

## ORIGINAL ARTICLE

# Electrosynthesis and characterization of a novel electrochromic copolymer of *N*-methylpyrrole with cyclopenta[2,1-*b*:3,4-*b'*]dithiophene

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Electrochemical copolymerization of *N*-methylpyrrole (NMPy) and cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) was performed in acetonitrile containing sodium perchlorate as a supporting electrolyte. Characterization of the resultant copolymer P(CPDT-co-NMPy) was performed by cyclic voltammetry, UV–vis spectroscopy, Fourier transform infrared spectroscopy and scanning electron microscopy. The P(CPDT-co-NMPy) film has distinct electrochromic properties and exhibits four different colors (reddish brown, pale khaki, pale sea green and light blue) under various potentials. The maximum contrast ( $\Delta T\%$ ) and response time of the copolymer film at 750 nm were measured as 47.0% and 2.20 s, respectively. An electrochromic device (ECD) based on P(CPDT-co-NMPy) and poly(3,4-ethylenedioxythiophene) was constructed and characterized. The optical contrast ( $\Delta T\%$ ) at 630 nm was found to be 40.2%, and the response time was measured as 1.77 s. The coloration efficiency of the device was calculated to be 476 cm<sup>2</sup> per C at 630 nm. The ECD also has satisfactory optical memories and redox stability.

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## INTRODUCTION

Conducting polymers (CPs) form an important class of functional materials that have been widely researched because of their interesting electrical and optical properties. Recent advances in the field of CPs have led to a variety of materials with greater potential for practical applications, including polymer solar cells,<sup>1,2</sup> sensors,<sup>3</sup> light-emitting diodes,<sup>4</sup> membranes<sup>5</sup> and electrochromic devices (ECDs).<sup>6,7</sup>

Electrochromism is defined as a property that is inherent in some materials and enables the materials to electrochemically switch between different colored states as a result of oxidation–reduction reactions.<sup>8</sup> The color change results from the generation of different electronic absorption bands that correspond to changes between at least two states.<sup>9</sup> The electronic absorption bathochromically shifts upon the oxidation process, and the color contrast between redox states is related to the polymer band gap.<sup>10</sup> Currently, researchers are investigating how to fine-tune the electrochromic properties of CPs by controlling the band gap of the polymers via the choice of the ideal heteroaromatic ring.

Copolymerization is an easy way to control the electrochromic properties of CPs. This procedure allows one to obtain materials with controlled properties without the experimental disadvantages associated with the preparation of new homopolymers (that is, complex synthetic routes to develop sophisticated monomers).<sup>11</sup> Thus,

copolymerization of distinct monomers or homopolymerization of hybrid monomers can lead to interesting combinations in the properties of the corresponding homopolymer.<sup>12</sup>

Recently, a great deal of attention has been focused on the class of conjugated polyheterocyclic polymers because of their electrical conductivity, chemical stability and satisfactory processability. Among these polymers, polypyrrole and its derivatives such as poly(*N*-methyl pyrrole) (PNMPy) have been extensively investigated due to the excellent retention of their electrical, chemical, thermal and mechanical properties.<sup>13–16</sup> Attempts have been made regarding the copolymerization of pyrrole and NMPy with other heterocyclic monomers to improve the stability, reversibility and switching properties of the resulting polymer.<sup>17–19</sup> In addition, there is much interest in molecules containing fused-ring systems, of which polythiophene is the best-known example. Cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) and its derivatives, which have strong electron-donating properties as types of the fused aromatic rings, have attracted great attention. Using these compounds as building blocks offers the possibility of forming homopolymers, copolymers with narrower band gaps and, thus, broader light-absorption properties for applications in electronic devices.<sup>20–23</sup> Because of the fully coplanar structure, the intrinsic properties based on dithiophene can be altered, leading to further

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extended conjugation, lower HOMO–LUMO energy band-gap and stronger intermolecular interaction.<sup>22</sup> Therefore, it is expected that the introduction of CPDT units into the main chain of PNMPy might produce a tunable band-gap polymer, which could be an ideal characteristic for electronic materials used in ECDs. To the best of our knowledge, electrochemical copolymerization of NMPy with CPDT has not previously been reported. On the basis of the considerations mentioned above, copolymers based on NMPy and CPDT were successfully synthesized via the electrochemical oxidation of NMPy/CPDT mixtures. The electrochromic and spectroelectrochemical properties of the copolymer were studied in detail. The copolymer film exhibited four different colors (reddish brown, pale khaki, pale sea green and light blue). In addition, we constructed and extensively characterized dual-type ECDs based on P(NMPy-co-CPDT) and poly(3,4-ethylenedioxythiophene) (PEDOT). In the neutral state, the device shows reddish brown coloring, whereas the oxidized state shows light blue coloring.

## EXPERIMENTAL PROCEDURE

### Materials

NMPy (Aladdin, 99%), CPDT (Trademax Pharmaceuticals & Chemicals Co., Shanghai, China, 98%), commercial high-performance liquid chromatography grade acetonitrile (ACN, Tedia Company, Inc., Fairfield, CT, USA), poly(methyl methacrylate) (PMMA, Shanghai Chemical Reagent Company, Shanghai, China), propylene carbonate (PC, Shanghai Chemical Reagent Company), (3,4-ethylenedioxythiophene, 98%, Aldrich Chemical Company, Inc, Milwaukee, WI, USA) and lithium perchlorate ( $\text{LiClO}_4$ , Shanghai Chemical Reagent Company, 99.9%) were used directly without further purification. Sodium perchlorate ( $\text{NaClO}_4$ , Shanghai Chemical Reagent Company, 98%) was dried in 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:  $<10\ \Omega\ \square^{-1}$ , purchased from Shenzhen CSG Display Technologies, Shenzhen, China) was successively washed with ethanol, acetone and de-ionized water in an ultrasonic bath and then dried by a constant stream of  $\text{N}_2$ .

### Electrochemistry

Electrochemical synthesis and experiments were performed in a one-compartment cell with a CHI 760 C Electrochemical Analyzer controlled with a computer. The working and counter electrodes for the cyclic voltammetric (CV) experiments were two platinum wires, each with a diameter of 0.5 mm, placed 0.5 cm apart during the experiments. The electrodes were cleaned before each test. An Ag wire was used as a pseudo-reference electrode. The pseudo-reference electrode was calibrated externally using a 5 mM solution of ferrocene ( $\text{Fc}/\text{Fc}^+$ ) in the electrolyte ( $E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.20\ \text{V}$  vs Ag wire in 0.2 M  $\text{NaClO}_4/\text{ACN}$ ).<sup>24</sup> The potentials are reported in reference to the Ag-wire electrode. The half-wave potential ( $E_{1/2}$ ) of  $\text{Fc}/\text{Fc}^+$  measured in a 0.2 M  $\text{NaClO}_4/\text{ACN}$  solution was 0.28 V vs SCE. Thus, the potential of the Ag wire was assumed to be 0.08 V vs SCE.<sup>25</sup> All of the electrochemical experiments were carried out at room temperature under a nitrogen atmosphere. All electrochemical polymerization and CV tests were performed in an ACN solution containing 0.2 M  $\text{NaClO}_4$  as a supporting electrolyte.

### Characterizations

The copolymer films that were generated in this study were characterized by CV. Infrared spectra were recorded on a Nicolet 5700 Fourier transform infrared spectroscopy spectrometer, where the samples were dispersed in KBr pellets. UV–vis spectra were measured on a Perkin-Elmer Lambda 900 UV–vis near-infrared spectrophotometer (PerkinElmer, Inc., Shelton, CT, USA). Scanning electron microscopy measurements were taken using a Hitachi SU-70 thermionic field emission scanning electron microscope (Hitachi, Tokyo, Japan). Digital photographs of the polymer films were taken by a Canon Power Shot A3000 IS digital camera (Canon, Kuala Lumpur, Malaysia).

### Spectroelectrochemistry

Spectroelectrochemical data were recorded on Perkin-Elmer Lambda 900 UV–vis-near-infrared spectrophotometer connected to a computer. A three-electrode cell assembly was used in which the working electrode was an ITO glass, the counter electrode was a stainless-steel wire, and an Ag wire was used as the pseudo-reference electrode. The copolymer films that were used for spectroelectrochemistry were prepared by potentiostatically depositing the polymer onto the ITO electrode (the active area:  $0.9\ \text{cm} \times 2.1\ \text{cm}$ ). The measurements were carried out in an ACN solution containing 0.2 M  $\text{NaClO}_4$ .

### Preparation of the gel electrolyte

A gel electrolyte based on PMMA and  $\text{LiClO}_4$  was plasticized with PC to form a highly transparent and conductive gel. ACN was also included as a high vapor-pressure solvent to allow easy mixing of the gel components. The composition of the casting solution by weight ratio of ACN:PC:PMMA: $\text{LiClO}_4$  was 70:20:7:3. The gel electrolyte was used for construction of the polymer cell.<sup>25</sup>

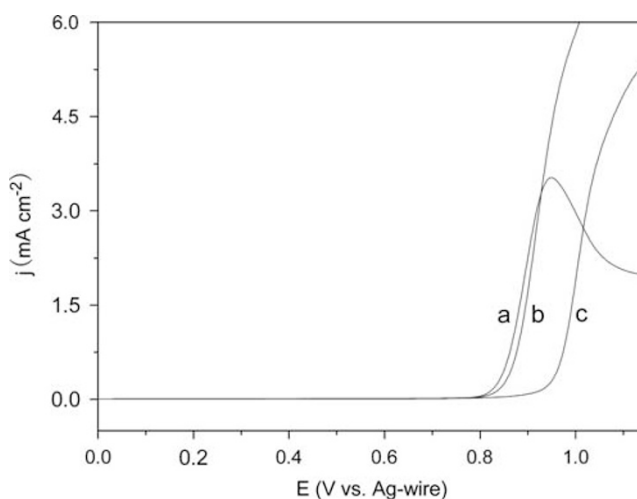
### Construction of electrochromic devices

ECDs were constructed using two complementary polymers, namely, P(CPDT-co-NMPy) as the anodic material and PEDOT as the cathodic material. Both P(CPDT-co-NMPy) and PEDOT films were electrodeposited on two ITO glass electrodes (the active area was  $1.8\ \text{cm} \times 2.5\ \text{cm}$ ) at +1.1 and +1.4 V, respectively. The ECDs were built by placing the two polymer films (one oxidized, the other reduced) directly across from each other and separated by a gel electrolyte.

## RESULTS AND DISCUSSION

### Electrochemical polymerization and characterization

**Electrochemical polymerization.** The anodic polarization curves of 0.004 M CPDT and 0.004 M NMPy in ACN solution containing 0.2 M  $\text{NaClO}_4$  are shown in Figure 1. The onset oxidation potentials ( $E_{\text{onset}}$ ) of CPDT and NMPy in the solution are approximately +0.85 V (Figure 1a) and +0.96 V (Figure 1c), respectively. The small distinction (0.11 V) between the onset oxidation potentials for the two monomers implies that copolymerization of CPDT and NMPy can be feasibly performed.<sup>26</sup> As observed in Figure 1b, the  $E_{\text{onset}}$  of the CPDT/NMPy at 1:1 mixture is 0.87 V, which is between the  $E_{\text{onset}}$  values for CPDT and NMPy. This intermediate value indicates that an interaction occurs between the two monomers in 0.2 M  $\text{NaClO}_4/$



**Figure 1** Anodic polarization curves of (a) 0.004 M CPDT, (b) 0.004 M CPDT and 0.004 M NMPy, and (c) 0.004 M NMPy in 0.2 M  $\text{NaClO}_4/\text{ACN}$ . Scanning rate:  $100\ \text{mV s}^{-1}$ .  $j$  denotes the current density. A full color version of this figure is available at *Polymer Journal* online.

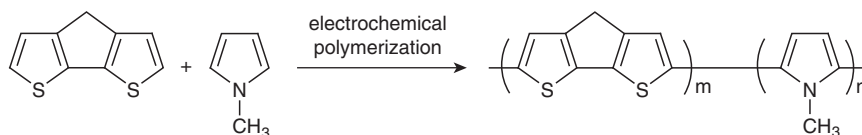
ACN.<sup>27</sup> The synthetic route of the copolymer of CPDT and NMPy is illustrated in Scheme 1.

Figure 2 displays the successive CV curves of 0.004 M CPDT, 0.004 M NMPy and the CPDT/NMPy mixture at 1:1 (0.004 M CPDT and 0.004 M NMPy) in an ACN solution containing 0.2 M NaClO<sub>4</sub> at a potential scan rate of 100 mV s<sup>-1</sup>. As observed from this figure, the CVs show features that are similar to other CPs, such as polythiophene and polypyrrole, during potentiodynamic syntheses. As the CV scan continued, the polymer films were formed on the working electrode surface. The increase in the redox wave current densities imply that the amount of CPs deposited onto the electrode was increasing. In Figure 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 +0.8 and -0.3 V and its reverse anodic peak at +0.63 V). The CV curves of NMPy (Figure 2c) show an oxidation peak at +0.65 V and a reduction peak at +0.5 V. However, the CV curve of the CPDT/NMPy mixture (prepared at 1:1 ratio) exhibits an anodic peak and a cathodic peak at +0.62 and +0.27 V, respectively (Figure 2b). These values are different from the values obtained

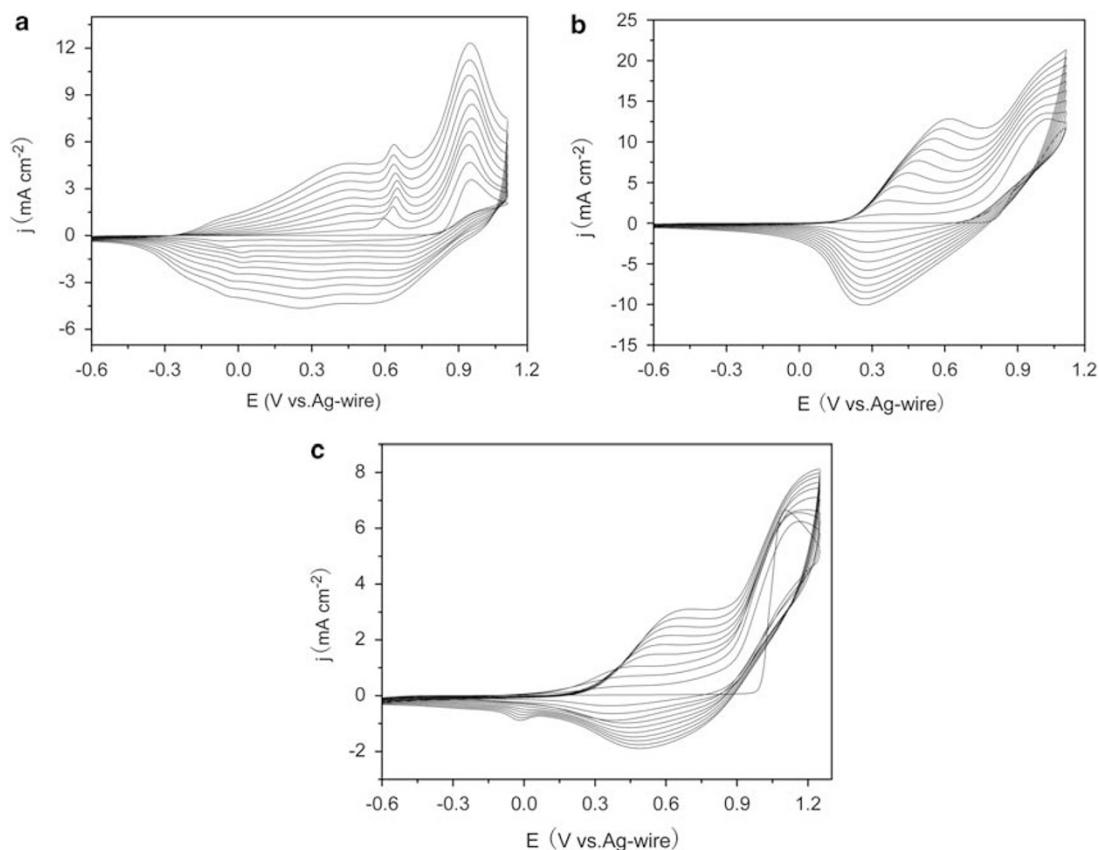
for CPDT and NMPy individually, indicating that a new polymer consisting of both CPDT and NMPy units was formed.<sup>28</sup> This evidence of a newly formed copolymer was not supported by other characterization techniques.

**Electrochemistry of the P(CPDT-co-NMPy) film.** P(CPDT-co-NMPy) film for use in CV tests was prepared potentiostatically using a 1:1 feed ratio of CPDT/NMPy on a platinum wire at +1.1 V. The film was washed with ACN, and redox switching in monomer free solution of ACN containing 0.2 M NaClO<sub>4</sub> showed a single, well-defined redox process as shown in Figure 3a. The peak current density response increased with an increase in the scan rate, indicating that the resulting copolymer film has good electrochemical activity and adhesion (Figure 3b). In addition, anodic and cathodic peak currents revealed a linear relationship as a function of scan rate for the copolymer, implying that the electrochemical processes of the copolymer are reversible and not diffusion limited.<sup>29</sup>

**FT-IR spectra of polymers.** The Fourier transform-infrared spectroscopy spectra of PCPDT, PNMPy and P(CPDT-co-NMPy) obtained



**Scheme 1** Synthetic route of the copolymer of CPDT and NMPy.



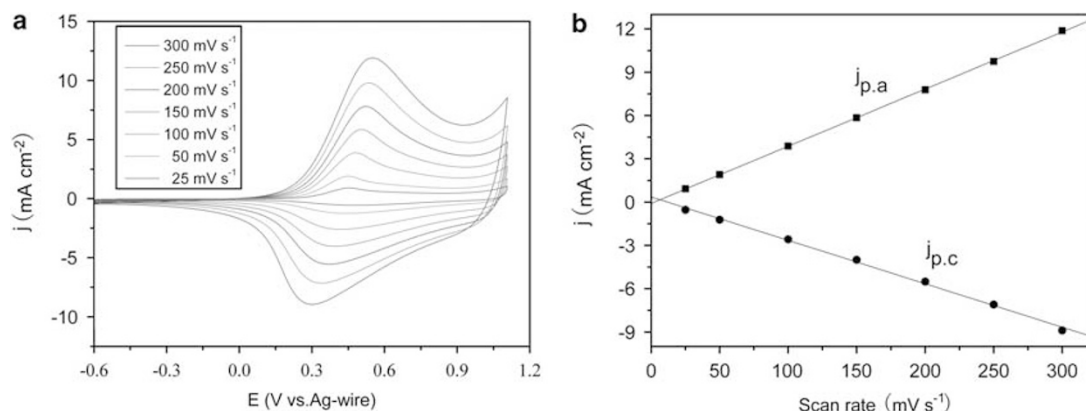
**Figure 2** Successive CV curves of (a) 0.004 M CPDT, (b) the mixture of 0.004 M CPDT and 0.004 M NMPy and (c) 0.004 M NMPy in ACN containing 0.2 M NaClO<sub>4</sub>. Scanning rate: 100 mV s<sup>-1</sup>. *j* denotes the current density. A full color version of this figure is available at *Polymer Journal* online.

under different applied potentials are shown in Supplementary Figure S1. In the spectrum of PCPDT (Supplementary Figure S1a), the peak at  $1633\text{ cm}^{-1}$  is due to the  $\text{C}=\text{C}$  stretching vibration of the thiophene ring, and the  $810\text{ cm}^{-1}$  band reflects the stretching mode of C-S. The absorption bands at  $989$  and  $943\text{ cm}^{-1}$ , which can be assigned to the pentadiene groups, are labeled in the figure.<sup>30</sup> According to the spectrum of PNMPy (Supplementary Figure S1c), the bands at  $2950$  and  $2933\text{ cm}^{-1}$  are attributed to the asymmetric and symmetric methyl C-H stretching; the peak at  $1384\text{ cm}^{-1}$  is assigned to the C-N stretching mode<sup>31</sup>; the bands at  $769$  and  $727\text{ cm}^{-1}$  show the C-H deformations of PNMPy. The spectra of P(CPDT-co-NMPy) (see Supplementary Figure S1b) contains the characteristic peaks of both PCPDT and PNMPy. For instance, the bands at  $1635$ ,  $993$ ,  $949$  and  $815\text{ cm}^{-1}$  indicate the presence of CPDT units. The bands at  $1388$  and  $761\text{ cm}^{-1}$  that originated from NMPy units are also observed. However, some apparent differences are shown between the copolymer and the homopolymers. For example, the peaks at  $2950$  and  $2933\text{ cm}^{-1}$  in the spectrum of PNMPy almost disappear in the copolymer, and the bands at  $993$  and  $949\text{ cm}^{-1}$  in the spectrum of the copolymer are weaker than the bands at  $989$  and  $943\text{ cm}^{-1}$  of PCPDT, indicating that the interactions between CPDT and NMPy units occur in the copolymers. All of the above features indicate that the copolymer contains both CPDT and NMPy units, which has yet to be supported by other characterization techniques.

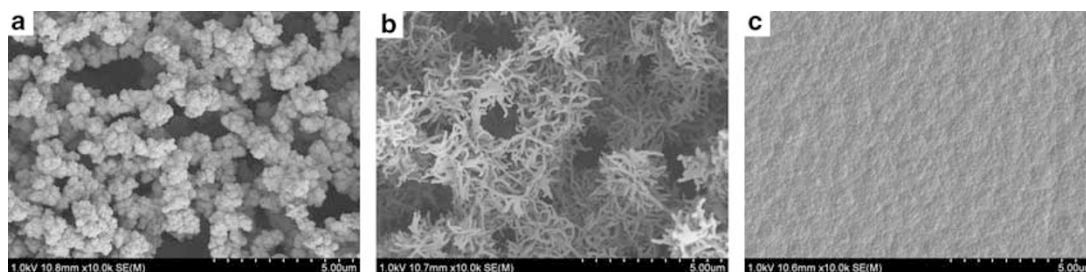
**Morphology.** The morphology of polymer films was investigated by scanning electron microscopy. Figure 4 shows the scanning electron microscopy images of PCPDT, P(CPDT-co-NMPy) and PNMPy, which were potentiostatically applied onto ITO electrodes and

de-doped before characterization. As shown in Figure 4a, PCPDT has granular particle clusters with a more porous structure. PNMPy film reveals a regular, smooth morphology with a compact surface that has nodules of very low average diameter (Figure 4c). However, the copolymer exhibits a porous texture with eucheuma-like clusters (Figure 4b). The difference in morphology between the copolymer and homopolymers also confirms the occurrence of copolymerization between CPDT and NMPy units.

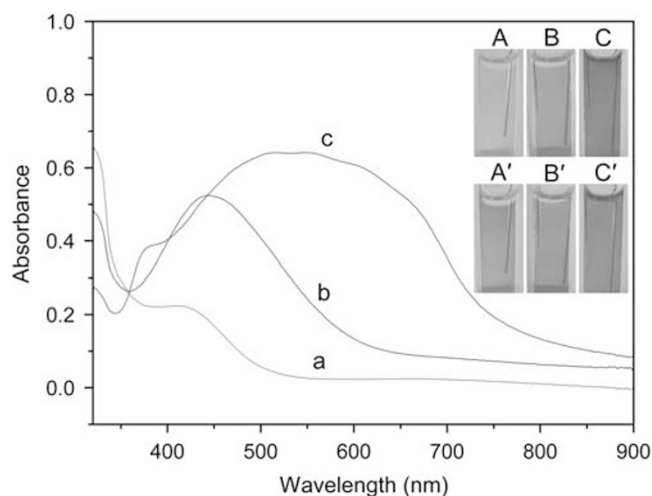
**UV-vis spectra of polymers.** Figure 5 depicts the UV-vis spectra of de-doped (a) PNMPy, (b) P(CPDT-co-NMPy) and (c) PCPDT that were deposited onto an ITO electrode with the same polymerization charge ( $3.2 \times 10^{-2}\text{ C}$ ) at  $+1.25$ ,  $+1.1$  and  $+1.1\text{ V}$ , respectively. For the PNMPy film (Figure 5a), there was a broad absorption at  $380\text{--}500\text{ nm}$  centered at  $425\text{ nm}$ , which was due to the  $\pi\text{--}\pi^*$  transition. Conversely, the spectrum of the PCPDT film shows a much broader absorption that appeared from  $345$  to  $740\text{ nm}$  with a maximum at approximately  $550\text{ nm}$  and a weak shoulder at  $380\text{ nm}$  (Figure 5c). The spectrum of P(CPDT-co-NMPy) shows both the characteristic absorptions of PCPDT and PNMPy, located at  $444\text{ nm}$  (Figure 5b). However, there is a slight red shift of the main absorption for the copolymer film in contrast to pure PNMPy due to the incorporation of CPDT. This observation further confirms the occurrence of copolymerization.<sup>32</sup> Furthermore, the colors of the polymer films on ITO in the de-doped and doped states were also recorded, as shown in the insets of Figure 5. PNMPy displays a light yellowish green color in the de-doped state and is pale cyan in the doped state (see insets A and A'), and PCPDT switches from purple to blue (see insets C and C'). The P(CPDT-co-NMPy) film change from



**Figure 3** (a) CV curves of the copolymer at different scan rates in the monomer-free solution of ACN containing  $0.2\text{ M NaClO}_4$ . (b) Graph of the scan rate dependence of the anodic and cathodic peak current densities.  $j_{p,a}$  and  $j_{p,c}$  denote the anodic and cathodic peak current densities, respectively. A full color version of this figure is available at *Polymer Journal* online.



**Figure 4** SEM images of (a) PCPDT, (b) P(CPDT-co-NMPy) and (c) PNMPy potentiostatically deposited on the ITO electrode.



**Figure 5** UV-vis spectra of de-doped (a) PNMPy, (b) P(CPDT-co-NMPy) and (c) PCPDT deposited on ITO at the neutral state. Insets: (A) light yellowish green, (B) reddish brown and (C) purple are the de-doped films and (A') pale cyan, (B') light blue and (C') blue are the doped films of PNMPy, P(CPDT-co-NMPy) and PCPDT, respectively. A full color version of this figure is available at *Polymer Journal* online.

a reddish brown color (inset B) to light blue (inset B'). The color of P(CPDT-co-NMPy) was significantly different from that of the two individual homopolymers, further confirming the formation of a copolymer consisting of both CPDT and NMPy units.

In addition, the optical band gap ( $E_g$ ) of polymer is deduced from the absorption band edges ( $\lambda_{\text{onset}}$ ). The  $E_g$  of the P(CPDT-co-NMPy) film was calculated as 2.12 eV, which was less than that of PNMPy (2.46 eV) and greater than that of PCPDT (1.68 eV). The effect of copolymerization between CPDT and NMPy leads to an obvious decrease in the  $E_g$  as compared with that of PNMPy, which implies that the introduction of CPDT units into PNMPy can reduce the  $E_g$  of the copolymer.

The UV-vis spectra of the de-doped copolymers produced at 2:1, 1:1 and 1:2 NMPy/CPDT feed ratios were also studied (see Supporting Information, Supplementary Figure S2). The absorption spectra of the resulting copolymers show a continuous red-shift and a reduction in the band gap as the feed ratio of NMPy/CPDT decreases. This observation implies that an increase in the CPDT units in polymer chain occurs. Fine-tuning in the band gap is achieved by tailoring the comonomer feed ratio of copolymerization.

Table 1 clearly summarizes the onset oxidation potential ( $E_{\text{onset}}$ ), maximum-absorption wavelength ( $\lambda_{\text{max}}$ ), low energy absorption edges ( $\lambda_{\text{onset}}$ ), HOMO and LUMO energy levels and the optical band gap ( $E_g$ ) values of PNMPy, PCPDT and the copolymers (prepared with the feed ratio of PNMPy/PCPDT at 2:1 (COP1), 1:1 (COP2) and 1:2 (COP3), respectively). HOMO energy levels of the monomers and copolymers were calculated using the formula  $E_{\text{HOMO}} = -e(E_{\text{onset}} + 4.4)$  (vs SCE), and LUMO energy levels ( $E_{\text{LUMO}}$ ) of each was calculated by the subtraction of the optical band gap ( $E_g$ ) from the HOMO levels.<sup>33</sup>

### Electrochromic properties of P(CPDT-co-NMPy) film

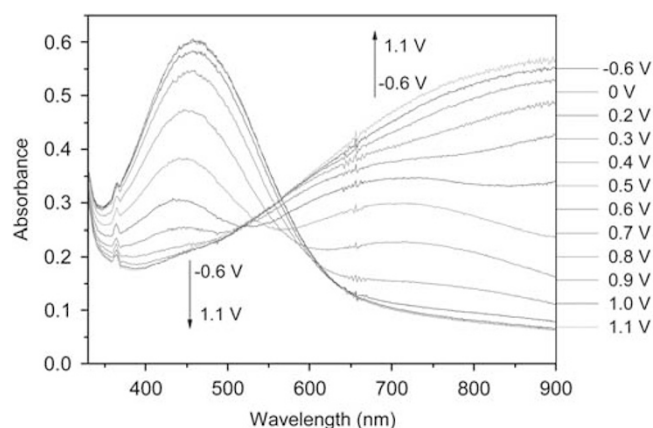
*Spectroelectrochemical properties of P(CPDT-co-NMPy) film.* Spectroelectrochemistry is a useful method for studying the changes in the absorption spectra and characterizing the electronic structures of conjugated polymers as a function of the applied voltage. The P(CPDT-co-NMPy) film-coated ITO electrode (prepared potenti-

**Table 1** The onset oxidation potential ( $E_{\text{onset}}$ ), maximum absorption wavelength ( $\lambda_{\text{max}}$ ), low energy absorption edges ( $\lambda_{\text{onset}}$ ), HOMO and LUMO energy levels and optical band gap ( $E_g$ ) values of PNMPy, PCPDT, and the copolymers (prepared with the feed ratio of NMPy/CPDT at 2:1, 1:1 and 1:2, respectively)

Compounds	$E_{\text{onset}}$ , vs (Ag-wire) (V)	$\lambda_{\text{max}}$ (nm)/ $\lambda_{\text{onset}}$ (nm)	$E_g^a$ (eV)	HOMO (eV)	LUMO <sup>b</sup> (eV)
PNMPy	+0.36	425/504	2.46	-4.84	-2.38
COP1	+0.20	437/563	2.20	-4.68	-2.48
COP2	+0.17	444/586	2.12	-4.65	-2.53
COP3	+0.15	460/616	2.01	-4.63	-2.62
PCPDT	-0.25	546/738	1.68	-4.23	-2.55

<sup>a</sup>Calculated from the low-energy absorption edges ( $\lambda_{\text{onset}}$ ).

<sup>b</sup>Calculated by the subtraction of the optical band gap ( $E_g$ ) from the HOMO level.

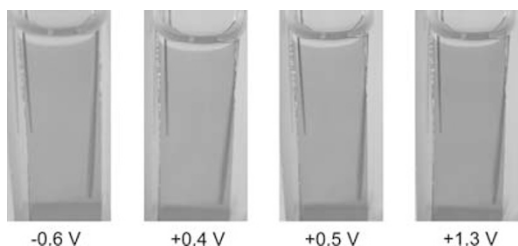


**Figure 6** Spectroelectrochemical spectra of P(CPDT-co-NMPy) with applied potentials between -0.6 and +1.1 V in monomer-free ACN solution containing 0.2 M NaClO<sub>4</sub>. Applied potentials range from -0.6 to +1.1 V. A full color version of this figure is available at *Polymer Journal* online.

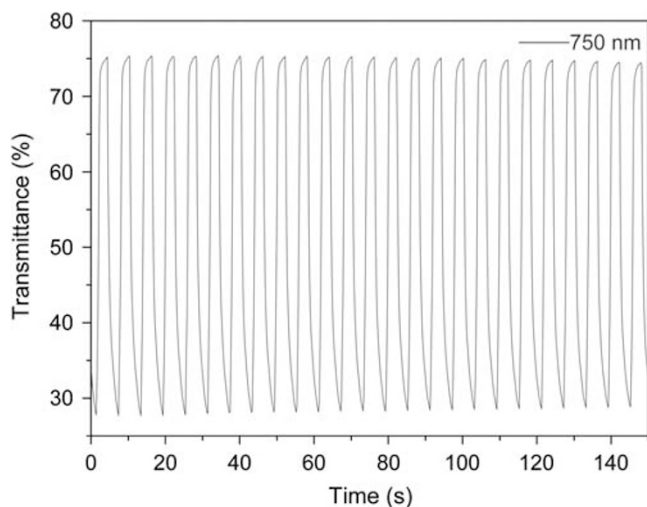
statically at +1.1 V) was switched between the neutral (-0.6 V) and doped (+1.1 V) states in an ACN solution containing 0.2 M NaClO<sub>4</sub> to obtain the in situ UV-vis spectra (Figure 6). At the neutral state, the copolymer film exhibited an absorption band at 458 nm due to the  $\pi-\pi^*$  transition. The intensity of the P(CPDT-co-NMPy)  $\pi-\pi^*$  electron transition absorption decreased, whereas a charge carrier absorption band located at approximately 750 nm increased dramatically upon oxidation.

In addition, it was interesting to find that the P(CPDT-co-NMPy) film showed a multicolor electrochromism. To study the range of colors, a wide interval of potentials (-0.6 to +1.3 V) was applied on the as-prepared P(CPDT-co-NMPy) films. As observed from Figure 7, P(CPDT-co-NMPy) film exhibited four different colors during neutral and oxidized states. The reddish brown color of the film at the neutral state (-0.6 V) turned into a pale tan color (+0.4 V) and pale sea green (+0.5 V) at the intermediately doped states and then into a light blue color in the fully doped state (+1.3 V). This multicolor property gives these materials the potential for use in applications for smart windows or displays.<sup>34</sup>

*Electrochromic switching of P(CPDT-co-NMPy) film in solution.* It is important that polymers can switch rapidly and exhibit a noteworthy color change for electrochromic applications.<sup>35</sup> For this purpose, a double-potential step chronoamperometry technique was used to



**Figure 7** Colors of the P(CPDT-co-NMPy) film at different applied potentials in an ACN solution containing 0.2 M NaClO<sub>4</sub>. A full color version of this figure is available at *Polymer Journal* online.



**Figure 8** Electrochromic switching response for P(CPDT-co-NMPy) film monitored at 750 nm in 0.2 M NaClO<sub>4</sub>/ACN solution between -0.6 and +1.1 V with a residence time of 3 s.

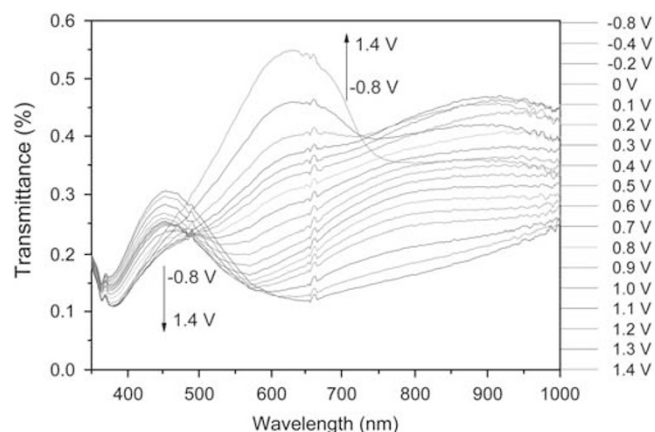
investigate the switching ability of P(CPDT-co-NMPy) film between its neutral and fully doped state (Figure 8). The dynamic electrochromic experiment for P(CPDT-co-NMPy) films was carried out at 750 nm. The potential was interchanged between -0.6 V (the neutral state) and +1.1 V (the oxidized state) at regular intervals of 3 s. One important characteristic of electrochromic materials is the optical contrast ( $\Delta T\%$ ), which can be defined as the difference in transmittance between the redox states. The  $\Delta T\%$  of the P(CPDT-co-NMPy) was found to be 47.0% at 750 nm, as shown in Figure 8.

The coloration efficiency (CE) is also an important characteristic for the electrochromic materials. CE can be calculated using the following equations<sup>36</sup>

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

where  $T_b$  and  $T_c$  are the transmittances before and after coloration, respectively.  $\Delta OD$  is the change of the optical density, which is proportional to the amount of color centers created.  $\eta$  denotes the CE.  $\Delta Q$  is the amount of injected charge per unit sample area. The CE value for the P(CPDT-co-NMPy) film was measured as 117.7 cm<sup>2</sup> C<sup>-1</sup> (at 750 nm) in the fully doped state, which had a reasonable CE.

Response time, one of the most important characteristics of electrochromic materials, is the time needed to perform switching between the neutral state and the oxidized state of the materials. The



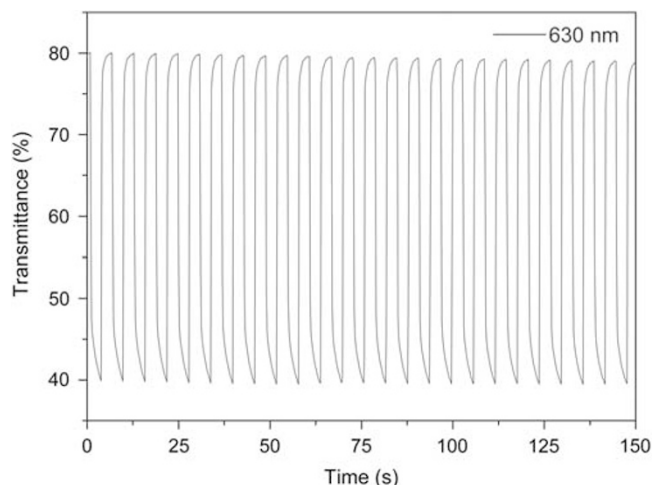
**Figure 9** Spectroelectrochemical spectra of the P(CPDT-co-NMPy)/PEDOT device at various applied potentials between -0.8 and +1.4 V. A full color version of this figure is available at *Polymer Journal* online.

response required to attain 95% of total transmittance difference was determined to be 2.20 s from the reduced to the oxidized state and 1.02 s from the oxidized to the reduced state. Thus, P(CPDT-co-NMPy) can be rapidly switched to the reduced state, which can be attributed to the ease of charge transport in the conducting film when it is reduced. Based on this information, the distinct optical contrast, the satisfactory CE and switching property make P(CPDT-co-NMPy) a promising electrochromic material.<sup>24</sup>

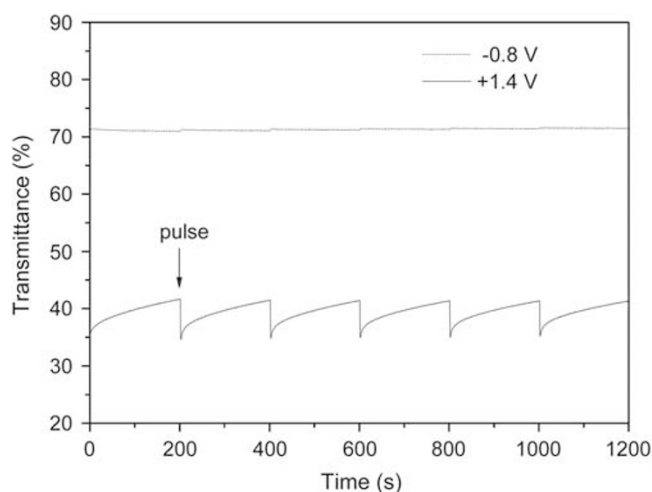
### Spectroelectrochemistry of electrochromic devices

**Spectroelectrochemical properties of ECDs.** A dual-type ECD consisting of P(CPDT-co-NMPy) and PEDOT was constructed, and its spectroelectrochemical behavior was also studied. Before composing the ECD, the anodic polymer film (P(CPDT-co-NMPy)) was fully reduced and the cathodic polymer film (PEDOT) was fully oxidized. The P(CPDT-co-NMPy)/PEDOT device was switched between -0.8 and +1.4 V. The spectroelectrochemical results are shown in Figure 9. At -0.8 V, the P(CPDT-co-NMPy) layer was in its neutral state, and PEDOT was in the oxidized state. Under these conditions, the device color was reddish brown. Thus, there was maximum absorption at approximately 450 nm due to  $\pi$ - $\pi^*$  transition of P(CPDT-co-NMPy), which was the electrochromic layer. As the applied potential increased, the P(CPDT-co-NMPy) layer started to oxidize, and the intensity of the peak due to the  $\pi$ - $\pi^*$  transition decreased. Concurrently, the PEDOT layer was reduced, and the evolution of a new intense absorption was observed at approximately 630 nm ( $\pi$ - $\pi^*$  transition of PEDOT itself). The dominant color of the device during this time was blue at +1.4 V.

**Switching of ECD.** Kinetic studies were also performed to test the percentage of transmittance changes and the response time of the P(CPDT-co-NMPy)/PEDOT ECD. Under a potential input of -0.8 and +1.4 V at regular intervals of 3 s, the optical response at 630 nm is illustrated in Figure 10. The optical contrast ( $\Delta T\%$ ) was calculated to be 40.2%. The response time was found to be 1.77 s at 95% of the maximum transmittance difference from the neutral state to the oxidized state and 0.53 s from the oxidized state to the neutral state. The CE of the device (the active of area: 1.8 × 2.5 cm) was calculated to be 476 cm<sup>2</sup> C<sup>-1</sup> at 630 nm. The spectroelectrochemical spectra and the optical response of the PNMPy/PEDOT device were also investigated (see Supporting Information, Supplementary Figures S3 and S4). This ECD showed a maximum optical contrast ( $\Delta T\%$ ) of



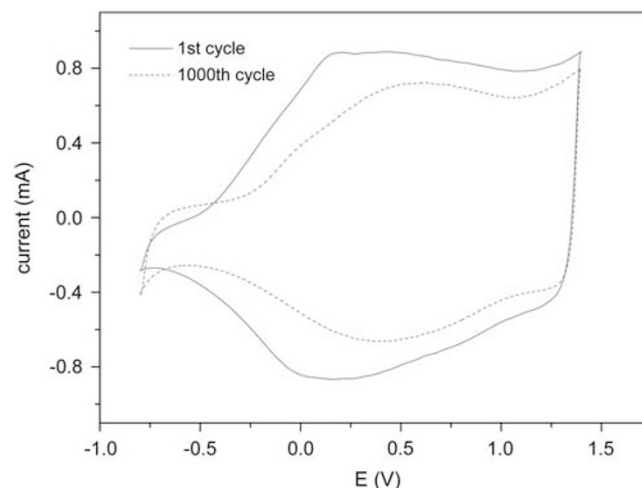
**Figure 10** Electrochromic switching, optical transmittance change monitored at 630 nm for the P(CPDT-co-NMPy)/PEDOT device between  $-0.8$  V and  $+1.4$  V with a residence time of 3 s. A full color version of this figure is available at *Polymer Journal* online.



**Figure 11** Open circuit stability of the P(CPDT-co-NMPy)/PEDOT device monitored at 630 nm.

20.4%, a response time of 0.37 s, and a CE of  $271 \text{ cm}^2 \text{ C}^{-1}$  at 620 nm. The P(CPDT-co-NMPy)/PEDOT device demonstrated high optical contrast (40.2%) and high CE ( $476 \text{ cm}^2 \text{ C}^{-1}$ ) as compared with the P(NMPy)/PEDOT device as a result of the introduction of CPDT units into the polymer backbone.

**Open circuit memory of ECD.** The optical memory in ECDs is an important characteristic as it is directly related to its application and energy consumption during the use of ECDs.<sup>35</sup> The optical spectrum for the P(CPDT-co-NMPy)/PEDOT device was monitored at 630 nm as a function of time at  $-0.8$  and  $+1.4$  V by applying the potential for 1 s for every 200-s time interval. As shown in Figure 11, in the reddish brown-colored state, the device showed a true permanent memory as there was nearly no transmittance change under the applied potential or open-circuit conditions. In the 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.



**Figure 12** Cyclic voltammogram of the P(NMPy-co-CPDT)/PEDOT device as a function, repeated with a scan rate of  $500 \text{ mV s}^{-1}$ .

**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 characteristic for ECD.<sup>37</sup> For this reason, the P(CPDT-co-NMPy)/PEDOT device was tested by CV of the applied potential between  $-0.8$  and  $+1.4$  V with  $500 \text{ mV s}^{-1}$  to evaluate the stability of the device (Figure 12). After 1000 cycles, 75.2% of its electroactivity was retained. These results show that this device has reasonable redox stability.

## CONCLUSION

A new copolymer based on NMPy and CPDT was electrochemically synthesized and characterized. The experiments revealed that the introduction of CPDT units can reduce the band gap ( $E_g$ ) of the copolymer, with the new copolymer having an optical band gap of 2.12 eV. Furthermore, the new copolymer had a reversible redox process and exhibited electrochromic behavior. The maximum contrast ( $\Delta T\%$ ) and response time of the copolymer film was measured as 47.0% and 2.20 s at 750 nm.

Additionally, an ECDs based on P(CPDT-co-NMPy) and PEDOT was constructed and characterized. An electrochromic switching experiment revealed that the copolymerization with CPDT can enhance the electrochromic properties. For the device, the maximum contrast and response time were 40.2% and 1.77 s at 630 nm. This ECD also shows satisfactory optical memory and redox stability. As one of the most important parameters of ECDs, CE was calculated to be  $476 \text{ cm}^2 \text{ C}^{-1}$ . Considering these features, this device is a promising candidate for commercial applications.

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