Syntheses of electroactive layers based on functionalized anthracene for electrochromic applications

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Abstract

A new monomer (DTAT) was synthesized via linking 3,4-ethylenedioxythiophene (EDOT) on anthracene. The polymer, P(DTAT) was electrosynthesized by anodic oxidation of the corresponding monomer in 0.1 M LiClO$_4$ acetonitrile (ACN) solution. The optical properties, the absorption spectra and the kinetics, were examined. Spectroelectrochemical analysis showed that P(DTAT) has an electronic band gap (due to π–π* transition) of 1.57 eV at 776 nm.

Copolymers of DTAT with EDOT were prepared in ACN/LiClO$_4$ (0.1 M) solvent–electrolyte couple by varying applied potential. The incorporation of an EDOT into the full conjugated backbone, DTAT, affects its optical behavior resulting in different colors; a claret red neutral state, gray and red intermediate states and a blue oxidized state.

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Keywords: Conducting polymers; Electrochemical copolymerization; Electrochromism; Electrochromic materials; Electrochromic devices

1. Introduction

In the last two decades, polymers with a regular alternating arrangement of an aromatic π-electron system are currently receiving attention for various important technological applications. Research was focused on their conducting, electroluminescent and photoluminescent properties and their potential application in electronic and electro-optic devices, in particular in light emitting diodes (LED) [1,2]. Enhanced delocalization of π-electrons through the π-conjugation on the backbone would improve optical and electric properties of the polymers, including semiconducting properties in the doped state [3].

Also, reactivity of the monomer will affect the properties of the resulting polymer. Due to their availability and relative ease of polymerization, electron-rich heterocycles such as thiophene (Th) and 3,4-ethylenedioxythiophene (EDOT) are the most common monomers used for electropolymerization [4,5]. Derivatization of the monomer structure prior to polymerization, synthesis of copolymers, and association of the conducting polymer (CP) with other materials in order to prepare hybrid materials where the properties of both components are associated with a possible synergic effect [6].

Anthracene polymers having extended π-conjugation are also of considerable interest for their photoluminescence and electroluminescent properties [7,8]. It is known that the *ortho* position substitutions (Th, EDOT) of the phenyl ring modify the degree of conjugation (extended π–π* bonding system) [9]. Palladium catalyzed cross-coupling reaction of organometallic species with arylhalides (the Stille coupling) provides this extension in organic compounds. Development of synthetic methodology makes it possible to design oligomers, which permits color and charge injection tunable. Due to the conjugated structures of the corresponding monomers, these polymeric systems presented the advantage of being electrosynthesized at much lower oxidation potentials than that of thiophene [10]. Switching the polymer between two or more redox states generates different visible region electronic absorption bands [11].

In the first part of this study, the electrosynthesis of a conducting polymer P(DTAT), obtained from a newly synthesized monomer with anthracene core unit was achieved. The optoelectrochemical behavior and switching ability of the polymer were investigated. Second part of the study was devoted to investigate

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changes in the optical properties of DTAT through copolymerization. Moreover, the copolymer of P(DTAT-co-EDOT) was used as the anodically coloring material to construct an electrochromic device against the cathodically coloring material PEDOT.

2. Experimental

2.1. Materials

Bromine, acetone, EDOT, *n*-butyl lithium and tributyltin chloride were obtained from Aldrich Chemicals and used as received. Acetic acid (Aldrich) and dry tetrahydrofuran (THF) (Aldrich) were used without further purification.

The electrolysis solvents, acetonitrile (ACN) and dichloromethane (DCM) (Merck) were used without further purification. The supporting electrolyte, lithium perchlorate (LiClO$_4$) (Aldrich) was used as received.

2.2. Synthesis of 2,3-dihydro-5-(10-(2,3-dihydrothieno [3,4-b][1,4]dioxin-5-yl)anthracen-9-yl)thieno[3,4-b] [1,4]dioxine

A palladium-catalyzed Stille coupling was used as the key reaction to build the target molecule (**3**, DTAT). Synthetic approaches of necessary intermediates are outlined in Scheme 1. 9,10-Dibromoanthracene (**1**) was prepared with bromine in acidic medium in accordance with the previously reported procedure [12]. Tributyltin substituted EDOT (**2**) was prepared in 70% yield by lithiation with *n*-butyl lithium and subsequent quenching with tributyltin chloride [13]. Through coupling of tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (4 mmol) (**2**) with **1** (1 mmol) in THF (100 ml), 2,3-dihydro-5-(10-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)anthracen-9-yl)thieno[3,4-b][1,4]dioxine (**3**, DTAT) was obtained in 41% yield. Column chromatography (silica, hexane/DCM, 3:2) gave DTAT as a yellow solid.

2.3. Nuclear magnetic resonance spectroscopy

^{1}H NMR spectrum of DTAT was obtained with a Bruker-Instrument-NMR Spectrometer (DPX-400) in CDCl$_3$, and chemical shifts (δ) were given relative to tetramethylsilane.

2.4. Synthesis of polymers

The redox behavior of DTAT was examined by cyclic voltammetry. The measurements were carried out in a one compartment, three-electrode system in an ACN solution containing
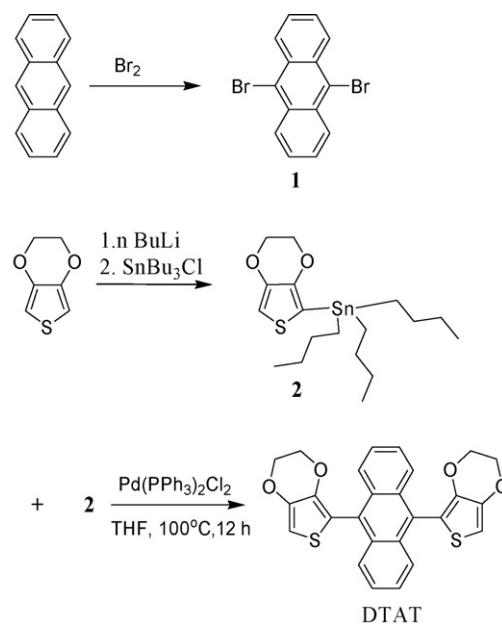

Scheme 1. Stille coupling route to EDOT-anthracene.

0.1 M of LiClO$_4$ as the supporting electrolyte. A Pt wire and a Ag wire (0.35 V vs. SCE) were used as the counter and pseudo-reference electrodes, respectively. The polymerization proceeds with the oxidation of DTAT on an ITO-coated glass working electrode (Scheme 2). P(DTAT) film was washed with ACN in order to remove excess supporting electrolyte and unreacted monomer after the potentiodynamic electrochemical polymerization.

DTAT and EDOT were electrolyzed to synthesize the conducting copolymer with properties different than their corresponding homopolymers. The oxidative electrochemical copolymerization of DTAT and EDOT was performed via repeated potential cycling and potentiostatic techniques (Scheme 3). 1.3×10^{-3} M of DTAT were dissolved in 0.1 M LiClO$_4$ in ACN and 1.3×10^{-3} M of EDOT were introduced into a single compartment electrolysis cell. A three-electrode cell assembly was used with the same electrodes described before.

2.5. Preparation of the gel electrolyte

The gel electrolyte used for electrochromic device was prepared using LiClO$_4$:ACN:PMMA:PC in the ratio of 3:70:7:20 by weight. After the dissolution of LiClO$_4$ in ACN, poly(methyl methacrylate) (PMMA, *M*: 120,000) was plasticized by 1,2-propylenecarbonate. The mixture was stirred and heated until the highly conducting transparent gel was produced.
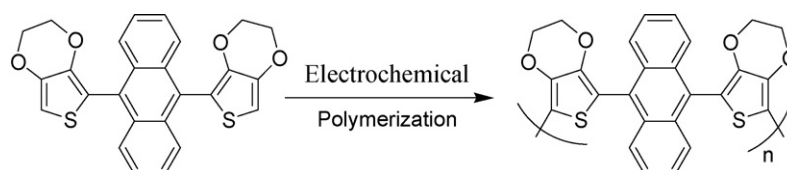
Scheme 2. Electrochemical polymerization of DTAT in LiClO$_4$ (0.1 M)/ACN.
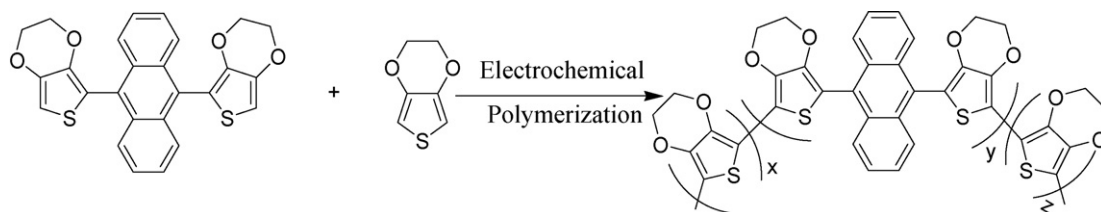
Scheme 3. Electrochemical copolymerization of DTAT with EDOT.
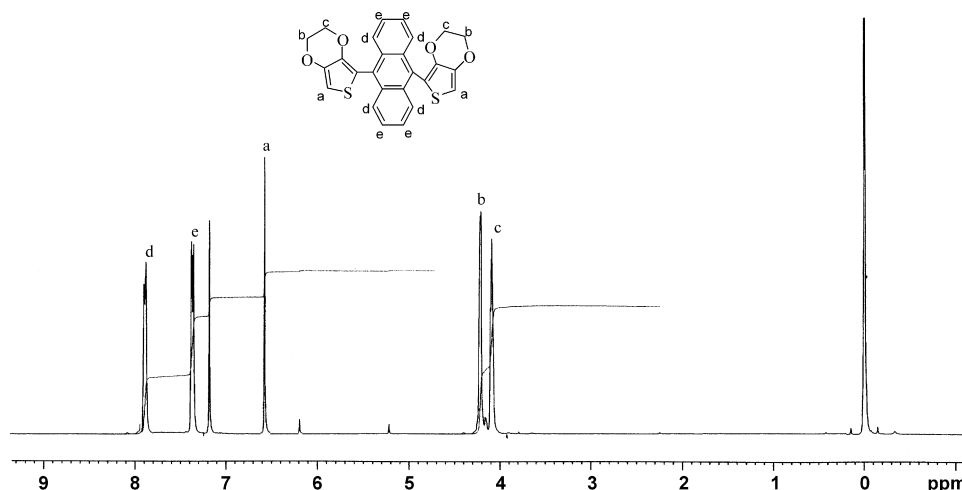
Fig. 1. ^{1}H NMR spectrum of DTAT.

3. Results and discussion

3.1. ^{1}H NMR spectrum of DTAT

^{1}H NMR spectrum of monomer (Fig. 1): $C_{26}H_{18}O_4S_2$, δ_H (CDCl$_3$) 4.1 (t, 4H), 4.36 (t, 4H), 6.6 (s, 2H), 7.3 (t, 4H), 7.9 (d, 4H).

The protons at ethylene bridge of EDOT are observed at 4.1 ppm. The α-proton of EDOT is at 6.6 ppm. The protons of anthracene unit are observed at 7.3 and 7.9 ppm.

3.2. FTIR spectra

FTIR spectrum of DTAT shows the following absorption peaks (Fig. 2): 3060 cm^{-1} (aromatic C–H stretching of benzene), 1633 cm^{-1} (C–O stretching of EDOT), 1355–1446 cm^{-1} (ring stretching of thiophene moiety of EDOT), 1650 cm^{-1} (aromatic C=C stretching), 1554 cm^{-1} (ring stretching of benzene), 1059 cm^{-1} (ring vibration of substituted benzene), 771 cm^{-1} (C–H stretching of EDOT) and 709 cm^{-1} (C–S stretching of thiophene moiety of EDOT) [14].

FTIR spectrum of electrochemically synthesized P(DTAT) showed the characteristic peaks of the monomer. The peaks related to C–H$_\alpha$ stretching of EDOT disappeared completely. The new broad band at around 1641 cm^{-1} was due to polyconjugation. The strong absorption peak at 1121 and 668 cm^{-1} were attributed to the incorporation of ClO$_4{}^-$ ions.

FTIR spectrum of electrochemically synthesized P(DTAT-co-EDOT) showed the characteristic peaks of both monomers. Intensity of peak 1633 cm^{-1} arising from aliphatic C–O stretchings (EDOT) increased. This is an evidence of the copolymerization of DTAT with EDOT. The new broad band at around 1640 cm^{-1} was due to polyconjugation. The strong absorption peak at 1122 and 668 cm^{-1} were attributed to the incorporation ClO$_4{}^-$ ions into the polymer film during doping process.
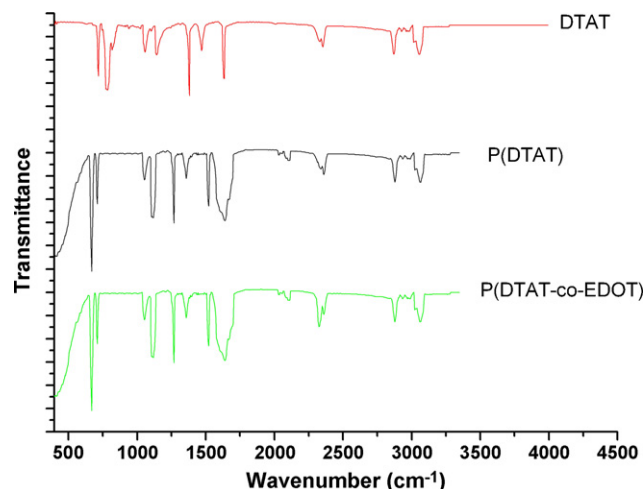

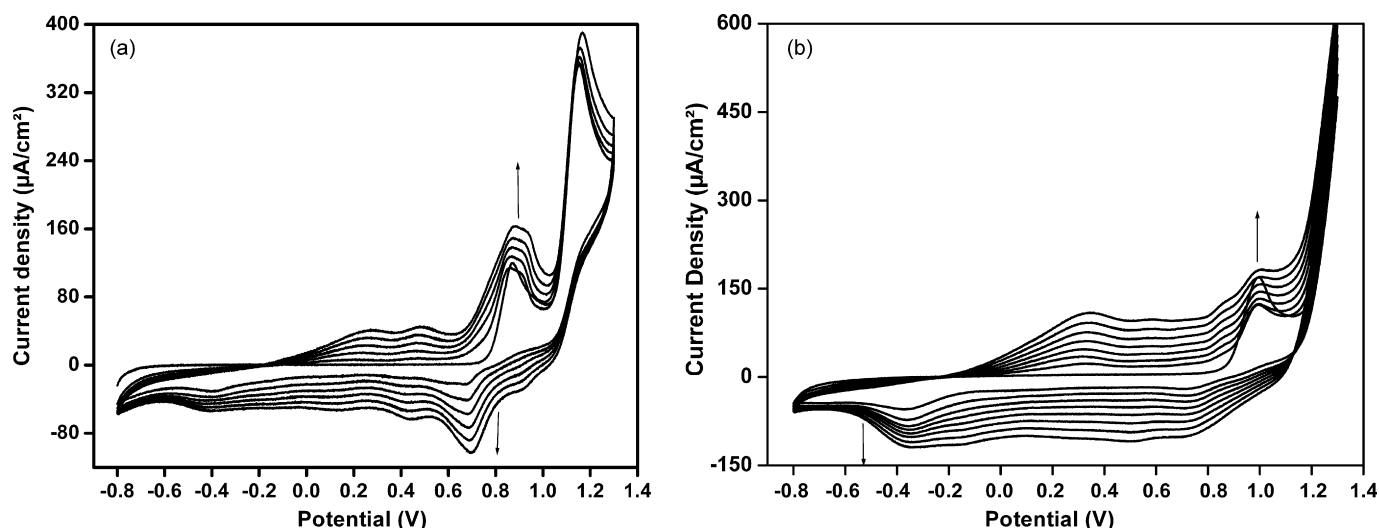
Fig. 2. FTIR spectra of DTAT, P(DTAT) and P(DTAT-co-EDOT).

Fig. 3. Cyclic voltammogram of electrodeposition of (a) P(DTAT) and (b) P(DTAT-co-EDOT) in 0.1 M LiClO₄/ACN electrolyte–solvent couple.

3.3. Electrochemical studies

3.3.1. Electrooxidation of the monomer

The redox behavior of DTAT (1.3×10^{-3} M) in ACN containing 0.1 M LiClO$_4$ solvent–electrolyte couple was studied. Potential scanning was performed between -0.8 and 1.3 V with a scan rate of 200 mV s^{-1}. The voltammogram exhibited reversible redox waves at $E_{p,a} = 0.87$ V and $E_{p,c} = 0.65$ V, and an irreversible oxidation at 1.2 V which refers to the further oxidation of the monomer. The redox activity of the polymer occurs around 0.6 V after the first cycle, the quasi reversible process with an average potential $(0.87 - (0.87 - 0.65)/2) = 0.76$ V is related to a monomer site that does not allow polymerization that occurs on another site that irreversible oxidized at 1.2 V. The reduction wave at 0.65 V is the reduction of the radical cation during each cycle. The enhancement of the current after the first cycle should be due to the overlapping of the oxidation current of the polymer or to the enhancement of the surface area of the electrode due to the polymer precipitation.

Electrochemical copolymerization of DTAT with EDOT was carried out in 0.1 M LiClO$_4$/ACN solution via potentiodynamic electrolysis. Upon repeated scanning of the potential between -0.8 and 1.3 V at 200 mV s^{-1}, formation of electroactive P(DTAT-co-EDOT) film on the ITO electrode was observed. A broad oxidation wave and a narrower peak were observed at about 0.3 and 0.9 V, respectively, whereas a broad reduction peak appeared at -0.3 V (Fig. 3b). The broad, oxidation peak, at 0.3 V during the second voltammetric cycle can be attributed to the appearance of oligomeric species (dimers, trimers, etc.) with variable chain lengths.

3.3.2. Scan rate dependence of P(DTAT) and P(DTAT-co-EDOT)

Well-defined oxidation and reduction peaks, at 0.87 and 0.65 V confirmed the electroactivity of film. The anodic and cathodic peak current intensities increased regularly with the number of cycles due to the progressive growth of the P(DTAT) film on the electrode surface. The intensity of these peaks
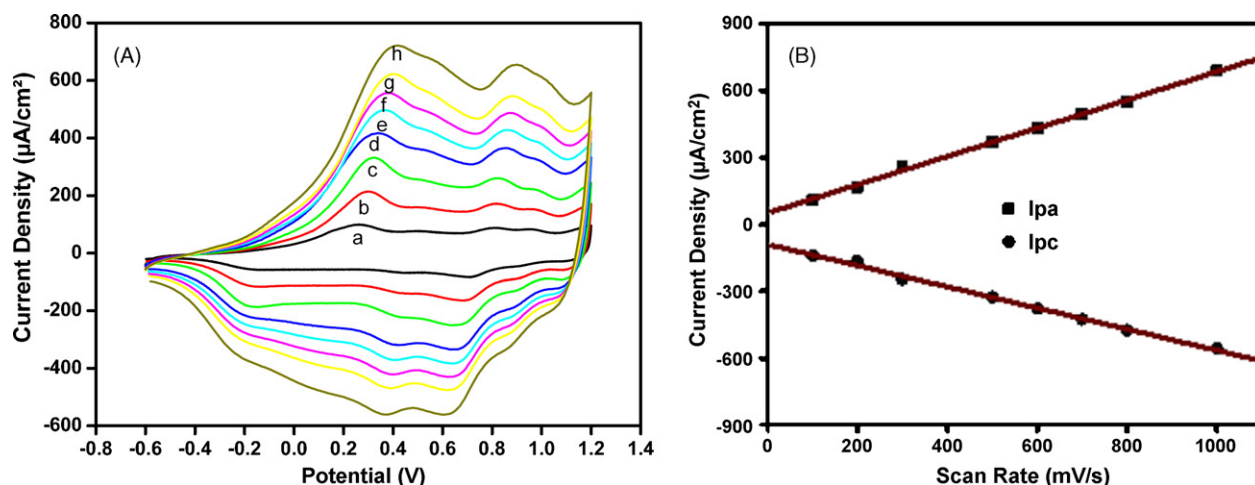

Fig. 4. (A) Cyclic voltammograms of P(DTAT) performed at various scan rates (a) 100, (b) 200, (c) 300, (d) 500, (e) 600, (f) 700, (g) 800 and (h)1000 mV s^{-1}. (B) Scan rate dependence of P(DTAT).
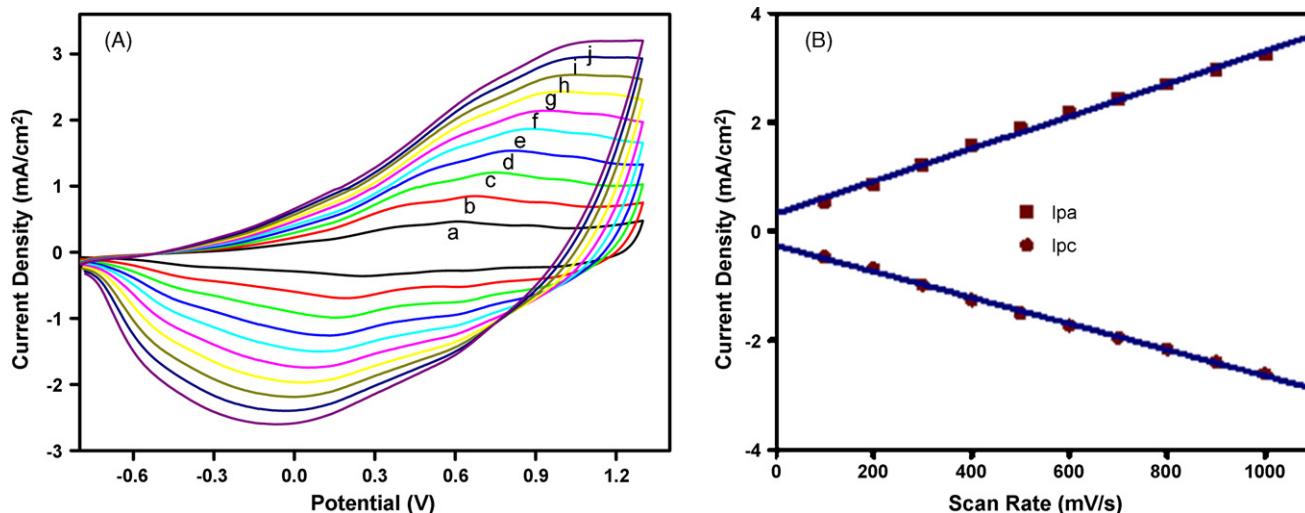
Fig. 5. (A) Cyclic voltammograms of P(DTAT-co-EDOT) performed at various scan rates. (a) $100\,mV\,s^{-1}$, (b) $200\,mV\,s^{-1}$, (c) $300\,mV\,s^{-1}$, (d) $400\,mV\,s^{-1}$, (e) $500\,mV\,s^{-1}$, (f) $600\,mV\,s^{-1}$, (g) $700\,mV\,s^{-1}$, (h) $800\,mV\,s^{-1}$, (i) $900\,mV\,s^{-1}$ and (j) $1000\,mV\,s^{-1}$. (B) Scan rate dependence of P(DTAT-co-EDOT).

increased linearly with the scan rate (v) in between 100 and $1000\,mV\,s^{-1}$, which is characteristic of a reaction of surface-localized electroactive species (Fig. 4A).

P(DTAT-co-EDOT) film also exhibited an electroactivity. The film was reversibly driven between the oxidized and neutral states, at various scanning rates, and the $I_{p,a}$ values varied linearly with the sweep rate (Fig. 5A).

Anodic and cathodic peak currents revealed a linear relationship as a function of scan rate for both polymers, indicating that electrochemical processes are not diffusion controlled (Figs. 4B and 5B).

3.4. Optical properties

The UV–vis absorption properties of P(DTAT) film, prepared using cyclic voltammetry, were investigated. In the neutral state the polymer exhibits one transition from the valence band to conduction band (π–π^*). The band gap energy which is measured as the onset of the π–π^* absorption was calculated from Fig. 6 for P(DTAT). According to de Broglie equation, the band gap (E_g) is found to be 1.57 eV (776 nm) for P(DTAT).

A spectroelectrochemical series for P(DTAT) in 0.1 M LiClO$_4$/DCM is shown in Fig. 6. The neutral form of the polymer shows a distinct π–π^* transition at 505 nm. Stepwise oxidation of the polymer results in the formation of a radical cation as the color changes from yellow to blue oxidized state. Further oxidation of the polymer forms a new absorption band around 1008 nm due to the formation of bipolarons.

3.5. Spectroelectrochemical studies of copolymers obtained by different applied potentials

The composition of the copolymer depends on monomer concentrations, the reactivity of monomer radical cations and applied potential. In order to investigate electronic structure of the copolymers obtained by different applied potentials, spectroelectrochemistry studies were performed. Polymers were

obtained via constant potential polymerizations at 0.9, 1.1 and 1.3 V.

As the applied potential was close to the oxidation potential of EDOT, a copolymer with a higher content of EDOT separated by anthracene units was synthesized. Band gap (E_g) of the copolymer increases and λ_{max} of the copolymer shifts and becomes closer to 600 nm (Fig. 7). Conversely, a higher DTAT concentration results in a copolymer with a decreased applied potential (at 0.9 V).

Table 1 is a good summary of comparison of the homopolymer, PEDOT and copolymers prepared via applying different potentials. Maximum absorption wavelengths are between those of the PEDOT and the homopolymer. Introduction of EDOT to the polymer chain leads to a slightly increase in the band gap. These numerical values also support the copolymerization phenomenon.

Copolymerization of DTAT with EDOT enhanced the optical properties of P(DTAT). Although P(DTAT) film showed two
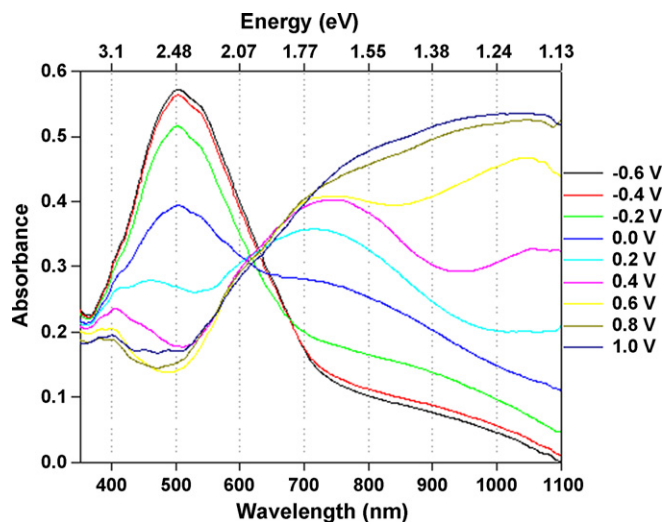

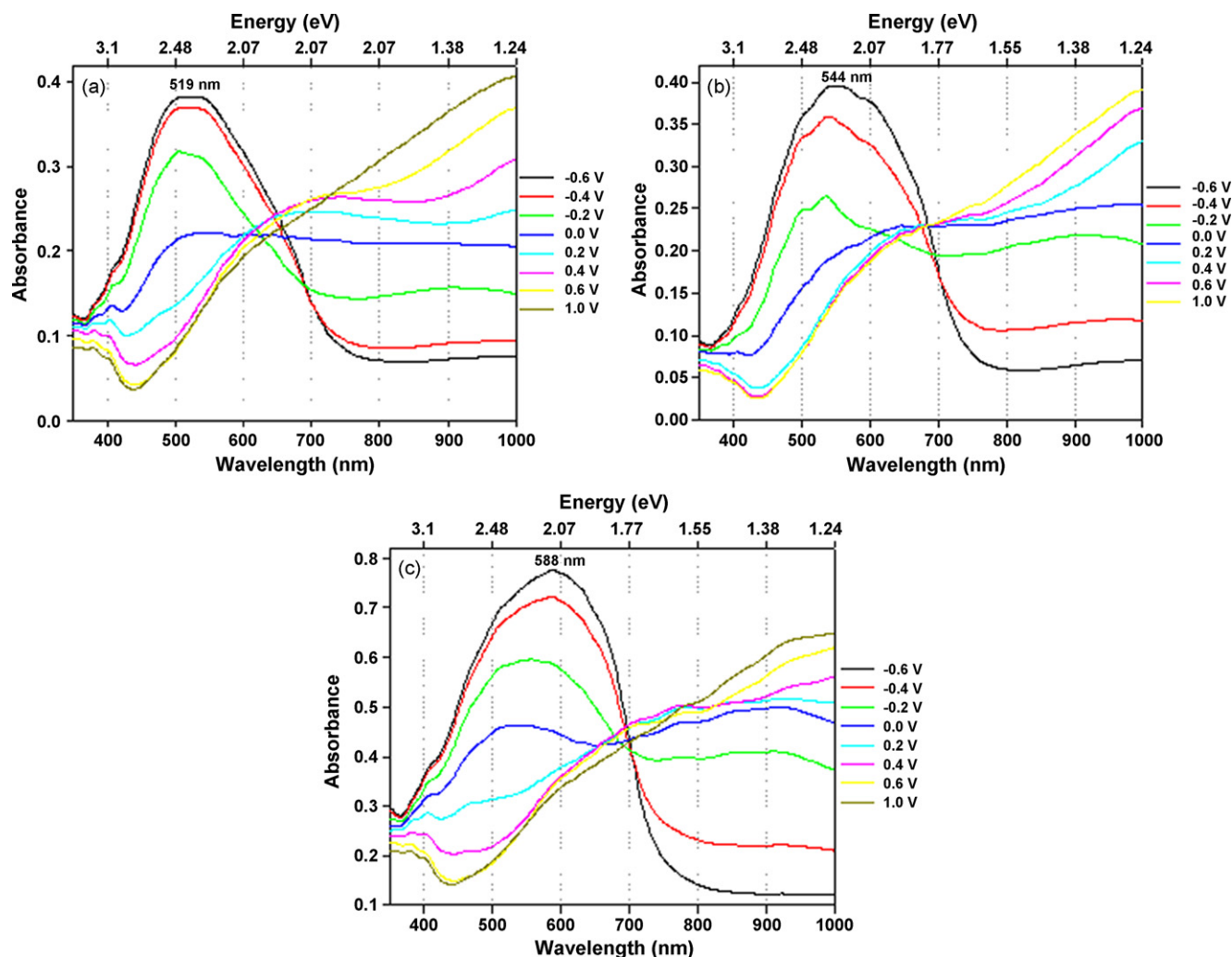Fig. 6. Optoelectrochemical spectrum of P(DTAT) in 0.1 M LiClO$_4$/DCM.

Fig. 7. Spectroelectrochemistry of copolymers synthesized at (a) 0.9 V, (b) 1.1 V and (c) 1.3 V.

distinct colors, P(DTAT-co-EDOT) film exhibited multichromic properties with a claret red neutral state, a gray and a red intermediate states, and a blue oxidized state.

3.6. Relative luminance

The luminance of a polymer film is a quantity that is highly dependent on the light source and is usually reported relative to the background luminance of a standard light source. Relative luminance studies are unique and valuable since, unlike chronoabsorptometry experiments that monitor a single wavelength, they allow the examination of the spectral changes across

the entire visible region for a polymer. In a typical experiment, the polymer, immersed in a monomer-free electrolyte solution inside a quartz cuvette, is placed in front of a standard light source (D65) in a specially designed light booth that excludes all external light. Color and luminance (L) changes were then monitored as the potential was increased. According to the CIE (Commission Internationale de I'Eclairage) system of colorimetry, the color is made up of three attributes; luminance (L), hue (a), and saturation (b) (Fig. 8).

A background measurement was also made using a blank ITO slide in the same electrolyte solution. When the polymer was held in its neutral state, it is very absorptive and does not permit much of the light to the colorimeter. However, upon oxidation, first the polymer becomes more transmissive (1.2 V) and a large amount of light reaches the colorimeter and than becomes less transmissive at the reduced state (−0.3 V).

3.7. Electrochromic switching

The ability of a polymer film to switch rapidly between its redox states is important for electrochromic applications. Response time of the polymer films to the applied potential was

Table 1
Electrochromic properties of copolymers, P(DTAT) and PEDOT

Material	Applied potential	λ_{max} (nm)	E_g (eV)
P(DTAT)	1.2	505	1.573
P(DTAT-co-EDOT) (1)	0.9	519	1.579
P(DTAT-co-EDOT) (2)	1.1	544	1.584
P(DTAT-co-EDOT) (3)	1.3	588	1.591
PEDOT	1.2	600	1.600
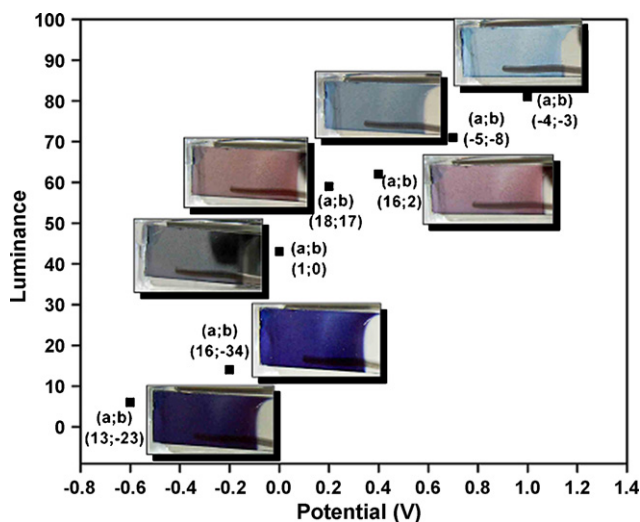
Fig. 8. Relative luminance changes of P(DTAT-co-EDOT) film with applied potential. (a, hue; b, saturation).

Fig. 10. Optoelectrochemical spectrum of P(DTAT-co-EDOT)/PEDOT device.

measured with chronoabsorptometry. In this technique, the polymer film was kept at its fully oxidized state for 5 s, and then it was stepped to its reduced form and kept at this state for another 5 s before being switched back to the initial potential again. Time is needed to switch between the redox states were recorded as the switching time. The optical contrast in the reduced and oxidized forms were measured and noted as $\Delta T\%$.

For electrochromic switching studies, P(DTAT) film was synthesized as described in Section 2.3. The film was stepped between its reduced (-0.6 V) and oxidized states (1.0 V). During switching, the $\Delta T\%$ at 500 nm was monitored as a function of time (Fig. 9). The response time to reach the 33% optical contrast was found to be 1.0 s.

Copolymerization of DTAT with EDOT caused several changes in the electrochromic properties of P(DTAT). Percent transmittance of the copolymer film was found to be 11%. The response time to full contrast was 2.1 s.
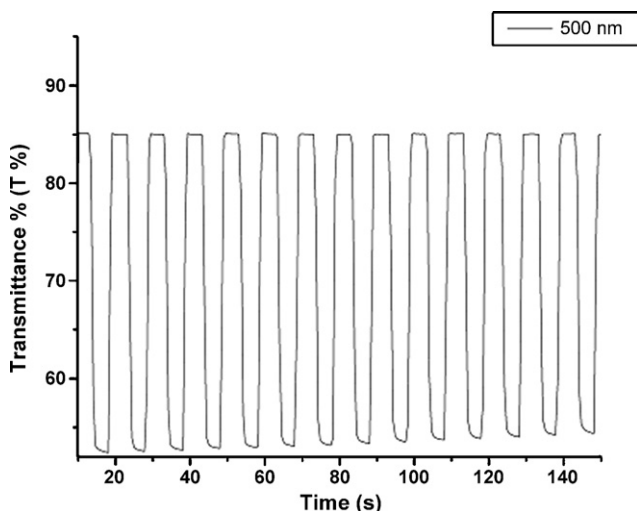
3.8. Spectroelectrochemistry of ECDs

Electrochromic devices prepared using conducting polymers was constructed by sandwiching a gel electrolyte between the polymers previously deposited on ITO. In this study, P(DTAT-co-EDOT) was used as the anodically coloring material while PEDOT used as the cathodically coloring material. Films were deposited onto ITO glass electrode via potentiodynamic electrolysis as described in Section 2.3. 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 concept of complementary conducting polymers in dual polymer ECDs yields highly transmissive and absorptive states with high optical contrast. A problem with the designed ECDs was the poor anodically coloring behavior of P(DTAT-co-EDOT) layer which switches between claret red (-1.5 V) and blue (1.5 V). Colored reduced state caused to lose the transmissive property of the PEDOT layer in the ECDs (Fig. 10). There
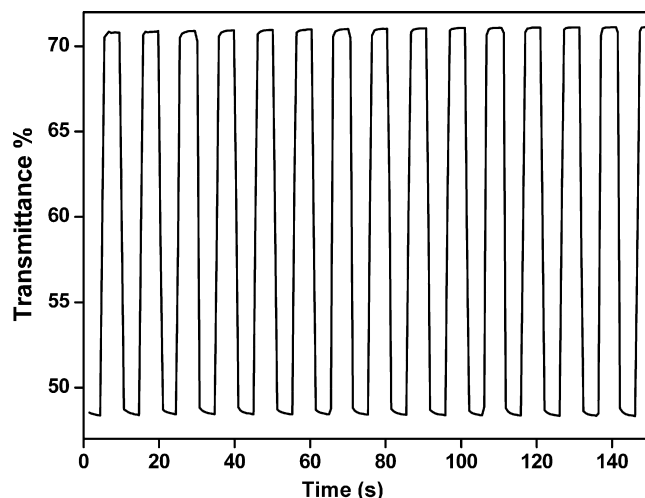

Fig. 9. Electrochromic switching for P(DTAT) at 500 nm.

Fig. 11. Kinetic study of P(DTAT-co-EDOT)/PEDOT device.

was a maximum absorption at 541 nm due to the π–π^* transition of the electrochromic layer, P(DTAT-co-EDOT). Upon application of positive potentials, P(DTAT-co-EDOT) layer started to get oxidized and the intensity of the peak due to the π–π^* transition decreased and there appears to be a second intense absorption at around 615 nm due to the reduction of PEDOT layer.

The response time that needed to switch between the two colored states and the device's stability during repeated cycles were evaluated by stepping the potential between -1.5 and $+1.5$ V with a residence time of 5 s. The percent transmittance change at 620 nm was found to be 23% for P(DTAT-co-EDOT)/PEDOT with 1.2 s switching time (Fig. 11).

4. Conclusion

Synthesis of monomer; 2,3-dihydro-5-(10-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)anthracen-9-yl)thieno[3,4-b][1,4]dioxine (DTAT) was successfully achieved. The electrochemical oxidative polymerization of DTAT was performed via potentiodynamic method using $LiClO_4$ as the supporting electrolyte in ACN. Spectroelectrochemical analyses showed that P(DTAT) has an electronic band gap (due to π–π^* transition) of 1.57 eV at 776 nm. It has a yellow color in the fully reduced form and a blue color in the fully oxidized state.

The incorporation of an EDOT into the conjugated backbone unit via copolymerization results in different emission colors: a claret red neutral state, gray and red intermediate states and a blue oxidized state. The dual-type complementary colored polymer ECD was constructed and its characteristics were examined. The color changes were observed between claret red and blue.

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