

# Optoelectrochemical properties of poly(5,12-dihydrothieno[3',4':2,3][1,4]dioxocino[6,7-b]quinoxaline-co-2,2'-bithiophene) and its electrochromic device application

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## Abstract

In this study we investigated the electrochromic properties and electrochromic device application of poly(5,12-dihydrothieno[3',4':2,3][1,4]dioxocino[6,7-b]quinoxaline (DDQ)-co-2,2'-bithiophene (BT)). Copolymerization was successfully achieved electrochemically in acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte by direct anodic oxidation on platinum and indium tin oxide coated glass electrodes. The structure and morphology of the copolymer were investigated by infrared spectroscopy and scanning electron microscopy (SEM). Spectroelectrochemical analysis of the resulting copolymer reflected electronic transitions at 504 nm and ~800 nm revealing a  $\pi-\pi^*$  transition and polaron formation, respectively. Dual-type polymer electrochromic devices (ECDs) based on P(DDQ-co-BT) were constructed with poly(3,4-ethylenedioxythiophene) (PEDOT). Spectroelectrochemistry, switching ability and stability experiments showed that the copolymer concerned can be a good anode material for electrochromic devices.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

In the late 1970s, conjugated polymers were proclaimed as futuristic new materials that would lead to the next generation of electronic and optical devices. Polythiophenes are an important representative class of conjugated polymers that form some of the most environmentally and thermally stable materials that can be used as nonlinear optical devices, polymer LEDs, electrochromic or smart windows,

sensors, electromagnetic shielding materials, artificial noses and muscles, solar cells, microwave absorbing materials, new types of memory devices, nanoswitches, and transistors (Skotheim *et al* 1998, Chandrasekhar 1999).

Creative new design and development strategies led to interesting new materials and enhanced performance in certain devices. The ability of molecular designers in understanding how to gain control over the structure in polythiophenes makes the synthesis of polythiophenes a critical subject in the development of new advanced materials (McCullough *et al* 1993).

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It is important to realize that structure plays a dominant role in determining the physical properties of conducting polymers. Research has focused on directing the structure and function of these materials through synthesis. Synthesis can help to determine the magnitude of  $\pi$  overlap along the backbone and eliminate structural defects. Material assembly (and/or processing) determines the interchain overlap and dimensionality. Planarization of the backbone and assembly of the backbone in the form of  $\pi$  stacks lead to better materials and device performance in almost every category, ranging from electrical conductivity to stability. The most striking conclusions are control of regularity and order in the polymeric structure, which leads to remarkable enhancements in the electronic and photonic properties of these novel materials (Roncali 2007). This of course leads to the exciting prospect that the properties of polythiophenes can be selectively engineered through synthesis and assembly. A large portion of both the pioneering and future work in conjugated polymers strongly depends on synthetic chemists creating new polymers that can be fabricated into new devices and whose physics and chemistry can be understood in detail (McCullough 1998).

Electrochromics (ECs) are materials which exhibit different colors as a function of applied potential. Both inorganic and organic materials have been used as EC materials. A wide variety of electrochromic materials are presently known, ranging from metal oxides such as  $\text{WO}_3$  (Granqvist 1999) and mixed-valence metal complexes like Prussian blue (Tacconi *et al* 2003) to organic molecules. In the realm of organic electrochromic systems, both small molecules like viologens (Mortimer 1999) and conjugated polymers (Argun *et al* 2004, Varis *et al* 2006, Ak *et al* 2007a) have been shown to display electrochromism. There is still a lot to do for further improvement in terms of switching speeds, stability, contrast, and ease of synthesis and processing.

For conducting polymers, the electrochromism is related to doping–undoping processes. The doping modifies the electronic structure of the polymer, and produces new electronic states in the band gap, and thus causes color changes. Electronic absorption shifts bathochromically upon doping, and the color contrast between the undoped and doped states is related to the polymer band gap. A major focus in the study of electrochromic polymeric materials is to control the colors through main-chain and pendant group structural modifications and copolymerization. Copolymerization can lead to an interesting combination of the properties (Ak *et al* 2006, Turkaslan and Toppare 2007).

For these reasons, we synthesized a new monomer, namely 5,12-dihydrothieno[3',4':2,3][1,4]dioxocino[6,7-b]quinoxaline (DDQ), and report the electrochemical copolymerization of this monomer with 2,2'-bithiophene (BT). The resultant copolymers were characterized via cyclic voltammetry (CV), SEM and conductivity measurements. The optoelectrochemical and electrochromic properties, such as the relative luminance, change of color upon redox switching, and long-term switching stability of the copolymer, were determined. Besides, we utilized a dual-type ECD, where P(DDQ-co-BT) was used as the anodically coloring and PEDOT as the cathodically coloring electrochromic materials.

## 2. Experimental details

### 2.1. Materials

5,12-dihydrothieno[3',4':2,3][1,4]dioxocino[6,7-b]quinoxaline (DDQ) was synthesized according to the literature (Ak *et al* 2007b). 2,2'-bithiophene (BT, Aldrich), tetrabutylammonium tetrafluoroborate (TBAFB, Aldrich), acetonitrile (MeCN, Aldrich), poly(methyl methacrylate) (PMMA, Aldrich) and propylene carbonate (PC, Aldrich) were used as received without further purification.

### 2.2. Instrumentation

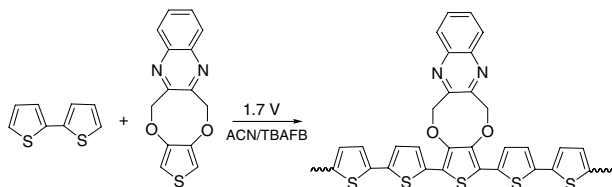
A Voltalab PST50 model potentiostat was used for the CV and chronocoulometry studies. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 510 FTIR spectrometer. Surface morphologies of the copolymer film were investigated by JEOL JSM-6400 scanning electron microscope. An Agilent 8453 UV–visible spectrophotometer was used to conduct the spectroelectrochemical experiments of copolymer and characterize the devices. Colorimetry measurements were done via a Minolta CS-100 chromameter.

### 2.3. Electrochemical experiments

Electrochemical syntheses and examinations were performed at room temperature in a one-compartment cell using a Voltalab PST 50 potentiostat–galvanostat. The working and reference electrodes for cyclic voltammetric experiments were platinum and silver wire. The polymers were deposited on an indium tin oxide (ITO) coated glass (1 cm<sup>2</sup>) for UV–visible spectral measurements. All samples were grown in MeCN solution containing 0.1 M TBAFB. For the deposition of polymer on ITO, the polymerization time was 1 min, whereas it was 30 min on the platinum electrode. For spectroelectrochemical studies thin films are required, hence very short polymerization times are quite appropriate. On the other hand, free standing films are required for several characterizations, and this can be achieved by producing 30  $\mu\text{m}$  thick films on platinum electrodes. Solutions were deaerated by a dry nitrogen stream and maintained at a slight nitrogen overpressure during experiments. In order to remove the electrolyte and monomers, the polymer films were rinsed with MeCN.

### 2.4. Synthesis of copolymers of DDQ with 2,2'-bithiophene (P(DDQ-co-BT))

2,2'-bithiophene was used as the comonomer for the synthesis of conducting copolymer of DDQ. The ratio of the monomers (BT:DDQ) was 1:4. Since BT is a very electroactive monomer, use of excess DDQ was found to be appropriate. DDQ (50 mg) was dissolved in 5 ml of MeCN and 5  $\mu\text{l}$  of BT were introduced into the single compartment electrolysis cell. TBAFB was used as the supporting electrolyte. A constant potential of 1.7 V was applied for 10 min under the inert atmosphere. Scheme 1 shows the copolymerization reaction.



**Scheme 1.** Electrochemical synthesis of P(DDQ-co-BT).

### 2.5. Spectroelectrochemistry

In order to carry out the spectroelectrochemical experiments, copolymer films were deposited on ITO-coated glass. They were used both for the spectroelectrochemistry and electrochromic measurements in MeCN/TBAFB. A silver wire and a platinum wire were employed as a reference and a counter electrode respectively in running the experiments.

### 2.6. Preparation of the gel electrolyte

Gel electrolyte was prepared by using TBAFB:MeCN:PMMA:PC in the ratio of 3:70:7:20 by weight. After TBAFB was dissolved in MeCN, PMMA was added into the solution. In order to dissolve PMMA, vigorous stirring and heating was required. PC, as a plasticizer, was introduced to the reaction medium when all of the PMMA was completely dissolved. The mixture was stirred and heated until the highly conducting transparent gel was produced.

### 2.7. Construction of electrochromic devices

Poly(3,4-ethylenedioxythiophene) (PEDOT) was potentiostatically deposited on the ITO working electrode by applying +1.5 V in MeCN/TBAFB (0.1 M) solvent–electrolyte.

P(DDQ-co-BT) was coated at +1.7 V in MeCN/TBAFB (0.1 M). It is important to balance the charge capacities of the devices prior to assembly. Otherwise, there would be incomplete electrochromic reaction and residual charges would remain during the redox process. Therefore, redox charges of the anodically and cathodically coloring polymers were matched by chronocoulometry. In order to obtain the complementary operating conditions, anodically coloring polymers were fully reduced and the cathodically coloring polymer was fully oxidized. The device was constructed by sandwiching the gel electrolyte between the anodically and the cathodically coloring polymers.

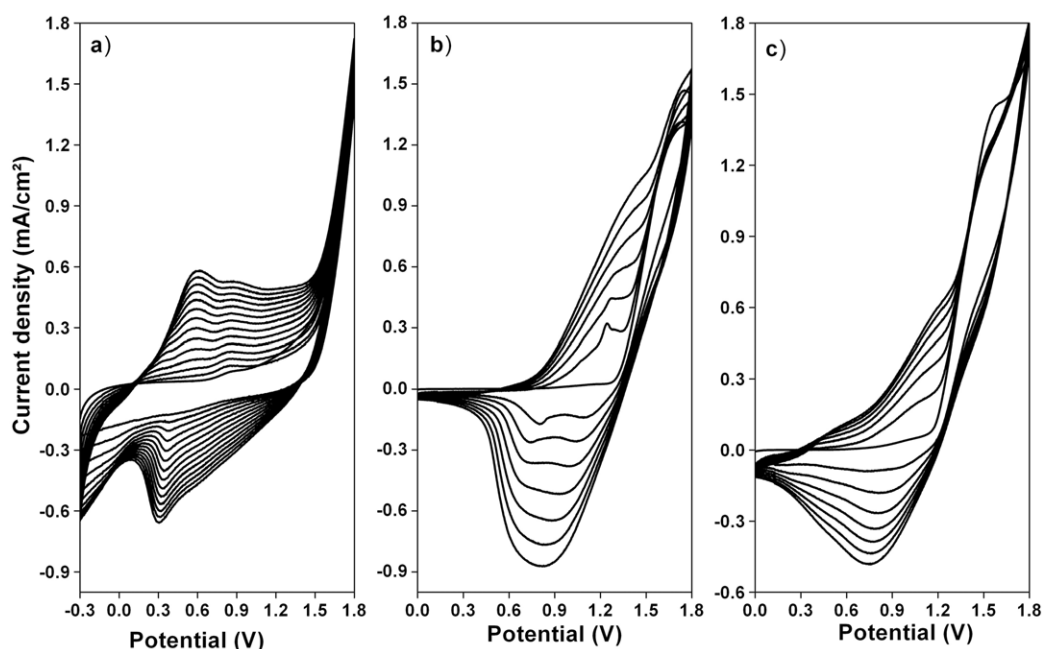
### 2.8. Colorimetry measurements

The sample was illuminated from behind by a D50 (5000 K) light source in a light booth specially designed to exclude external light. Background measurements were taken using a blank device containing two ITO glasses held together by the gel electrolyte.

## 3. Results and discussion

### 3.1. Cyclic voltammetry

The cyclic voltammogram of DDQ indicated an oxidation peak at 0.58 V and a reduction peak at 0.29 V. When the range between  $-0.3$  and  $+1.8$  V was scanned, the electroactivity increased with increasing scan number (figure 1(a)). In order to investigate the CV behavior of the copolymer, we performed the same CV runs in the presence of BT under the same experimental conditions. There was a drastic change in the voltammogram, in terms of the increase in the current increments between consecutive cycles. The oxidation potential of the material was different than those of DDQ and



**Figure 1.** Cyclic voltammograms of (a) DDQ, (b) pure BT, and (c) DDQ in the presence of BT in 0.1 M TBAFB MeCN.

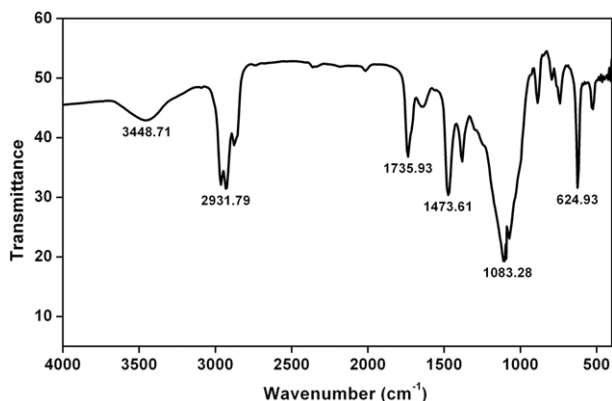


Figure 2. FTIR spectrum of P(DDQ-co-BT).

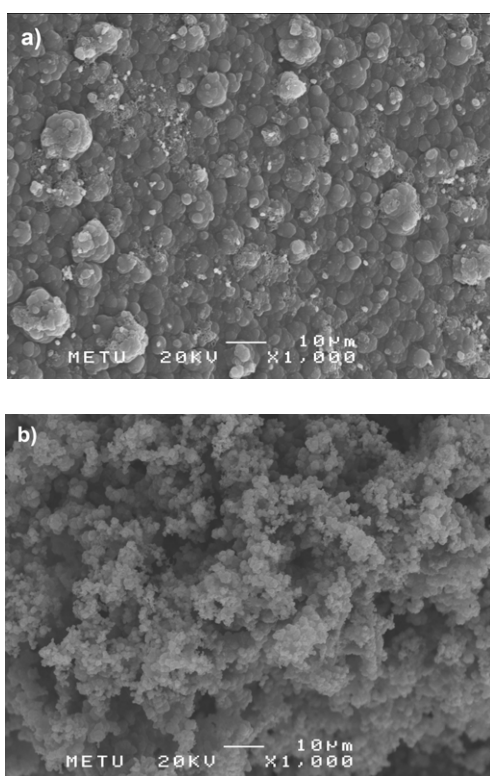


Figure 3. SEM micrographs of (a) P(BT), (b) P(DDQ-co-BT).

BT, which in fact could be interpreted as the formation of copolymer (figures 1(b) and (c)).

### 3.2. FTIR spectroscopy

In the FTIR spectrum of the P(DDQ-co-BT) (figure 2) the following absorption bands were observed: 2931.78  $\text{cm}^{-1}$  (aliphatic C-H), 1473–1381  $\text{cm}^{-1}$  (aromatic C=C stretching), 1134, 1017 (C-H in plane bending of benzene and thiophene), 624  $\text{cm}^{-1}$  (C-S-C stretching), 795  $\text{cm}^{-1}$  (C-H<sub>β</sub> out-of-plane bending of 2,5-disubstituted bithiophene), 1640  $\text{cm}^{-1}$  (polyconjugation), 1083  $\text{cm}^{-1}$  (BF<sub>4</sub><sup>-</sup> ions into the polymer film).

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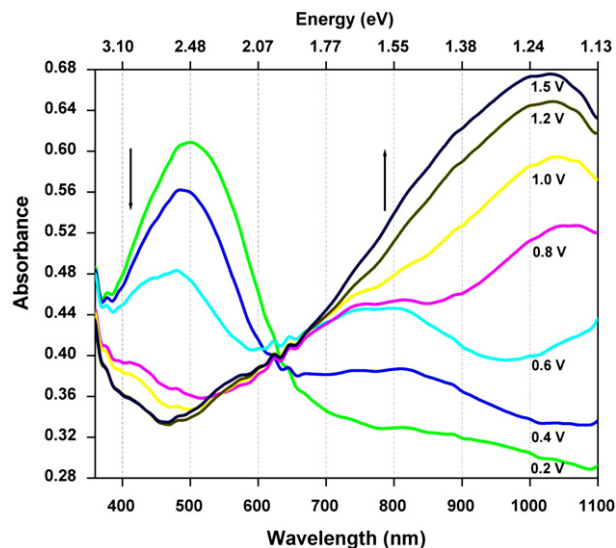


Figure 4. Optoelectrochemical spectrum of P(DDQ-co-BT) at applied potentials between +0.2 and +1.5 V in MeCN/TBAFB (0.1 M).

### 3.3. Conductivity measurements

Electrical conductivity measurements were carried out by using the four-point probe technique. The conductivity of P(DDQ-co-BT) film was measured as  $2.3 \times 10^{-2} \text{ S cm}^{-1}$ .

### 3.4. Scanning electron microscopy (SEM)

The properties of conducting polymers are strongly dependent on their morphology and structure. The solution side of the P(DDQ-co-BT) film revealed a porous-like surface structure (figure 3(b)) which was significantly different than that of the granular-like structure of pure P(BT) (figure 3(a)). The difference in morphology can be due to the copolymerization.

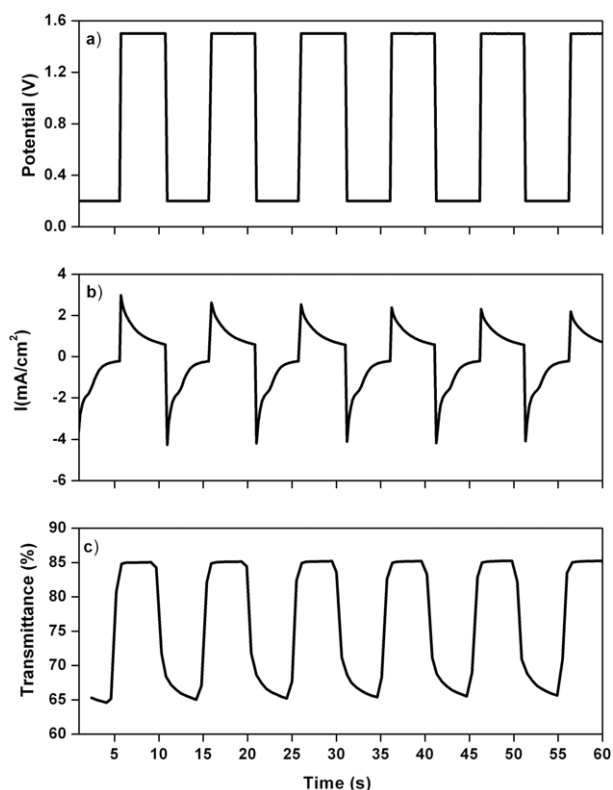
### 3.5. Electrochromic properties of conducting polymer

The best way of examining the changes in optical properties of conducting polymers upon voltage change is spectroelectrochemistry. This also gives information about the electronic structure of the polymer, such as the band gap ( $E_g$ ) and the intergap states that appear upon doping. The film was deposited on ITO via potentiostatic electrochemical polymerization of 0.01 M DDQ with 0.01 M bithiophene in the presence of MeCN/TBAFB (0.1 M) at +1.7 V. The polymer was switched between +0.2 and +1.5 V in a monomer free MeCN/TBAFB solvent/electrolyte couple to obtain the UV-vis spectra series. The electronic band gap ( $E_g$ ) was found to be 1.76 eV and  $\lambda_{\text{max}}$  was 504 nm at 0.2 V (figure 4). Upon oxidation of the polymer, the intensity of the  $\pi$ - $\pi^*$  transitions reduced and the formation of the charge carrier bands beyond 800 nm were observed while the color of the polymer changed from red to blue.

The colors of the electrochromic materials were defined accurately by performing colorimetry measurements. The CIE system was used as a quantitative scale to define and compare colors. Three attributes of color, hue ( $a$ ), saturation ( $b$ ) and luminance ( $L$ ), were measured, and these are recorded in table 1.

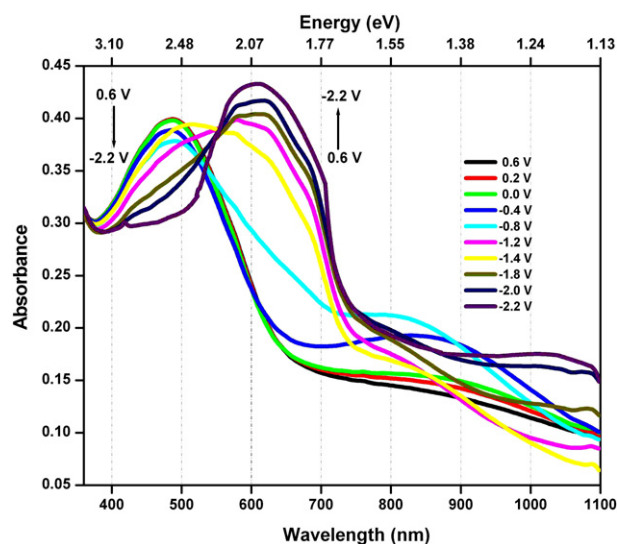
**Table 1.** Optical and electrochromic properties of copolymer and device.

Polymer	$\lambda_{\max}$ (nm) ( $\pi-\pi^*$ )	Switch. time (s)	Optical contrast	$E_g$ (eV) (Band gap)	Colors and $L a b$ values	
					Oxidation ( $L a b$ )	Reduction ( $L a b$ )
P(DDQ-co-BT)	505	1.1	21	1.76	Blue (66, -5, 20)	Red (51, 52, 46)
P(BT)	480	1.6			Blue (77, -11, -30)	Orange (60, 10, 22)
Device	$\lambda_{\max}$ (nm) P(DDQ-co-BT)	$\lambda_{\max}$ (nm) PEDOT	Switch. time (s)	Optical contrast	Colors and $L a b$ values	
					Oxidation ( $L a b$ )	Reduction ( $L a b$ )
P(DDQ-co-BT)/ PEDOT device	490	609	1.6	20	Blue (50, -6, -19)	Red (61, 18, 7)

**Figure 5.** (a) Potential–time, (b) current–time and (c) transmittance–time profiles of the P(DDQ-co-BT).

### 3.6. Electrochromic switching

For electrochromic applications, the ability of a polymer to switch rapidly and exhibit a striking color change are important. Electrochromic switching studies can monitor these types of properties. A square-wave potential step method coupled with optical spectroscopy, known as chronoabsorptometry, is used to probe switching times and contrast in these polymers. In this double potential step experiment, the potential is set at an initial potential for a set period of time, and is stepped to a second potential for a set period of time, before being switched back to the initial potential again. During the experiment, the % transmittance (%T) at  $\lambda_{\max}$  (504 nm) of the polymer is measured using a UV–vis spectrophotometer. The polymer film was synthesized on ITO-coated glass slides using a constant potential. The %T was then monitored at  $\lambda_{\max}$  while the polymer was switched from +0.2 to +1.5 V. The contrast was measured as the difference between %T in the oxidized (86%) and

**Figure 6.** Optoelectrochemical spectrum of the P(DDQ-co-BT)/PEDOT device at applied potentials between +0.6 and -2.2 V.

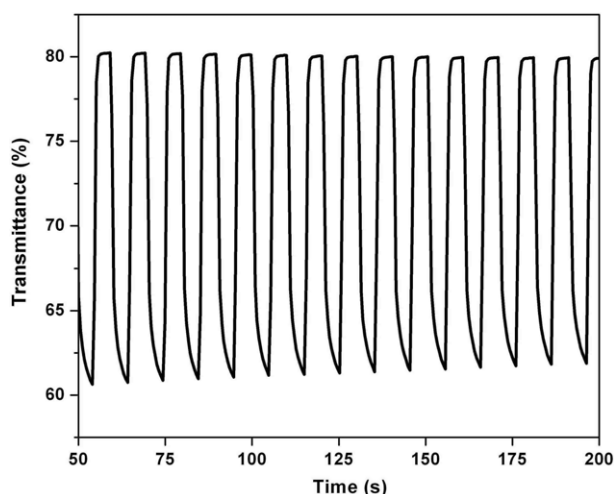
reduced forms (65%), and  $\% \Delta T$  noted as 21. Figure 5 shows potential–time, current–time and transmittance–time profiles of the P(DDQ-co-BT) film recorded during double-step spectrochronoamperometry.

### 3.7. Spectroelectrochemistry of the ECDs

Spectroelectrochemical studies of the ECDs were performed to investigate the variation of the optical properties of the devices upon applied potential. The optoelectrochemical spectrum of the P(DDQ-co-BT)/PEDOT device is shown in figure 6. At +0.6 V, the anodically coloring polymer dominated the device, revealing a maximum at 490 nm with a red color. At this voltage, PEDOT was in its oxidized state, exhibiting a transmissive sky blue color. Upon increase in the applied potential, a second absorption at around 800 nm was observed, which was an indication of the charge carrier band formation. Further increase resulted in the formation of a new band at 609 nm due to the reduction of PEDOT. At -2.2 V, PEDOT was in its most reduced state and the blue color of the polymer was dominant. Thus, upon varying the applied potential from +0.6 to -2.2 V, a color change from red to blue was observed.

### 3.8. Switching of the ECDs

Response time, one of the most important characteristics of electrochromic devices, is the time needed to perform



**Figure 7.** Electrochromic switching, optical contrast change monitored at 650 nm for the device between  $-2.0$  and  $2.2$  V.

a switching between two states. Chronoabsorptometry was performed to estimate the response time of the device and its stability during consecutive scans. On switching between square wave potentials ( $+0.6$  V and  $-2.2$  V) with a residence time of 5 s, the optical contrast ( $\Delta T\%$ ) at 650 nm was found to be 20%, with 1.6 s switching time (figure 7).

### 3.9. Stability of the ECDs

Redox stability of the devices toward multiple redox switching usually limits the utility of electrochromic materials in ECD applications. The main reasons for device failure are high applied voltages and environmental conditions. Cyclic voltammetry was employed to figure out the long term stability of the devices. To test the stability of the device, the potential was swept repeatedly between 0.0 and  $-2.3$  V with a scan rate of  $500$  mV s $^{-1}$ . Between the 1st and 1000th cycles only a limited decrease ( $\sim 10\%$ ) in the current response was observed (figure 8), which shows that the ECDs have good environmental and redox stability.

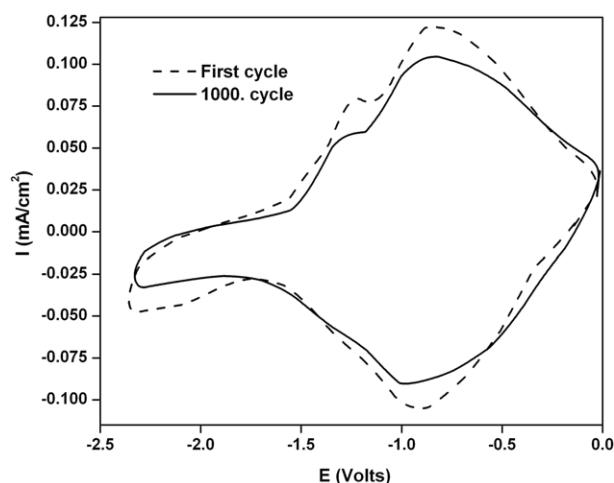
## 4. Conclusion

Synthesis of a new copolymer of 5,12-dihydrothieno[3',4':2,3][1,4]dioxocino[6,7-b]quinoxaline (DDQ) was successfully achieved in a MeCN/TBAFB (0.1 M) solvent–electrolyte couple. The copolymer was characterized by CV, SEM and FTIR studies. Spectroelectrochemical analyses revealed that the copolymer has an electronic band gap of 1.76 eV. The contrast was measured as the transmittance difference in the reduced and oxidized forms and noted as 21 %T at 504 nm.

In the second part of the study, a dual-type complementary colored polymer ECD was assembled with a configuration of ITO/P(DDQ-co-BT) || gel electrolyte || PEDOT/ITO, and its characteristics were examined. Electrochromic switching study results showed that the optical contrast ( $\% \Delta T$ ) and switching time were 20% and 1.6 s at 650 nm. In addition, the device has good environmental and redox stability.

## Acknowledgment

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**Figure 8.** Cyclic voltammogram of the P(DDQ-co-BT)/PEDOT ECD as a function of repeated scans at  $500$  mV s $^{-1}$  (after 1st and 1000th cycles).

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