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Synthesis and electro-optical properties of a new copolymer based on EDOT and carbazole

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ABSTRACT

A new copolymer of 3,4-ethylenedioxythiophene (EDOT) and 5-(2-ethylhexyl)-1,3-bis(9-methyl-9H-carbazol-3-yl)-5H-thieno[3,4-c]pyrrole-4,6-dione (CzPDICz) was electrochemically synthesized using different monomer feed ratios. The resulting copolymer films were investigated in terms of their electrochemical and electro-optical behaviors. Properties of the obtained copolymer films through different monomer feed ratios were compared to each other and to individual poly(ethylenedioxythiophene; PEDOT) and homopolymer of CzPDICz in order to observe the differences in the properties with respect to PEDOT and P(CzPDICz). Copolymers exhibited well adherence on the electrode surface with having non-diffusional redox process. The monomer feed ratios were prepared as 9:1; 4:1, and 1:1 (EDOT:CzPDICz) and changes in the electrochemical and spectroelectrochemical behavior were noted with increasing CzPDICz ratio in the monomer mixture. Although no appreciable change in the optical band gap values of the copolymers was noted as compared to PEDOT, the neutral blue copolymers exhibited grayish color in their semi-oxidized states and transparent green in their fully oxidized states.

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KEYWORDS

3,4-Ethylenedioxythiophene (EDOT); carbazole; conjugated polymers; copolymers

1. Introduction

Conjugated polymers (CPs) have been one of the most popular topics over the past decades [1,2] since they have opened a huge gate through the next generation electronics such as solar cells,[3–6] light emitting diodes,[7,8] electronic displays,[9–11] electrochromic devices [12,13], and biosensors.[14,15] These applications depend on the properties of CPs which can be tuned via modifications of the molecular structure.[16,17] Since the band gap energy is one of the most crucial properties of conjugated polymers in above-mentioned applications, there has been extensive research on band gap tuning. Among them, alternating sequence of the appropriate donor (D) and acceptor (A) units is widely used which induces a reduction in the band gap energy.[18–21] Copolymerization is another way to adjust the properties of CPs which leads materials with intermediate properties between two homo-polymers,[22–24] thus allowing modification of the physical properties of the conducting polymers.

3,4-Ethylenedioxythiophene (EDOT) is a commonly used polythiophene derivative for copolymer synthesis via electrochemical methods since this monomer can be electropolymerized at reasonable anodic potentials with having good adherence on the electrode surface. [25] Moreover, high conductivity and stability of PEDOT

make this monomer useful in CP studies.[26] There are various investigations about electrochemically prepared copolymers from novel conjugated molecules and EDOT in the literature.[27–29] Carbazole derivatives, on the other hand, are one of the attractive conjugated molecules for electronic applications due to its ease of functionalization not only at the nitrogen atom but also at 2,7- and 3,6- positions. In several studies, nitrogen atom of the carbazole units was functionalized with various alky groups for enhancing the solubility of the resulting polymer.[30] On the other hand, introducing acceptor units on the nitrogen atom was found to be effective on tuning the electrochromic properties.[31–33] There are also several studies reporting copolymerization of carbazole derivatives with various donor units including thiophene and EDOT.[34,35] Recently, Ateş et al. reported the electrochemical properties and capacitive behavior of a copolymer which is prepared from 4-vinylbenzyl 9H-carbazole-9-carbodithioate and EDOT as co-monomers.[36]

In the light of the above considerations, we have successfully synthesized a new carbazole derivative, 5-(2-ethylhexyl)-1,3-bis(9-methyl-9H-carbazol-3-yl)-5H-thieno[3,4-c]pyrrole-4,6-dione (CzPDICz), including thienopyrroledione unit as a strong acceptor and methyl substituted carbazole as a donor.

After the synthesis of CzPDICz, it was electropolymerized to obtain its corresponding polymer P(CzPDICz). Since the band gap of obtained polymer was found to be much larger than that of PEDOT, copolymers of EDOT and CzPDICz monomers were prepared using different monomer feed ratios by repetitive potential cycling in order to investigate its effect on band gap tuning. Changes in the properties of the copolymers and homopolymers were comparatively investigated in terms of their electrochemical and electro-optical properties. To the best of our knowledge, there have been no reports about the electrochemical copolymerization of CzPDICz with EDOT so far.

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma Aldrich Chemicals and used as received unless otherwise noted. Electrochemical studies were performed by using platinum (Pt) disk as a working electrode (WE), Pt wire as a counter electrode (CE) and silver–silver chloride (Ag/AgCl; in 3 M NaCl (aq) solution) as a reference (RE) electrode. The cyclic voltammograms (CVs) were recorded with Gamry Reference 300 model potentiostat-galvanostat. Electropolymerizations of co-monomers and electrochemical studies were performed in dichloromethane (DCM) containing 0.1 MTBAPF₄ as a supporting electrolyte. Acetonitrile (ACN) was used as a solvent for spectroelectrochemical studies of the polymer films.

Spectroelectrochemical measurements were performed using a Carry 60 model UV–Vis spectrometer combined with Gamry PCI4/300 potentiostat–galvanostat. Indium tin oxide (ITO, Delta Tech. 8–12 Ω, 0.7 cm × 5 cm) coated glass, Pt wire, and Ag wire were used as WE, CE, and pseudo RE, respectively. Fluorescence measurements were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer.

Structural characterization of monomer was revealed by using ¹H and ¹³C NMR spectra, recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer. All measurements were performed at room temperature and ambient conditions.

2.2. Synthesis of CzPDICz

Monomer (CzPDICz) synthesis was achieved via Suzuki coupling reaction as shown in Scheme 1.[37]

2.2.1. General procedure for the monomer synthesis

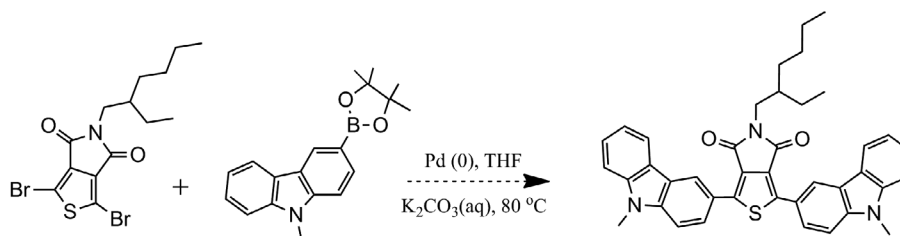
1,3-dibromo-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (0.3 mmol), 9-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (0.6 mmol), and 5% of Pd (0) were dissolved in freshly distilled tetrahydrofuran (THF; 20 mL) and stirred under nitrogen gas (N₂) for 15 min. Potassium carbonate (K₂CO₃; 10 mmol) was dissolved in 5 mL distilled water and degassed for 10 min. Then, 1 mL of aqueous K₂CO₃ solution was added to the reaction mixture. The mixture was purged with N₂ for 30 min and refluxed for 50 h at 73 °C. At the end of reaction, the crude product was washed with DCM and water. The collected organic phase was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. Further purification was done using silica gel column chromatography (3 DCM: 1 Hexane). Final product was obtained as yellow solid (120 mg, 64%).

¹H NMR (CDCl₃) d: 8.9 ppm (s, 1H), 8.4 ppm (dd, 1H), 8.23 ppm (d, 1H), 7.5 ppm (t, 1H), 7.42 ppm (t, 2H), 7.3 ppm (t, 1H), 5.29 ppm (s, 3H), 3.61 ppm (d, 2H), 1.92 ppm (m, 1H), 1.32 ppm (m, 8H), 0.9 ppm (dt, 6H).

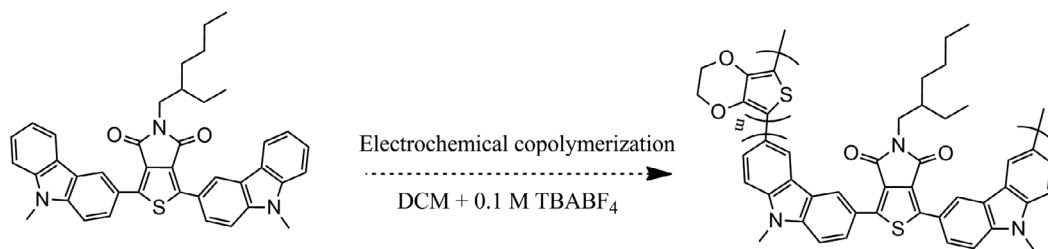
¹³C NMR (CDCl₃) d: 163.73, 145.7, 141.71, 141.56, 128.45, 126.33, 126.25, 123.09, 122.87, 122.130, 120.80, 120.40, 119.64, 108.768, 108.58, 53.40, 38.24, 31.6, 29.24, 23.97, 22.65, 14.1, 10.6 ppm.

2.3. Copolymer synthesis

EDOT and CzPDICz were dissolved in DCM separately to prepare 0.025 M stock solutions of each monomer. Then the monomer solutions were mixed in the ratio of 9:1, 4:1, and 1:1 (EDOT:CzPDICz; v:v) in separate vials. Copolymerization of CzPDICz with EDOT was achieved via potential cycling between –0.8 and +1.5 V vs. Ag/AgCl in DCM–TBAPF₄ electrolytic medium as shown in Scheme 2. For spectroelectrochemical investigations, copolymers were deposited on ITO working electrode (50 mC cm⁻²) by constant potential electrolysis at 1.5 V vs. Ag wire.



Scheme 1. Synthesis route of monomer CzPDICz.



Scheme 2. The electrochemical copolymerization of EDOT and CzPDICz.

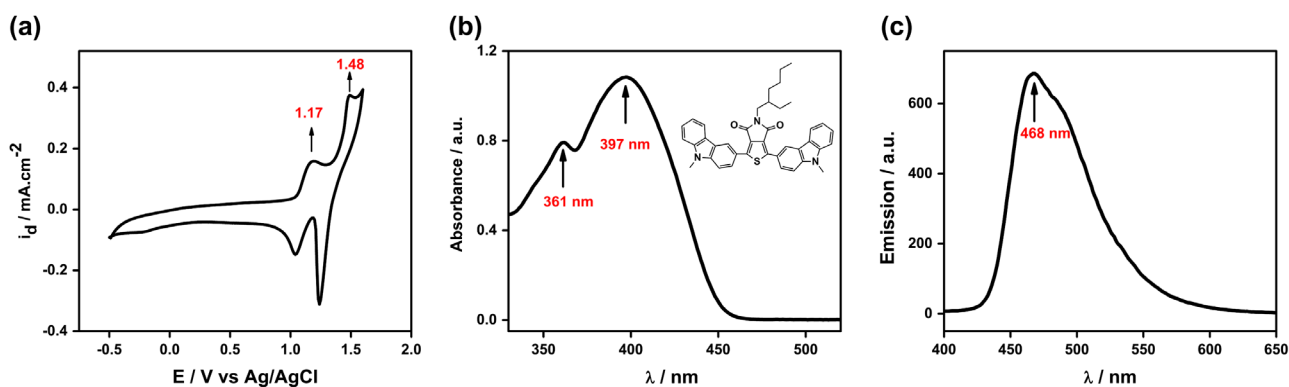


Figure 1. CV (a); electronic absorption spectrum (b) and emission spectrum (c) of CzPDICz. Inset of (b) chemical structure of CzPDICz.

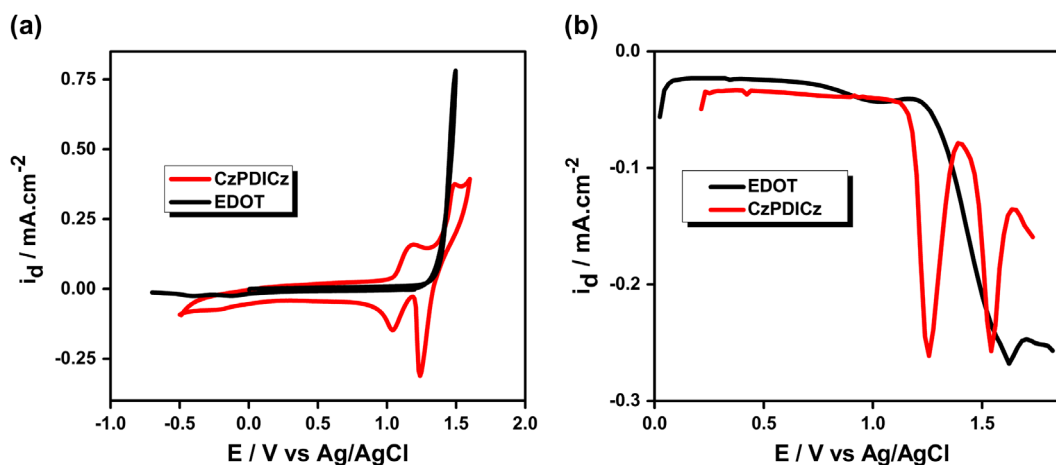


Figure 2. CVs (a) and DPVs (b) of CzPDICz and EDOT during their anodic scans.

3. Results and discussion

3.1. Electrochemical and optical properties of CzPDICz

Before the copolymerization studies, electrochemical and optical properties of the monomer, CzPDICz, were investigated. CV of the monomer recorded in DCM–TBABF₄ electrolytic medium is given in Figure 1(a). As seen from the figure, CzPDICz exhibits two reversible oxidation peaks at 1.20 and 1.47 V. However, no reduction peak was observed during the cathodic scan. Electronic absorption spectrum of CzPDICz in DCM shows one major absorption band at 397 nm (Figure 1(b)) and the monomer solution exhibits

yellow and fluorescent yellow colors under daylight and UV light, respectively. Emission spectrum of CzPDICz is given in Figure 1(c). Comparison of absorption and emission maxima of the monomer solution reveals 71 nm Stokes shift indicating the conformational changes of the molecules upon excitation.[38]

After electrochemical and optical characterization of the monomer is completed, its electrochemical polymerization was monitored via potentiodynamic and potentiostatic methods in DCM–TBABF₄ electrolytic medium. However, no sign of polymerization was observed when the potential was cycled repetitively between 0.0 and +1.20 V (first oxidation potential of the monomer). When

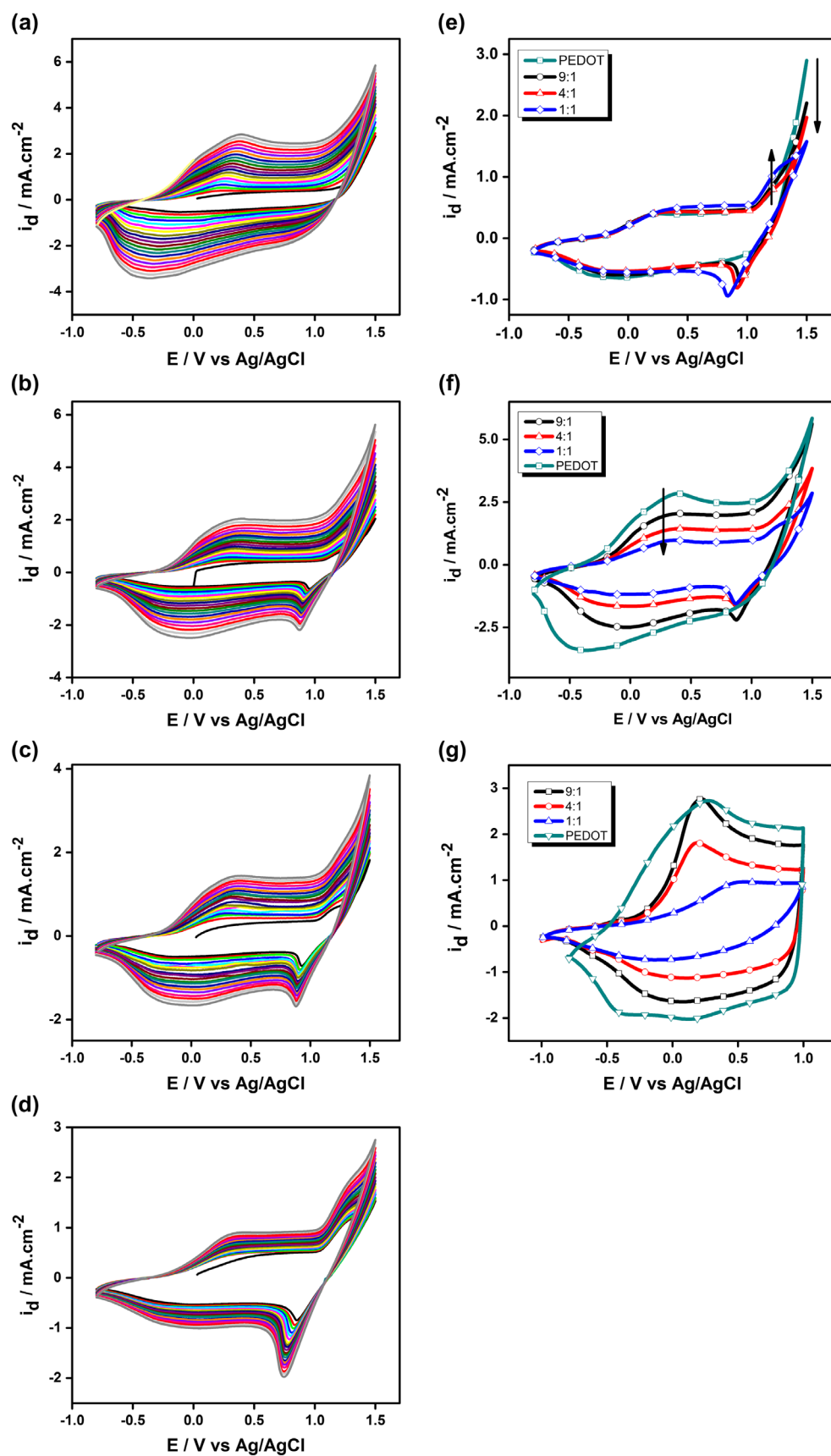


Figure 3. CVs of EDOT (a) and EDOT/CzPDICz monomer feed ratios of 9:1 (b); 4:1 (c) and 1:1 (d) during electropolymerization on Pt WE between -0.8 and 1.5 V in 0.1 M DCM- TBABF_4 with a scan rate of 100 $\text{mV}\cdot\text{s}^{-1}$. The second (e) and the last (f) CVs of the electropolymerization cycles, (g) CVs of PEDOT and resulting copolymers in monomer free solution containing 0.1 M TBABF_4 in ACN.

scan limit was extended to +1.50 V (slightly greater than the second oxidation peak) small amount of deposition on the electrode surface was observed but due to its low adherence on the surface, no polymer film was obtained on the working electrode surface. In the case of potentiostatic attempt, a small quantity of boron trifluoride diethyl etherate (60 μL to 3.0 mL electrolytic solution) was added not only to resolve the adherence problem and also to lower the oxidation potential of monomer by lowering aromatization energy. Then, the potential was set to 1.30 V which resulted in the formation of a very thin film on the surface of the working electrode.

3.2. Synthesis and the electrochemical properties of the copolymers

Prior to copolymerization studies, CV and differential pulse voltammograms (DPV) of CzPDICz and EDOT were recorded in DCM-TBAPF₄ electrolytic medium and the results are given in Figures 2(a) and 3(b), respectively. As seen from the figure, the oxidation potentials of CzPDICz and EDOT are compatible to obtain a copolymer via electrochemical techniques.[22]

Copolymers were prepared utilizing CV technique by applying 20 repetitive cycles between a certain potential range of -0.8 and 1.5 V in an electrolytic solution of 0.1 M DCM-TBAPF₄ (Figure 3). As seen from the Figure 3(a)–(d), after the first anodic scan, a new redox couple starts to intensify upon successive cycling in the case of EDOT and co-monomer mixtures with different feed ratios which indicates polymer deposition on the working electrode surface. When the second and last cycles recorded during electropolymerizations were compared (Figure 3(e) and (f), respectively), a decrease in the current densities were noted with increasing CzPDICz/EDOT ratio (i.e. from 1:9 to 1:1) due to decreasing electroactivity of copolymer as compared to PEDOT. The characteristic anodic and cathodic peaks (1.2 and 1.0 V, respectively) of CzPDICz becomes clearly noticeable in the co-monomer mixture and their intensities increase with increasing CzPDICz/EDOT ratio (Figure 3(e)). Appearance of these characteristic anodic–cathodic peaks of CzPDICz in the CVs of polymer films indicates incorporation of CzPDICz in to polymer matrix. The decrease in the current density by increasing the CzPDICz in the monomer feed ratio further proves the copolymer formation during repetitive potential cycling.[39]

After completion of electropolymerization (20 repetitive cycles) monomeric or oligomeric parts were removed by washing the polymer films with DCM and the CVs of PEDOT and copolymer films were recorded in monomer free solution between -1.0 and 1.0 V (Figure 3(g)). Although current density decreases with decreasing EDOT in the feed ratio, characteristic capacitive behavior of PEDOT was still observable in the copolymer films.

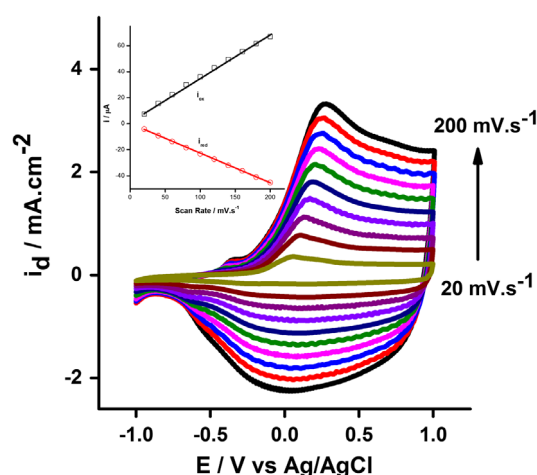


Figure 4. The CVs of the copolymer (4:1) with increasing scan rate from 20 to 200 mV s^{-1} with 20 mV increments. (0.1 M DCM-TBAPF₄ monomer free solution, on Pt working electrode vs. Ag/AgCl). Inset: Variation of anodic and cathodic current densities vs. voltage scan rate.

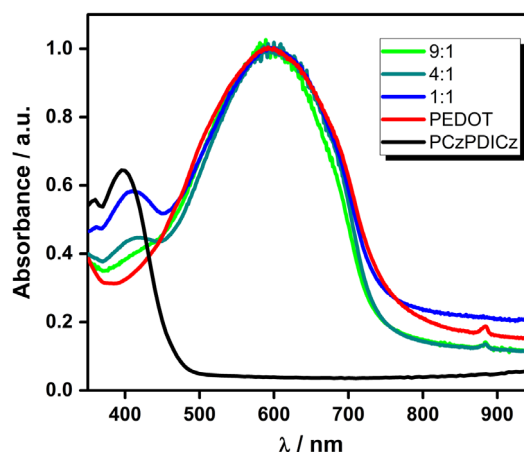


Figure 5. Normalized electronic absorption spectra of the copolymer and homopolymer films in their neutral forms recorded in ACN.

It is important to note that, when the monomer feed ratio reaches to 1, the problem observed during homopolymerization of CzPDICz was also noted; causing loss of some part of polymer film from the electrode surface into the electrolytic solution. However, the remaining polymer film on the surface was still enough to reflect a different behavior from PEDOT (See Figure 3(f) and (g)).

The copolymer films were scanned with increasing scan rates between -1.0 and 1.0 V in order to observe their scan rate dependency. The copolymers exhibited a linear increase in current densities with increasing scan rates indicating well adhering electroactive polymer film on the electrode surface and the non-diffusional redox behavior [40] even at high scan rates. The scan rate dependence of the copolymer (4:1) was demonstrated in Figure 4 as a representative example.

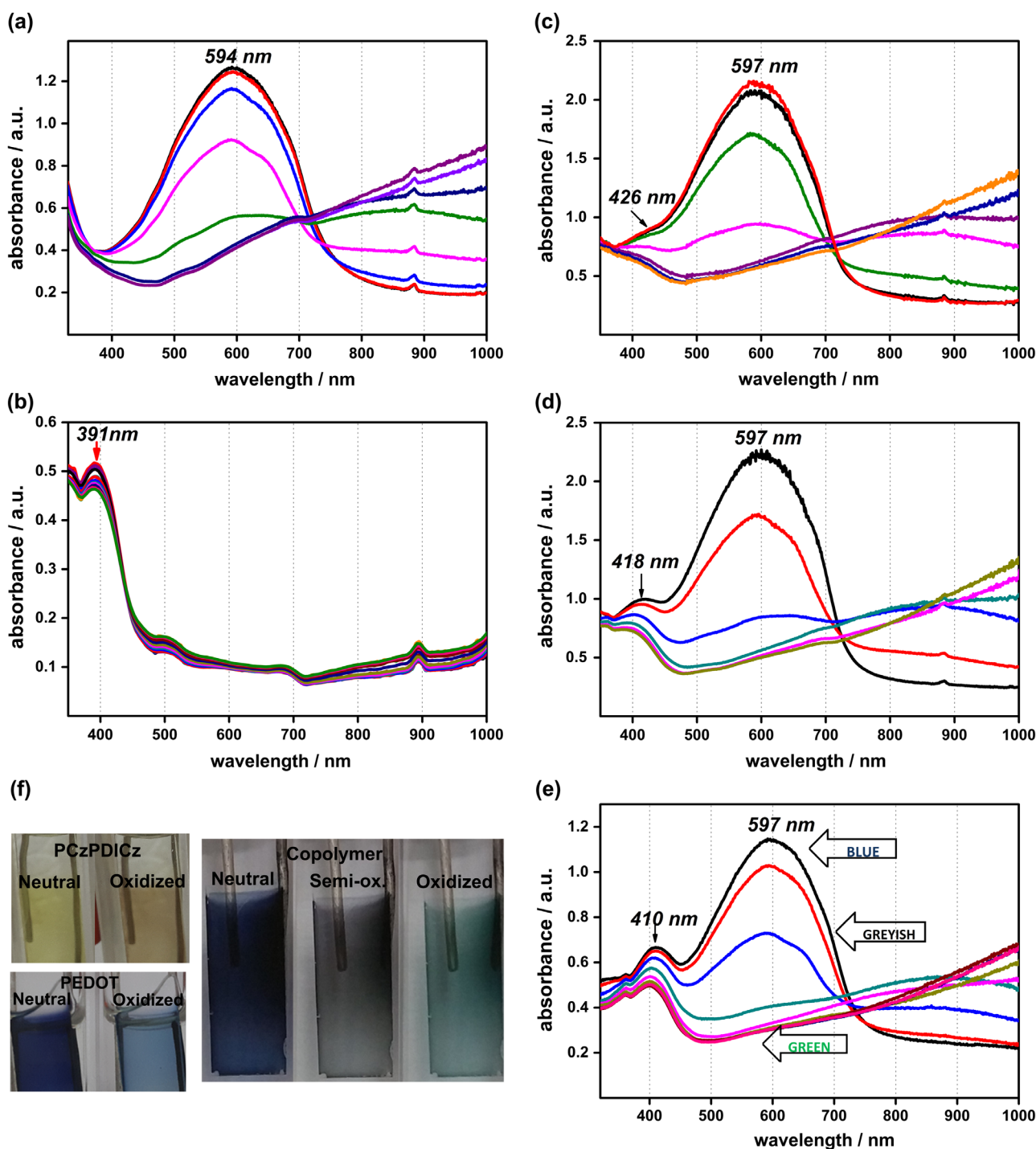


Figure 6. Collected electronic absorption spectra of PEDOT (a); PCzPDICz (b); copolymers of 9:1, 4:1, 1:1 (c, d, e, respectively) during potential scanning from -1.0 to 1.0 V in 0.1 M ACN-TBAPF₄ monomer free solution with scan rate of 20 mV s⁻¹ and colors of homopolymers and copolymers in their neutral and oxidized states (f). (For PCzPDICz, potential scanning range is between -0.5 and 1.2 V).

3.2. Spectrochemical properties of the copolymers

The copolymer films were also investigated in terms of their optical behaviors. The copolymers were obtained on ITO working electrode surface via constant potential electrolysis by applying 1.5 V potential until the same amount of charge of 50 mC cm⁻² passed through the system. For comparison

sake, EDOT and CzPDICz homopolymers (PEDOT and PCzPDICz) were also prepared on the ITO working electrode surface. After washing with DCM, polymer film-coated electrodes were dipped into monomer free electrolytic solution and were brought into their neutral form by applying -1.0 V potential for 60 s. Electronic absorption spectra of

homo and copolymers are given in Figure 5. As seen from the figure, all copolymer films exhibit a strong absorption band having maximum at around 595 nm originating from PEDOT unit. However, in the case of copolymer films, apart from 595 nm band, there exists another band at about 410 nm which is originating from CzPDICz. It is noteworthy to mention that the intensity of this shorter wavelength band increases with increasing CzPDICz/EDOT ratio in the electrolytic solutions clearly indicating incorporation of CzPDICz units into the copolymer structure.

Electro-optical properties of the copolymer films deposited on ITO electrode via constant potential electrolysis were also investigated by monitoring the changes in the electronic absorption spectra under a voltage pulse and the results are depicted in Figure 6.

As seen from the figure, both 410 and 595 nm bands lose their intensities during oxidation of the copolymer films which is accompanied by the appearance of new intensifying band located at 850 nm due to formation of charge carriers (i.e. polarons). Upon further oxidation, another band beyond 1000 nm was also noted indicating the bipolaron formation (Figure 6). These changes in the electronic absorption spectra were also accompanied by a color change from blue to transparent blue for PEDOT,[29] yellow to deep yellow for P(CzPDICz), and blue to transparent green for the copolymer films in their neutral and oxidized states, respectively. The different colors of PEDOT (transparent blue) and copolymer films (transparent green) in their oxidized states can be explained in terms of differences in their electronic absorption spectra. A close inspection of Figure 6(e) reveals that the copolymer films absorb visible light in two regions, a band around 410 nm and another one beyond 700 nm, which are essential values for the appearance of green color.[41] Moreover, a grayish color was observed in semi-oxidized states of copolymers which were not observed during oxidation of the homopolymers (Figure 6(f)).

CVs recorded during in-situ spectroelectrochemical studies are also given in Figure 7. As seen from the figure, the intensity in current decreases by the increasing amount of CzPDICz in monomer feed ratio. Moreover, onset oxidation potentials of copolymer films approach to that of CzPDICz homopolymer (0.51 V) with increasing concentration of CzPDICz in the electrolytic solution.

Optical band gap values of the copolymers and homopolymers were calculated from the onsets of $\pi-\pi^*$ transition bands in their neutral absorption spectra and the results are depicted in Table 1. The band gap energies of the copolymers did not show appreciable difference from that of PEDOT albeit they became much lower when compared to band gap of CzPDICz homopolymer (see Table 1).

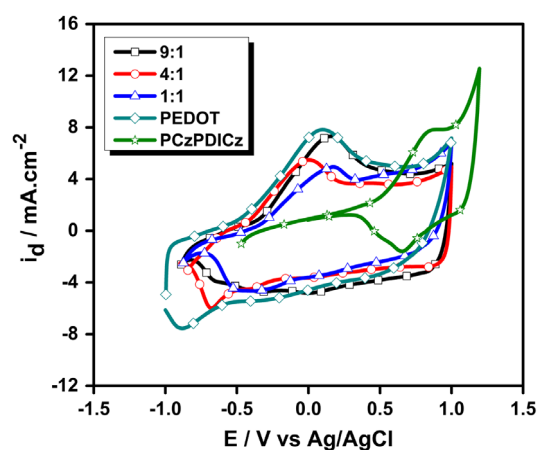


Figure 7. CVs of copolymer and homopolymer films on ITO WE, recorded in 0.1 M ACN-TBAPF₄ monomer free solution with scan rate of 20 mV s⁻¹.

Table 1. Electrochemical and optical properties of the copolymers and homopolymers.

Copolymers (EDOT: CzPDICz)	$E_{\text{ox}}^{\text{onset}}$ (V)	Absorption λ_{max} (nm)	$E_{\text{g}}^{\text{optical}}$ (eV)
P(9:1)	-0.32	426–590	1.67
P(4:1)	-0.42	418–597	1.67
P(1:1)	-0.35	410–594	1.66
PEDOT	-0.45	594	1.64
P(CzPDICz)	0.51	391	2.64

The percent transmittance values ($T\%$) of the copolymer films at their low lying energy bands were calculated as 27, 32, and 43% for P(9:1), P(4:1), and P(1:1), respectively and $T\%$ of the PEDOT film was calculated as 35%. As seen from the transmittance data, the copolymer formation results with higher $T\%$ values with increasing CzPDICz ratio in the co-monomer mixture.[42] However, the inverse trend was observed for their high energy bands. At their high energy bands, the transmittance percents were found as 15, 14, and 11% for P(9:1), P(4:1), and P(1:1), respectively, further indicating the increasing amount of CzPDICz contribution in the copolymers.

To get insight into morphological differences between homopolymer and copolymer (feed ratio 9:1) films, scanning electron microscopy (SEM) images were taken and are shown in Figure 8. As seen from the figure, the morphology of PEDOT is quite regular with a growth of long curved shapes (Figure 8, left) and the image of P(CzPDICz) is appeared as pollen flowers (Figure 8, right). On the other hand, the morphology of the copolymer film exhibited a smoother surface pattern than that of both homopolymer film surfaces which can be used as a further support for the copolymer formation.

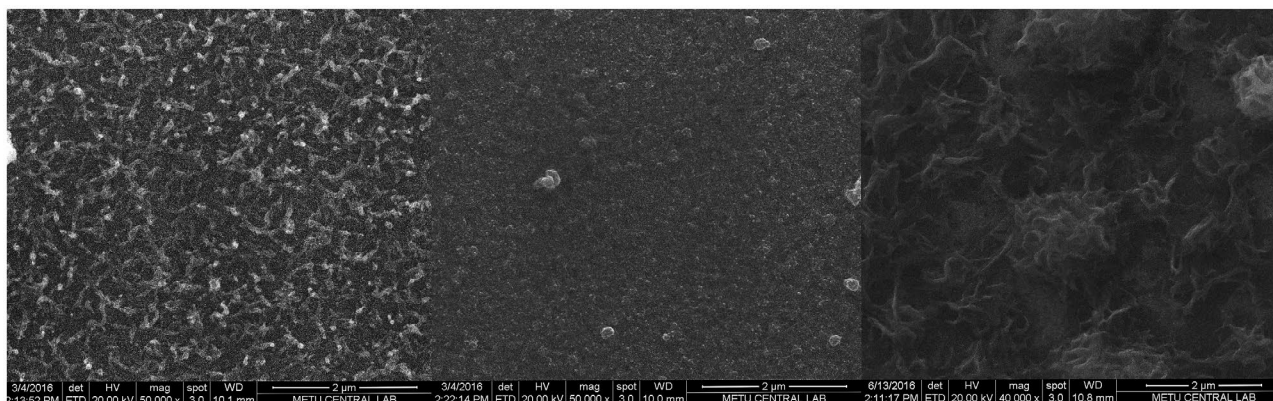


Figure 8. SEM images of PEDOT, copolymer (feed ratio 9:1) and P(CzPDICz) films (left to right).

4. Conclusion

In this study, synthesis of a new carbazole (CzPDICz) derivative bearing a strong acceptor unit, and its electrochemical copolymerization with EDOT was reported. The changes in the electrochemical and optical behavior of the copolymer films were investigated with respect to PEDOT and P(CzPDICz) using different monomer feed ratios. The lowest oxidation potential and optimum film formation with well adherence on the electrode surface were obtained from 4:1 EDOT/CzPDICz feed ratio. The copolymer demonstrates blue color in its neutral form as in PEDOT, but transparent green in its oxidized form different from PEDOT (transparent blue). Although copolymer formation lowered both onset oxidation potential (from 0.51 to -0.41 V) and band gap values (from 2.64 to 1.67 eV) as compared to homopolymer of CzPDICz, these values did not exhibit any appreciable difference from that of PEDOT. In summary, the new copolymers exhibited lower band gap values as compared to P(CzPDICz) and different electrochromic response as compared to PEDOT. The copolymers exhibit blue and green colors in their neutral and oxidized states and grayish color in semi-oxidized state which makes them a potential candidate for electrochromic device applications.

Disclosure statement

No potential conflict of interest was reported by the authors.

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