



# A new low-voltage-driven polymeric electrochromic

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## ABSTRACT

Design, synthesis, and properties of a novel donor-acceptor-donor type low-voltage-driven green polymeric electrochrome, **P1**, which is based on 8-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-11-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)acenaphtho[1,2-b]quinoxaline (**1**) are highlighted. It is noted that **P1** has an ambipolar (n- and p-doping processes) character in 0.1 M tetrabutylammonium hexafluorophosphate/dichloromethane solution and switches to a transmissive blue state upon oxidation. Furthermore, this new polymeric electrochromic candidate exhibits high redox stability, high coloration efficiency and/or contrast ratio, high percent transmittance (%T) and low response time (1.0 s) with a band gap of 1.10 eV–1.25 eV.

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## 1. Introduction

The development of organic  $\pi$ -conjugated polymers has been intensively pursued since they offer great potential for advanced technological applications. In particular, they have become one of the most favored electrochromes in devices [1,2], optical displays [3], smart windows [4,5], mirrors [6,7], and camouflage materials [8,9] due to their low cost, compatibility and tunable intrinsic (electronic, optical, and conductivity) properties offered by the structural design of the starting materials [10–12]. Recent efforts in the field of polymeric electrochromics (PECs) have focused on the design of macromolecular conjugated systems based on alternating electron-rich (donor, D) and –poor (acceptor, A) units [13]. Fortunately, these D-A systems did not only allow a fine tuning of the band gap ( $E_g$ ) of the as-prepared organic materials [14–17] but also provided access to a wide range of neutral state red, blue [18,19] and more recently green [20–27] (*Red, Green and Blue constitute the primary additive colour-space, RGB*) PECs. Nevertheless, the number of low-voltage-driven D-A systems which reflect and/or transmit the green leg of RGB colour-space is still meager due to common difficulties of producing the green color (i.e. at least two absorption bands in the visible region which could deplete simultaneously during the redox processes). Therefore, it is a challenging task to attain novel low-voltage-driven neutral state green PECs in the context of color-changing systems including smart glass and/or innovative high performance polymeric RGB display technologies [22,28–30], memory devices [31], and e-papers [28].

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In this connection, recently a series of neutral state green PECs based on D-A systems was designed and synthesized by our group [32,33]. Taking into account these results, we turned our attention to a new hybrid material which was based on acenaphthoquinone scaffold and EDOT units, namely 8-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-11-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)acenaphtho[1,2-b]quinoxaline (**1**). It was envisaged that this newly designed system, **1**, would provide a low-voltage-driven PEC which would exhibit the green color in its neutral form when electrochemically polymerized to give **P1** (Chart 1). EDOT units as D-parts would both assure linear polymer chains and play key roles on the redox behavior by intermolecular charge transfer within D-A system. Furthermore, it might be possible to get a low band gap material when acenaphthoquinoxaline unit [34–37] was incorporated in the main chain as the A-unit. In this article, we wish to report the design, synthesis and properties of a new low-voltage-driven green polymeric electrochrome, **P1**, which switches to a highly transmissive blue state upon doping. Furthermore, this ambipolar PEC candidate exhibits high redox stability, high coloration efficiency (CE), high percent transmittance (%T) and/or contrast ratio and low response time (1.0 s) with a band gap of 1.10 eV–1.25 eV. A comparison of this PEC **P1** with its hexylthiophene D-unit analogue (**P2**) [36] was also given.

## 2. Experimental

### 2.1. Materials

All chemicals were purchased from Aldrich Chemical and used as received unless otherwise noted. 0.1 M tetrabutylammonium

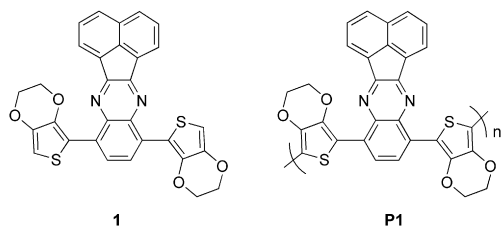


Chart 1.

hexafluorophosphate (TBAH) dissolved in dichloromethane (DCM) and acetonitrile (ACN) was used as electrolyte solution.

## 2.2. Methods

A platinum disk (0.02 cm<sup>2</sup>) and a platinum wire were used as working and counter electrodes, respectively, as well as a silver wire as a pseudo-reference electrode (calibrated externally using 5 mM solution of ferrocene/ferrocenium couple). Repetitive cycling or constant potential electrolysis was used to obtain the polymer films. Electro-optical properties were investigated by using an indium tin oxide (ITO, Delta Tech. 8–12 Ω, 0.7 cm × 5 cm) electrode as well as a platinum wire as counter electrode and a Ag wire as a pseudo-reference electrode. In order to equilibrate the redox behavior of the polymer film and to obtain repeated results, the coated polymer films were switched between their neutral and oxidized states several times before electroanalytical and optical studies. Electroanalytical measurements were performed using a Gamry PCI4/300 potentiostat–galvanostat. The electro-optical spectra were monitored on a Hewlett–Packard 8453A diode array spectrometer. Photographs of the polymer films were taken by using a Canon (PowerShot A75) digital camera. **4–5** [38] and **8** [37] were prepared according to literature procedures.

## 2.3. Synthesis of 8,11-dibromoacenaphtho[1,2-b]quinoxaline (**7**)

Solutions of **5** (266 mg, 1 mmol) and **6** (182 mg, 1 mmol) in 20 ml HOAc were heated to 80 °C overnight while stirring magnetically. The flask was cooled to room temperature and extracted with CHCl<sub>3</sub>

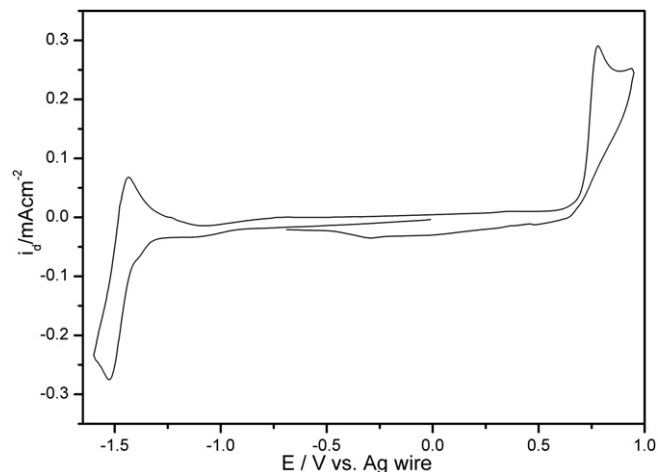
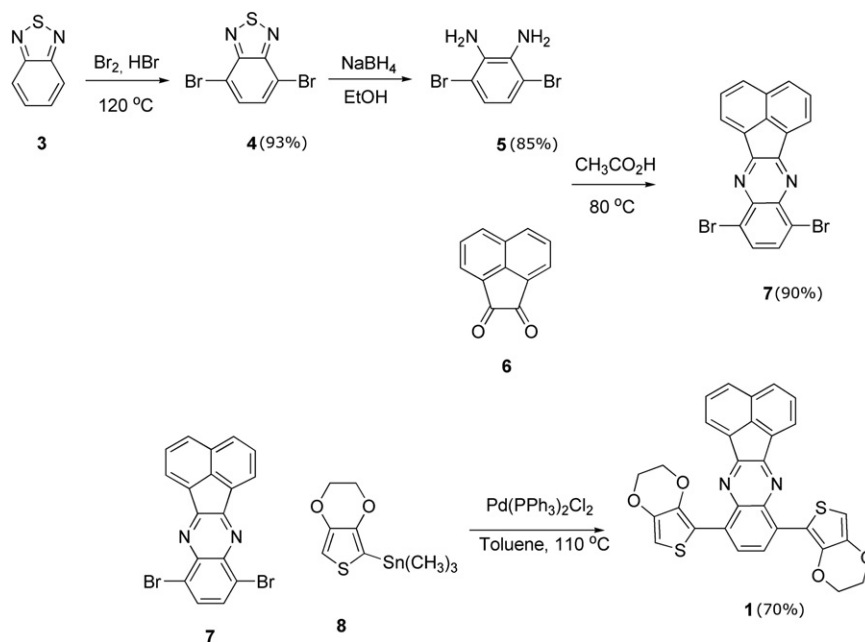


Fig. 1. Cyclic voltammogram of **1** in 0.1 M TBAH/DCM at a scan rate of 100 mV/s.

(3 × 100 ml) after neutralization with saturated NaHCO<sub>3</sub>. Organic part was washed with water (2 × 100 ml), dried over MgSO<sub>4</sub> and filtered. The solvent was removed under reduced pressure to give **7** as white solid in 90% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.50 (d, J = 7.0 Hz, 2H), 8.10 (d, J = 7.1 Hz, 2H), 7.86 (s, 2H), 7.81 (t, J = 7.1 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 155.1, 140.1, 137.3, 132.7, 130.9, 130.3, 130.0, 128.8, 124.4, 123.3. Anal. Calcd for C<sub>18</sub>H<sub>8</sub>N<sub>2</sub>Br<sub>2</sub>: C 52.46, H 1.96, N 6.80; found: C 52.41, H 1.98, N 6.71.

## 2.4. Synthesis of 8,11-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)acenaphtho[1,2-b]quinoxaline (**1**)

To argon degassed solutions of **7** (300 mg, 0.73 mmol) and **8** (450 mg, 1.46 mmol) in dry toluene (15 ml) were added Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (100 mg) and the mixture was heated under reflux overnight. After cooling to room temperature, the solvent was removed under reduced pressure and the crude mixture was chromatographed on silica gel by eluting with *n*-hexane:chloroform (1:1, v/v) to give **1** as orange solid in 70% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.27–8.21 (m, 2H), 8.13 (s, 2H), 7.92 (dd, J = 8.0–1.4 Hz, 2H), 7.65 (dd, J = 8.0–1.0 Hz,



Scheme 1. Synthesis of **1**.

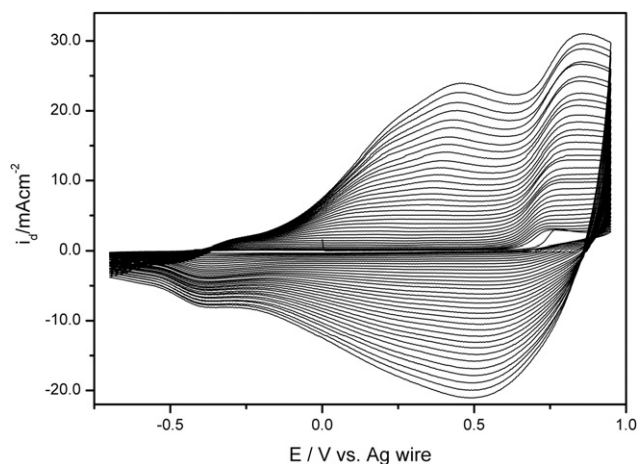


Fig. 2. Repeated scan electropolymerization of **1** in 0.1 M TBAH/DCM at a scan rate of 100 mV/s.

2H), 6.34 (s, 2H), 4.20 (bs, 4H), 4.10 (bs, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 152.3, 141.6, 140.2, 132.6, 129.8, 129.7, 128.6, 128.0, 126.6, 123.7, 122.9, 113.7, 103.7, 101.9, 65.0, 64.3; Anal. Calcd for  $\text{C}_{30}\text{H}_{18}\text{N}_2\text{O}_4\text{S}_2$ : C 67.40, H 3.39, N 5.24, S 12.00; found: C 67.35, H 3.44, N 5.19, S 11.79.

### 3. Results and discussion

#### 3.1. Synthesis

As depicted in Scheme 1, synthesis of **1** was carried out by following well-established literature procedures with slight modifications. Bromination of **3** afforded **4** [38], which was converted to diamine **5** [38] by treatment with  $\text{NaBH}_4$  in ethanol. Condensing diamine **5** with **6** resulted in the formation of quinoxaline **7** and finally, Stille coupling reaction of **7** with **8** [37] gave the target D-A system. Initial characterization of **1** was based on  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data along with the combustion analysis which firmly established the structure.

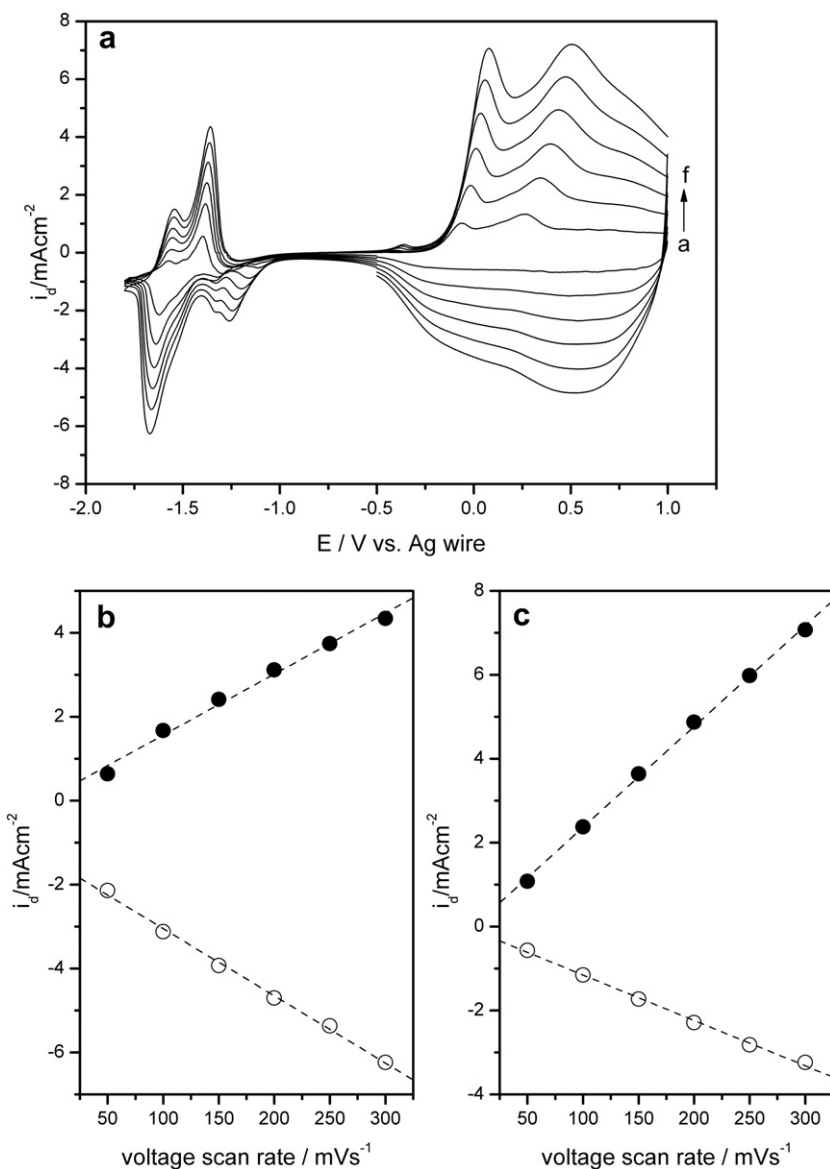
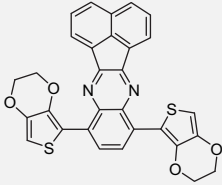
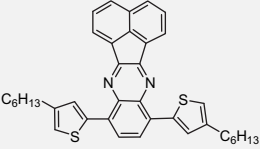


Fig. 3. (a) Scan rate dependence of the polymer film in 0.1 M TBAH/DCM at different scan rates, a: 50 mV/s; b: 100 mV/s; c: 150 mV/s; d: 200 mV/s; e: 250 mV/s; f: 300 mV/s; Relationship of anodic (●) and cathodic (○) current peaks as a function of scan rate for (b) n- and (c) p-doped P1 film in 0.1 M TBAH/DCM.

**Table 1**  
The structures and properties of quinoxaline based polymers **P1** and **P2**.

Monomer	$E_{m}^{ox}$ (V)	Polymer	$E_{p,1/2}^{ox}$ (V)	$E_{p,1/2}^{red}$ (V)	$\lambda_{max}$ (nm)	$E_g$ (eV)	Solubility
 <p style="text-align: center;"><b>1</b></p>	+0.78	<b>P1</b>	-0.02	-0.52	320 415 690	1.25 <sup>b</sup> 1.10 <sup>c</sup>	+
 <p style="text-align: center;"><b>2</b></p>	+1.10	<b>P2</b>	+0.85 <sup>a</sup>	-1.25 <sup>a</sup>	430 675	1.2 <sup>b</sup>	-

<sup>a</sup> Estimated from corresponding reference [36].

<sup>b</sup> Calculated from the onset of absorption band.

<sup>c</sup> Calculated from CV and DPV measurements (onset potentials).

### 3.2. Electrochemistry and polymerization of **1**

In order to investigate the redox behavior of **1**, cyclic voltammetry studies were performed in 0.1 M TBAH/DCM solution. It was noted that **1** exhibited ambipolar redox behavior (Fig. 1). As illustrated in Fig. 1, during anodic scan an irreversible oxidation peak at 0.78 V vs. Ag wire ( $E_{m,a}^{ox} = 0.43$  V vs. Fc/Fc<sup>+</sup>) which was attributed to the oxidation of the D-units in the system was observed. On the other hand, the presence of a reversible reduction peak with a half peak potential of -1.49 V can be ascribed to the formation of stable radical anion during cathodic scan (Fig. 1). These results were in line with the electronic nature of D-units in compounds **1** and **2**, since EDOT was electron-rich which predicated lower oxidation (and higher reduction) potential(s) on D-A type system **1** when compared to hexylthiophene of **2** (1.10 V) [36], as expected.

The formation of an electroactive polymer film, **P1**, was observed when the potential was cycled between -0.7 V and 0.95 V. The appearance of a new reversible redox couple with a concomitant increase in the current intensity of this couple after each successive cycle was evident during anodic scan (Fig. 2).

It was also noteworthy that **P1** showed an ambipolar character (both n- and p-type doping processes), as in the case of **1**, when its redox behavior was elaborated in monomer free electrolyte solution. **P1** exhibited a well-defined reversible redox couple during p-doping ( $E_{p,1/2}^{ox}$ ) at -0.14 V (Fig. 3a). However, a linear dependence of the peak currents as a function of scan rates confirmed both a nondiffusional redox process and a well-adhered electroactive polymer film (Fig. 3b,c). The p-doping process takes place much easier for **P1** when compared to **P2** (Table 1).

On the other hand, the n-doping of **P1** which principally took place in the A-(acenaphtho[1,2-*b*]quinoxaline) units of the polymer backbone was reversible and quite stable with a well-defined half peak potential ( $E_{p,1/2}^{red}$ ) of -1.49 V. The ambipolar nature of **P1** with superior n- and p-doping processes suggested that it was an excellent candidate for device applications such as capacitors, electrochromics and n-p type transistors [39]. It is well-known that a rectangular shape of voltammogram which should ideally be persistent even at high scan rates indicating a rapid charge/

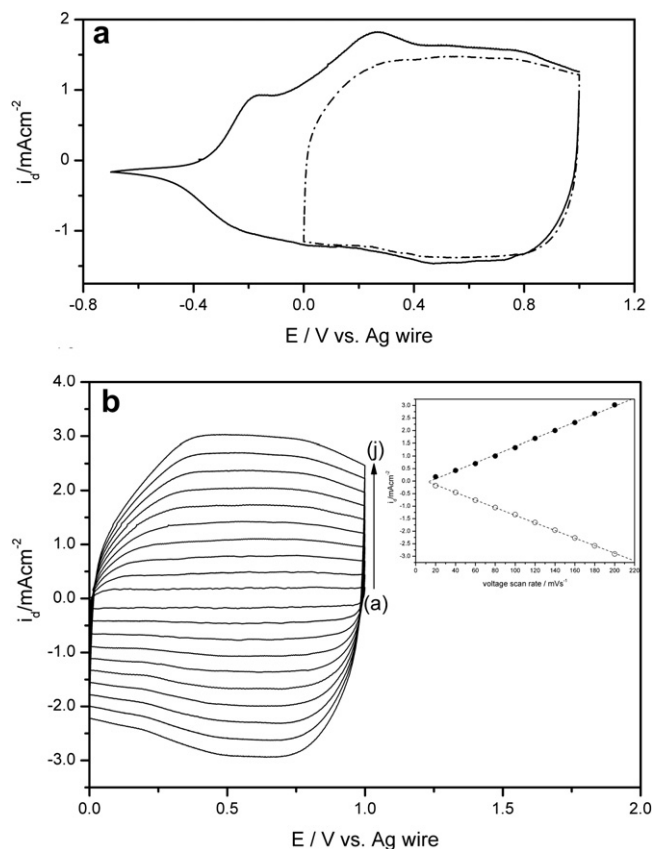
discharge (doping/dedoping) process is the characteristic feature of the electrochemical capacitors. To investigate the utility of **P1** as a capacitor, it was cycled in a potential range of 0.0 V–1.0 V as a function of scan rate (Fig. 4). It was found that **P1** had a rectangular shaped voltammogram which was sustained even at high scan rates acquiring rapid charge/discharge process (Fig. 4b).

### 3.3. Electro-optical properties of **P1**

The optical properties of **P1** were investigated by monitoring the changes in electronic absorption spectra upon doping process. Electrodeposition of the polymer film on ITO glass slide was followed by washing with DCM to get rid off the residual monomers and/or oligomeric species. The neutralization of the polymer film was achieved at -0.7 V. The polymer film was green in its neutral state as noted above. It is worth to mention that **P1** has three well-defined absorption maxima (at 320 nm, 415 nm, and 690 nm) including deep valleys (371 nm and 503 nm) controlling the hue and brightness of the green color in the neutral form (Fig. 5) [20].

As the polymer film **P1** was oxidized, the intensities of the bands decreased simultaneously at low doping levels and a broad absorption band centered on 810 nm started to intensify due to the formation of charge carriers, as depicted in Fig. 5. Upon further oxidation, the bipolaron band (at 930 nm) at 0.50 V formed, which was also monitored synchronously with cyclic voltammetry (Fig. 5, inset). The absorption bands at 320, 415 and 690 nm reached its minimum intensity during this process (p-doping). On the other hand, a true n-doping behavior of the polymer film was confirmed by *in situ* monitoring the UV-vis spectra during reduction process (Fig. 6). The  $\pi$ - $\pi^*$  transition bands began to diminish concurrently with intensifying of new absorption bands at 468, 540, 760, and 1000 nm.

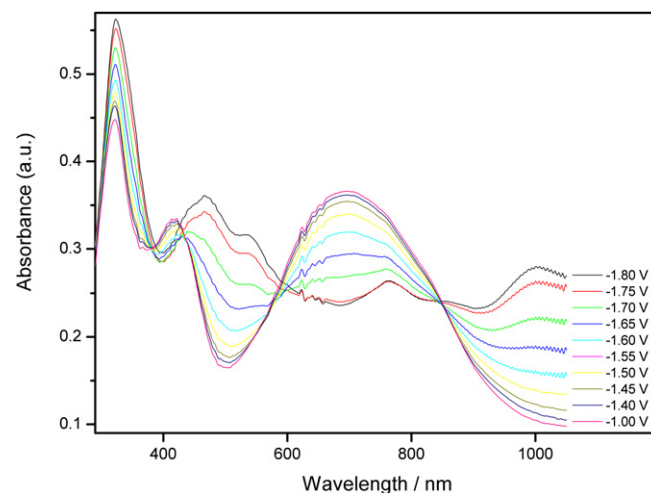
These changes in electronic absorption spectra of **P1** upon p- and n-doping processes nicely reflected by color changes from green to a transmissive blue and gray-purple color, respectively (Fig. 7). Interestingly, it was found that the polymer film was dissolved when it was exposed to a potential of -1.70 V leading in turn a homogeneous green solution and heaped particles in solution (Fig. 7 inset). Although it is not clear yet, we assume that the ion



**Fig. 4.** (a) (solid line) Cyclic voltammetry and (– –) capacitance effect of P1 film at a scan rates of 100 mV/s (b) capacitance effect of P1 film as a function of scan rate at (a) 20, (b) 40, (c) 60, (d) 80, (e) 100, (f) 120, (g) 140, (h) 160, (i) 180, and (j) 200 mV/s (inset) relationship of anodic (●) and cathodic (○) current peaks as a function of scan rate for P1 film in 0.1 M TBAH/DCM.

flux was so effective that the polymer was solubilized during n-doping (probably, the interactions of the doped polymer and tetrabutylammonium ions of the electrolyte played a key role on the solubility) after which the polymer chains was aggregated.

The band gap ( $E_g$ ) value which was calculated from the onset of the low energy end of  $\pi$ - $\pi^*$  transition band (at 690 nm) for green

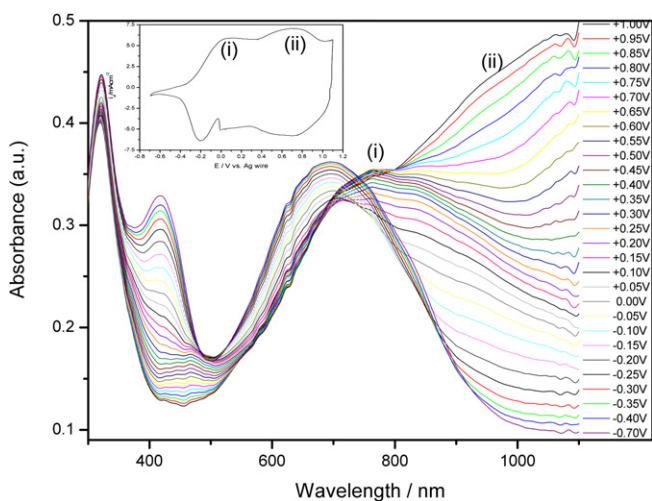


**Fig. 6.** Electronic absorption spectra of P1 ( $7.5 \text{ mC/cm}^2$ ) on ITO in 0.1 M TBAH/DCM at various applied potentials between  $-1.0$  and  $-1.8 \text{ V}$ .

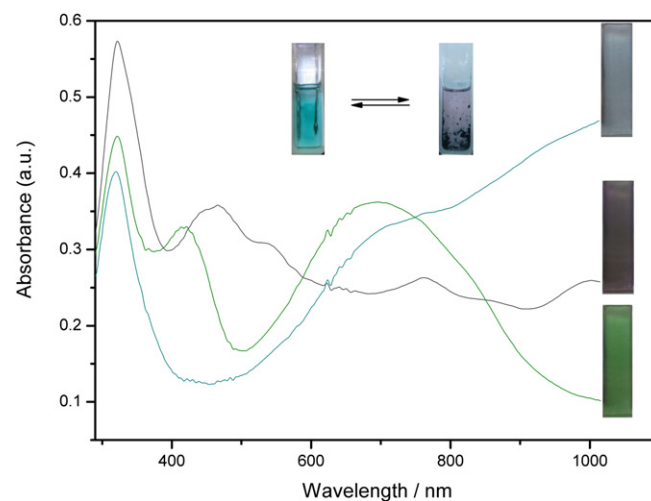
polymer was 1.25 eV. In comparison to spectroelectrochemical method, the  $E_g$  value was also estimated by both cyclic (CV) and differential pulse voltammetry (DPV) techniques which is one of the best methods to determine  $E_g$  value due to the elimination of capacitive current during process [35,40]. The values of  $E_g$  from the onsets of redox waves obtained by the two electrochemical methods (CV and DPV) were found to be 1.10 eV (Fig. 8). On the basis of CV and DPV, the highest molecular orbital and lowest unoccupied molecular orbital levels with respect to ferrocene/ferrocenium (4.8 eV) were calculated to be 4.12 eV and 3.02 eV, respectively.

#### 3.4. Switching and stability of P1

The development of optical and electrochromic devices mainly depends on the stability and the switching ability of electroactive polymer film between its redox states. Therefore, the stability of polymer film P1 was investigated between neutral and oxidized states at a scan rate of 200 mV/s under air atmosphere. No significant change in redox response of the polymer was observed at the end of a thousand cycles. In addition, the switching ability of the

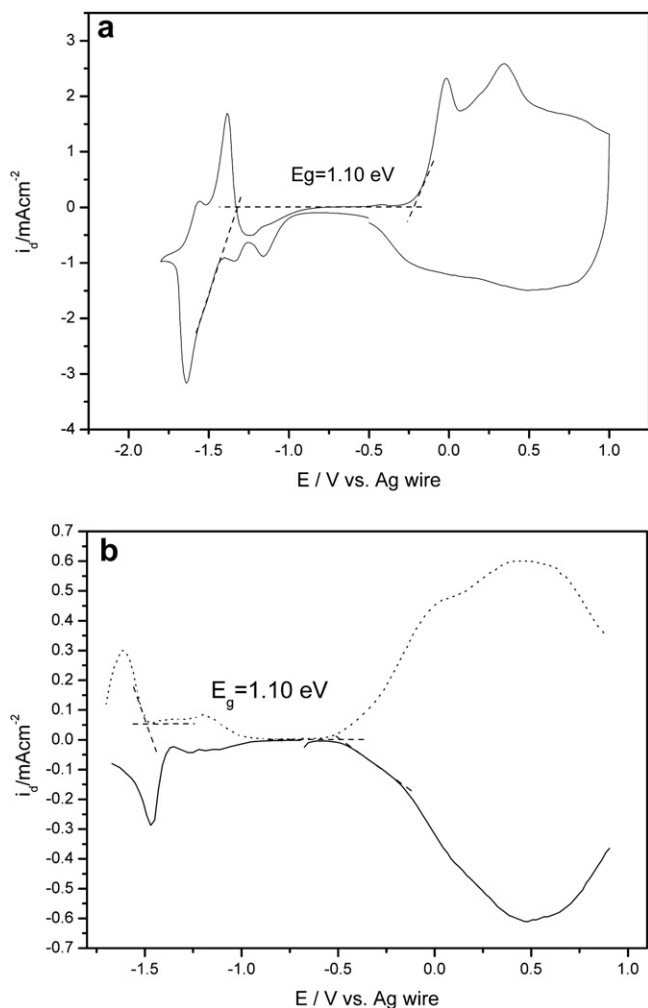


**Fig. 5.** Electronic absorption spectra of P1 ( $7.5 \text{ mC/cm}^2$ ) on ITO in 0.1 M TBAH/DCM at various applied potentials between  $-0.7$  and  $1.0 \text{ V}$ .



**Fig. 7.** Electronic absorption spectra and the color on ITO in 0.1 M TBAH/DCM at  $-0.7 \text{ V}$  (at neutral state),  $-1.7 \text{ V}$  (at reduced state) and  $1.0 \text{ V}$  (at oxidized state).





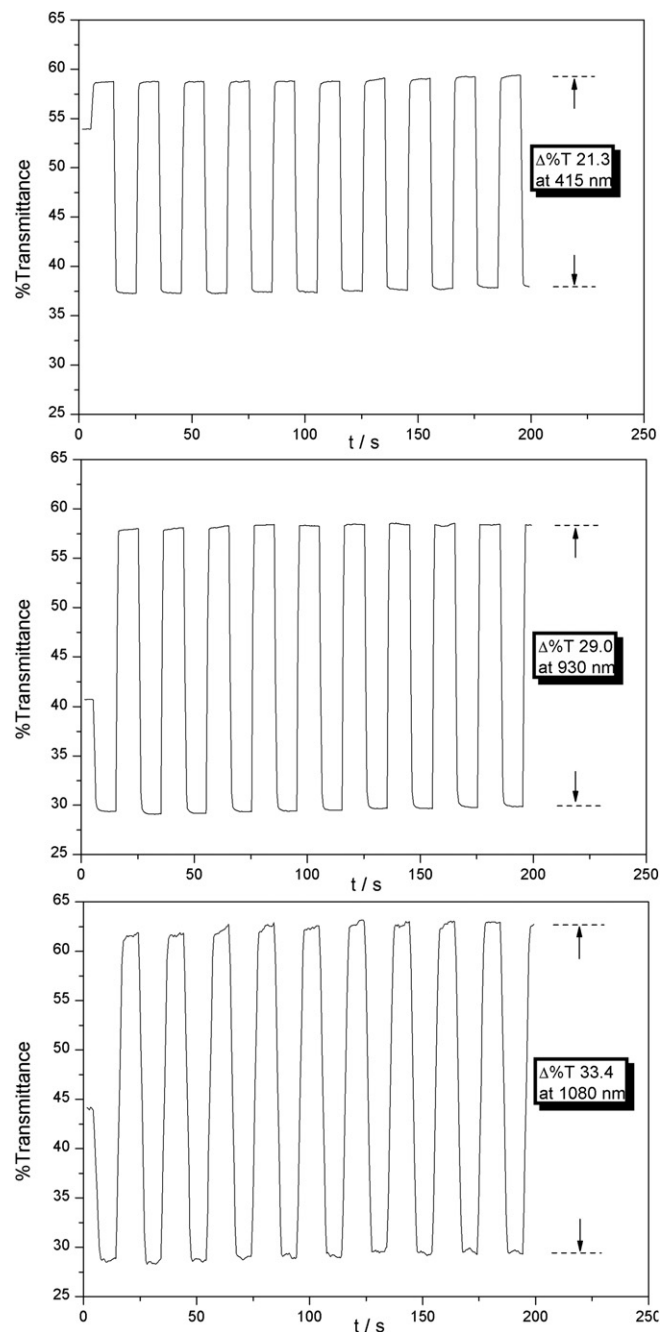
**Fig. 8.** (a) Cyclic voltammetry, and (b) differential pulse voltammetry of P1 in 0.1 M TBAH/DCM.

polymer film between its neutral and doped states in the electrolyte solution was examined and the changes in the electro-optical responses were monitored *in situ*. The changes in percentage transmittance ( $\Delta T\%$ ) between the neutral (at  $-0.70 \text{ V}$ ) and oxidized states (at  $1.0 \text{ V}$ ) were found as 21.3% for 415 nm, 29.0% for 930 nm and 33.4% for 1080 nm in the near infrared region (Fig. 9). Response time from the neutral to oxidized states or vice versa was found to be 1.0 s, which is the necessary time for 95% of the full optical switch (after which the naked eye could not sense the color change). The stability and/or robustness of **P1** along with a low response time clearly imply that this material is amenable for use in electrochromic devices and/or optical displays.

CE is a useful term for measuring the power efficiency of the electrochromic devices and can be calculated via optical density using the following equations [41];

$$\Delta OD = \log \frac{T_{\text{colored}}}{T_{\text{bleached}}} \quad \text{and} \quad CE = \log \frac{\Delta OD}{Q_d}$$

where  $Q_d$  is the injected/ejected charge during a redox step;  $T_{\text{colored}}$  and  $T_{\text{bleached}}$  are the transmittance in the oxidized and neutral states, respectively. On the basis of these equations, the CE of **P1** was found to be  $225 \text{ cm}^2/\text{C}$  which was higher than that of PEDOT ( $173 \text{ cm}^2/\text{C}$ ), an industrially important polymer [19]. This feature makes the polymer an attractive electrochromic material.



**Fig. 9.** Optical transmittance changes for P1 at 415 nm, 930 nm and 1080 nm in 0.1 M TBAH/DCM while the polymer was switched between  $-0.7 \text{ V}$  and  $1.0 \text{ V}$  with a switch time of 10 s.

#### 4. Conclusion

In summary, design, synthesis and properties of a new low-voltage-driven green polymeric electrochrome, **P1**, which was based on D-A approach, were disclosed. It was noted that **P1** has green color in the neutral state and switches to a transmissive blue state upon oxidation. The band gap of the polymer film was found to be 1.10 eV–1.25 eV. Moreover, high redox stability, high CE and contrast ratio, and low response time (1.0 s) of this novel material make **P1** an excellent candidate for electrochromic applications. Work along these lines is currently underway in our laboratories.

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