability, high optical contrast ration, multicolor with the same material, high stability and long cycle life with fast response time [10]. To achieve color change in electrochromic polymers, absorption in the visible region should be monitored by means of an externally applied potential. Upon doping, electronic states change due to the formation of polaronic and bipolaronic bands causing a change in the absorption characteristics of the polymer [11,12].

For produce a novel electrochromic polymer with special properties, copolymerization is an easy, facile way. 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 [13]. 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 [14].

Among numerous kinds of electrochromic materials, polythiophenes are a class of excellent one because of their high electrical conductivity and good redox property. They exhibit fast switching times, outstanding stability and high contrast ratios in the visible and NIR regions [15]. Meanwhile, polythiophenes have facile band gap (E_g) tunability through structural modification reported extensively in past few years [16–18]. On the other hand, pyrene and its derivatives are valuable fluorescent probes due to their unique fluorescence properties, and it is interesting to note that fine tuning in the band gap and neutral state color of the polymer can be achieved by copolymerization with pyrene [19,20]. Furthermore, copolymerization offers an effect way of controlling the electrochromic properties of conducting polymers. Copolymers can lead to an interesting combination of the properties observed in the corresponding homo-polymers [21]. Besides, it is well known that the pursuit of new high-quality electrochromic materials is still the main goal of scientists in the field of electrochromic devices.

According to above considerations, in this work, we electrochemically synthesized copolymer based on 4H-cyclopenta[2,1-b:3,4-b’]dithiophene (CPDT) and pyrene via the electrochemical oxidation of pyrene/CPDT mixtures. The electrochromic and spectroelectrochemical properties of the copolymer are studied in detail. The copolymer film reveals five different colors (reddish brown, brown, purple, indigo and blue). In addition, we construct and characterize dual type electrochromic devices based on P(CPDT -co-pyrene) and PEDOT in detail. Neutral state of device shows reddish brown color while oxidized state reveals blue color.

2. EXPERIMENTAL

2.1. Materials

4H-Cyclopenta[2,1-b:3,4-b’]dithiophene (CPDT) was purchased from Trademax Pharmaceuticals & Chemicals Co. Shanghai China and was used as received, the pyrene(98%) was purchased from J&K Chemical Co. Beijing China. Commercial high-performance liquid chromatography grade acetonitrile (ACN, Tedia Company, INC. USA) are used directly without further purification. Sodium perchlorate ($NaClO_4$, Shanghai Chemical Reagent Company, China, 98%) was dried in vacuum at 60 ºC for 24 hours before use. All other reagents were used as received without further treatment. 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 nitrogen flow.

2.2. Electrochemistry

The electrochemical syntheses and experiments were carried out in a one-compartment cell with a CHI 760 C Electrochemical Analyzer(Shanghai ChenHua Instrument Co. China) under computer control with a platinum wires with a diameter of 0.5 mm as working electrode, a platinum ring as counter electrode, and a silver wire (Ag wire) as pseudo reference electrode. The working and counter electrodes were placed 0.5 cm apart during the experiments. The electrolytic solution consisted of 0.2 M $NaClO_4$ in ACN solution. The electrodeposition was performed in 0.2 M $NaClO_4$/ACN solution containing monomers or a monomer mixture potentiodynamically at a scan rate of 100 mV s^{-1}. Ag wire, the pseudo reference was calibrated externally with a 5 mM solution of ferrocene (Fc/Fc^+) in the electrolyte ($E_{1/2}(Fc/Fc^+) = +\ 0.20$ V *vs*. Ag wire in 0.2 M $NaClO_4$/ACN) [15]. $E_{1/2}$ of Fc/Fc^+ measured in the 0.2 M $NaClO_4$/ACN solution was 0.28V *vs*. SCE. Thus, the potential of Ag wire was assumed to be 0.08V *vs*. SCE. Cyclic voltammetry(CV) of polymer was carried out with the same electrode set-up in monomer-free electrolyte solution. All of the electrochemistry experiments were carried out at room temperature under nitrogen atmosphere.

2.3. Characterizations

The obtained copolymer films were studied by cyclic voltammetry. Infrared spectra were recorded on a Nicololet 5700 FT-IR spectrometer (Thermo Nicolet Co., Wisconsin, USA), where the samples were dispersed in KBr pellets. UV–vis spectra were carried out on a Perkin-Elmer Lambda 900 UV–vis-near-infrared spectrophotometer (PerkinElmer Inc., Massachusetts, USA). Scanning electron microscopy (SEM) measurements were taken by using a JEOL JSM-6380LV SEM (JEOL Ltd., Tokyo, Japan). Digital photographs of the polymer films were taken by a Canon Power Shot A3000 IS digital camera.

2.4. Spectroelectrochemistry

The spectroelectrochemical data were recorded on Perkin-Elmer Lambda 900 UV-vis-near-infrared spectrophotometer under control of a computer. A three-electrode cell assembly was used, where the working electrode was an ITO-coated glass slides, the counter electrode was a stainless steel wire, and an Ag wire was used as pseudo-reference electrode. The potentials were reported versus Ag wire. The polymer films for spectroelectrochemistry were prepared by potentiostatic deposition on ITO-coated glass slides (the active area: 2.1 cm×0.8 cm). The measurements were all carried out in ACN solution containing 0.2 M $NaClO_4$.

2.5. Preparation of the gel electrolyte

A gel electrolyte based on poly(methyl methacrylate) (PMMA) (MW: 350,000) and $LiClO_4$ was plasticized with propylene carbonate (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 [22].

2.6. Fabrication of electrochromic devices

Electrochromic devices (ECDs) were fabricated with two complementary polymers, namely P(CPDT-co-pyrene) as the anodically coloring material and PEDOT as the cathodically coloring material. Both the P(CPDT-co-Pyrene) and PEDOT films were electrodeposited onto two ITO-coated glass (active area: 1.8 cm×2.5 cm) at 1.35V and 1.4 V, respectively. ECDs were fabricated 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 characterization

3.1.1. Electrochemical polymerization

The anodic polarization curves of 0.004 M CPDT and 0.004 M pyrene in ACN solution containing 0.2 M $NaClO_4$ are shown in Fig. 1.The onset oxidation potential ($E_{pa\ onset}$) of CPDT in the solution was 0.85 V (Fig. 1a), while that of pyrene was 1.12 V (Fig. 1c). It is well known that successful electrochemical copolymerization of different monomers is due to the fact that the $E_{pa\ onset}$ of the monomers are close to each other [23, 24]. However the distinction of the $E_{pa\ onset}$ between CPDT and pyrene is 0.27 V. From this point, it seems that it is hard to achieve the electrochemical copolymerization of CPDT and pyrene. But according to the results of our experimental, the copolymerization could be carried out, when the concentration of pyrene is higher than 3mM while the concentration of CPDT is lower than 5mM. As can be seen from Fig. 1b, the $E_{pa\ onset}$ of the CPDT/pyrene mixture was approximately 0.9 V, which is much lower than that of pyrene, indicated the existence of the interaction between two monomers in 0.2 M $NaClO_4$/ACN [25, 26]. The synthetic route of the copolymer of CPDT and pyrene is illustrated in Scheme 1.

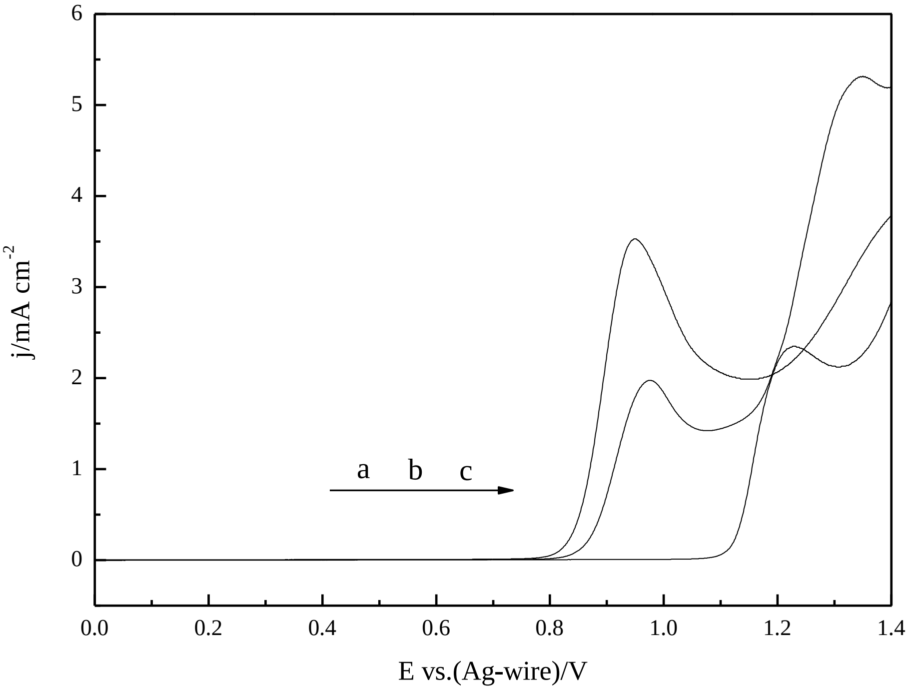
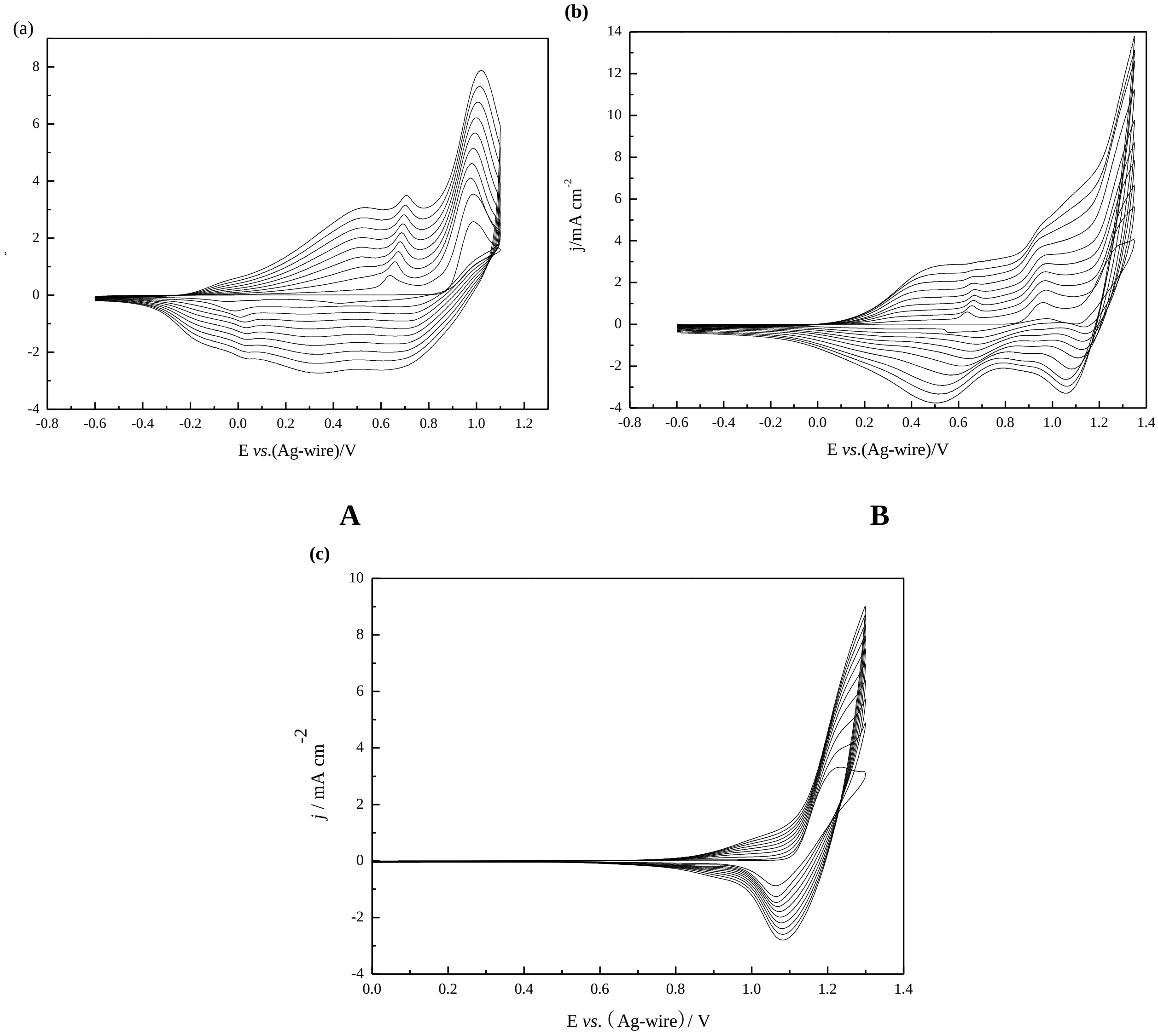


Figure 1. Anodic polarization curves of (a) 0.004 M CPDT, (b) 0.004 M CPDT and pyrene， (c) 0.004 M pyrene in 0.2 M $NaClO_4$/ACN. Scanning rates: 100 mV s^{-1}. *j* denotes the current density, E denotes the potential.

Scheme 1. The synthetic route of the copolymer.

The successive CV curves of 0.004 M CPDT, 0.004 M pyrene and the CPDT/pyrene mixture (0.004 M CPDT and 0.004 M pyrene) in 0.2 M $NaClO_4$/ACN are illustrated in Fig. 2. As shown in Fig. 2a, a characteristic oxidation peak of the monomer CPDT was observed at 0.95 V accompanied by a reversible redox couple of its polymer (a broad cathodic peak between +0.8V and −0.3V and its reverse anodic peak at +0.63 V). The CV curves of pyrene showed an oxidation peak at +1.1 V and a reduction peak at +1.05 V. (Fig. 2c). However, the CV curve of the CPDT/pyrene mixture exhibited a broad anodic peak between around 0.63V and 0.95V (Fig. 2b), which were different from those of CPDT and pyrene, indicated the formation of a new copolymer (CPDT-co-pyrene) consisting of both CPDT and pyrene units [27-29]. In addition, as can be seen from Fig. 2, there was an obvious increase of current density (*j*) of the CPDT/pyrene mixture compared with those of CPDT and pyrene, this can also implied the formation of a copolymer [28].



A **B**

C

Figure 2. Successive CV curves of (a) 0.004 M CPDT, (b) 0.004 M CPDT and 0.004 M pyrene, (c) 0.004 M pyrene in 0.2 M $NaClO_4$/ACN. Scanning rates: 100 mV s^{-1}. *j* denotes the current density, E denotes the potential.

3.1.2. Electrochemistry behavior of P(CPDT-co-pyrene) films

Figure 3 shows the electrochemical behavior of the P(CPDT-co-pyrene) film (prepared on platinum wires by sweeping the potentials from –0.6 and 1.35 V for ten cycles) at different scan rates between 25 and 300 mV s^{-1} in 0.2 M $NaClO_4$/ACN. As can be seen from Fig. 3a, the P(CPDT-co-pyrene) film is cycled repeatedly between doped and dedoped states without significant decomposition. The peak current densities (*j*) are proportional to the potential scan rates (Fig. 3b), indicated a reversible redox process of the polymer adhered well to the platinum wire electrode [30]. This also demonstrated that the electrochemical processes of P(CPDT-co-pyrene) were reversible and not diffusion limited [31].

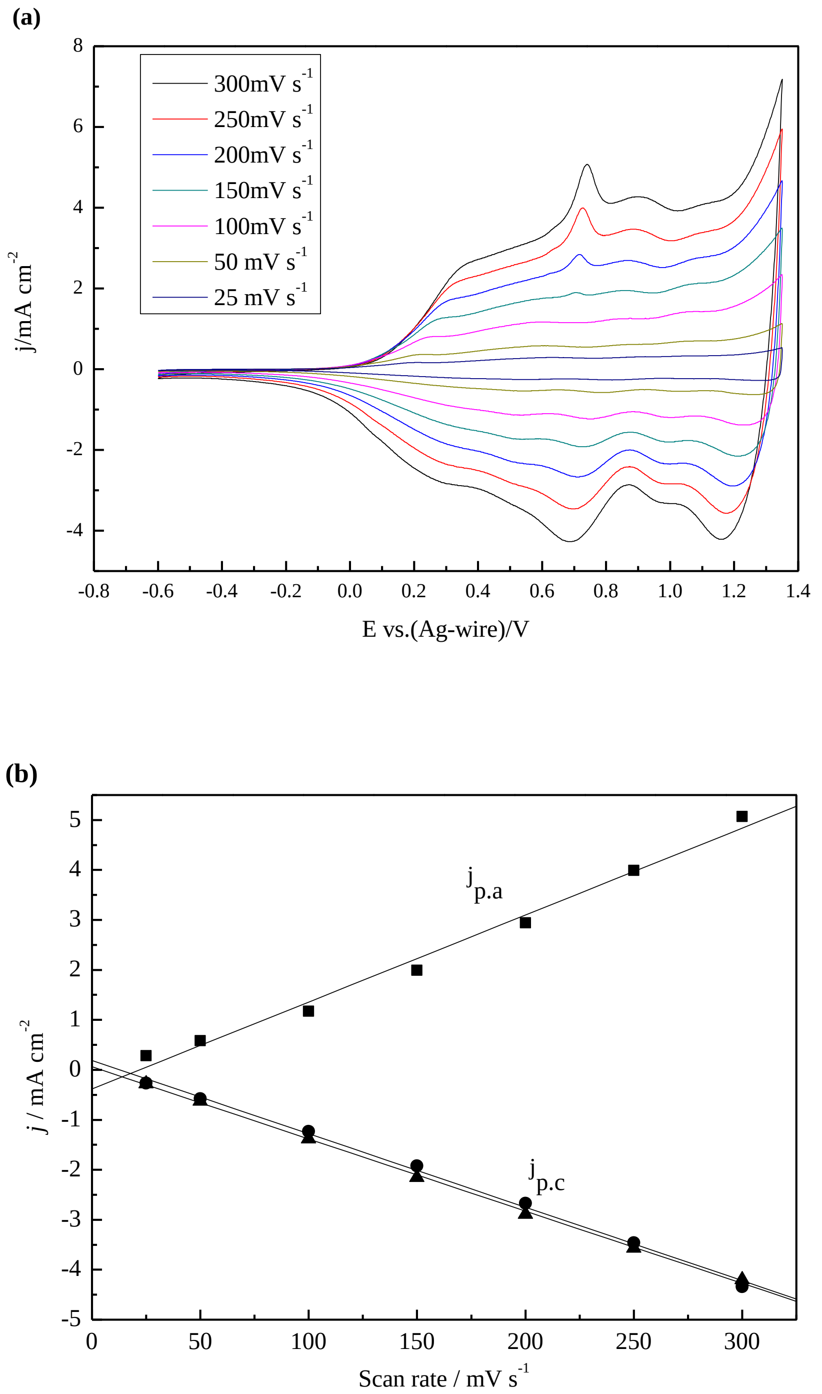


Figure 3. (a) CV curves of the P(CPDT-co-pyrene) film at different scan rates between 25 and 300 mV s^{-1} in the monomer-free 0.2 M $NaClO_4$/CAN solution. (b) Scan rate dependence of the P(CPDT-co-Pyrene). j_{pa} and j_{pc} denote the anodic and cathodic peak current densities, respectively, j denotes the current density, E denotes the potential.

3.1.3. FTIR spectra

To obtain sufficient amount of polymers for characterization, the titanium (Ti) sheet (the active of area is 1.0 cm × 2.5 cm) are employed as working electrodes. The polymers are synthesized potentiostatically in the solution of 0.2 M $NaClO_4$/ACN containing 0.004 M CPDT and 0.004 M pyrene monomers or their mixture. Fig. 4 shows the FT-IR spectra of PCPDT, polypyrene and P(CPDT-co-pyrene). In the spectrum of PCPDT (Fig. 4a), the peak at 1635 cm^{-1} is due to C=C stretching vibration of thiophene ring and the 810 cm^{-1} band reflects the stretching mode of C–S. While the absorption bands at 987 and 940 cm^{-1}, which can be assigned to the pentadiene groups, are labeled in the figure. In the spectrum of polypyrene (Fig. 4b), the peaks at 845 and 817 cm^{-1} reflected substituted benzene ring. The above mentioned bands of PCPDT and polypyrene could also be found in the FT-IR spectrum of P(CPDT-co-pyrene) (Fig. 4c). Compared with corresponding homopolymers, these features indicated that copolymer contains both CPDT and pyrene units.

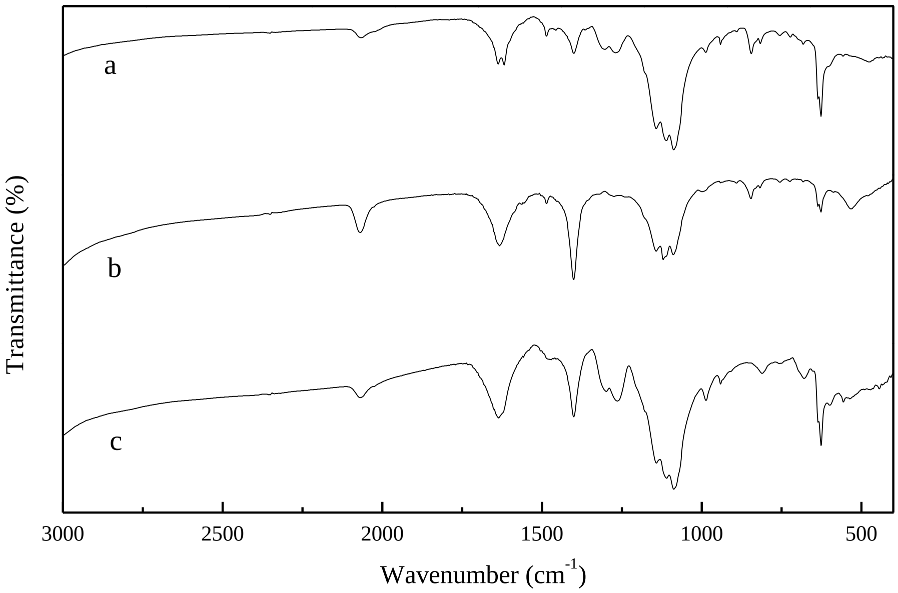


Figure 4. The FT-IR spectra of (a) PCPDT, (b) Polypyrene and (c) P(CPDT-co-pyrene) obtained at 1.1V, 1.3V and 1.3V potentiostatically from 0.2 M $NaClO_4$/ACN solution, respectively.

3.1.4. Scanning electron microscopy

Scanning electron micrographs (SEM) of polymers provide their clear surface and bulk morphologies, which are closely related to their optical and electrical properties [32]. PCPDT, P(CPDT-co-pyrene) and polypyrene are deposited on ITO electrode (0.5 cm × 0.5 cm) at 1.1V, 1.3V and 1.3V potentiostatically from 0.2 M $NaClO_4$/ACN solution, respectively, and then dedoped. The SEMs of them are shown in Fig. 5. In this case, The PCPDT film exhibits granular particle clusters with more porous structure were dispersed on the side of film (Fig. 5a). Polypyrene exhibits an accumulation state of clusters of globules (Fig. 5c). While P(CPDT-co-pyrene) shows a crowed network morphology with a little amounts of flakes (Fig. 5b), which are significantly different from two corresponding homopolymers. The difference of morphology between the copolymer and homopolymers well confirmed the occurrence of copolymerization between CPDT and pyrene.

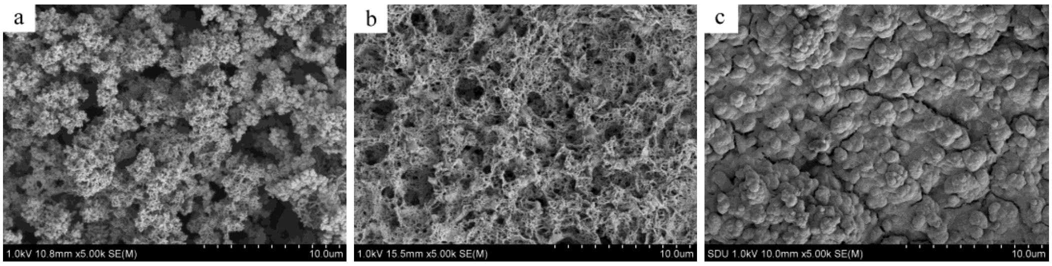


Figure 5. SEM images of (a) PCPDT, (b) P(CPDT-co-pyrene) and (c) polypyrene deposited potentiostatically on ITO electrode.

3.1.5. UV–vis spectra of the polymers

Fig. 6 depicts the UV–vis spectra of dedoped (a) PCPDT, (b) P(CPDT-co-pyrene) and (c) polypyrene deposited on ITO electrode with the same polymerization charge (3.2×10^{-2} C) at +1.1V, +1.35V and +1.3V, respectively. For PCPDT film (Fig. 6a), there was a broad absorption at 350–700 nm with a maximum at around 520 nm and a weak shoulder at 360 nm. On the other hand, the spectrum of polypyrene film showed a absorption appeared at 350 nm (Fig. 6c). While, the spectrum of the P(CPDT-co-pyrene) exhibited both the characteristic absorptions of PCPDT and polypyrene, located at 360nm and a shoulder at 460 nm (Fig. 6b). However, there was a little bit red shift of the main absorption of copolymer film in contrast to pure polypyrene due to the incorporation unit of CPDT, further confirming the occurrence of copolymerization [28]. The spectrum of P(CPDT-co-pyrene) were significantly shift from those of two individual homopolymers, further confirmed the formation of copolymer consisting of both CPDT and pyrene units.

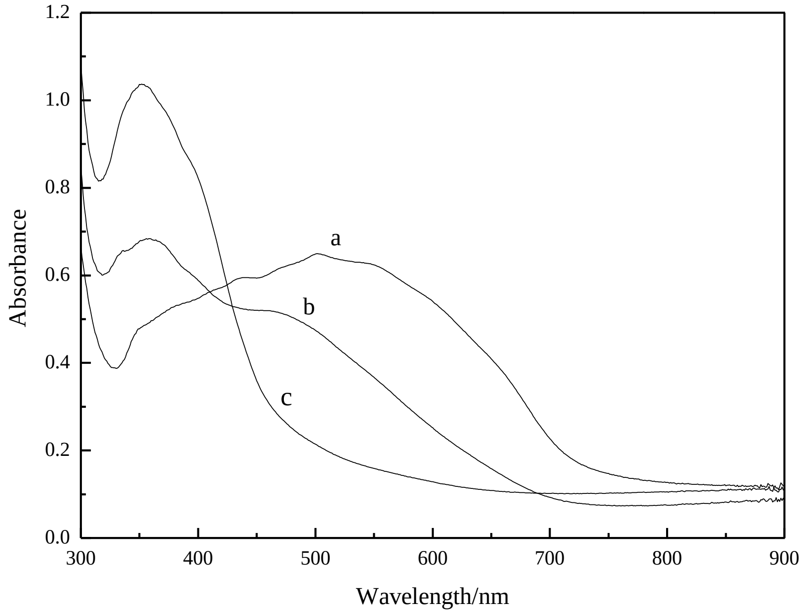


Figure 6. UV-vis spectra of (a) PCPDT, (b) P(CPDT-co-pyrene) and (c) polypyrene deposited on ITO at the neutral state.

Besides, the optical band gap (E_g) of polymer was deduced from the absorption band edges (λ_{onset}). The E_g of the P(CPDT-co-pyrene) film was calculated as 1.77 eV, which is lower than that of polypyrene (2.67 eV) and higher than that of PCPDT (1.68 eV). The effect of copolymerization between CPDT and pyrene led to an obvious decrease in the E_g comparing with that of pyrene, which implied that the introduction of CPDT units into pyrene can reduce the E_g of the copolymer.

Table 1 summarized 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 polypyrene, PCPDT and the copolymers (prepared with the feed ratio of pyrene/CPDT at 5:3 (COP1), 1:1 (COP2) and 3:5 (COP3), respectively) quite clearly. HOMO energy levels of them were calculated by using the formula $E_{HOMO} = -e(E_{onset} + 4.4)$ (vs. SCE) and LUMO energy levels (E_{LUMO}) of them were calculated by the subtraction of the optical band gap (E_g) from the HOMO levels [33].

Table 1. The onset oxidation potential (Eonset), maximum absorption wavelength (λmax), low energy absorption edges (λonset), HOMO and LUMO energy levels and optical band gap (Eg) values of pyrene, PCPDT and the copolymers (prepared with the feed ratio of pyrene/CPDT at 5:3, 1:1 and 3:5, respectively).

Compounds	E_{onset}, vs.(Ag-wire) (V)	λ_{max} (nm)/ λ_{onset} (nm)	E_g [a] (eV)	HOMO (eV)	LUMO[b] (eV)
Pyrene	+0.64	352/465	2.67	-5.12	-2.45
COP1	+0.11	356/671	1.85	-4.59	-2.74
COP2	-0.026	367/701	1.77	-4.45	-2.68
COP3	-0.061	376/710	1.75	-4.42	-2.67
PCPDT	-0.34	546/738	1.68	-4.14	-2.46

[a] Calculated from the low energy absorption edges (λ_{onset}).

[b] Calculated by the subtraction of the optical band gap (E_g) from the HOMO level.

3.2. Electrochromic properties of the copolymer

3.2.1. Spectroelectrochemical properties of the copolymer

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. P(CPDT-co-pyrene) coated ITO (prepared potentiostatically at 1.35 V vs. Ag wire) was switched between -0.6 and 1.30 V in 0.2 M $NaClO_4$/ACN solution in order to obtain the in situ UV-vis spectra (Fig. 7). In the neutral state, polymer film exhibited an absorption band at 370 nm with a shoulder at around 470 nm due to the π-π^* transition. As shown in Fig. 7, the intensity of the P(CPDT-co-pyrene) π–π^* electron transition absorption decreased while a charge carrier absorption band located at about 780 nm increased dramatically upon oxidation. The appearance of the charge carrier band could be attributed to the evolution of polaron and bipolaron bands.

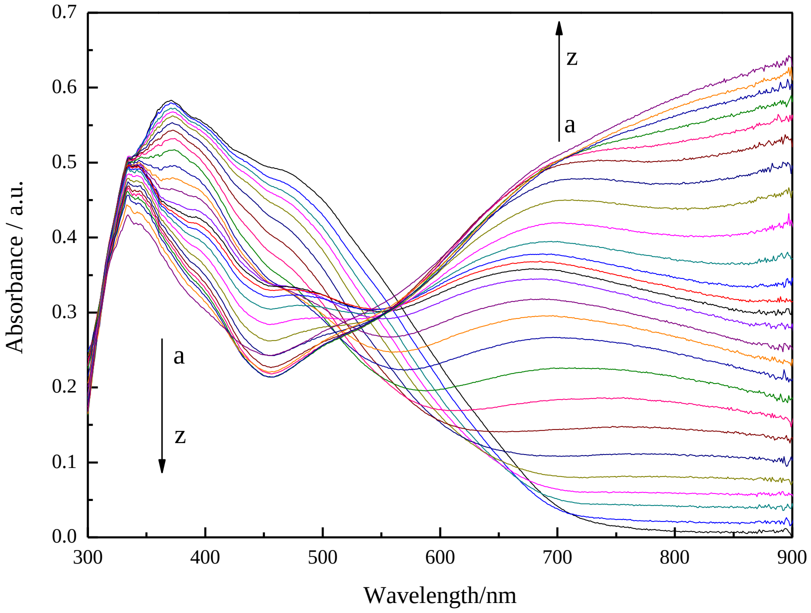


Figure 7. Spectroelectrochemical spectra of P(CPDT-co-pyrene) with applied potentials between –0.6 V and +1.35 V in monomer-free 0.2 M $NaClO_4$ / ACN. Applied potentials are the following: (a) –0.6V; (b) 0.2V; (c) 0.3 V; (d) 0.35 V; (e) 0.4V; (f) 0.45 V; (g) 0.5 V; (h) 0.55 V; (i) 0.6 V; (j) 0.65 V; (k) 0.675 V; (l) 0.7 V; (m) 0.73 V; (n) 0.75 V; (o) 0.77 V; (p) 0.8 V; (q) 0.85 V; (r) 0.9 V; (s) 0.95 V; (t) 1.0 V; (u) 1.05 V; (v) 1.1 V; (w) 1.15 V; (x) 1.2 V; (y) 1.25 V; (z) 1.3 V.

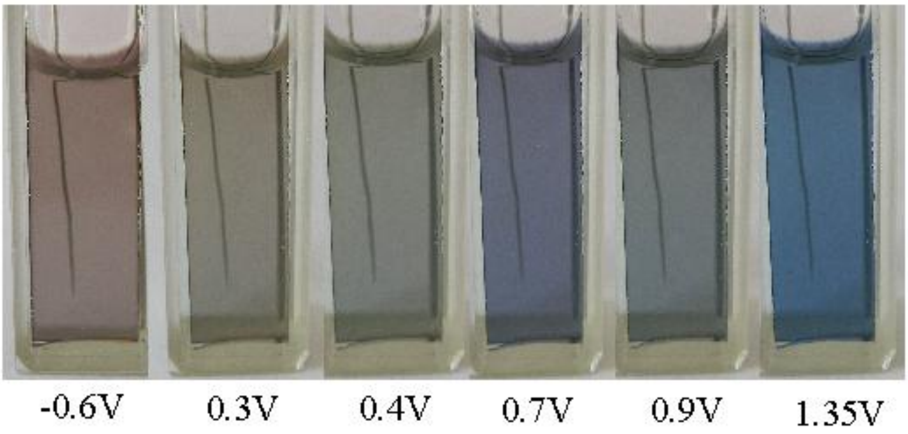


Figure 8. The images of P(CPDT-co- pyrene) film at –0.6 V (the neutral state), 0.3 V (the intermediate doped state), 0.4 V (the intermediate doped state), 0.7 V (the intermediate doped state), 0.9 V (the intermediate doped state) and 1.35 V (the full doped state).

In addition, it is interesting to find that the P(CPDT-co- pyrene) film shows a multicolor electrochromism. In order to study the range of colors, a wide interval of potentials (−0.6 V to +1.35

V) was applied on the as-prepared P(CPDT-co-pyrene) films. As can be seen from Fig. 8, P(CPDT-co-pyrene) film showed kinds of colors in neutral and oxidized states. The reddish brown color of the film at neutral state (−0.6 V) turned into brown color (+0.3 V) and celadon color (+0.4 V), and then into purple color (+0.7 V) and indigo color (+0.9 V), at last into blue color at full doped state (+1.35 V). This multicolor property possesses significant potential applications in smart windows or displays and so on.

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

It is important that polymers can switch rapidly and exhibit striking color changes, revealing superior results in electrochromic applications [34]. The dynamic electrochromic experiment for P(CPDT-co-pyrene) was carried out at 750 nm, where the maximum transmittance differences between redox states were observed in the visible region. Square wave potential step method was coupled with optical spectroscopy, named chronoabsorptometry, to investigate the switching ability of P(CPDT-co-pyrene) between its neutral and full doped state (Fig. 9). The potential was interchanged between – 0.6 V (the neutral state) and 1.35 V (the oxidized state) at regular intervals of 3 s. One important characteristic is the optical contrast (ΔT %), which can be defined as the transmittance difference between the redox states. The maximum ΔT % of the P(CPDT-co-Pyrene) was found to be 35.7% at 750 nm, as showed in Fig. 9.

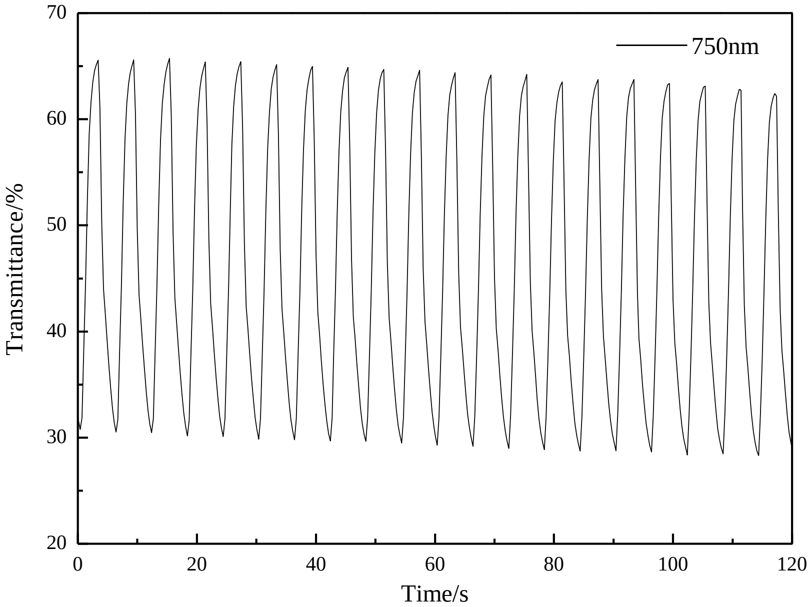


Figure 9. Electrochromic switching (750 nm) for P(CPDT-co-pyrene) film monitored in 0.2 M $NaClO_4$/ACN solution under an applied square voltage signal between –0.6 V and +1.35 V with a residence time of 3 s.

The coloration efficiency (CE) is also an important characteristic for the electrochromic materials. CE can be calculated by using the equations and given below [35]:

$$\Delta \mathrm{OD} = \lg\left(\frac{T_{\mathrm{b}}}{T_{\mathrm{c}}}\right) \text{ and } \eta = \frac{\Delta \mathrm{OD}}{\Delta \mathrm{Q}}.$$

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(CPDT-co-pyrene) film was measured as 67.94 $\mathrm{cm}^2\ \mathrm{C}^{-1}$ (at 750 nm) at full doped state, which had reasonable coloration efficiency.

The 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 [31, 34]. The response required to attain 95% of total transmittance difference was found to be 2.49 s from the reduced to the oxidized state and 2.14 s from the oxidized to the reduced state.

3.3. Characterization of the electrochromic devices (ECDs)

3.3.1. Spectroelectrochemical properties of ECDs

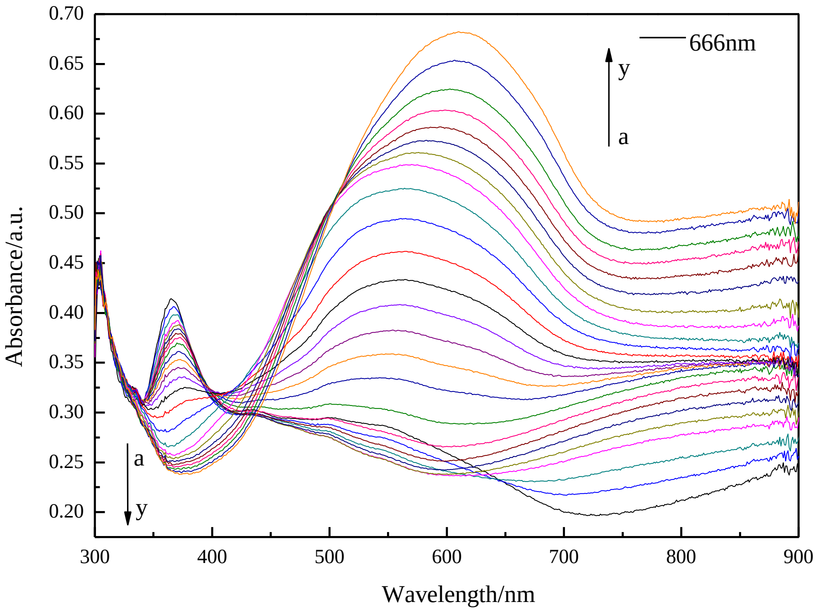


Figure 10. Spectroelectrochemical spectra P(CPDT-co-Pyrene) device at various applied potentials from –0.8 to +1.4 V. Applied potentials are the following: (a) -0.8V; (b) -0.4V; (c) -0.2 V; (d) 0 V; (e) 0.1V; (f) 0.2 V; (g) 0.3 V; (h) 0.4 V; (i) 0.5 V; (j) 0.6 V; (k) 0.65 V; (l) 0.7 V; (m) 0.75 V; (n) 0.8 V; (o) 0.85 V; (p) 0.9 V; (q) 0.95 V; (r) 1.0 V; (s) 1.05 V; (t) 1.1 V; (u) 1.15 V; (v) 1.2 V; (w) 1.25 V; (x) 1.3 V; (y) 1.35 V.

A dual-type ECD consisting of P(CPDT-co-pyrene) and PEDOT was constructed, and its spectroelectrochemical behaviors were also studied. Before we composed the ECD, the cathodically coloring polymer (P(CPDT-co-pyrene)) was fully oxidized while the anodically coloring polymer film (PBTBE) was fully reduced. P(CPDT-co-pyrene) /PEDOT ECDs were switched between –0.8 and +1.4 V. The spectroelectrochemical result show P(CPDT-co-pyrene) layer was in its neutral state and PEDOT was in oxidized state at –0.8 V, and the device color was reddish brown. As the applied potential increased, the P(CPDT-co-pyrene) layer start to be oxidized while PEDOT layer is reduced. This led to a new absorption at 610 nm due to the reduced state of PEDOT (Fig. 10), and the dominated color of the device was dark blue at +1.4 V.

3.3.2. Switching of ECDs

Kinetic studies were also done to test the response time of P(CPDT-co-pyrene)/PEDOT ECDs. Under a square potential input of –0.8 and +1.4 V at regular intervals of 2 s, the optical response at 666 nm, as illustrated in Fig. 11. The response time is found to be 0.29 s at 95% of the maximum transmittance from the neutral state to oxidized state and 0.50 s from the oxidized state to the neutral state, and Δ*T* % is calculated to be 28.8 %. The CE of the device (the active of area is 1.8 cm × 1.8 cm) is calculated to be 920 cm^2 C^{-1} at 666 nm.

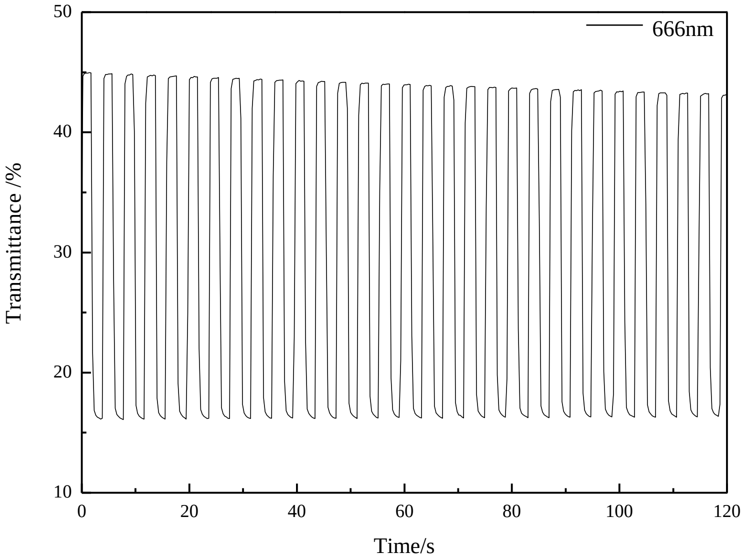


Figure 11. Optical response (at 666 nm) as a function of time of P(CPDT-co-pyrene)/PEDOT device by applying square potentials between –0.8 V (the neutral state) and +1.4 V (the oxidized state) with a residence time of 2 s.

3.3.3. Open-circuit memory of ECDs

The optical memory in the electrochromic devices is an important parameter since it is directly related to its application and energy consumption during the use of ECDs [36]. The optical spectra for

P(CPDT-co-pyrene) were monitored at 666 nm as a function of time at -0.8 and +1.4 V by applying the potential for 1 s for 200 s time intervals, respectively. As shown in Fig. 12, both blue and reddish brown states were highly stable, and the device kept its color without loss. Thus, this device showed good optical memory, which also indicated this ECD has potential applications.

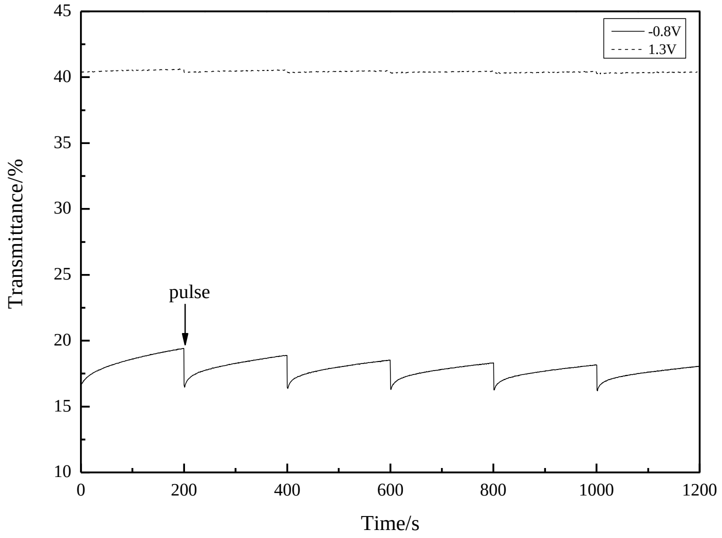


Figure 12. Open circuit stability of the P(CPDT-co-pyrene) /PEDOT ECDs monitored at 666 nm.

3.3.4. Stability of ECD

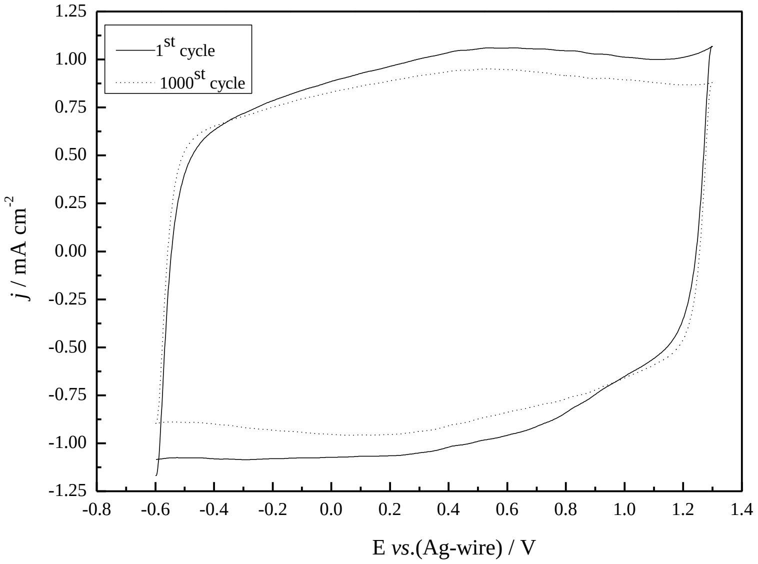


Figure 13. Cyclic voltammogram of P(CPDT-co-pyrene)/PEDOT device as a function of repeated scans 500 mV/s.

Redox stability is another important parameter for ECDs. The stability of devices toward multiple redox switching usually limits the application of electrochromic materials in ECD utility [35]. For this reason, the P(CPDT-co-pyrene)/PEDOT ECD was tested by cycling of the applied potential between -0.6 and +1.3 V with 500 mV/s to evaluate the stability of the devices (Fig. 13). After 1000 cycles, 91.3% of its electroactivity is retained and the changes in anodic (j_{pa}) and cathodic peak current densities (j_{pc}) are 11.4% and 10.5%, respectively. These results indicate that this ECD had a reasonably redox stability.

4. CONCLUSION

In this study, a new electrochromic copolymer of 4H-cyclopenta[2,1-b:3,4-b']dithiophene with pyrene was successfully synthesized by the electrochemical oxidation of their monomer mixture in 0.2 M $NaClO_4$/ACN solution. The obtained copolymer P(CPDT-co-pyrene) was studied by several means such as cyclic voltammetry, UV–vis spectra, FT-IR spectra and scanning electron microscopy. According to the spectroelectrochemical analyses, the copolymer film has distinct electrochromic properties and shown different colors (reddish brown, brown, purple, indigo and blue) under various potentials. Maximum contrast (ΔT %) and response time of the copolymer film are measured as 35.7% and 2.49 s at 750 nm. Even the response time is little longer than most novel copolymers', but it also promptly enough for electrochromic device (ECD) application. The dual type electrochromic device (ECD) based on P(CPDT-co-pyrene) and PEDOT is constructed and its electrochromic properties are also studied. The studies show that the optical contrast (ΔT %) and response time are 28.8% and 0.50 s at 666 nm. The coloration efficiency (CE) of the device is calculated to be 920 $cm^2\ C^{-1}$ at 630 nm. This ECD also shows good optical memories and reasonable redox stability. Considering these results, this device is a promising candidate for commercial applications. So based on this study, we concluded that the copolymer which included 4H-cyclopenta[2,1-b:3,4-b']dithiophene and pyrene units is really suitable for electrochromic application.

ACKNOWLEDGEMENTS
The work was financially support by the National Natural Science Foundation of China (20906043), the Promotive research fund for young and middle-aged scientists of Shandong Province (2009BSB01453), the Natural Science Foundation of Shandong province (ZR2010BQ009), the open foundation of the State key Laboratory of Electronic Thin Films and Integrated Devices(KFJJ201114) and the Taishan Scholarship of Shandong Province.

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