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Dual Type Complementary Colored Polymer Electrochromic Devices Based on Conducting Polymers of Poly(hexanedioic acid bis-(2-thiophen-3-yl-ethyl ester))

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In this study, dual type polymer electrochromic devices (ECDs) based on homopolymer and copolymer of hexanedioic acid bis-(2-thiophen-3-yl-ethyl ester) with 3,4-ethylene dioxithiophene (EDOT) were constructed, where PEDOT functioned as the cathodically coloring layer. Spectroelectrochemistry, switching ability, stability, open circuit memory and color of the devices were investigated. Results of the kinetic studies showed these devices exhibit switching times around 1.8 s with an optical contrast of 24–25.3%. The device utilizing the homopolymer revealed color variation between yellow and blue, whereas the one with the copolymer was between orange and blue. Both devices have good open circuit memory under atmospheric conditions, which might be useful in many applications.

Keywords electrochromic devices, conducting polymers, hexanedioic acid bis-(2-thiophen-3-yl-ethyl ester)

Introduction

Electrochromism is a persistent color change with a variation in applied potential (1). The color change is due to the energy difference between the π -bonding orbital (conduction band) and the π^* -antibonding orbital (valence band), which usually lies within the visible region. Upon oxidation, the intensity of the π to π^* transition decreases, and the two low-energy transitions emerge to produce a second color (2). Attachment of different functional groups to polymers results in a change of band gap values (3). Since coloration of the polymer is closely related to the band-gap, it is possible to control their colors by structural modification. The polythiophene family has proven to be of special interest for this purpose due to their stability under ambient and use conditions. Another strategy to control the electrochromic properties is copolymerization, which can result in an interesting combination of the properties observed in the corresponding

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homopolymers (4). In our previous work, conducting homo and copolymers of hexanedioic acid bis-(2-thiophen-3-yl-ethyl) ester (HABTE) were synthesized electrochemically in the presence of tetrabutylammonium tetrafluoroborate as the supporting electrolyte, in acetonitrile/borontrifluoride ethyl-ether solvent mixture (8:2, v/v) (5). Polymers were characterized via various techniques including spectroelectrochemistry, kinetic studies and colorimetry measurements. Results indicated the possible use of these materials in electrochromic devices due to their nice electrochromic properties like short switching time. An electrochromic device is a kind of electrochemical cell, composed of optically transparent electrodes coated with complementary electrochromic materials and separated by an electrolyte, which may be a liquid or a solid (6). For commercial applications of electrochromic materials, an electrochromic device having high stability (7), rapid response time (8), efficient color change (9–11) are very important.

In this study, we constructed dual-type electrochromic devices based on poly(hexanedioic acid bis-(2-thiophen-3-yl-ethyl) ester), its copolymer with thiophene, and poly(3,4-ethylenedioxythiophene). Devices were assembled in sandwich configuration with electrochromic materials deposited on ITO glass electrodes and a gel electrolyte. For the construction of the devices, PEDOT was used as the cathodically coloring, PHABTE and P(HABTE-co-Th) were used as the anodically coloring materials.

Experimental

Materials

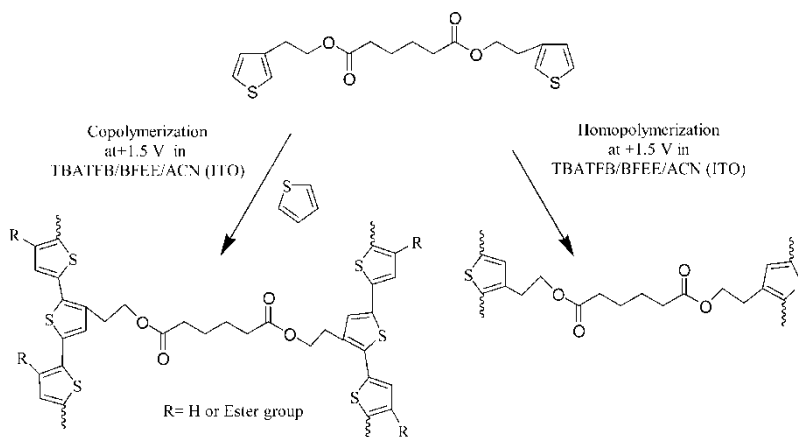
Propylene carbonate (PC), tetrabutylammonium tetrafluoroborate (TBAFB), PMMA, were purchased from Aldrich and were used without further purification. Borontrifluoride ethylether (BFEE) were purchased from Sigma. Acetonitrile (Merck) was distilled before use. The gel electrolyte was prepared from an acetonitrile solution containing poly(methyl methacrylate) and TBAFB. The acetonitrile was slowly evaporated under stirring and a few drops of propylene carbonate were added to decrease the vapor pressure of the gel electrolyte yielding a highly conducting transparent gel. The ratio of the composition of TBAFB:PMMA:PC:ACN was 3:7:20:70 by weight (12).

Instruments

Characterization of the devices' optical properties were carried out using a HP8453A UV-VIS spectrophotometer. A device without the active polymer layer, was used as a reference. The colorimetry measurements were done by a Coloreye XTH Spectrophotometer (GretagMacbeth). Cyclic Voltammetry and electropolymerizations were performed by Solartron 1285 potentiostat/galvanostat.

Electrochemistry

A three-electrode cell containing ITO-coated glass slides as the working electrode, a platinum flag as the counter electrode, and a silver wire as the pseudo-reference electrode was used for deposition of polymer films at 1.5 V in a single compartment cell, in the presence of 10^{-2} M HABTE, 0.2 M TBAFB in AN/BFEE (8:2, v/v) for the homopolymer synthesis. The copolymer was achieved in the same electrolytic system with addition of 10^{-2} M thiophene. Poly(3,4-ethylenedioxy thiophene) (PEDOT) was synthesized at 1.5 V in single compartment cell in the presence of 0.2 M TBAFB in AN. All electrochemical studies were performed using a Solartron 1285 potentiostat/galvanostat (Scheme 1).



Scheme 1. Electrochemical polymerization of HABTE.

Construction of ECDs

The redox sites of anodically and cathodically coloring films were matched by stepping the potentials between the ultimate oxidized and reduced states. Thus, potential stepping applied were 0.0 V to +1.6 V for PHABTE and P(HABTE-co-Th) and -1.0 V to +1.5 V for PEDOT. ECDs were built by arranging oxidized and neutral electrochromic polymer films facing each other separated by a gel electrolyte. The devices were dried under atmospheric conditions.

Results and Discussion

Results of our previous (5) study showed that the homopolymer of HABTE is an anodically coloring electrochromic material with a band gap of 1.92 eV. The color of the polymer changes between blue and yellow upon doping and dedoping, with a switching time less than 1.5 s. Similar behavior was observed for the copolymer where the λ_{\max} was 470 nm and the switching time was found to 2.1 s with a variation of color between orange and blue.

In this study, we assembled the dual transmissive/absorptive type devices of PHABTE or P(HABTE-co-Th) with PEDOT using transparent ITO electrodes. ITOs were coated with anodically coloring materials (PHABTE or P(HABTE-co-Th)) at 1.5 V in the presence of 0.2 M TBAFB acetonitrile/borontrifluoride ethyl-ether (8:2,v/v). Prior to construction, the charge capacities of the electrochromic layers were balanced in order to achieve complete electrochromic reaction and eliminate the residual charge formation during the coloring/bleaching processes, since the reverse situation will result in residual coloration of the ECD in the bleached state. To minimize the effect of charge imbalances in ECD, we matched the redox charges of the two complementary polymer films by chronocoulometry and provided a balanced number of redox sides for switching. In order to achieve complementary operating conditions (oxidation of one layer during reduction of the other), the anodically coloring polymer films were fully reduced and the cathodically coloring polymer, PEDOT, was fully oxidized. The ion exchange between the electrochromic layers was achieved by coating ITOs with gel electrolyte while ITOs were positioned in a way to face electrochromic layers to each other.

Spectroelectrochemistry

A spectroelectrochemical study of the ECDs was performed to examine the spectral changes that occur during redox switching which are important for electrochromic applications. Optoelectrochemical spectra of the dual-type PHABTE/PEDOT ECD as a function of applied voltage are shown in Figure 1(a). In this study applied

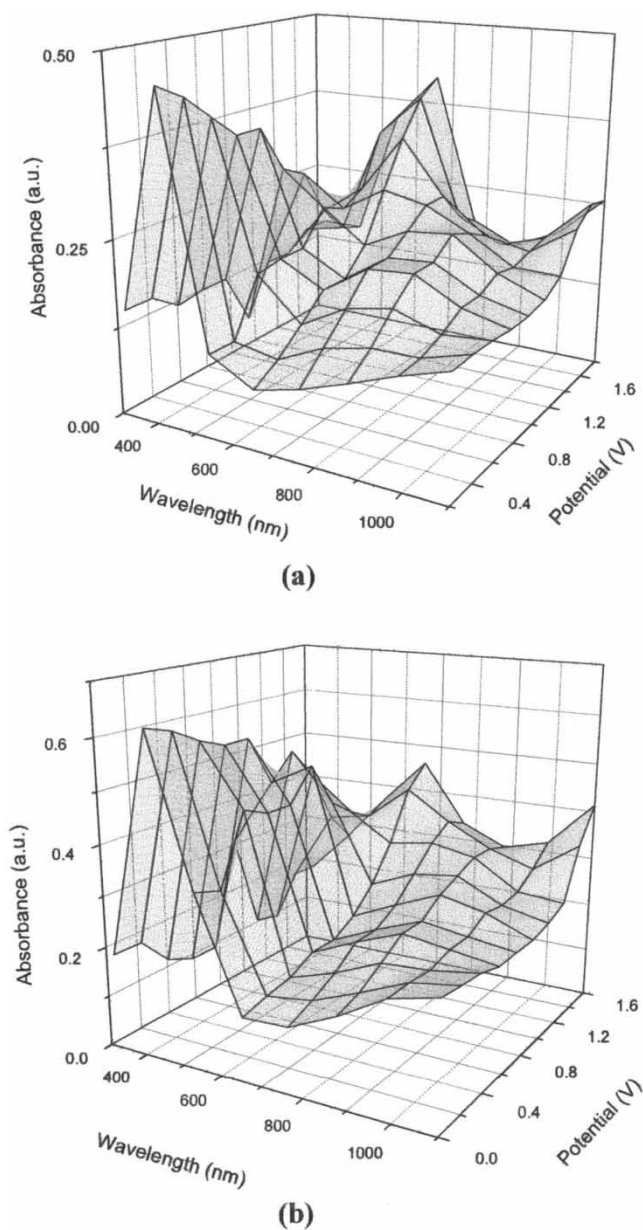


Figure 1. (a) Optoelectrochemical spectrum of PHABTE/PEDOT ECD at applied potentials between 0.2 and +1.8 V; (b) Optoelectrochemical spectrum of P(HABTE-co-Th)/PEDOT ECD at applied potentials between 0.0 and +1.6 V.

potentials were supplied by a Solartron 1285 potentiostat/galvanostat where the reference and the counter electrodes were shortcut to achieve a two electrode system. The wavelength for maximum electronic absorption was 448 nm at 0.2 V where the color of the device was yellow. The yellow color was attributed to the absorption of reduced PHABTE (π - π^* transition), since PEDOT was in its oxidized form (highly transparent). Upon application of positive potentials, PHABTE layers started to oxidize and the intensity of the peak due to π - π^* transition decreased and there appears to be a second absorption at around 800 nm due to the formation of charge carrier bands. At this point, both anodically and cathodically coloring polymers were in their partially oxidized states. Further positive potentials results in the evolution of a new peak around 619 nm due to π - π^* transition of PEDOT itself, which was followed by a decrease in the intensity at π - π^* transition of anodically coloring electrochromic layer. At this stage, the color of the device started to alter from yellow to blue. At 1.8 V, PEDOT and PHABTE layers were in fully reduced and oxidized states, respectively.

A similar type of spectroelectrochemical behavior was observed in the case of P(HABTE-co-Th)/PEDOT device. Figure 1(b) presents spectroelectrochemistry of the P(HABTE-co-Th)/PEDOT device, which clearly shows absorbance features of both PEDOT and P(HABTE-co-Th). At 0.0 V, the entire device was an orange color ($\lambda_{\max} = 467$ nm due to π - π^* transition of P(HABTE-co-Th)). The color of the device changed to blue ($\lambda_{\max} = 646$ nm due to π - π^* transition of PEDOT) upon further applied positive potentials. From 1.0 V to 1.6 V, the gradual coloration was primarily due to the reduction of PEDOT. In fact, at 0.0 V, the spectrum of P(HABTE-co-Th)/PEDOT ECD appeared very similar to that of P(HABTE-co-Th) in the reduced state and at 1.6 V device spectrum appeared very similar to that of PEDOT in a reduced state.

Switching Characteristics

The kinetics of color change within devices were investigated performing fast spectral scans *in situ*, while applying the potential step square wave form. This technique provides information about the kinetics of color-switching as depicted in Figure 2 (a) and (b) which demonstrates the transmittance change at a selected wavelength (maximum contrast; at 619 nm and 646 nm for PHABTE/PEDOT and P(HABTE-co-Th)/PEDOT ECD respectively). During the experiment, potentials were stepped between +0.2 and +1.8 V for PHABTE/PEDOT, 0.0 and +1.6 V for P(HABTE-co-Th) /PEDOT device with a residence time of 5 s. Results showed that time required to reach % 95 of ultimate % T was 1.8 s and 1.9 s for PHABTE/PEDOT and P(HABTE-co-Th) /PEDOT electrochromic devices, respectively. The optical contrast was measured as the difference between %T in the bleached and colored states and was found to be 25.3% and 24% for PHABTE/PEDOT and P(HABTE-co-Th)/PEDOT ECD, respectively.

Electrochromic Memory

Electrochromic memory, defined as the ability of an ECD to hold its color and/or optical density while the current is off. In order to investigate electrochromic memory of the devices, the experiment was performed by polarizing the devices in their two extreme states (yellow/blue and orange/blue for PHABTE/PEDOT and

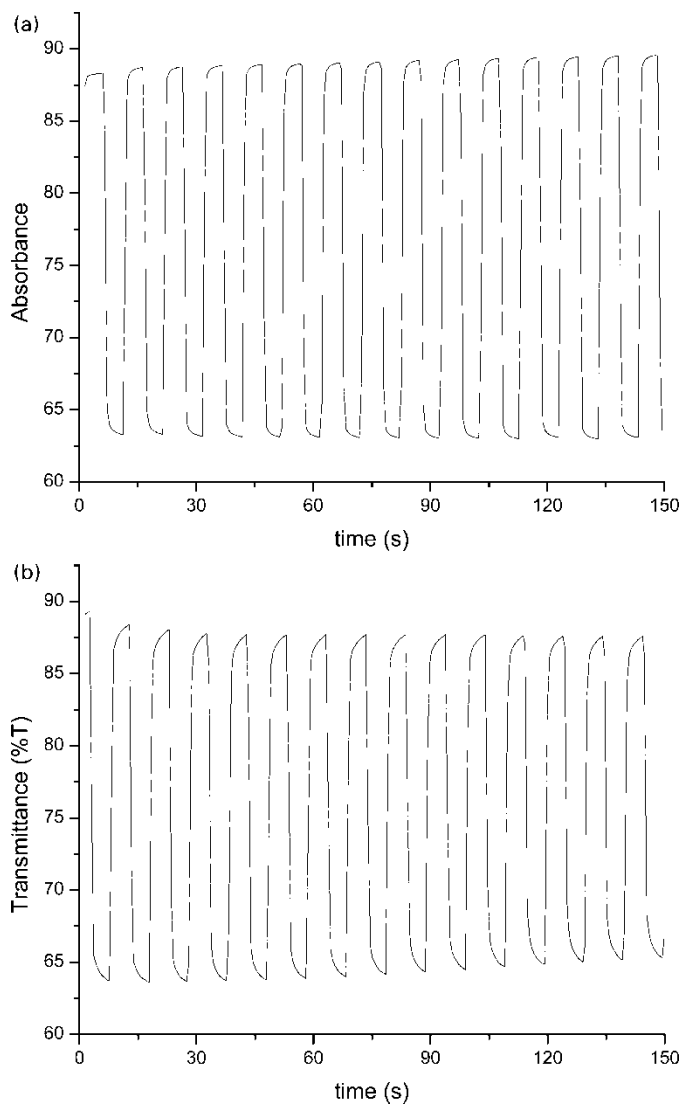
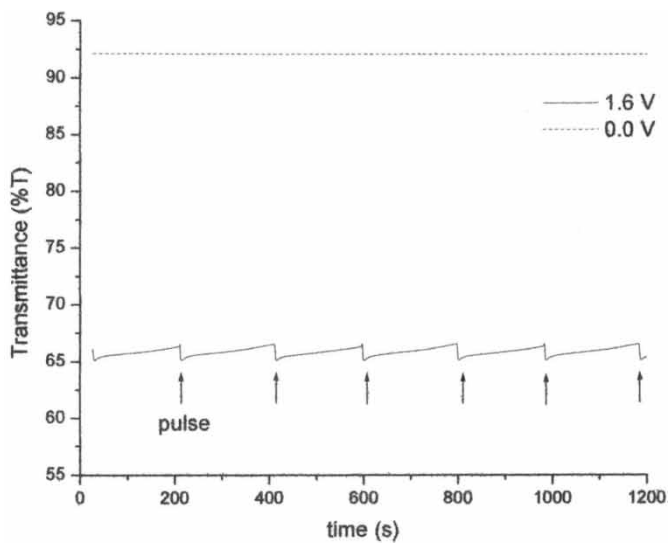
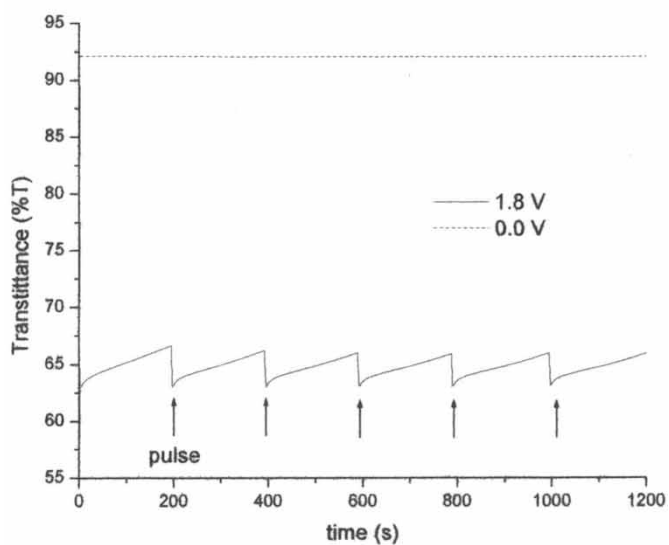


Figure 2. (a) Electrochromic switching, optical absorbance change monitored at 619 nm for PHABTE/PEDOT ECD between 0.0 V and 1.4 V; (b) Electrochromic switching, optical absorbance change monitored at 646 nm for P(HABTE-co-Th)/PEDOT between 0.0 V and 1.4 V.

P(HABTE-co-Th)/PEDOT respectively) by an applied pulse (0.2/1.8 V and 0.0/1.6 V for PHABTE/PEDOT and P(HABTE-co-Th)/PEDOT, respectively) for 1 second and kept at open circuit conditions for 200 s. The variation of the optical spectrum was simultaneously followed at 646 and 619 nm for P(HABTE-co-Th)/PEDOT and PHABTE/PEDOT, respectively as a function of time under open circuit conditions. (Figure 3 (a) and (b)). When P(HABTE-co-Th)/PEDOT polarized in the blue colored state initially, the device presents %T = 65.0%, while after 200 s, it changes to 66.5% under open circuit conditions which was remarkable. A similar, but less pronounced effect was observed for the case of PHABTE/PEDOT. These results indicate that this system does not truly



(a)



(b)

Figure 3. Onen circuit memory of (a) P(HABTE-co-Th)/PEDOT; (b) PHABTE/PEDOT

reach to equilibrium under open circuit conditions. However, this matter can be overcome by the application of current pulses to freshen the fully colored state. At bleached states, namely yellow and orange colored states, a true permanent memory effect was observed.

Stability

Redox stability is an important requirement for the production of reliable electrochromic devices with long lifetimes. Main reasons for device failure are different applied voltages and environmental conditions. In this study, CV was exploited as a method to evaluate the stability of the devices. For this purpose, we performed non-stop cycling of the applied potential between 0.0–2.0 V for both ECDs with 500 mV/s

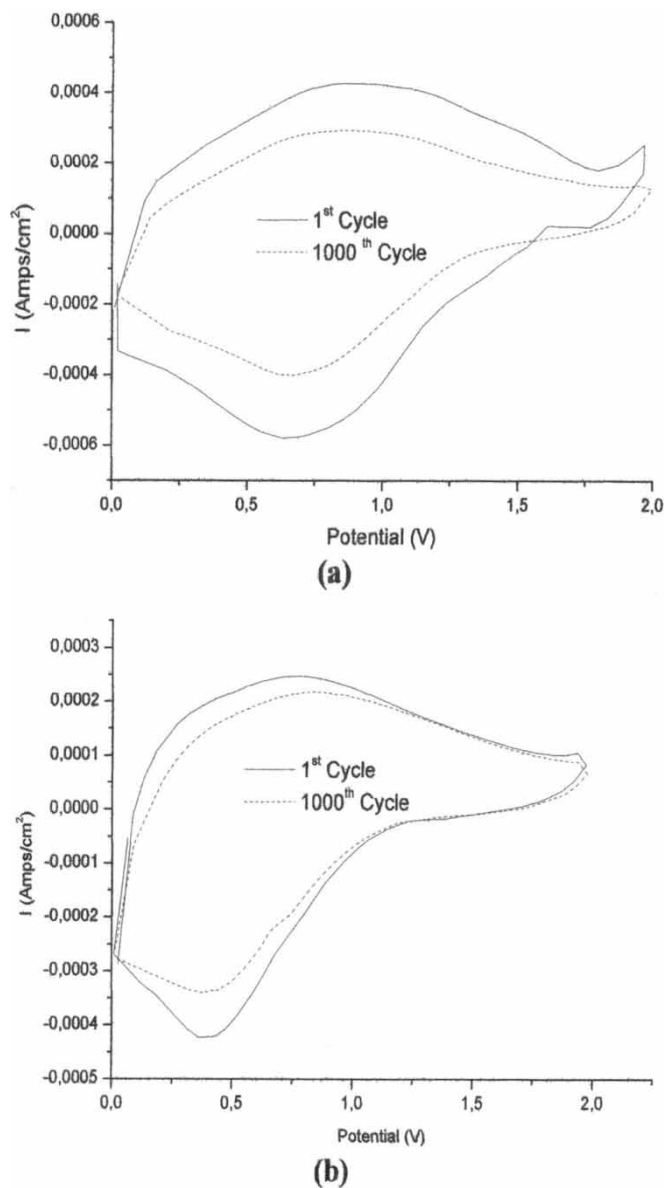


Figure 4. Cyclic Voltammogram of (a) PHABTE/PEDOT, (b) P(HABTE-co-Th)/PEDOT electrochromic devices as a function of repeated scans 500 mV/s; 1st cycle and after the 1000th.

Table 1
Colorimetry data

Electrochromic device	Color	L	a	b
PHABTE/PEDOT	Blue (at 1.8 V)	30	7	-39
	Yellow (at 0.2 V)	54	7	57
P(HABTE-co-Th)/PEDOT	Blue (at 1.6 V)	27	1	-31
	Orange (at 0.0 V)	47	31	46

scan rate. As seen in Figure 4 (a) and (b), even after the 1000th run, both devices showed only a slight decrease (9%) in electroactivity accompanied by unperturbed color change from bleached to colored state, where P(HABTE-co-Th)/PEDOT seems to be more stable upon switching for longer times. These results showed that both ECDs have good environmental and redox stability, which make them promising materials for future applications.

Colorimetry

Colorimetric analysis is a well established characterization technique in the field of electrochromic polymers since it allows quantitative measure of the color. Color is made up of three attributes; hue, saturation and luminance; color systems such as the often-used CIE system are used as a quantitative scale to define and compare colors (4). Colorimetry measurements were performed by using the Coloreye XTH Spectrophotometer. The relative luminance (L) and the a (hue) and b (saturation) values of the devices (Table 1) were measured at the bleached and colored state. The color of the PHABTE/PEDOT switches from a yellow to blue and P(HABTE-co-Th)/PEDOT switched between orange to blue.

Conclusions

We demonstrated the construction and characterization of dual type electrochromic devices based on conducting polymers of HABTE and PEDOT in sandwich configuration with gel electrolyte. Device contrast ratios (measured as $\% \Delta T$) and switching time of devices were 25.3 and 1.8 s for PHABTE/PEDOT device, 24.0% and 1.9 s for P(HABTE-co-Th)/PEDOT device, respectively. These devices exhibit low switching voltages and switching times with good switching stability in atmospheric conditions. In both cases, reversible color change between blue and yellow, blue and orange was observed for PHABTE/PEDOT and P(HABTE-co-Th)/PEDOT, respectively. Results of the electrochromic memory experiments implied the good performance of the devices at open circuit conditions, which might be very useful in many applications.

Acknowledgements

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