



Hunting black color via absorption engineering: EDOT and thiophene-benzothiadiazole based black-to-transmissive copolymer and its electrochromic device application

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ABSTRACT

Neutral state black electrochromics are prominent materials for smart applications such as displays, car rear views, e-papers etc. This work has aimed to obtain a neutral state black electrochromic polymer, by tuning the optical absorbance to whole visible region. Two monomers, 4,7-bis(5-(thiophen-2-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (TTBTT) and 3,4-ethylenedioxythiophene (EDOT), were selected according to their complementary absorbance behaviors, and they were combined in the same polymer backbone via electrochemical copolymerization technique. Copolymerization was performed using three different monomer feed ratios (2:1, 1:1 and 1:2 (EDOT: TTBTT)). Even though all the copolymers exhibited dark to transmissive colors from neutral to oxidized states, changing the monomer feed resulted in different optical contrast, switching response and color hues for each copolymer. The higher optical contrast (from 17% to 27%) and faster switching response (from 3.6 s to 1.8 s) were recorded as EDOT unit increase in the copolymer chain. A dual type electrochromic device was also constructed using the copolymer and the resulting device was successfully changed its color from black to transmissive.

1. Introduction

For the last decades, electrochromic polymers (ECPs) and their applications have been one of the most important research areas. The tunable optical properties make ECPs the potential candidates in various applications such as optical sensors [1–3], solar cells [4,5], displays [6–8], field effect transistors [9] and many other optoelectronics [10–12]. Scientists have a special interest in black-to-transmissive ECPs due to their ability of absorbing the entire visible range in the optical spectrum. Black-to-transmissive ECPs play an important role in organic electronic applications such as car-rear views [13], electrochromic windows [14], electronic papers [15], etc. Material scientists and polymer/organic chemists are constantly designing and synthesizing new structures or modifying current systems to generate black ECPs. To achieve black electrochromic, new structural design is primarily based on the donor-acceptor-donor (DAD) strategy [16,17]. Alternatively, black ECPs are also obtained by copolymerization technique [18,19].

An electrochromic (EC) copolymer consists of at least two different

monomers, and can be synthesized either by chemical or electrochemical techniques. Among them, electrochemical copolymerization technique is quite easy and quick way to obtain an EC copolymer as a thin film on the electrode surface. Moreover, optoelectronic properties of a copolymer can be altered by changing the monomer feed ratios. The most frequently used monomer in copolymer synthesis is “3,4-Ethylenedioxythiophene (EDOT)”, since it can be polymerized at low anodic potentials while maintaining good electrode surface adhesion [20,21]. EDOT is an improved form of the thiophene unit, including an alkoxy bridge on the third and fourth carbon position of thiophene. The alkoxy bridge prevents undesired polymerization on these positions. Besides, the electron donating oxygen atoms on the alkoxy bridge allows EDOT to be polymerized easily. The resulting polymer (PEDOT) exhibits a narrow band gap with outstanding stability, conductivity, and optical contrast [22]. With these remarkable characteristics, EDOT unit enhances the electrochemical and optical properties of the copolymer in which it is inserted [23].

Benzothiadiazole, on the other hand, is another widely used

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conjugated unit in the literature. It provides a good planarity and longer conjugation length to the resulting polymer chain [24,25]. The low band gap DAD type electrochromic polymers based on thiophene derivatives and benzothiadiazole have been commonly reported in the literature. The utilization of thiophene as a donating moiety and benzothiadiazole as an accepting moiety is a well-studied and successful strategy to producing low band gap materials. Previously reported by our group that, increasing thiophene number from one to two in the thiophene-benzothiadiazole-thiophene segment caused better conjugation and more effective intramolecular charge transfer in the resulting ECP [26].

In the literature, there are also various reports about combination of thiophene-benzothiadiazole DAD type of units with different monomers, including thienothiophene [27,28], dibenzosilole [29,30], cyclopentadithiophene [31], fluorene [32,33], carbazole [34], and longer oligothiophenes [35], to produce low band gap copolymers.

In this article, under the light of the information above, we investigated the electrochemical and optical properties of a copolymer, which is synthesized by combining a thiophene-benzothiadiazole based DAD type of monomer (4,7-bis(5-(thiophen-2-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole) (TTBTT) and EDOT in the same polymer matrix. The homopolymers of these units have a complementary optical absorption behavior. For this reason, we mainly focused on covering the entire visible region via combination of these monomers and obtaining a black ECP. By changing the monomer feed ratios, the more covering the visible region, in other words, the darker color, was tried to optimized. Resulting copolymers with different monomer feed ratios were investigated in terms of their electrochemical and optical properties.

2. Experimental

All measurements were performed at room temperature and ambient conditions. Reagents and solvents (tetrabutylammonium perchlorate (TBAClO₄), 3,4-ethylenedioxythiophene (EDOT), acetonitrile (ACN) and dichloromethane (DCM)) were purchased from Merck or Sigma Aldrich and used as received. Gamry PCI4/300 potentiostat-galvanostat and Carry 60 model UV-Vis spectrometer combined with Gamry were used for the electrochemical and spectroelectrochemical measurements, respectively. Electropolymerizations were performed via cyclic voltammetry using ITO (Delta Tech. 8–12, 0.7 cm × 5 cm) coated glass working electrode (vs Ag wire as pseudo-reference, and platinum wire as counter electrodes). All polymerizations were conducted in TBAClO₄-ACN/DCM (5:2 v/v), and the polymer behaviors were investigated in TBAClO₄-ACN electrolyte systems. The color values of the polymer films (L: brightness; a: hue, b: saturation) were reported according to “The International Commission of Illumination, CIE,” color coordinates. Gel electrolyte for electrochromic device application was prepared by mixing TBAClO₄ - poly(methyl methacrylate) - propylene carbonate - ACN in the following ratio 3:7:20:70 (w/w), respectively [36].

2.1. Electrosynthesis of homopolymers and copolymers

TTBTT had been already synthesized in one of our previous study [26]. For the current study, 0.025 M solutions of EDOT and TTBTT were prepared in DCM and these solutions were used in all polymerizations. Homopolymers and copolymers were obtained on ITO-glass electrode (electroactive area of 1.2 cm²) by 10 repetitive cyclings (at a scan rate of 100 mV/s) using cyclic voltammetry in 0.2 M TBAClO₄-ACN/DCM (5:2 v/v). The polymerization potential range for TTBTT is between 0.0 V and 1.5 V. For EDOT and copolymers, -0.3 V and 1.5 V potential range was used. Copolymerizations were performed using different monomer feed ratios of 2:1, 1:1 and 1:2 (TTBTT: EDOT). After polymerizations completed, the resulting polymer films were washed in ACN to get rid of monomeric or oligomeric species, and then taken into monomer free electrolyte solution of 0.2 M TBAClO₄-ACN for further studies.

2.2. Electrochromic device (ECD) fabrication

For ECD fabrication, copolymer and PEDOT films, deposited on ITO-glass electrodes were used as the anodically and the cathodically coloring materials, respectively. The copolymer (in its neutral state) and PEDOT (in its oxidized state) films were sandwiched by plain gel electrolyte in between. Resulting ECD was left to dry overnight.

3. Results and discussion

3.1. Electrochemical and optical characterization of homopolymers

The CV behaviors of TTBTT and EDOT monomers were investigated in the anodic region and their oxidation onset potentials were observed at 1.16 V for TTBTT and 1.3 V for EDOT (Fig. 1, blue lines). The small difference in the oxidation onset values of the monomers indicates the suitability of copolymerization, since the applied potential must be enough to oxidize both monomers [11].

Fig. 1 shows the CVs of the homopolymers during the

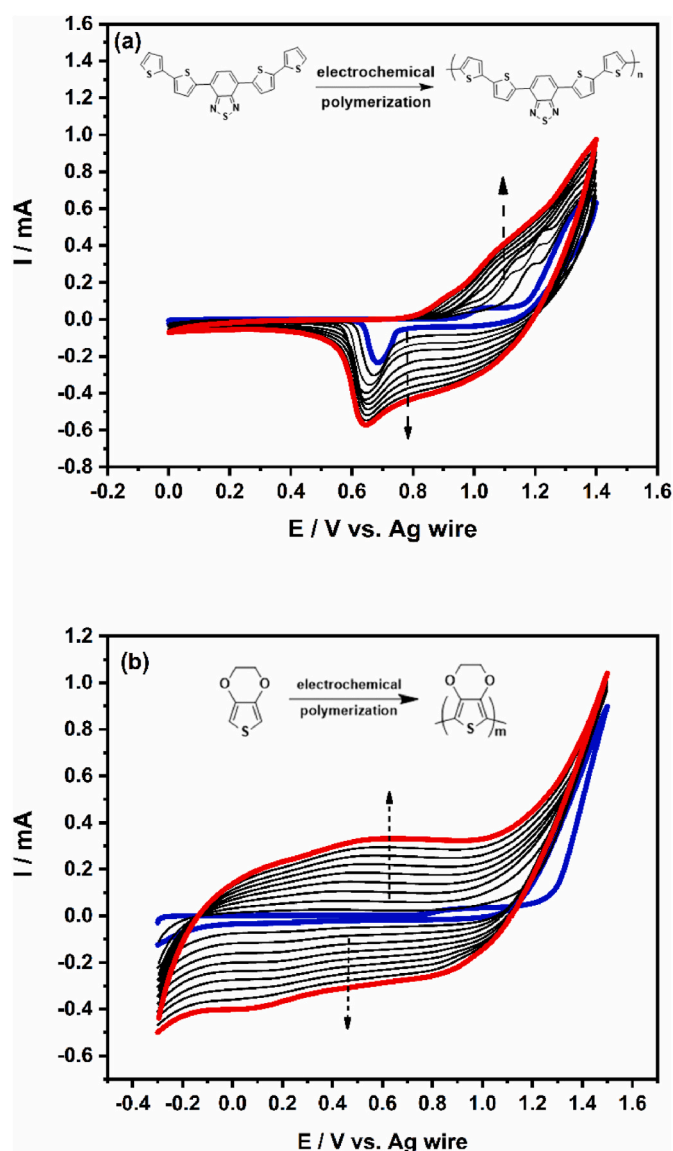


Fig. 1. Cyclic voltammograms collected during electropolymerization of a) TTBTT (between 0.0 V and 1.5 V) and b) EDOT (between -0.3 V and 1.5 V). (10 repetitive cyclings at 100 mV/s) Insets: Electrochemical polymerization routes for TTBTT and EDOT.

electrochemical polymerization. As seen from the figure, increase in the current intensity (for both EDOT and TTBTT) in each successive scan shows the electroactive polymer film formation on the working electrode surface. Moreover, the colored film on the working electrode surface, which can be clearly observed with the naked eye also indicates the polymer formation [37]. After polymerizations were completed, the polymer films removed from the cell, washed with ACN to get rid of the monomeric or oligomeric species, and taken into monomer free electrolyte solution. PEDOT is a well known polymer and lots of studies have already showed the electrochemical and optical stability of PEDOT film [22,23,38,39]. Fig. 2 shows the CV and UV behaviors of homopolymers. Cyclic voltammograms of PEDOT and P(TTBTT) were collected at a scan rate of 25 mV/s, between -0.8 V and 1.1 V for PEDOT and 0.0 V and 1.5 V for P(TTBTT). As seen from Fig. 2a, PEDOT starts to oxidize at about -0.3 V and gives a broad oxidation peak with having a maximum at 0.21 V. Oxidation onset of P(TTBTT) is observed at about 0.85 V, reaching the maximum at 1.23 V.

Optical absorption behaviors of homopolymers were demonstrated in Fig. 2b. As seen from the figure, P(TTBTT) exhibited two absorption maximum at 394 and 466 nm, as shown in our previous study [26]. PEDOT, on the other hand, gave the maximum of its optical absorption band at 588 nm. The optical band gap energy values of homopolymer films (calculated from their absorption onsets of the lower energy bands) were calculated as 1.88 eV for P(TTBTT) and 1.65 eV for PEDOT.

In order to examine the spectrochemical behaviors, UV-Vis spectra of homopolymers were monitored during a slow anodic scan up to their fully oxidized states, and the resulting spectra were shown in Fig. 3. As it can be followed in Fig. 3a, absorption maxima of P(TTBTT) starts to lose its intensity upon oxidation at about 0.9 V, and continues to decrease, which is accompanied by the appearance of a newly intensifying band at about 618 nm. Upon further oxidation (at about 1.3 V), a second newly formed band at about 996 nm rises its intensity. These new bands can be attributed to formation of charge carriers (polarons and bipolarons, respectively) [40,41]. Similarly for PEDOT, decrease in intensity of the neutral peak at 588 nm accompanies with an increase of the new peaks are intensified at about 890 nm and 1030 nm (See Fig. 3b). These changes in the electronic absorption spectra of homopolymer films were also observed as color changes. The colors of P(TTBTT) film is brown in its neutral state and cosmos blue in its fully oxidized state. On the other hand, PEDOT film is dark blue in the neutral and transmissive sky blue in the oxidized state. Colors and related L-a-b values of the homopolymers are given in Fig. 3c.

Further optical parameters of the homopolymer films, such as switching time (t_{ox}), percent transmittance (T %) and coloration efficiency (CE), were elucidated via kinetic studies, by subjecting the polymer films into square wave input of 0.0 V and 1.5 V for P(TTBTT) and -0.8 V and 1.1 V for PEDOT in 10 s intervals. The visible transmittance was monitored during switching as a function of time.

Switching time and CE values were reported at 95% of the full optical contrast, at which the human eye is more sensitive. CE was calculated using the following equation: $CE = \Delta OD / Q_d$, where Q_d is the injected/ejected charge per unit area during a redox step, and ΔOD is the optical density which is calculated as " $\log(T_{ox}/T_{red})$ ", where T_{ox} and T_{red} are the percent transmittance in the oxidized and neutral states, respectively [42]. The way of measuring T % and switching time was shown in Fig. 4, using the kinetic data of PEDOT, recorded at 588 nm. PEDOT film exhibited 46% T change at 588 nm with possessing 1.0 s switching time (at 95% optical contrast) and the optical behavior kept its stability during many scans between -0.8 V and 1.1 V. On the other hand, when monitoring P(TTBTT), it was observed that optical contrast showed a decrease even after 10 switches, especially in polaron/bipolaron region. Fig. 5a shows the kinetic behavior of P(TTBTT). While the polymer film keeps its optical stability at 394 nm and 466 nm with having the optical contrast of 14.5% and 5.5%, respectively, the T % values at 618 nm starts to decrease from 20.5% to 16%. Moreover at 996 nm, a decrease is also recorded from 35% to 30%, even after 10 switches. If it needs to be explained, the kinetic study was performed on the same film by repetitive 20 switches firstly at 394 nm, following by at 466 nm, then at 618 nm and finally at 996 nm. 80 switches at total shows that, after about 50 switches, the polymer film could not sustain its optical stability.

To examine the electrochemical behavior, the same polymer film that subjected to kinetic study was used and scanned between 0.0 V and 1.5 V for 20 times. Resulting CVs were shown in Fig. 5b. As seen from the figure, 35% lost in both anodic and the cathodic current intensities was recorded after 20 scans. On the other hand, it was observed that the polymer film is still electroactive even if the neutral and oxidized colors are little faded.

Switching time of P(TTBTT) was elucidated from kinetic data and found as 4.7 s at 394 nm, 4.9 at 466 nm, 2.8 s at 618 nm and 2.6 s at 966 nm. Moreover, CEs were also calculated and found to be 41 cm^2/C and 95 cm^2/C at 394 nm and 466 nm, respectively. When the optical properties are evaluated, it can be concluded that P(TTBTT) film did not show promising properties by possessing relatively long switching times and poor optical and electrochemical stability. This is most probably due to two thiophene units in the monomer, which increase the D/A ratio of the polymer chain and decrease the intramolecular charge transfer. Moreover, stiffness of the polymer may also suffer when D/A ratio is high [26,43]. The electrochromic properties of homopolymers were summarized in Table 1.

3.2. Electrochemical and optical characterization of copolymers

Since the main aim of this study is obtaining black electrochromism, it was majorly focused on the optical absorption behaviors of the homopolymers. P(TTBTT) and PEDOT has their maximum absorption wavelengths at 466 nm and 588 nm, respectively. In the light of

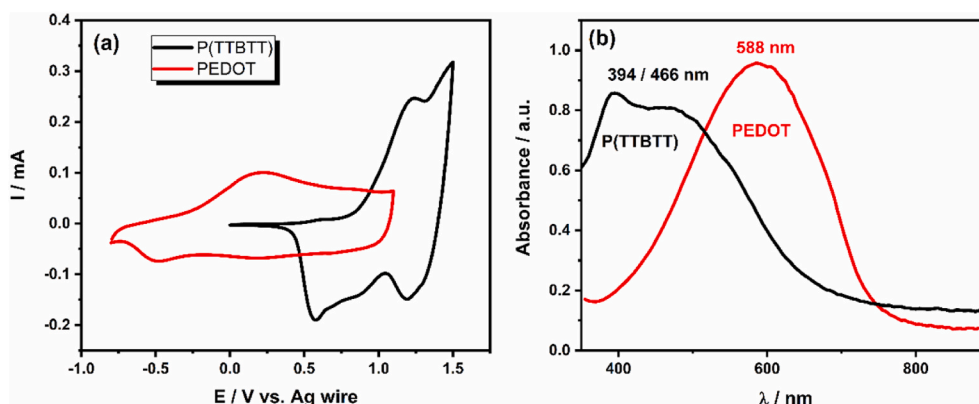


Fig. 2. a) Cyclic voltammograms of homopolymers collected at 25 mV/s, b) Neutral state UV-Vis spectra of homopolymer films measured in 0.1 M $\text{TBAClO}_4/\text{ACN}$.

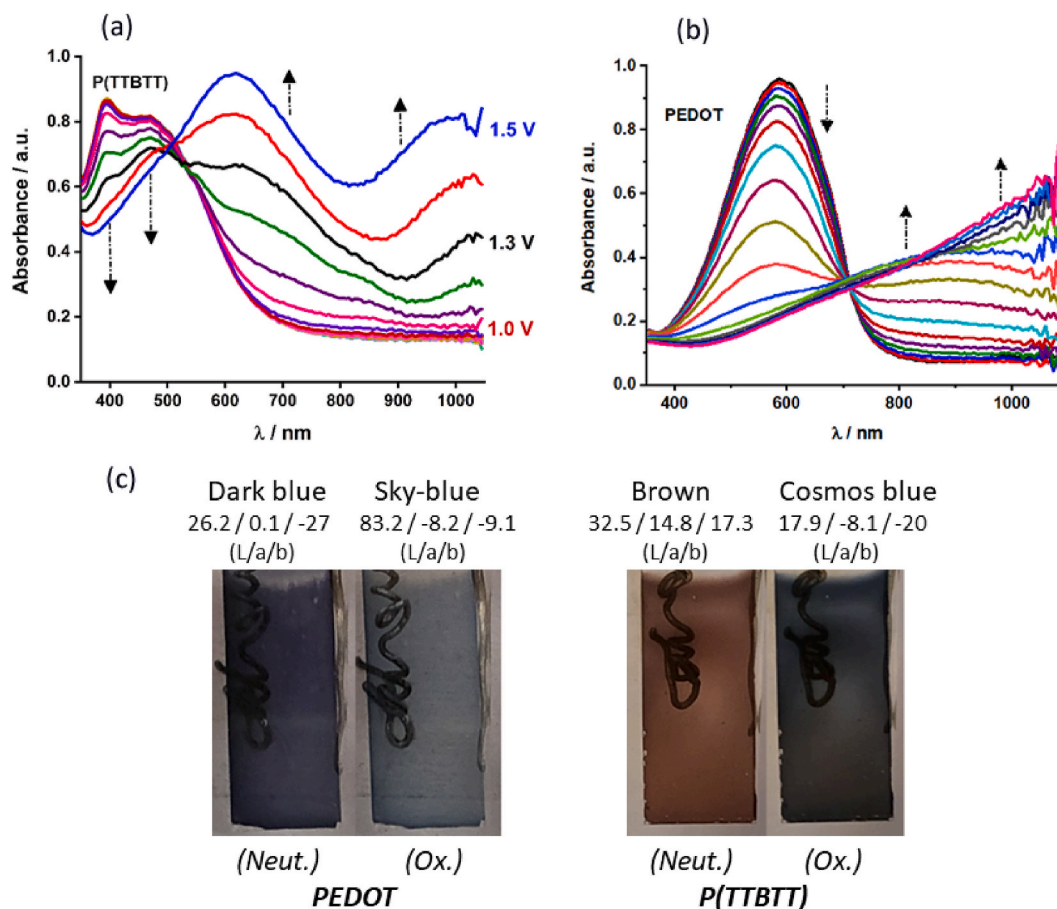


Fig. 3. UV-Vis spectra of homopolymers during anodic scan, a) From -0.3 V to 1.5 V for P(TTBTT). b) From -0.8 V to 1.1 V for PEDOT, at a scan rate of 25 mV/s c) Colors and L-a-b values of homopolymers in neutral and oxidized states. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

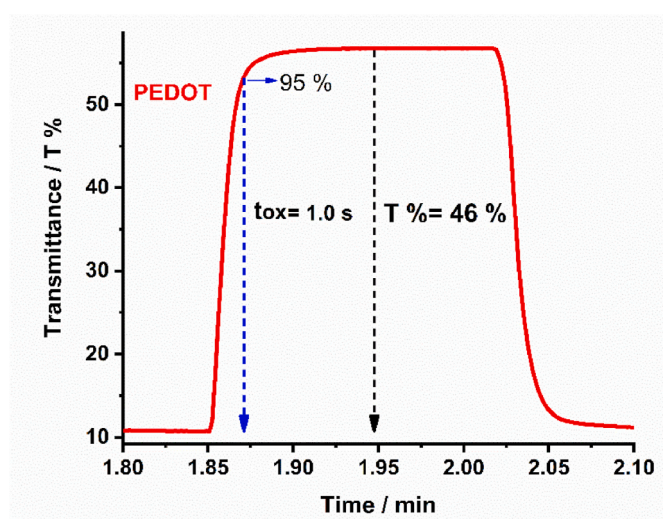


Fig. 4. 6th curve of PEDOT, taken from kinetic data during 10 s switching at -0.8 V and 1.1 V, used for revealing the percent transmittance, response time and coloration efficiency values.

information about the UV-Vis bands of the homopolymers, it can be possible to cover the more visible region and obtain a darker electrochromic polymer by combining these units in the same polymer backbone. The optimum coverage of the visible region can be obtained by changing the monomer feed ratio. Moreover, the low electrochemical

and optical stability of P(TTBTT) may be overcome by introducing EDOT unit into the copolymer matrix. For this aim, the copolymerization was performed using different monomer feed ratios as follows: 2:1, 1:1 and 1:2 (TTBTT:EDOT). Each copolymerization was performed under the same conditions:

- 1) In the same electrolytic medium of 0.2 M $TBAClO_4$ - ACN/DCM,
- 2) 10 repetitive cyclings between -0.3 V and 1.5 V,
- 3) 1.2 cm^2 electroactive film deposition area on the working electrode surface.

Fig. 6 shows the CVs during three copolymerizations and the resulting CVs of the copolymers. As seen from Fig. 6a, b and 6c, the current intensities of CVs increases in each successive scan, which shows the electroactive polymer formation on the working electrode surface. As EDOT ratio increase in the monomer mixture, the copolymerization CVs match more to EDOT polymerization pattern. When the ratio is 2:1 (TTBTT: EDOT), the oxidation peak of TTBTT at about 0.85 V and its reversible peak at about 0.6 V can be observed clearly (Fig. 6a). As the EDOT ratio increases, the first CV becomes more flat, and the peak at about 0.6 V in the reduction side loses its intensity, which resembles to PEDOT's behavior more (Fig. 6b and c).

Same look was also observed in the copolymer CVs. As seen in the inset of Fig. 6a, the polymer redox CV looks like dominating by both polymers, (early oxidation coming from PEDOT and two oxidation regions before and after 0.5 V along with the reversible peak at about 0.6 V). As EDOT ratio increases in the copolymer chain, the redox behavior becomes more flat and includes broader oxidation and reduction peaks,

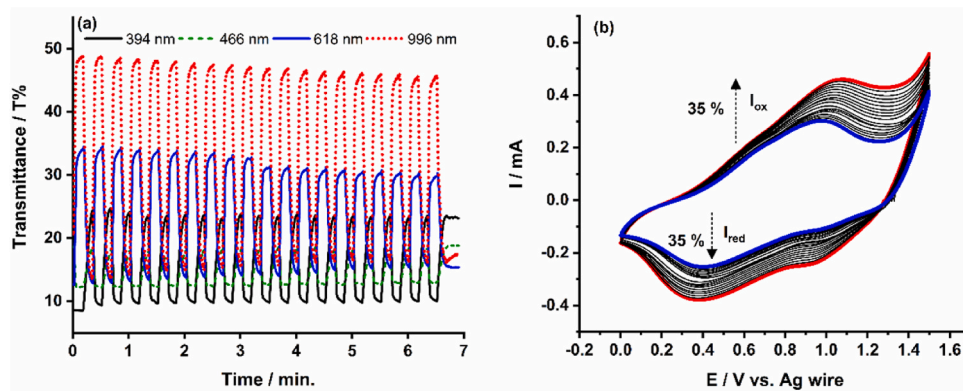


Fig. 5. a) Chronoabsorptometry experiment for P(TTBTT) film, switched between 0.0 V and 1.5 V with switch time of 10 s, b) 20 repetitive CVs of P(TTBTT) film scanned between 0.0 V and 1.5 V, at a scan rate of 200 mV/s.

Table 1
Summary of the electrochromic properties of homopolymers and copolymers.

	PEDOT	P(TTBTT)	Copol2:1	Copol1:1	Copol1:2
λ_{\max} (nm)	588	394/466	520	550	570
E_g (eV)	1.65	1.88	1.67	1.66	1.65
T %	46	5.5/16	17	21	27
t_{ox} (s) (95%)	1.0	4.7/4.9	3.6	3.0	1.8
CE (cm ² /C) (95%)	356	41/95	117	134	182
Colors (neutral)	dark blue	Brown	nut brown	black	black
Colors (oxidized)	sky blue	cosmos blue	bronze gray	olive black	dark gray

looking more like pristine PEDOT (insets of Fig. 6b and c). It can be concluded that the different copolymerization behaviors and copolymer CV patterns prove the successful copolymerizations [44,45]. Moreover, all copolymer films appeared as a dark color on the working electrode surface, which is different than those of homopolymers. This can be evaluated as a further proof of copolymer formation [45].

Scan rate dependence of homopolymer P(TTBTT) was not promising. In other words, there was no direct relationship between the current intensity with respect to the scan rate, especially at high scan rates. For that reason, it is estimated that increasing EDOT feed can improve the scan rate dependence behavior. For this aim, anodic and cathodic current responses of the copolymers were monitored as a function of scan rate (at 25, 50, 75, 100, 125, 150, 175 and 200 mV/s) and the resulting CVs were shown in Fig. 6d, e and 6f. Current intensity vs scan rate graphs were obtained from the related CV data (insets of Fig. 6d, e and 6f). It was seen that as EDOT ratio increases, current responses were found to be directly related to the scan rates, indicating a well adhering electroactive polymer film on the working electrode surface [46]. Copol2:1 deviated from the linearity after 100 mV/s, which can be due to low EDOT ratio in the copolymer matrix. On the other hand, linearity between current and scan rate was accomplished by Copol1:1 and Copol1:2. Moreover, these results also indicate a non-diffusional redox process for Copol1:1 and Copol1:2.

UV-Vis spectra of the copolymer films were monitored during a slow anodic scan from -0.8 V to 1.5 V at a scan rate of 25 mV/s, and the resulting spectra were depicted in Fig. 7 (a-b-c).

The maximum wavelengths of the neutral absorption bands of the copolymers were measured at 520 nm for copol2:1, 550 nm for copol1:1 and 570 nm for copol1:2. The sequential red-shift in the optical absorption bands clearly shows the contribution of more EDOT moiety into the copolymer chain [47]. Moreover, the initial oxidation of copol1:1 is observed about 0.1 V earlier than that of copol2:1, on the other hand, about 0.1 V later than that of copol 1:2. The oxidation delay shows the effect of monomer feed on the copolymerization. In other words, as

EDOT ratio increases in the copolymer matrix, oxidation becomes easier for the whole copolymer chain.

During oxidation, the intensity of the neutral band of each copolymer decreased accompanying by formation of newly intensifying bands (beyond 800 nm and 900 nm, most probably due to formation of polarons and bipolarons, respectively). The bipolaron bands intensified after 0.8 V for copol2:1, 0.7 V for copol1:1 and 0.5 V for copol1:2, probably due to more EDOT contribution in the copolymer matrix. The band gap values were calculated from the onset of the low energy bands and found as 1.67 eV (for Copol2:1), 1.66 eV (for Copol1:1) and 1.65 eV (for Copol1:2).

Another observation regarding UV-Vis behavior can be evaluated as follows: The intensity of absorption peak at about 394 nm resulting from the presence of TTBTT unit is lowest in copol1:2, since EDOT units exists more. Moreover, it can be observed that, the spectral density in the visible region decreases more in fully oxidized state, as EDOT unit increases (Fig. 7 a-b-c).

UV-Vis spectra were also used to determine the incorporation mode (random, alternating or block wise) of the copolymers. Random or alternating copolymers are expected to show different optical spectra than their homopolymers. On the other hand, block wise copolymers might include the peaks at superpositions of their homopolymers [48]. As seen from UV-Vis spectra of homopolymers and the copolymers in this work, the absorption behaviors of all copolymers are different than their homopolymers, indicating the copolymerization mode of random or alternative, rather than block wise type [49].

The copolymer films were also subjected into square wave inputs of -0.8 V and 1.5 V in 10 s revealing times at their maximum of the optical absorption bands (Fig. 7d-e-f). As EDOT ratio increased in the copolymer matrix, the optical contrast increased as 17%, 21% and 27% for Copols 1:2, 1:1 and 1:2, respectively. The switching times were measured from the kinetic data at 95% of the optical contrast and found to be 3.6 s (for Copol2:1 at 520 nm), 3.0 s (for Copol1:1 at 550 nm) and 1.8 s (for Copol1:2 at 570 nm). It can be concluded that the more EDOT unit incorporated in the copolymer matrix increases the optical contrast and results in a faster switching response for the resulting copolymer. The CE values were also calculated for each copolymer and showed an increasing trend with increasing EDOT ratio in the copolymer chain. CE values and other electrochromic properties of the copolymers were summarized in Table 1.

The homopolymers (PEDOT and P(TTBTT)) were insoluble in common organic solvents. As their homopolymers, the solubility of copolymers were also tested in DCM, ACN, chloroform and acetone and found as insoluble.

While all the copolymer films exhibited dark colors in their neutral states, the degree and shade of the darkness changed as increasing EDOT ratio. Fig. 8 shows the colors and L-a-b values of the copolymer films in their neutral and oxidized states. Copol2:1 exhibited neutral state nut

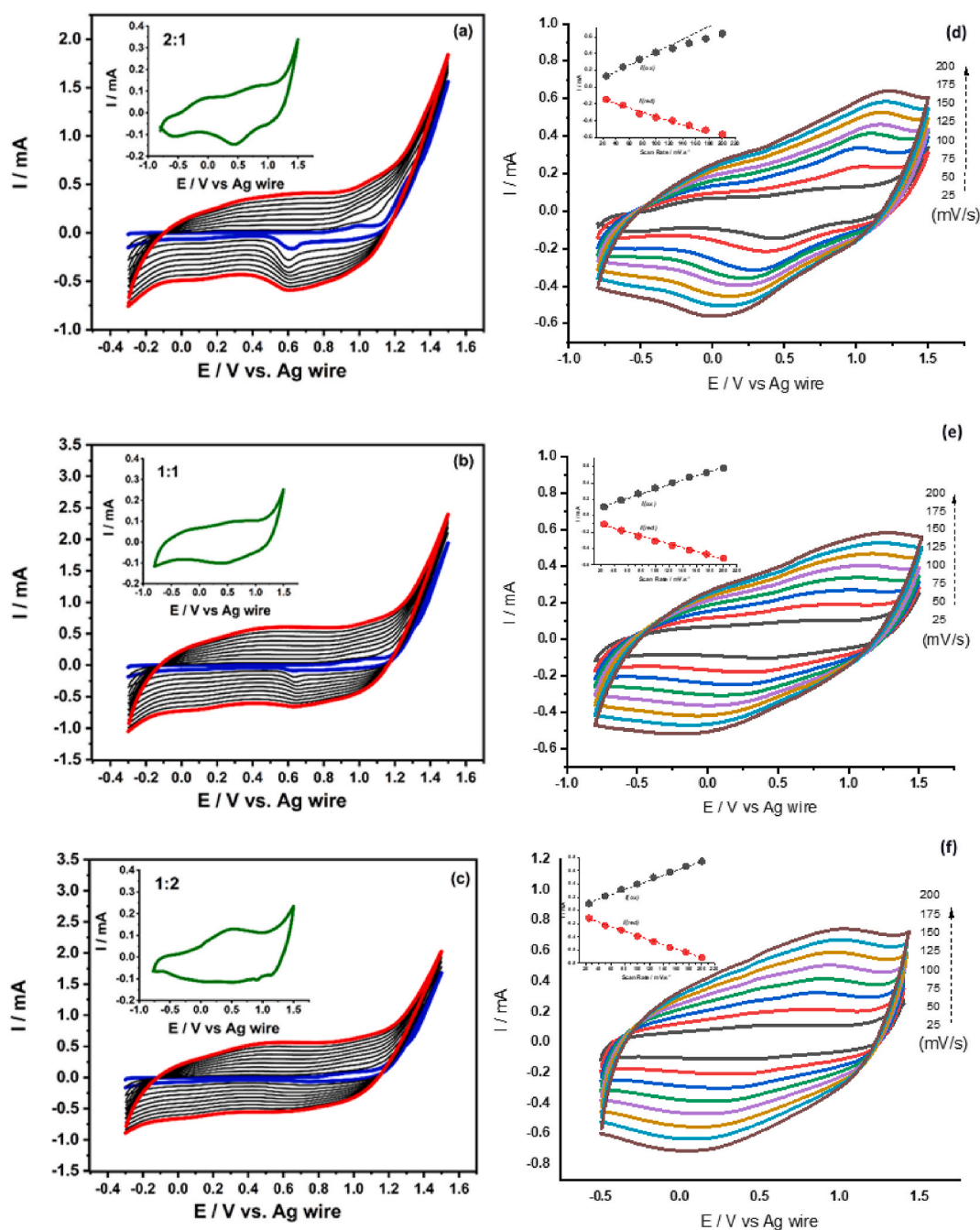


Fig. 6. CVs during copolymerizations with the monomer feed (TTBT:EDOT) of a) 2:1, b) 1:1 and c) 1:2, performed between -0.3 V and 1.5 V at a scan rate of 100 mV/s (insets: Resulting CVs of the copolymers recorded in the potential range of -0.8 V and 1.5 V, at a scan rate of 25 mV/s). CVs of copolymers d) 2:1, e) 1:1 and f) 1:2, recorded at the scan rates of 25 , 50 , 75 , 100 , 125 , 150 , 175 , 200 mV/s (insets: Current intensities both in anodic and cathodic region as a function of scan rate).

brown color and this color little bleached to bronze-gray in its fully oxidized state. The more black color was observed in Copol1:1, which exhibited very dark black brown color in the neutral state. During oxidation, Copol1:1 revealed intermediate colors and finally became transmissive greenish-gray in the oxidized state. On the other hand, Copol1:2 showed the effect of PEDOT in its color by revealing a bluish black color. The color turned to transmissive grayish in the oxidized state. It can be concluded that, although Copol1:2 shows more optical contrast and faster switching response than other two copolymers due to more EDOT ratio in the copolymer matrix, the Copol1:1 exhibits darker color which meets the expectations about obtaining the “black electrochromic”. For this reason, copol1:1 was used for the electrochromic device application.

3.3. Electrochromic device (ECD) application

ECD was constructed using Copol1:1 and PEDOT films as anodically and cathodically coloring polymers, respectively. The optical behavior of ECD were monitored in the potential range of -1.3 V and 1.75 V, and the collected CV and UV-Vis spectra were given in Fig. 9. As seen from Fig. 9a, the peak belonging to copolymer at 550 nm decreased during oxidation and a new peak around 600 nm appeared due to PEDOT reduction at the same time. This indicates that the ECD works successfully. The optical contrast of ECD was calculated as 6% at 550 nm (see Fig. 9b). Low optical contrast might be due to effect of blue color coming from the reduction state of PEDOT. T % and switching time was measured at 90% of the full optical contrast since the T % is already 6%

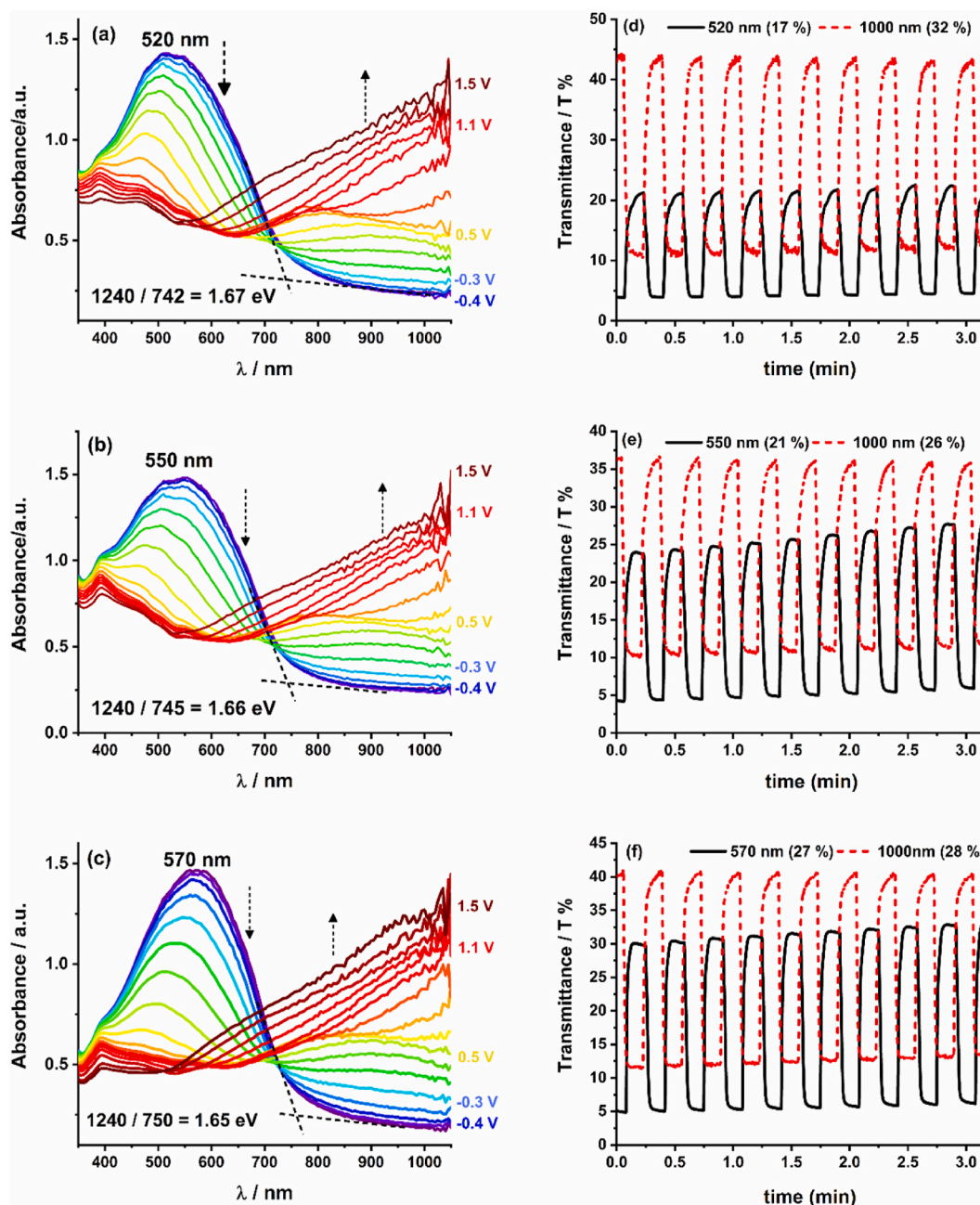


Fig. 7. UV-Vis spectra of copolymers during anodic scan from -0.3 V to 1.5 V for a) copol2:1, b) copol1:1 and c) copol1:2, at a scan rate of 25 mV/s. Chronoabsorptometry experiment of copolymers films of d) copol1:2, e) copol1:1 and f) copol1:2, switched between -0.8 V and 1.5 V with switch time of 10 s.

and the naked eye sensitivity is more suitable at 90% . Bleaching of ECD was completed in 1.8 s. The stability was also tested by scanning the device 100 times and no significant decrease in current intensity was recorded. Only 10% current lost was observed in the cathodic regime (Fig. 9c).

The color change of ECD was shown in Fig. 9d. For a sake of comparison, a bold type of text was placed behind the ECD. While the text is almost invisible in the neutral state of ECD, it becomes clearly visible in the bleached state. As seen from the figure that ECD works well from black to transmissive color states. After 250 switches, the color of the ECD little faded, but it was still electroactive, as in their pristine copolymer films. This phenomenon of having relatively low optical stability and not having sufficient optical contrast about black electrochromic polymers is widely reported in the literature. This is the main obstacle to commercializing them for certain applications [13,50].

However, studies by our group and by other scientists should be on the way to overcome these issues.

4. Conclusion

Black electrochromic polymers are promising materials due to their application areas. In this study, a black electrochromic polymer film was successfully obtained with the help of optical absorption engineering. The prediction was: the coverage of almost the entire visible region could be achieved with the help of the complementary absorption behaviors of homopolymers (PEDOT and P(TTBT)). Using this information, these units were combined in the same polymer matrix by electrochemical copolymerization technique. Different feed ratios resulted in different shades of black. On the other hand, the brown black color, which seems as "nearly true black" was obtained from $1:1$

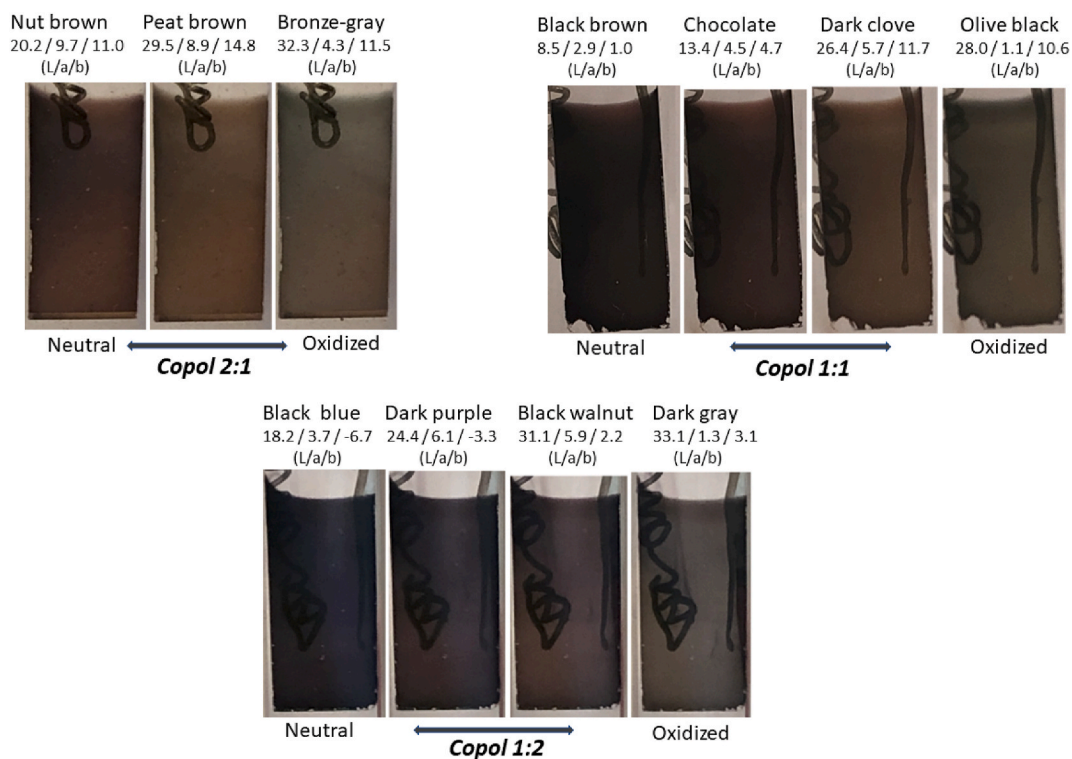


Fig. 8. Colors and L-a-b values of copolymers in their neutral to oxidized states. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

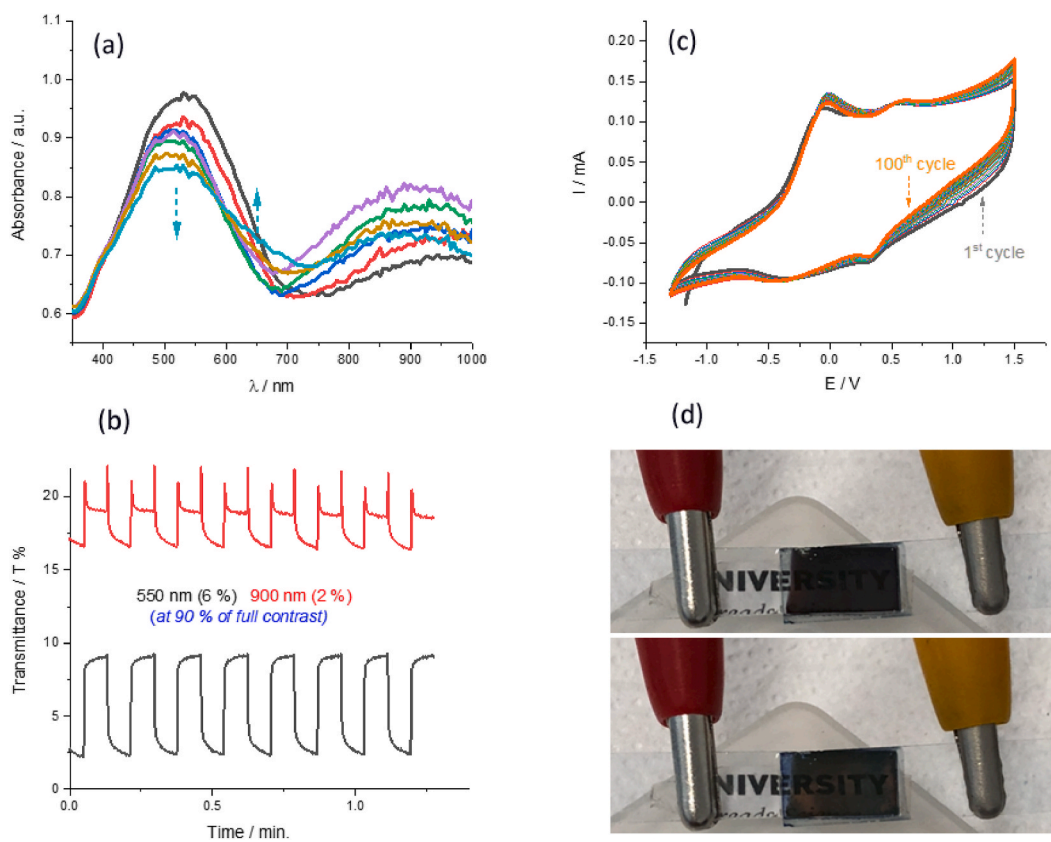


Fig. 9. a) UV-Vis spectra of ECD during a switching from -1.3 V to 1.75 V, b) Chronoabsorptometry experiment for ECD (switched between -1.3 V and 1.75 V with switching time of 10 s, c) CVs of ECD during 100 scans between -1.3 V and 1.75 V at a scan rate of 200 mV/s, d) Colors of ECD at neutral and oxidized states. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

monomer feed ratio. The copolymer worked well in the electrochromic device, switched fast, and showed black to transmissive behavior. Although the insolubility behavior can limit the application areas of the copolymer in photovoltaics, the proposed copolymer can be a good candidate in electrochromic device and electrochromic device-based sensor applications. With the help of absorption engineering, further studies are on the way to obtain black ECPs.

CRedit authorship contribution statement

Emine Gul Cansu Ergun: Conceptualization, Methodology, Software, Data curation, Writing – original draft, Investigation, Supervision, Writing – review & editing, share the responsibilities in this work. **Merve Akbayrak:** Conceptualization, Software, Data curation, Writing – original draft, Writing – review & editing, share the responsibilities in this work.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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References

- E.G.C. Ergun, Three in one sensor: a fluorometric, colorimetric and paper based probe for the selective detection of mercury(II), *New J. Chem.* 45 (2021) 4202–4209, <https://doi.org/10.1039/D1NJ00085C>.
- S. Roy, T. Mondal, D. Dey, M.V. Mane, S.S. Panja, A new thiophene-appended fluorescein-hydrazone-based chromo-fluorogenic sensor for the screening of Hg²⁺ ions in real water samples, *ChimistrySelect* 6 (2021) 10464–10479, <https://doi.org/10.1002/slct.202102692>.
- E.G.C. Ergun, G. Ertas, D. Eroglu, A benzimidazole-based turn-off fluorescent sensor for selective detection of mercury (II), *J. Photochem. Photobiol., A* 393 (2020), 112469, <https://doi.org/10.1016/j.jphotochem.2020.112469>.
- Y. Liang, Y. Wu, D. Feng, S.-T. Tsai, H.J. Son, G. Li, L. Yu, Development of new semiconducting polymers for high performance solar cells, *J. Am. Chem. Soc.* 131 (2009) 56–57, <https://doi.org/10.1021/ja808373p>.
- C. Wang, F. Liu, Q.M. Chen, C.Y. Xiao, Y.G. Wu, W.W. Li, Benzothiadiazole-based conjugated polymers for organic solar cells, *Chin. J. Polym. Sci.* 39 (2021) 525–536, <https://doi.org/10.1007/s10118-021-2537-8>.
- B.B. Carbas, D. Asil, R.H. Friend, A.M. Onal, A new blue light emitting and electrochromic polyfluorene derivative for display applications, *Org. Electron.* 15 (2014) 500–508, <https://doi.org/10.1016/j.orgel.2013.12.003>.
- M. Yasa, S. Sürmeli, T. Depci, L. Toppare, S.O. Hacıoğlu, Synthesis of a multifunctional quinoxaline and benzodithiophene bearing polymer and its electrochromic device applications, *Macromol. Chem. Phys.* 221 (2020), 1900470, <https://doi.org/10.1002/macp.201900470>.
- E.G.C. Ergun, D. Eroglu, An electrochemically and optically stable electrochromic polymer film based on EDOT and 1, 2, 3, 4-tetrahydrophenazine, *Org. Electron.* 75 (2019), 105398, <https://doi.org/10.1016/j.polymer.2022.125250>.
- P.B. Pati, S.P. Senanayak, K.S. Narayan, S.S. Zade, Solution processable benzoxadiazole and benzothiadiazole based D-A-D molecules with chalcogenophene: field effect transistor study and structure property relationship, *ACS Appl. Mater. Interfaces* 5 (2013) 12460–12468, <https://doi.org/10.1021/am403559a>.
- M. Akbayrak, A.M. Onal, Synthesis and electrochemical polymerization of diketopyrrolopyrrole based donor–acceptor–donor monomers containing 3,6- and 2,7-linked carbazoles, *Polym. Chem.* 7 (2016) 6110–6119, <https://doi.org/10.1039/C6PY01489E>.
- E.G.C. Ergun, B. Bezgin Carbas, Electrochromic copolymers of 2,5-dithienyl-N-substituted-pyrrole (SNS) derivatives with EDOT: properties and electrochromic device applications, *Mater. Today Commun.* 32 (2022), 103888, <https://doi.org/10.1016/j.mtcomm.2022.103888>.
- S. Qi, C. Wang, Z. Liu, Y. Han, F. Bai, Z. Chen, Electrochromic and photovoltaic properties of benzothiadiazole-based donor-acceptor conjugated polymers with oligo(ethylene glycol) side chains, *Dyes Pigments* 204 (2022), 110432, <https://doi.org/10.1016/j.dyepig.2022.110432>.
- T. Jarosz, K. Gebka, A. Stolarczyk, W. Domagala, Transparent to black electrochromism—the “holy grail” of organic optoelectronics, *Polymers* 11 (2019) 273, <https://doi.org/10.3390/polym11020273>.
- S.V. Vasilyeva, P.M. Beaujuge, S. Wang, J.E. Babiarz, V.W. Ballarotto, J. R. Reynolds, Material strategies for black-to-transmissive window-type polymer electrochromic devices, *ACS Appl. Mater. Interfaces* 3 (2011) 1022–1032, <https://doi.org/10.1021/am101148s>.
- P. Andersson, D. Nilsson, P.-O. Svensson, M. Chen, A. Malmström, T. Remonen, T. Kugler, M. Berggren, Active-matrix displays based on all-organic electrochemical smart pixels printed on paper, *Adv. Mater.* 14 (2002) 1460–1464, [https://doi.org/10.1002/1521-4095\(20021016\)14:20<1460::AID-ADMA1460>3.0.CO;2-S](https://doi.org/10.1002/1521-4095(20021016)14:20<1460::AID-ADMA1460>3.0.CO;2-S).
- W.T. Neo, Q. Ye, S.-J. Chua, J. Xu, Conjugated polymer-based electrochromics: materials, device fabrication and application prospects, *J. Mater. Chem. C* 4 (2016) 7364–7376, <https://doi.org/10.1039/C6TC01150K>.
- C. Chen, Q. Yan, Achieving excellent colorimetric properties of low-cost black to transmissive switching electrochromic polymers by incorporating of spacing units into copolymers of 3,4-propylenedioxythiophene and benzothiadiazole, *Dyes Pigments* 178 (2020), 108378, <https://doi.org/10.1016/j.dyepig.2020.108378>.
- R. Oliver, A. Muñoz, C. Ocampo, C. Alemán, E. Armelin, F. Estrany, Electrochemical characteristics of copolymers electrochemically synthesized from N-methylpyrrole and 3,4-ethylenedioxythiophene on steel electrodes: comparison with homopolymers, *Chem. Phys.* 328 (2006) 299–306, <https://doi.org/10.1016/j.chemphys.2006.07.013>.
- R. Yue, Z. Yao, J. Geng, Y. Du, J. Xu, P. Yang, Facile electrochemical synthesis of a conducting copolymer from 5-aminoindole and EDOT and its use as Pt catalyst support for formic acid electrooxidation, *J. Solid State Electrochem.* 17 (2013) 751–760, <https://doi.org/10.1007/s10008-012-1922-1>.
- M. Akbayrak, E.G. Cansu-Ergun, A.M. Onal, Synthesis and electro-optical properties of a new copolymer based on EDOT and carbazole, *Des. Monomers Polym.* 19 (2016) 679–687, <https://doi.org/10.1080/15685551.2016.1209627>.
- S. Singhal, P. Yadav, S. Naqvi, S. Gupta, A. Patra, Donor–acceptor–donor copolymers with 3,4-ethylenedioxythiophene moiety: electropolymerization and effect on optoelectronic and electrochromic properties, *ACS Omega* 4 (2019) 3484–3492, <https://doi.org/10.1021/acsomega.8b02811>.
- L. Groenendaal, G. Zotti, P.-H. Aubert, S.m. Waybright, J.r. Reynolds, Electrochemistry of poly(3,4-alkylenedioxythiophene) derivatives, *Adv. Mater.* 15 (2003) 855–879, <https://doi.org/10.1002/adma.200300376>.
- J. Roncali, P. Blanchard, P. Frère, 3,4-Ethylenedioxythiophene (EDOT) as a versatile building block for advanced functional π -conjugated systems, *J. Mater. Chem.* 15 (2005) 1589–1610, <https://doi.org/10.1039/B415481A>.
- C. Chen, Q. Yan, Achieving excellent colorimetric properties of low-cost black to transmissive switching electrochromic polymers by incorporating of spacing units into copolymers of 3,4-propylenedioxythiophene and benzothiadiazole, *Dyes Pigments* 178 (2020), 108378, <https://doi.org/10.1016/j.dyepig.2020.108378>.
- A.V. Akkuratov, P.A. Troshin, Conjugated polymers with benzothiadiazole, benzoxadiazole, and benzotriazole moieties as promising semiconductor materials for organic solar cells, *Polym. Sci. B* 56 (2014) 414–442, <https://doi.org/10.1134/S1560090414040010>.
- E.G. Cansu-Ergun, M. Akbayrak, A. Akdag, A.M. Onal, Effect of thiophene units on the properties of donor acceptor type monomers and polymers bearing thiophene-benzothiadiazole- scaffolds, *J. Electrochem. Soc.* 163 (2016) G153, <https://doi.org/10.1149/2.0711610jes>.
- L. Biniak, C.L. Chochos, N. Leclerc, G. Hadziioannou, J.K. Kallitsis, R. Bechara, P. Lévêque, T. Heiser, A [3,2-b]thienothiophene -alt- benzothiadiazole copolymer for photovoltaic applications: design, synthesis, material characterization and device performances, *J. Mat. Chem.* 19 (2009) 4946–4951, <https://doi.org/10.1039/B819177H>.
- L. Biniak, C.L. Chochos, G. Hadziioannou, N. Leclerc, P. Lévêque, T. Heiser, Electronic properties and photovoltaic performances of a series of oligothiophene copolymers incorporating both thieno[3,2-b]thiophene and 2,1,3-benzothiadiazole moieties, *Macromol. Rapid Commun* 31 (2010) 651–656, <https://doi.org/10.1002/marc.200900804>.
- E. Wang, L. Wang, L. Lan, C. Luo, W. Zhuang, J. Peng, Y. Cao, High-performance polymer heterojunction solar cells of a polysilafluorene derivative, *Appl. Phys. Lett.* 92 (2008), 033307, <https://doi.org/10.1063/1.2836266>.
- A.M. Onal, S. Eken, E.G.C. Ergun, Synthesis and Electrochemical polymerizations of Dithienosilole-based monomers bearing different donor units, *J. Electrochem. Soc.* 163 (2016) 69–74, <https://doi.org/10.1149/2.0521606jes>.
- A.J. Moule, A. Tsami, T.W. Bünnagel, M. Forster, N.M. Kronenberg, M. Scharber, M. Koppe, M. Morana, C.J. Brabec, K. Meerholz, U. Scherf, Two novel cyclopentadithiophene-based alternating copolymers as potential donor components for high-efficiency bulk-heterojunction-type solar cells, *Chem. Mater.* 20 (2008) 4045–4050, <https://doi.org/10.1021/cm8006638>.
- L.H. Slooff, S.C. Veenstra, J.M. Kroon, D.J.D. Moet, J. Sweelssen, M.M. Koetse, Determining the internal quantum efficiency of highly efficient polymer solar cells through optical modeling, *Appl. Phys. Lett.* 90 (2007), 143506, <https://doi.org/10.1063/1.2718488>.
- D. Veldman, Ö. Ipek, S.C.J. Meskers, J. Sweelssen, M.M. Koetse, S.C. Veenstra, J. M. Kroon, S.S. van Bavel, J. Loos, R.A.J. Janssen, Compositional and electric field dependence of the dissociation of charge transfer excitons in alternating

- polyfluorene copolymer/fullerene blends, *J. Am. Chem. Soc.* 130 (2008) 7721–7735, <https://doi.org/10.1021/ja8012598>.
- [34] N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletête, G. Durocher, Y. Tao, M. Leclerc, Toward a rational design of poly(2,7-carbazole) derivatives for solar cells, *J. Am. Chem. Soc.* 130 (2008) 732–742, <https://doi.org/10.1021/ja0771989>.
- [35] E. Bundgaard, F.C. Krebs, Low band gap polymers for organic photovoltaics, *Sol. Energy Mater. Sol. Cells* 91 (2007) 954–985, <https://doi.org/10.1016/j.solmat.2007.01.015>.
- [36] A. Cirpan, A.A. Argun, C.R.G. Grenier, B.D. Reeves, J.R. Reynolds, Electrochromic devices based on soluble and processable dioxathiophene polymers, *J. Mater. Chem.* 13 (2003) 2422–2428, <https://doi.org/10.1039/B306365H>.
- [37] H.C. Soyleyici, M. Ak, Y. Sahin, D. Odaci Demikol, S. Timur, New class of 2,5-di(2-thienyl)pyrrole compounds and novel optical properties of its conducting polymer, *Mater. Chem. Phys.* 142 (2013) 303–310, <https://doi.org/10.1016/j.matchemphys.2013.07.019>.
- [38] M.N. Gueye, A. Carella, J. Faure-Vincent, R. Demadrille, J.P. Simonato, Progress in understanding structure and transport properties of PEDOT-based materials: a critical review, *Prog. Mater. Sci.* 108 (2020), 100616, <https://doi.org/10.1016/j.pmatsci.2019.100616>.
- [39] Q. Pei, G. Zuccarello, M. Ahlsgog, O. Inganäs, Electrochromic and highly stable poly(3,4-ethylenedioxythiophene) switches between opaque blue-black and transparent sky blue, *Polymer* 35 (1994) 1347–1351, [https://doi.org/10.1016/0032-3861\(94\)90332-8](https://doi.org/10.1016/0032-3861(94)90332-8).
- [40] J. Bakalis, A.R. Cook, S. Asaoka, M. Forster, U. Scherf, J.R. Miller, Polarons, compressed polarons, and bipolarons in conjugated polymers, *J. Phys. Chem. C* 118 (2014) 114–125, <https://doi.org/10.1021/jp408910a>.
- [41] R.R. Chance, J.L. Bredas, R. Silbey, Bipolaron transport in doped conjugated polymers, *Phys. Rev. B* 29 (1984) 4491–4495, <https://doi.org/10.1103/PhysRevB.29.4491>.
- [42] C.L. Gaupp, D.M. Welsh, R.D. Rauh, J.R. Reynolds, Composite coloration efficiency measurements of electrochromic polymers based on 3,4-alkylenedioxythiophenes, *Chem. Mater.* 14 (2002) 3964–3970, <https://doi.org/10.1021/cm020433w>.
- [43] P. Sonar, E.L. Williams, S.P. Singh, A. Dodabalapur, Thiophene–benzothiadiazole–thiophene (D–A–D) based polymers: effect of donor/acceptor moieties adjacent to D–A–D segment on photophysical and photovoltaic properties, *J. Mater. Chem.* 21 (2011) 10532–10541, <https://doi.org/10.1039/C2PY20677C>.
- [44] S. Kiralp, P. Camurlu, G. Gunbas, C. Tanyeli, I. Akhmedov, L. Toppare, Electrochromic properties of a copolymer of 1–4-di [2, 5–di (2–thienyl)-1H1–pyrrolyl] benzene with EDT, *J. Appl. Polym. Sci.* 112 (2009) 1082–1087, <https://doi.org/10.1002/app.29544>.
- [45] T. Soganci, S. Soyleyici, H.C. Soyleyici, M. Ak, High contrast electrochromic polymer and copolymer materials based on amide-substituted poly (dithienyl pyrrole), *J. Electrochem. Soc.* 164 (2016) H11–H20, <https://doi.org/10.1149/2.0111702jes>.
- [46] K. Çelik, A. Kıvrak, B.B. Çarbas, A new electrochromic copolymer composed of 4,7-di(thiophen-2-yl)benzo[c] [1,2,5] thiadiazole and 3,4-ethylenedioxythiophene, *Turk. J. Chem.* 46 (2022) 1516–1523, <https://doi.org/10.55730/1300-0527.3456>.
- [47] E.G.C. Ergun, A. Cihaner, A new carborane based polymeric electrochrome, *J. Electroanal. Chem.* 707 (2013) 78–84, <https://doi.org/10.1016/j.jelechem.2013.08.026>.
- [48] M. Ak, H. Cetisli, L. Toppare, Blend or copolymer? Spectroelectrochemical evidence of copolymerization and blending of two electrochromic monomers, *Colloid Polym. Sci.* 291 (2013) 767–772, <https://doi.org/10.1007/s00396-012-2787-7>.
- [49] E.G.C. Ergun, B.B. Çarbas, Chasing the black electrochromism: a new electrochromic copolymer based on 4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole and ProDOT, *Polymer* 256 (2022), 125250, <https://doi.org/10.1016/j.polymer.2022.125250>.
- [50] S. Yan, L. Zhang, X. Lv, J. Sun, Y. Zhang, C. Zhang, Black-to-transmissive electrochromism in π -conjugated polymer-based materials and devices, *Adv. Photon. Res.* 3 (1) (2022), 2000199, <https://doi.org/10.1002/adpr.202000199>.