

Synthesis and characterization of a bifunctional amido-thiophene monomer and its copolymer with thiophene and electrochemical properties

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Abstract

A bifunctional amido-thiophene namely hexamethylene (bis-3-thiophene acetamide) (HMTA) was synthesized by the reaction of 3-thiophene acetic acid with hexamethylene diamine. Copolymerization in the presence of thiophene was achieved electrochemically in tetrabutylammonium tetrafluoroborate/acetonitrile (TBAFB/AN). Spectroelectrochemical analysis of the resulting copolymer [P(HMTA-co-Th)] reflected electronic transitions at 505 nm, 740 nm and ~1000 nm, revealing π to π^* transition, polaron and bipolaron band formation respectively. Switching ability was evaluated by a kinetic study via measuring the transmittance (%*T*) at the maximum contrast. Dual type polymer electrochromic devices (ECDs) based on P(HMTA-co-Th) and poly(ethylene dioxythiophene) (PEDOT) have been constructed. Spectroelectrochemistry, switching ability and stability of the devices were investigated by UV–vis spectroscopy and cyclic voltammetry. These devices exhibit low switching voltages (between 0.0 V and +1.6 V), short switching times with reasonable switching stability under atmospheric conditions.

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1. Introduction

During the last two decades there has been enormous interest in the area of conducting polymers (CPs) which display a wide range of applications. Recent advances in the field of the conducting polymers have led to a variety of material with greater potentials for practical

applications such as batteries [1,2], electronic devices [3], sensors and capacitors [4], electromagnetic radiation shielding, antistatic coating, gas separation membranes, nonlinear optics and electrochromic devices (ECDs) [5,6].

In the recent years, CPs have gained a lot of attention for ECDs. This is due to the fact that CPs are more processable than inorganic electrochromic materials and offer the advantage of a high degree of color tailorability [7–10]. This tailorability has been achieved through the modification of various polymer systems via monomer functionalization and copolymerization as well as with

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the use of blends, laminates and composites [11–14]. Complex colors are achieved by mixing two existing colors in a dual polymer device. Among conducting polymers, polythiophene and its derivatives have become a subject of considerable interest as electrochromic materials, owing to their chemical stability, ease of synthesis and structural versatility [15].

An ECD is an electrochemical cell, composed of optically transparent electrodes coated with complementary electrochromic materials and separated by an electrolyte, which may be liquid or solid. ECDs have been developed for mirrors, optical displays, camouflage materials, spacecraft thermal control, and solar control glazings for “smart windows” [15,16]. Electrochemical techniques such as cyclic voltammetry, coulometry, chronoamperometry and spectroscopic measurements are employed for characterization of both a single polymer electrode and electrochromic device, which enables us to decide whether they are suitable for commercial purposes. The requirements for high performance electrochromic device are high electrochromic efficiency, short response time, good stability, optical memory, optical contrast and color uniformity [17].

In this paper, we describe the synthesis of a bifunctional amido-thiophene monomer, hexamethylene (bis-3-thiophene acetamide) (HMTA) via by the reaction 3-thiophene acetic acid with hexamethylene diamine and its copolymer with thiophene via electropolymerization. The copolymer was characterized spectroelectrochemically. Dual type ECD was constructed with thiophene co-HMTA (anodically coloring polymer) and poly-3,4-ethylenedioxythiophene (PEDOT) (cathodically coloring polymer).

2. Experimental

2.1. Materials

Propylene carbonate (PC), tetrabutylammonium tetrafluoroborate (TBAFB), polymethylmetacrylate (PMMA), 3-thiophene acetic acid, hexamethylene diamine were purchased from Aldrich and used without further purification. Borontrifluoride ethylether (BFEE) was purchased from Sigma. Acetonitrile (AN) (Merck) and thiophene (Th) (Aldrich) were distilled prior to use. 3,4-Ethylenedioxythiophene (EDOT), was purchased from Aldrich and used as received.

2.2. Synthesis of hexamethylene (bis-3-thiophene acetamide)

A mixture of 3-thiophene acetic acid (0.80 g 5.6 mmol) and thionyl chloride (0.77 g, 6.5 mmol) was placed in 25 mL round bottom flask carrying a drying tube and refluxed for 1 h. A water aspirator vacuum was applied to remove the excess thionyl chloride. The liquid product was dropwise added to hexamethylene diamine (0.32 g, 2.81 mmol) in 20 mL dry THF in an ice bath under rapid stirring. The mixture was stirred for about 30 min. The product was collected by suction filtration and washed with THF to remove unreacted hexamethylene diamine and 3-thiophene acetic acid. A light-brownish solid product was obtained in 45% yield. Scheme 1 shows synthesis route for monomer.

2.3. Synthesis of copolymer of HMTA with thiophene [P(HMTA-co-Th)]

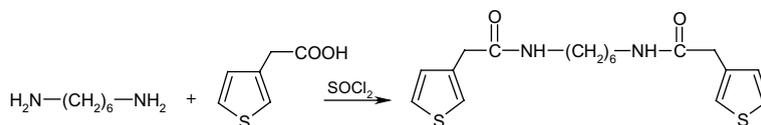
HMTA was coated on the working electrode surface from its dichloromethane solution. The electrolyses were carried out in acetonitrile with TBAFB (0.05 M) and thiophene (8×10^{-2} M) at 1.9 V vs. Ag^0/Ag^+ at room temperature. Free standing black films were formed in 1 h.

2.4. Electrochemistry

A three-electrode cell containing ITO-coated glass slides (Delta Technologies, $R = 8\text{--}12 \Omega \text{sq}^{-1}$) as the working electrode, a platinum foil as the counter electrode, and a silver wire as the pseudo-reference electrode were used for electrodeposition of polymer films by potentiodynamic methods. All electrochemistry was performed using a Solartron 1285 potentiostat/galvanostat.

2.5. Spectroelectrochemistry

Spectroelectrochemical studies were carried on a Agilent 8453 UV-vis spectrophotometer. Colorimetry measurements were done with a Coloreye XTH Spectrophotometer (GretagMacbeth). To carry out spectroelectrochemical and electrochromic studies, copolymer films were synthesized on ITO-coated glass. Copolymer films deposited on ITO-coated glass were used both for spectroelectrochemistry and electrochromic measurements in TBAFB (0.1 M)/AN with Ag/Ag^+ as the reference electrode and a Pt wire as the auxiliary electrode.



Scheme 1. Synthesis of the monomer, HMTA.

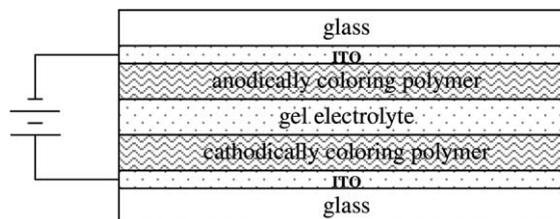
Films were deposited on ITO-coated glass slides and dried under atmospheric conditions.

2.6. Preparation of gel electrolyte

The gel electrolyte for electrochromic device based on poly(methyl methacrylate) (PMMA) was plasticized by 1,2-propylenecarbonate to form a highly transparent and conductive gel. A high vapor pressure solvent AN was used to dissolve the PMMA and to allow an easy mixing of the gel components. After stirring and heating, PC was used for plasticization. The composition of casting solution (by weight AN:PC:PMMA:TBAFB) was 70:20:7:3.

2.7. ECD construction and characterization

ECD were constructed by sandwiching the gel electrolyte between anodically and cathodically coloring polymers which were previously electrochemically deposited onto the ITO-coated glass from a 0.2 M TBAFB/AN:BFEE solution. The copolymer coated and the PEDOT coated electrodes were polarized at +1.6 V and 0.0 V in AN/TBAFB (0.1 M) solvent-electrolyte couple. Chronocoulometry was employed to match the redox charges of the two complimentary polymer films to maintain a balanced number of redox sites for switching. The spectroelectrochemical and kinetic studies of device were performed with Agilent 8453 UV-vis spectrophotometer. The colorimetry measurements were done by a Coloreye XTH Spectrophotometer (GretagMacbeth). Cyclic voltammetry study was performed by Solartron 1285 potentiostat/galvanostat



Scheme 2. Schematic representation of devices.

The construction of an absorption/transmission type device is depicted in Scheme 2.

3. Results and discussion

3.1. FTIR and NMR spectra

The structure of the monomer was confirmed by NMR and IR spectral analysis. ^1H NMR spectra of the monomer were taken by using a Bruker-instrument NMR spectrometer (DPX-400) with CDCl_3 as the solvent and tetramethylsilane as the internal standard. ^1H NMR spectrum of the monomer (Fig. 1) evidences resonance signals of thiophene (Th), Th- CH_2 , NH and CH_2 protons of relative intensities corresponding to the number and type of protons. ^1H NMR (δ , ppm) data for HMTA: 7.4–6.9 ppm (m 6H), 5.6 (br, 2H), 3.7 ppm (s 4H), 3.22 ppm (m 4H), 1.54 (m 4H), 1.25 ppm (m 4H).

Nicolet 510 FTIR Spectrophotometer was used for FTIR studies. The IR spectral characteristics of the monomer was discussed together with that of the

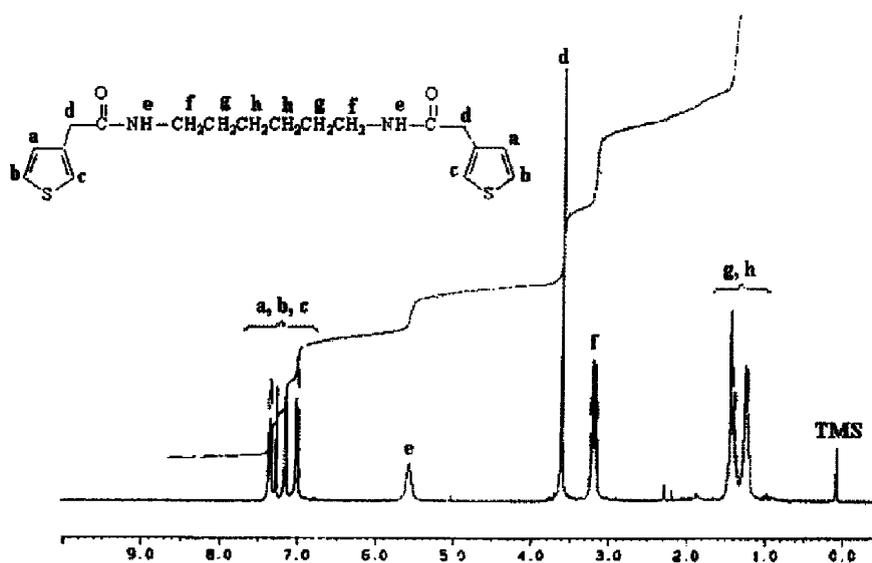


Fig. 1. ^1H NMR spectra of the HMTA.

copolymer. HMTA showed a characteristic, intense peak at 1640 cm^{-1} , which belongs to C=O stretching vibrations. Two peaks at 2948 cm^{-1} and 2867 cm^{-1} correspond to aliphatic methylene stretchings. The peak at 1251 cm^{-1} indicates C–O–C ester group vibrations while the peak at 3265 cm^{-1} is attributed to N–H stretching vibration. Also, the peak at 739 cm^{-1} is the result of aromatic C–H_x stretching of thiophene units.

FTIR spectrum of P(HMTA-co-Th) showed intense peak at 1082 cm^{-1} which belongs to dopant ions. A characteristic peak 1640 cm^{-1} belonging to carbonyl group of HMTA was also observed. These results prove copolymerization. Fig. 2 shows FTIR spectra of HMTA and its copolymer with thiophene.

3.2. Cyclic voltammetry

Redox behavior of HMTA was investigated via cyclic voltammetry (CV). CVs of HMTA in AN–TBAFB system implied that the precursor monomer is not electroactive since it lacks any redox peaks. Upon addition of Th into the reaction medium, an increasing redox peak with increasing scan number was observed (Fig. 3b).

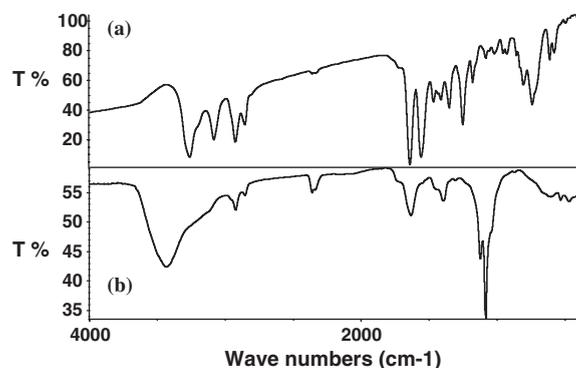


Fig. 2. IR spectrum of (a) HMTA and (b) P(HMTA-co-Th).

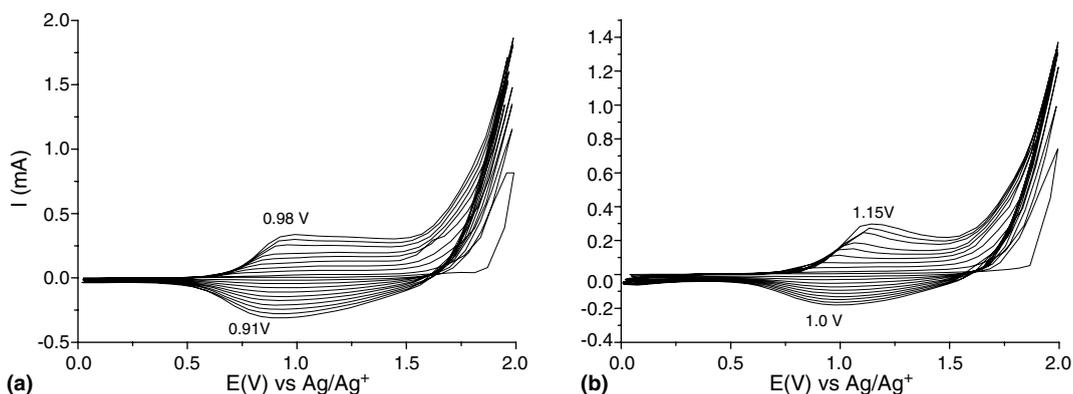


Fig. 3. Cyclic voltammogram of (a) pure polythiophene (b) HMTA in the presence of thiophene in 0.1 M TBAFB/AN.

The number of cycles observed up to a certain current value was different than that of pure polythiophene (PTh) (Fig. 3a).

3.3. Spectroelectrochemistry

3.3.1. In situ polymerization

Spectroelectrochemistry experiments reveal key properties of conjugated polymers such as band gap (E_g) and the intergap states that appear upon doping. We investigated the in situ electrochemical copolymerization by UV–vis spectrophotometer under 1.9 V at TBAFB/AN at every 10 s time interval (Fig. 4).

3.3.2. Spectroelectrochemistry of P(HMTA-co-Th)

The film was deposited on ITO via potentiostatic electrochemical copolymerization of HMTA (0.01 M) in the presence of TBAFB and Th in AN at 1.9 V. Copolymer coated ITO was investigated by UV–vis

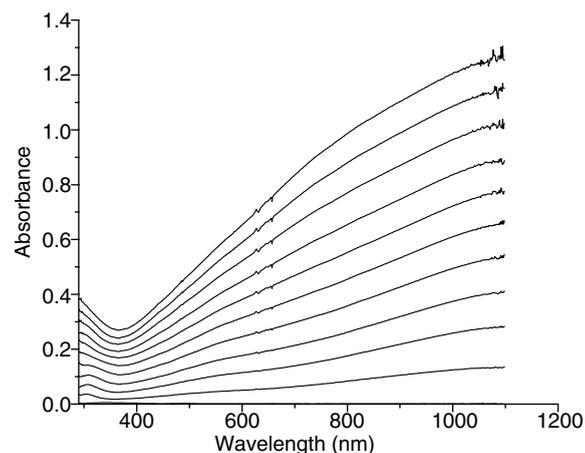


Fig. 4. In situ electrochemical copolymerization of HMTA with thiophene.

spectroscopy in the monomer free electrolytic system by switching between +0.2 V and +1.6 V (Fig. 5). The onset energy for the π - π^* transition (electronic band gap) was found to be 1.95 eV and λ_{max} was 505 nm. Appearance of the peak around 741 nm could be attributed to the evolution of polaron band. Upon further oxidation, appearance of another absorption was observed at longer wavelengths (>1000 nm) due to bipolaron charge carriers.

3.3.3. Spectroelectrochemistry of P(HMTA-co-Th)/PEDOT device

Spectroelectrochemical study of P(HMTA-co-Th)/PEDOT device at voltages varying between 0.0 V and +1.6 V is shown in Fig. 6. Due to π - π^* transition there is a maximum absorption at 496 nm revealing the red color. In that state PEDOT layer was in transparent blue color and device revealed red color. When the applied potential was increased due to reduction of PEDOT layer, blue color became dominant and maximum absorption was observed at 608 nm.

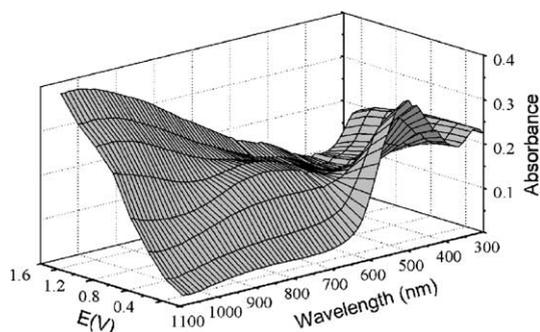


Fig. 5. Optoelectrochemical spectrum of P(HMTA-co-Th) as at applied potentials between 0.0 and +1.6 V in 0.1 M TBAFB/AN.

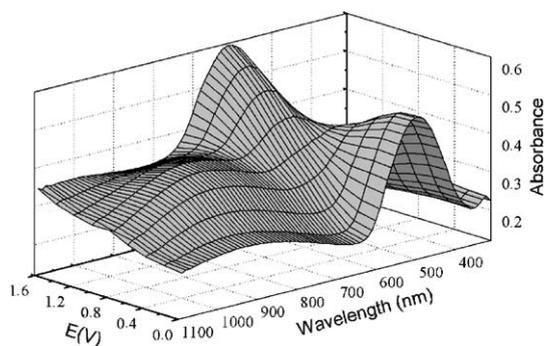


Fig. 6. Optoelectrochemical spectrum of P(HMTA-co-Th)/PEDOT device as at applied potentials between 0.0 and +1.6 V in 0.1 M TBAFB/AN.

3.4. Device characterization

3.4.1. Switching

One of the most important characteristics of ECDs is the response time needed to perform a switching between two colored states. A square wave potential step method coupled with optical spectroscopy known as chronoabsorptometry is used to probe switching times and contrast in these polymers. During the experiment, the % transmittance (%*T*) at the wavelength of maximum contrast was measured by using a UV–vis spectrophotometer. For P(HMTA-co-Th) maximum contrast ($\% \Delta T$) was measured as 20.02 and switching time was 1.1 s by stepping the potential between 0.0 V and +1.6 V with a residence time of 5 s. (Fig. 7). Switching time and $\% \Delta T$ values for P(HMTA-co-Th)/PEDOT device measured as 1.7 s and 23.95 respectively while stepping the potential between -0.5 V and +1.5 V. Fig. 8 shows potential–time (a), current–time (b) and transmittance–time (c) profiles of the P(HMTA-co-Th)/PEDOT device recorded during double step spectrochronoamperometry.

3.4.2. Stability

Redox stability is an important requirement for production of reliable electrochromic devices with long lifetimes. For this purpose we accomplished non-stop cycling of the applied potential between 0.0 and 1.6 V with 500 mV/s scan rate. As seen in Fig. 9 even after 1000th run, device showed only a slight decrease in electroactivity accompanied by unperturbed color change.

3.4.3. Open circuit memory

The color persistence in the electrochromic devices is an important feature since it is directly related to aspects

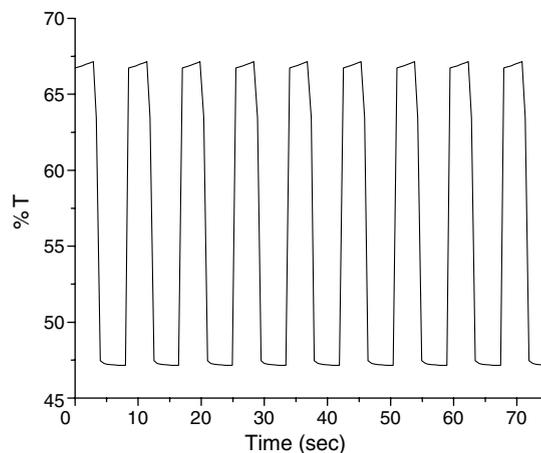


Fig. 7. Electrochromic switching, optical absorbance change monitored at 505 nm for P(HMTA-co-Th) between 0.0 V and 1.6 V.

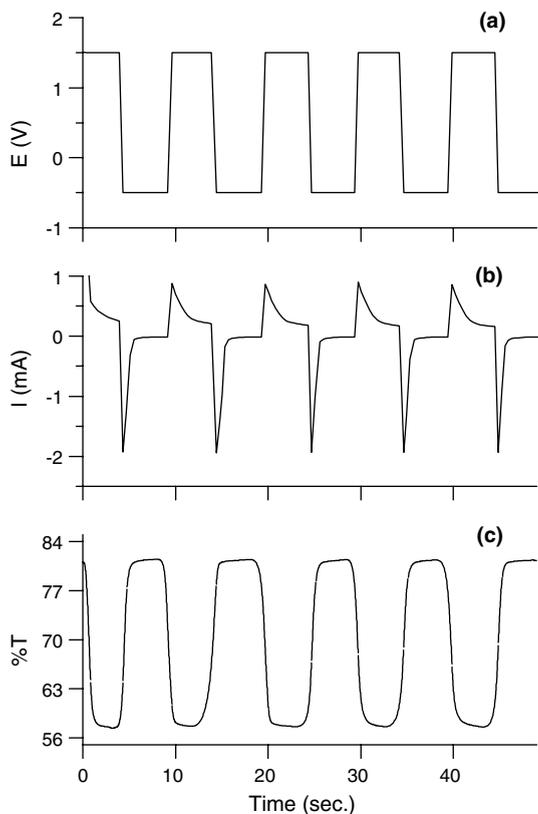


Fig. 8. Potential–time (a), current–time (b) and transmittance–time (c) profiles of the device recorded during double step spectrochronoamperometry.

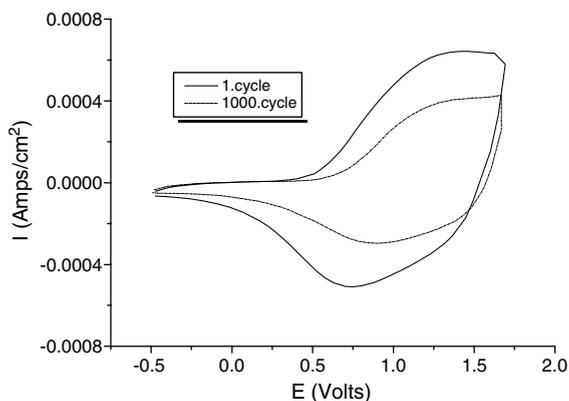


Fig. 9. Cyclic Voltammogram of the electrochromic device as a function of repeated scans 500 mV/s: after first cycle (plain), after 1000 cycles (dash).

involved in its utilization and energy consumption during use [17]. The optical memory of an EC material is defined as the time during which this material retains its color without applying potential [18]. We applied a pulse

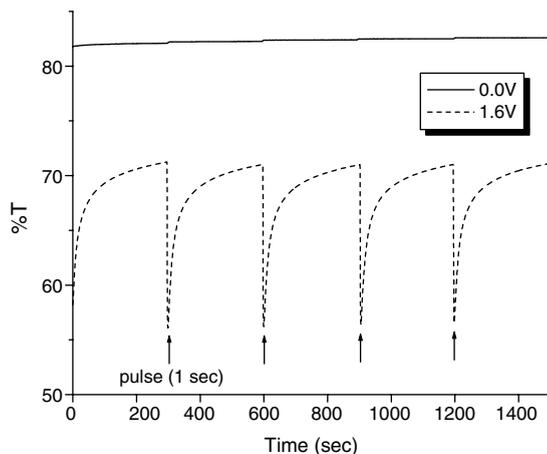


Fig. 10. Open Circuit memory of the device monitored by single-wavelength absorption spectroscopy at 633 nm. +1.6 and 0.0 V pulse are applied for 1 s every 300 s to recover the initial transmittance.

Table 1
Colorimetry data

P(HMTA-co-Th)/PEDOT device

Color	<i>L</i>	<i>A</i>	<i>b</i>
Blue	50	−6	−19
Red	61	18	7

(0.0 V or +1.6 V) for 1 s and held the cell in an open circuit condition for 200 s while the transmittance was monitored as a function of time. Simultaneously, the optical spectrum at 633 nm as a function of time at open circuit conditions was monitored (Fig. 10).

3.5. Colorimetry

CIE L^*a^*b system [The Commission Internationale de l'Éclairage (International Commission on Illumination)] is used for an objective description of the color of the ECDs, Luminance (L), hue (a) and saturation (b) are three attributes that are used to describe the color [19,20]. The L , a , b values measured at 0.0 V and +1.6 V were given in Table 1.

4. Conclusion

ECD was assembled with a configuration of ITO/Conducting Copolymer || Gel Electrolyte || PEDOT/ITO and characterized for their performance. Device exhibit low switching voltages (−0.5 to 1.5 V) and switching time with reasonable switching stability in atmospheric conditions. Reversible color change between blue and red states after cycling more than 1000 times was ob-

served. These results showed that ECD has good environmental and redox stability, which make them promising materials for future applications.

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