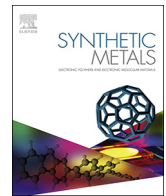




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Enhancing electrochemical and electrochromic performances of carbazole comprising monomer via copolymerization with 3,4-ethylenedioxythiophene (EDOT)

Isil Kalay^a, Deniz Yiğit^b, Mustafa Güllü^c, Tolga Depci^d, Levent Toppare^{e,f,g,h,*},
Serife O. Hacıoğlu^{d,*}

^a Department of Energy Systems Engineering, Faculty of Engineering and Natural Sciences, Iskenderun Technical University, 31200, Hatay, Turkey

^b Department of Pharmaceutical Basic Sciences, Faculty of Pharmacy, Lokman Hekim University, Sogutozu, 06510, Ankara, Turkey

^c Department of Chemistry, Faculty of Science, Ankara University, Beşevler, 06100, Ankara, Turkey

^d Department of Basic Sciences of Engineering, Faculty of Engineering and Natural Sciences, Iskenderun Technical University, 31200, Hatay, Turkey

^e Department of Chemistry, Middle East Technical University, Ankara, 06800, Turkey

^f Department of Polymer Science and Technology, Middle East Technical University, 06800, Ankara, Turkey

^g Department of Biotechnology, Middle East Technical University, Ankara, 06800, Turkey

^h The Center for Solar Energy Research and Application (GUNAM), Middle East Technical University, Ankara, 06800, Turkey

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ABSTRACT

In this study, two novel electrochromic copolymers (CoP1.3 and CoP1.5) were synthesized via electrochemical methods and characterized. The comonomers used in the synthesis were 3,4-ethylenedioxythiophene (EDOT) and a carbazole comprising monomer; 9-(2-(4-(Phenyldiazenyl) phenoxy) ethyl)-3,6-di(thiophen-2-yl)-9H-carbazole (M1). Carbazole containing monomer (M1) and EDOT were combined with two different comonomer feed ratios, 1: 3 and 1: 5 respectively in order to investigate the effect of increasing EDOT amount on electrochemical, spectroelectrochemical and electrochromic behaviors. The electrochemical and spectroelectrochemical characterizations of the electrochemically obtained copolymers were performed by cyclic voltammetry (CV) and UV-vis-NIR spectrophotometry. Both copolymers exhibited p-type doping with reversible oxidation potentials reported at 0.23 V/0.93 V for CoP1.3 and 0.30 V/0.98 V for CoP1.5. The difference between these oxidation potentials could be dedicated to the difference in electron density in the copolymer chains. Optical band gap values were calculated from neutral state absorptions as 1.21 eV and 1.18 eV for CoP1.3 and CoP1.5, respectively. Due to the higher EDOT amount in the copolymer backbone, the band gap for CoP1.5 is lower than that of CoP1.3. Both CoP1.3 and CoP1.5 exhibited multichromic behavior with different colors in the neutral and oxidized states. While both copolymers (CoP1.3 and CoP1.5) exhibited purple color in the neutral states, the colors turned to blue colors upon applied potentials. Optical contrast values were calculated as 31 % (at 555 nm), 55 % (at 1050 nm) and 38 % (at 1240 nm) for CoP1.3 and 34 % (at 565 nm), 25 % (at 975 nm) and 45 % (at 1170 nm) for CoP1.5. As a result of electrochromic switching studies, switching times (oxidation) were calculated as 2.5 s, 1.7 s, 1.9 s for CoP1.3 and 1.9 s, 1.8 s, 2.7 s for CoP1.5. Furthermore, addition of EDOT unit into copolymer backbone resulted in the obvious improvements in electrochemical, optical, electrochromic and kinetic properties. Copolymers exhibited full visible absorption with red-shifted neutral state absorption, lower optical band gap values compared to those of homopolymers.

1. Introduction

For several years conductive polymers have gained great importance for both academic and commercial applications due to their certain advantages and wide field of applications. Conjugated polymers

with desired properties can be synthesized via easy structural modifications and thus their mechanical, thermal and electrical properties can be controlled by proper molecular design. Conjugated polymers have many application fields such as transistors, biosensors, modified electrodes, light emitting diodes and electrochromic devices [1–4]. In

* Corresponding authors at: Iskenderun Technical University, Department of Engineering Science, 31200, Hatay, Turkey.

E-mail addresses: toppare@metu.edu.tr (L. Toppare), serife.hacioglu@iste.edu.tr (S.O. Hacıoğlu).

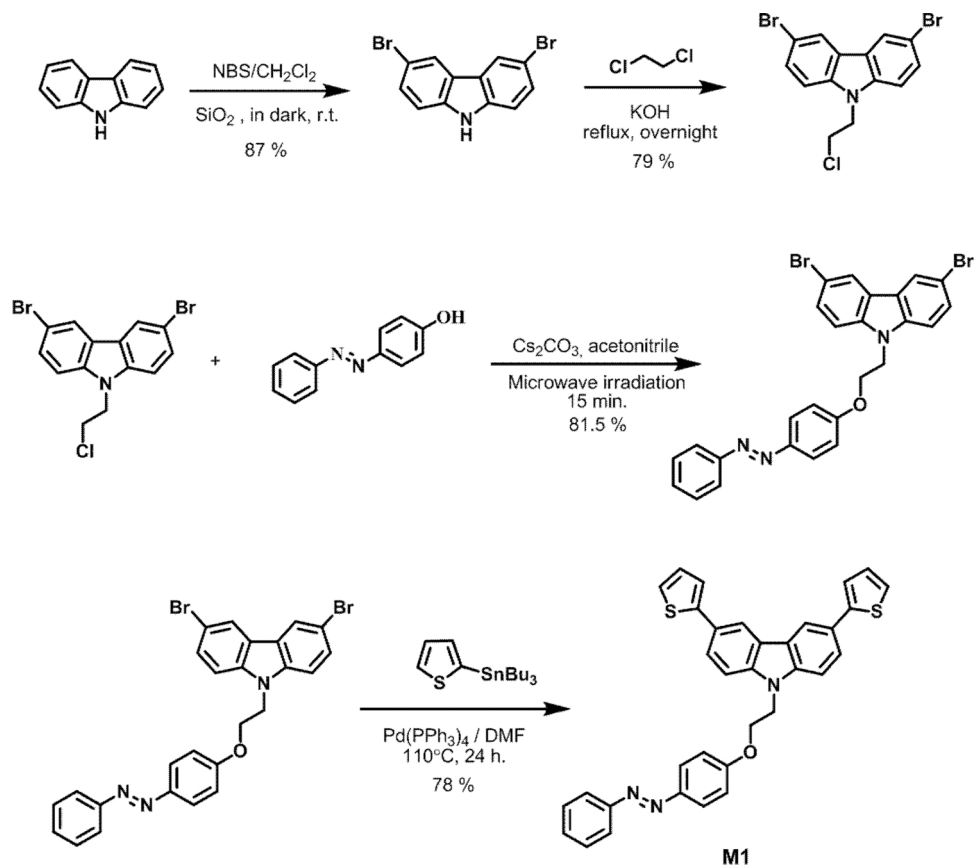
¹ Middle East Technical University, Department of Chemistry, 06800, Ankara, Turkey.

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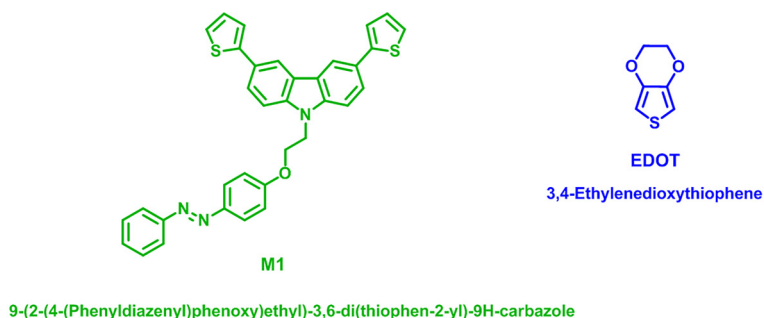
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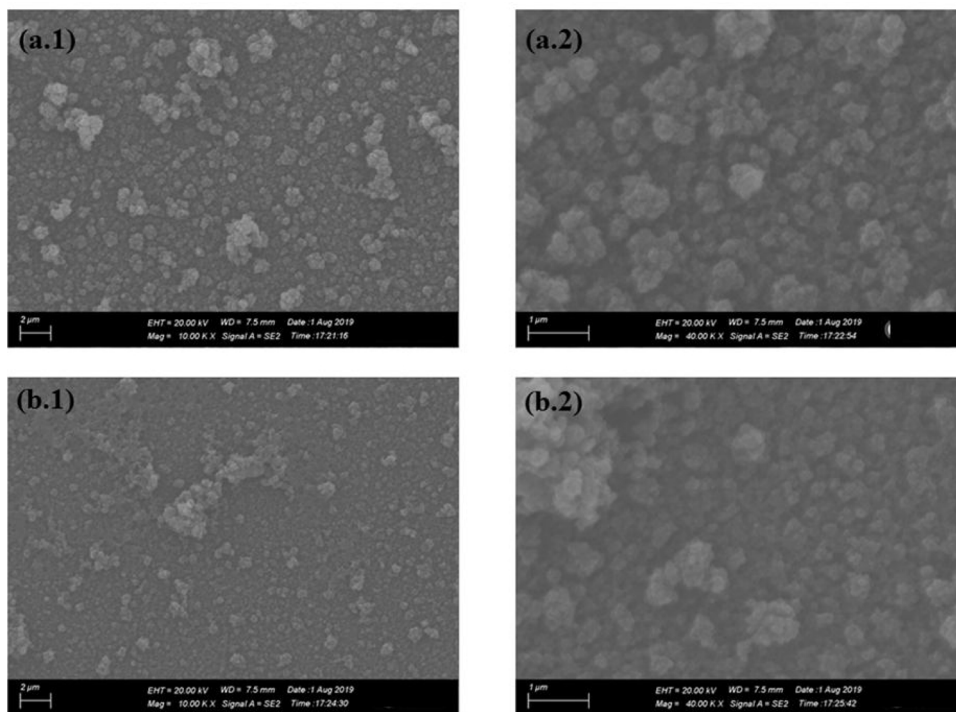
Scheme 1. Synthetic pathway for M1.



Scheme 2. Structures of monomers and electrochemically synthesized copolymers.

order to meet the need in both academic and commercial applications, studies have been going on to synthesize new conductive polymers with low optical band gap and good electrical conductivity. Band gap (E_g) and the highest occupied molecular orbital (HOMO)/ the lowest unoccupied molecular orbital (LUMO) energy levels are crucial

parameters that affect the electronic and optical properties of conjugated polymers. Design and synthesis of the low band gap polymers is extremely important in literature and many engineering strategies have been carried out for years for that purpose. One approach to design such polymers is to combine strong electron donor and acceptor units in the



Scheme 3. Surface characteristics of (a) CoP1.3 and (b) CoP1.5 (with 1000 and 4000 magnification) SEM images.

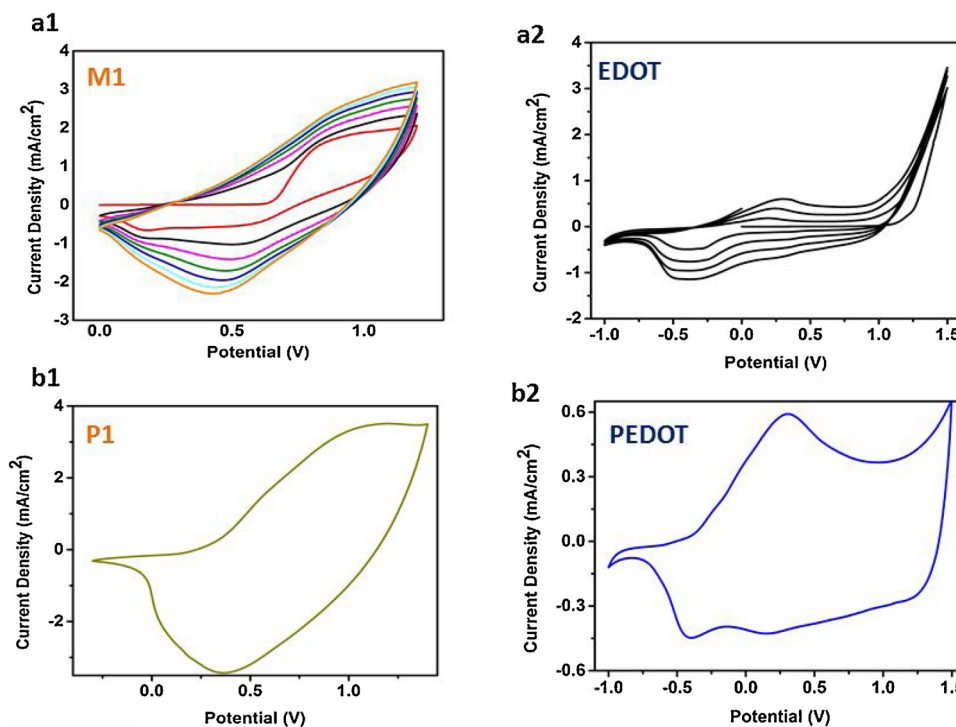


Fig. 1. Cyclic voltammograms of (a1) M1 and (a2) EDOT during electropolymerization on ITO surface, and (b1,b2) single scan cyclic voltammograms of homopolymers (P1 and PEDOT) in 0.1 M NaClO₄-LiClO₄/ACN solution.

polymer backbone, namely donor- acceptor approach [5].
 Modification of polymers can be performed via molecular engineering using different polymer backbones or special functional groups to increase the diversity [6]. Copolymerization is another mostly preferred technique that widely used for the improvement of electrochemical and optical properties like optical band gap, switching time, neutral and oxidized state colors and optical contrasts [7-9].

Copolymerization can be performed by chemical or electrochemical methods [10]. Both methods have some certain advantages and disadvantages. When copolymerization methods (chemical and electrochemical copolymerization) are compared, electrochemical copolymerization is an easy and fast way to synthesize a well-adhered copolymer film on the electrode surface and to investigate the electro-optical behavior of the resulting copolymer film. In literature, there are

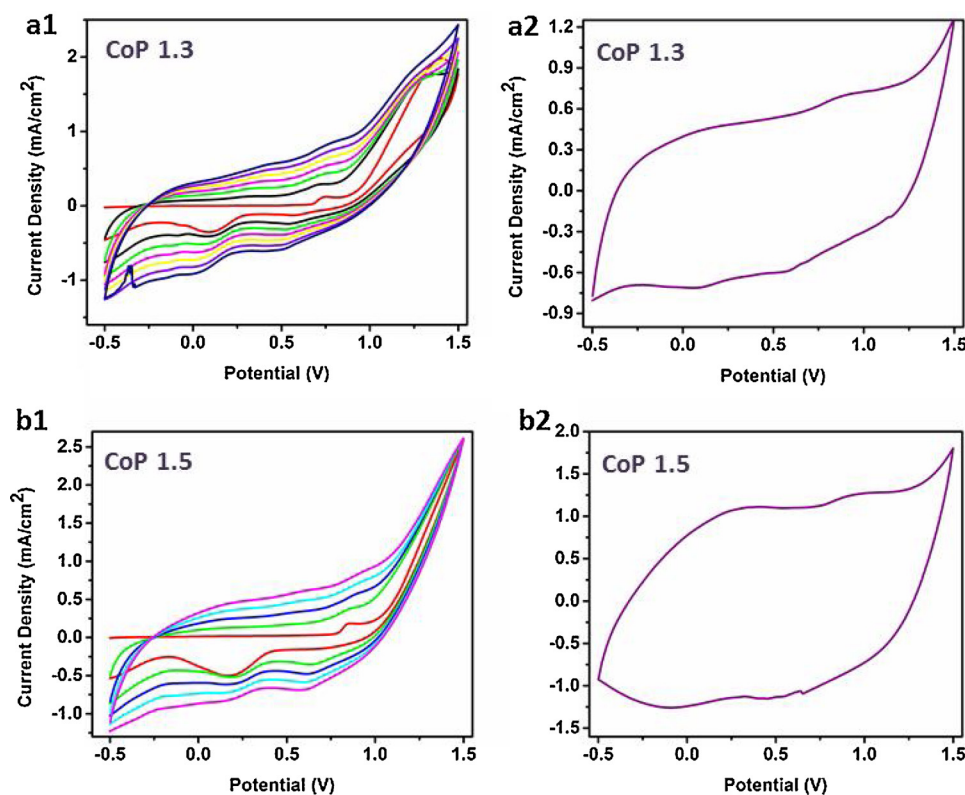


Fig. 2. Cyclic voltammograms of (a1) CoP1.3, (b1) CoP1.5 during the electro polymerizations 0.1 M NaClO₄-LiClO₄/ACN/DCM (95:5, v/v) solution and (a2, b2) single scan CVs of the copolymers in a monomer-free medium.

Table 1

Summary of electrochemical properties for CoP1.3 and CoP1.5.

	E_m^{ox} (V)	$E_{p-doping}$ (V)	$E_{p-dedoping}$ (V)	E_{doping}^{onset} (V)	HOMO (eV)	LUMO (eV)
CoP1.3	0.75/1.40	0.23/0.93	0.08/0.58	-0.57	-4.18	-2.97
CoP1.5	0.85	0.30/0.98	-0.08/0.47	-0.52	-4.24	-3.06

various studies on the synthesis and characterization of different copolymers via electrochemical techniques [11–14]. Generally, the resulting copolymers obtained either electrochemically or chemically exhibited better electrochemical, optical and spectroelectrochemical properties than the pristine homopolymers [15,16].

Another important and impressive property of conducting copolymers is electrochromism. Material that reversibly changes its color upon applied potential is called as electrochromic material [17]. For conducting polymers, electrochromism relates to the doping-dedoping process which changes the electronic structure of the polymer [18,19].

In literature different co-monomers were used during copolymerization process to obtain novel materials with improved electrochemical and electrochromic properties. [20–22] In this study, electrochemical copolymerization of carbazole comprising monomer (M1) and EDOT was performed to improve the above-mentioned properties such as band gap, optical contrast and switching times of carbazole comprising polymer. Carbazole unit is an aromatic heterocyclic organic compound that is consisting of two six-membered benzene rings fused on either side of a five-membered nitrogen-containing ring. The use of carbazole functional unit in literature is quite common. The most common application fields are related to photoconductors and charge-transporting materials [23–25]. There are many reasons which make it applicable in this variety of applications such as forming relatively stable radical cations, exhibiting relatively high charge carrier mobilities, introducing different substituents into the carbazole ring, having high thermal and photochemical stability [26]. As a result of these

certain advantages, there are a number of studies on carbazole based functional materials in literature [27–31]. Oral et al. synthesized polystyrene (PS) functionalized carbazole macromonomer via electrochemical oxidative polymerization process. After structural analyzes via ¹H NMR, FT-IR, UV-vis and cyclic voltammetry (CV) techniques, electrochromic properties of the polymer were investigated. Then, the polymer switching between greenish blue and dark blue upon applied potential was used in the construction of an electrochromic device with 38 % (at 640 nm) optical contrast and 1.1 s switching time values. In addition to these promising properties, 3,6-dithienylcarbazole based electrochemically obtained polymer was reported by our group with yellow color, 1.93 eV optical band gap and 22 % optical contrast which are not proper for electrochromic applications. To overcome these problems and obtain multifunctional 3,6-dithienylcarbazole derivatives, copolymerization is an easy and effortless method to combine electrochromic properties of the comonomers and obtaining low oxidation potentials. In terms of structure-property relationships, 3,4-ethylenedioxythiophene (EDOT) is a good candidate as a co-monomer due to the low band gap of resulting EDOT comprising polymers due to the presence of two electron donating oxygen atoms. Furthermore, incorporation of EDOT unit in the polymer chain results fast switching times, high conductivity and good stability in ambient conditions.

3,4-Ethylenedioxythiophene (EDOT) is another important electroactive conductive monomer consisting of thiophene unit, substituted at the 3 and 4 positions. EDOT is a widely used comonomer for electrocopolymerization reactions due to its low band gap with high stability

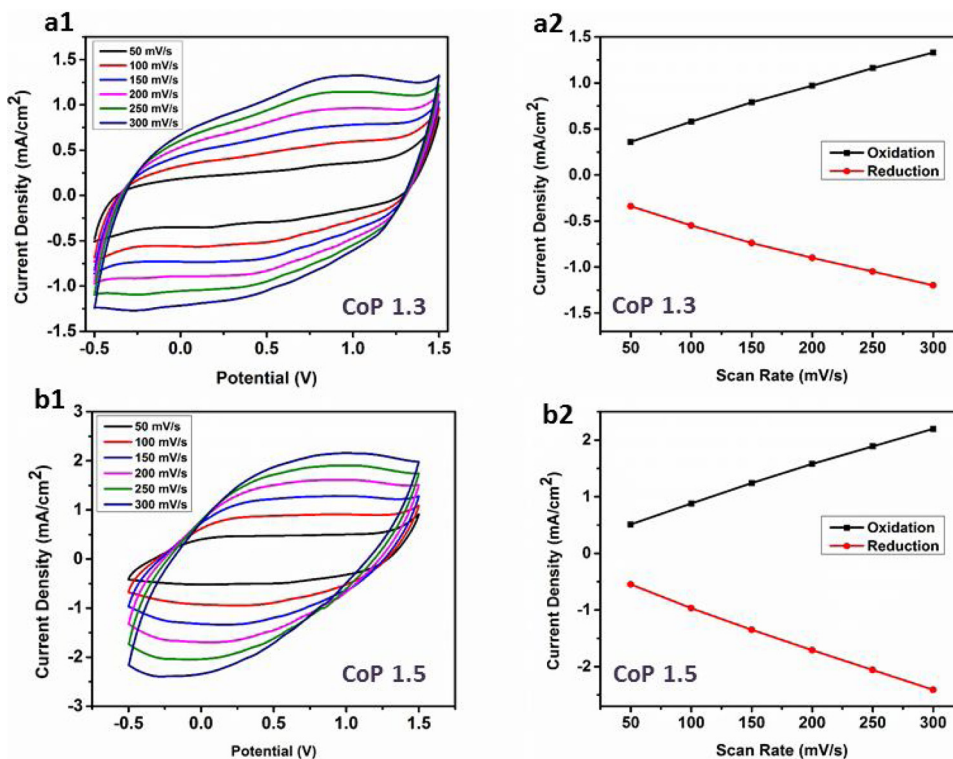


Fig. 3. Scan rate dependency for (a1, a2) CoP1.3 and (b1,b2) CoP1.5.

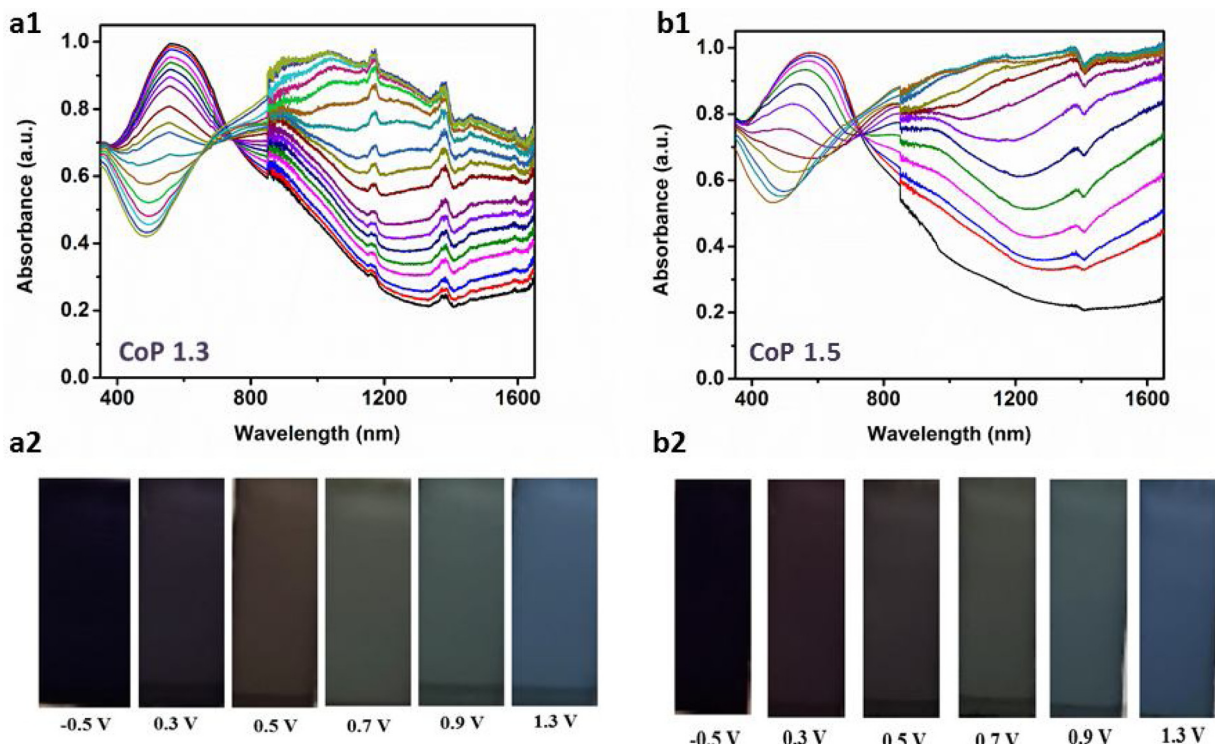


Fig. 4. Spectroelectrochemical studies of (a1, a2) CoP1.3 and (b1, b2) CoP1.5 in 0.1 M NaClO₄-LiClO₄/ACN solution upon stepwise oxidation between -0.5 V and 1.0 V with corresponding colors at neutral, oxidized and intermediate states.

and good conductivity. There are many articles in the literature on EDOT and its applications [32–34]. A perylene (PE) and EDOT bearing copolymer was synthesized by Hu et al. by electrochemical polymerization method. While the obtained copolymer is initially exhibited orange color, upon applied potential it changed its color to red brown

and light green with 25 % (516 nm) and 42 % (1100 nm) optical contrasts and high stability.

Copolymerization is often used to achieve novel polymers with desired properties that are expected to embody the advantages of both of the parent polymers which also enlarge the application fields and

Table 2
Summary of spectroelectrochemical properties of CoP1.3 and CoP 1.5.

	λ_{\max} (nm)	$\lambda_{\max}^{\text{onset}}$ (nm)	E_g^{op} (eV)	Polaron/Bipolaron (nm)
CoP1.3	575	1029	1.21	1050/1240
CoP1.5	594	1051	1.18	975/1170

display better electrochromic properties; additionally synthesis of multifunctional polymer with improved electrochromic behaviors is possible via this widely preferred technique. Low oxidation potential and high stability of EDOT makes it a possible candidate for copolymerizations to enhance the electrochemical properties of resulting copolymers. In literature copolymerization of EDOT with other monomers such as quinoxaline [35], benzimidazole [36], dithienylpyrrole [37], carbazole [38,39], anthracene [40], dithienylpyrrole [41] and 5-cyanoindole [42], has been reported. Celebi et al. reported the enhancing electrochromic and kinetic properties of quinoxaline derivatives by copolymerization with EDOT and resulting polymers were found to be promising candidates for optoelectronic technology since they have multicolored characters, fast switching times at around 1 s and high stabilities [35]. Then, copolymerization of dithienylpyrrole and EDOT was investigated by Camurlu et al. and the electrochemically obtained dithienylpyrrole and EDOT comprising copolymers revealed shorter switching times (around 0.5 s) higher optical contrast (around 36 %). Furthermore, this study stated that the color of the copolymers could be easily tuned by controlled increase in copolymerization potential [37]. In another study, functionalized carbazole and EDOT bearing copolymers exhibited five different colors under different applied potentials and higher optical contrast (50 % of 1100 nm) and coloration efficiency ($356.88 \text{ cm}^2 \text{ C}^{-1}$) [38]. Then, 5-cyanoindole was copolymerized with EDOT and resulting copolymers were used for ECD applications. The resulting ECD showed impressive performances such as; good optical contrast (48 % at 630 nm), high coloration efficiency ($680.88 \text{ cm}^2 \text{ C}^{-1}$), fast response time (0.8 s at 630 nm) with good optical memory and long-term stability [42]. As seen from the literature examples copolymerization with EDOT was widely investigated in order to enhance the electrochromic behaviors.

As reported in our previous works, monomer chains based on terthiophene, 2,5-dithienylpyrrole (SNS) and 3,6-dithienylcarbazole were combined with highly optically potent chromophore groups in the UV–vis region (azobenzene, coumarin and fluorescein) and interesting electrochemical and spectroelectrochemical characteristics were obtained for homopolymer derivatives. [43,44] Especially, poly(3,6-dithienylcarbazole)-based homopolymers containing azobenzene and coumarin units as pendant groups exhibited better electrochemical and optical properties than those of poly(terthiophene) and poly(2,5-

Table 3
Colorimetric measurements of CoP1.3 and CoP1.5.

Polymer	Applied potential (V)	L	a	b
CoP1.3	–0.5	0.931	2.008	–5.993
	0.3	12.00	6.695	–6.210
	0.5	22.97	8.953	6.758
	0.7	31.46	–3.851	3.805
	0.9	33.30	–7.968	–1.226
	1.3	32.96	–8.187	–17.620
CoP1.5	–0.5	0.586	1.906	–4.257
	0.3	12.110	12.350	–0.827
	0.5	18.660	4.648	0.117
	0.7	28.810	–3.265	4.117
	0.9	34.00	–8.710	–5.030
	1.3	32.07	–5.343	–21.07

dithienylpyrrole)-based homopolymers because of highly effective electroactive and photoactive nature of carbazole ring system. Furthermore, as reported in our recent work, azobenzene and coumarin functionalized thiophene comprising polymers were used both for electrochromic and organic solar cell applications [45]. In addition, in literature these chromophore groups were not widely used for organic solar cell applications. Improvement of electrochromic properties of azobenzene functionalized polymers will make them good candidates for variety of applications as multipurpose materials.

In light of our previously results, it is expected that better electrochromic behaviors can be obtained through the copolymerization of 3,6-dithienylcarbazole monomer bearing an azobenzene unit and EDOT, in this study. For this purpose, a carbazole comprising monomer (9-(2-(4-(phenyldiazenyl)phenoxy) ethyl)-3,6-di(thiophen-2-yl)-9H-carbazole) (M1) and EDOT were copolymerized electrochemically to improve the electrochemical and electrochromic properties of carbazole comprising homopolymer (poly-9-(2-(4-(phenyldiazenyl)phenoxy) ethyl)-3,6-di(thiophen-2-yl)-9H-carbazole) (P1). Electrochemical, spectroelectrochemical and kinetic studies were performed and significant improvements were observed on the electrochromic behaviors, optical contrast and switching time values by addition of EDOT unit onto the copolymer chain via electro-copolymerization technique.

2. Experimental

2.1. Materials and methods

3,4 Ethylenedioxythiophene (EDOT) is a commercially available monomer and purchased from Sigma-Aldrich Chemical Co. Ltd. and used without any further purification. GAMRY 600 potentiostat/galvanostat and JASCO V-770 were used for electrochemical studies and UV–vis-NIR spectral characterizations. Electrochemical, spectroelectrochemical and optical switching studies were performed under ambient temperature. Both electrochemical and spectroelectrochemical studies were performed in a three-electrode cell bearing an indium tin oxide (ITO)-coated glass electrode, platinum wire and Ag wire as the working electrode (WE), the counter electrode (CE) and as the reference electrode (RE), respectively. While electrochemical copolymerizations were performed in 0.1 M $\text{NaClO}_4\text{-LiClO}_4/\text{ACN}/\text{DCM}$ (95:5, v/v) solution at 100 mV s^{-1} scan rate, the other studies were performed in 0.1 M $\text{NaClO}_4\text{-LiClO}_4/\text{ACN}$, electrolyte/solvent couple. HOMO-LUMO energy levels were calculated using onset of oxidation potentials with Eqn1 and relative to the vacuum level (the value of standard hydrogen electrode (SHE) as -4.75 eV).



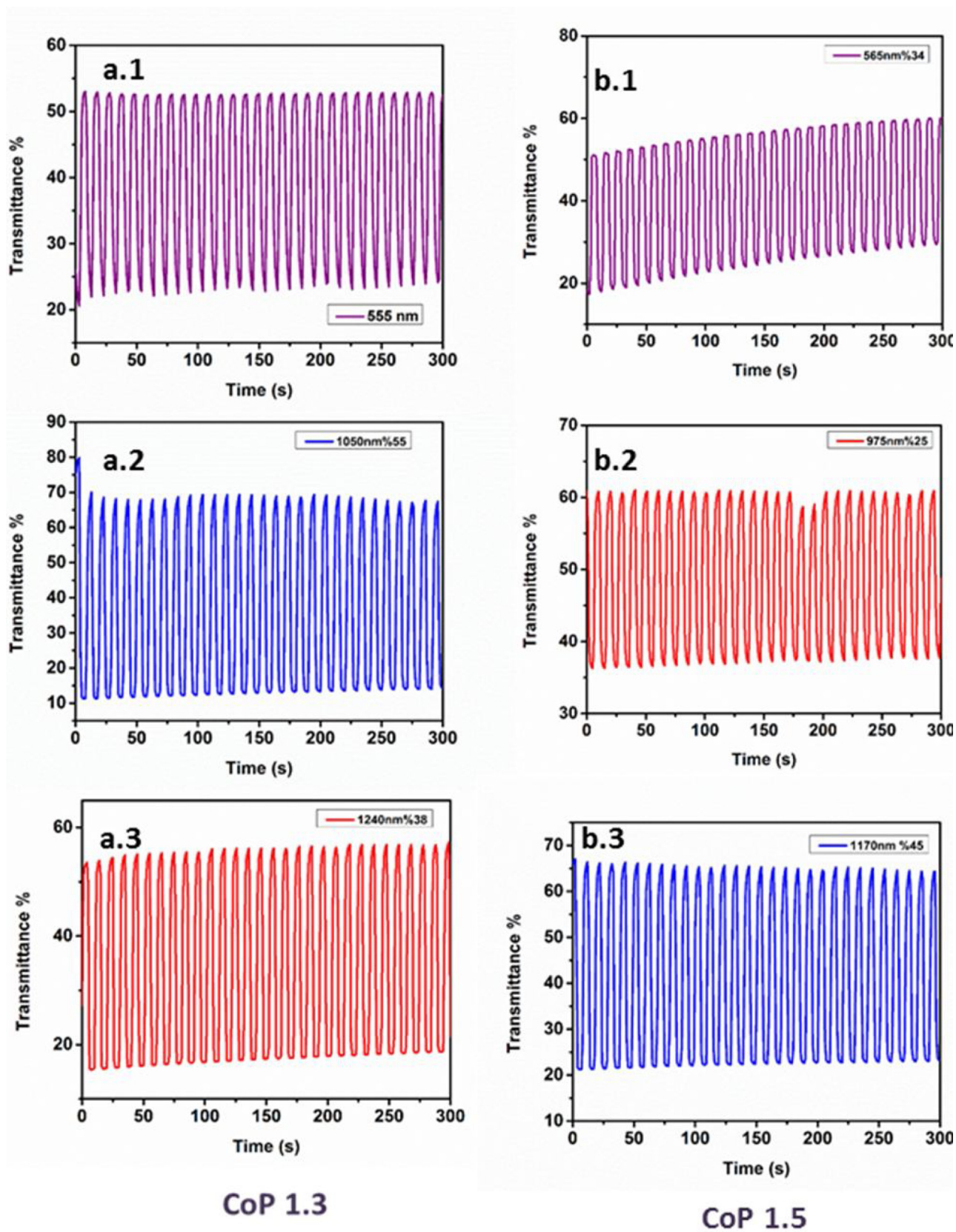


Fig. 5. Optical transmittance changes for CoP1.3 at (a1) 555 nm, (a2) 1050 nm and (a3) 1240 nm, for CoP1.5 at (b1) 650 nm, (b2) 975 nm and (b3) 1170 nm in 0.1 M NaClO₄-LiClO₄/ACN solution.

Table 4
The optical contrast and switching times values for CoP1.3 and CoP1.5.

	Wavelength (nm)	Optical Contrast (T %)	Switching Times Oxidation (s)	Switching Times Reduction(s)
CoP1.3	555	31	2.5	3.5
	1050	55	1.7	2.4
	1240	38	1.9	2.6
CoP1.5	565	34	1.8	1.9
	975	25	2.7	2.2
	1170	45	1.9	2.7

2.2. Synthesis of 9-(2-(4-(Phenyldiazenyl)phenoxy)ethyl)-3,6-di(thiophen-2-yl)-9H-carbazole (M1)

The monomer 9-(2-(4-(phenyldiazenyl)phenoxy)ethyl)-3,6-di(thiophen-2-yl)-9H-carbazole (M1) was synthesized via a synthetic method consisting of essentially two main steps. In the first step of reaction pathway, 3,6-dibromo-9H-carbazole moite and azobenzene chromophore unit was brought together through a microwave-assisted nucleophilic substitution reaction. Subsequently, palladium-catalyzed Stille cross-coupling reaction of 3,6-dibromo-9-(2-(4-(phenyldiazenyl)phenoxy)ethyl)-9H-carbazole and 2-(tributylstannyl) thiophene was performed in order to obtain the target monomer, 9-(2-(4-(phenyldiazenyl)phenoxy)ethyl)-3,6-di(thiophen-2-yl)-9H-carbazole (M1), as described in Scheme 1. The crude product was purified by column chromatography with hexane/ dichloromethane (90:10, v/v) a bright orange solid was obtained with 78 % yield [46].

FTIR ν/cm^{-1} 3068, 3039, 2934, 2864, 1599, 1580, 1483, 1360, 1241. ^1H NMR (400 MHz, CDCl_3 , Me_4Si) δ_{H} 4.37 (t, $J = 7.6$ Hz, 2 H), 4.66 (t, $J = 7.5$ Hz, 2 H), 6.86 (dd, $J = 8.7$ Hz and $J = 2.4$ Hz, 2 H), 7.09–7.49 (m, 9 H), 7.37–7.75 (dd, $J = 9.8$ Hz and $J = 2$ Hz, 2 H), 7.81–7.85 (m, 4 H), 8.32 (d, $J = 2$ Hz, 2 H). ^{13}C NMR (400 MHz, CDCl_3 , Me_4Si) δ_{C} 42.6, 66.2, 109, 114.6, 117.9, 122.2, 122.5, 123.4, 123.8, 124.7, 126.4, 128, 129, 130, 140.4, 145.4, 147.2, 160. MS (EI) calculated for $\text{C}_{34}\text{H}_{25}\text{N}_3\text{O}_2$ m/z : 555.7, found m/z : 555 (M^+ , 5), 519 (2), 473 (30), 422 (15), 357 (10), 317 (5), 262 (55), 183 (10), 139 (5), 77 (100). Anal. Calcd. for ($\text{C}_{34}\text{H}_{25}\text{N}_3\text{O}_2$): C, 73.48 %; H, 4.53 %; N, 7.56 %. Found: C, 73.65 %; H, 4.12 %; N, 7.31 %.

2.3. Electrochemical copolymerization of EDOT and M1

Electrochemical homopolymerizations and copolymerizations were performed as described before with CV in a 0.1 M $\text{NaClO}_4\text{-LiClO}_4/\text{DCM}/\text{ACN}$ (5/95, V/V). The structures of co-monomers and copolymer are illustrated in Scheme 2. Initially CVs for homopolymers (P1 and PEDOT) and then copolymers were recorded and reported. Copolymers CoP1.3, CoP1.5 were synthesized with a monomer feed ratio of (M1:EDOT) 1:3, 1:5 in order to investigate the effect of increasing EDOT amount in the copolymer backbone on electrochemical features of the resulting copolymers (CoP1.3 and CoP1.5).

The morphologies of copolymer films were investigated by scanning electron microscopy (SEM). All figures were recorded after copolymerization of M1 and EDOT in 0.1 M $\text{NaClO}_4\text{-LiClO}_4/\text{ACN}/\text{DCM}$ (95:5, v/v) solution on ITO surface with 1:3, 1:5(M1:EDOT) comonomer feed ratios. While compatibility of the co-monomers can be clearly seen from the SEM images, formation of porosity and network on the images can

Table 5
Comparison of electrochemical, spectroelectrochemical and kinetic properties of copolymers with P1.

	E_{m}^{ox} (V)	$E_{\text{p-doping}}$ (V)	HOMO (eV)	LUMO (eV)	λ_{max} (nm)	E_{g}^{op} (eV)	Optical Contrast (T %)	Switching Times Oxidation (s)	Colors
CoP1.3	0.75/1.40	0.23/0.93	-4.18	-2.97	575	1.21	31 and 38 (555 and 1240 nm)	2.5 and 1.9 (555 and 1240 nm)	Purple-blue
CoP1.5	0.85	0.30/0.98	-4.24	-3.06	594	1.18	34 and 45 (565 nm and 1170 nm)	1.8 and 1.9 (565 nm and 1170 nm)	Purple-blue
P146	0.98	0.58	-5.35	-3.42	370/415	1.93	6 and 22 (415 nm and 1100 nm)	2.8 and 3.0 (415 nm and 1100 nm)	Yellow-green

be dedicated to the formation of copolymers (CoP1.3 and CoP1.5) on an ITO electrode (Scheme 3) [47].

3. Results and discussion

3.1. Electrochemical properties

Cyclic Voltammetry (CV) is a multi-purpose electrochemical technique that can be used both for electropolymerization (electro-synthesis) and electrochemical characterization. Redox potentials, HOMO-LUMO energy levels and band gap are crucial parameters for electrochemical characterizations and they can be easily determined from the CV curves. The main purpose of this study is to enhance the electrochemical, electrochromic and spectroelectrochemical features of carbazole and thiophene comprising polymer P1 which was electrochemically synthesized and characterized before. For that purpose, carbazole comprising monomer (M1) and EDOT were used in two different comonomer feed ratios, 1:3 and 1:5 respectively. CVs were recorded both for homopolymers and copolymers in order to compare the results clearly. Corresponding voltammograms for both electrochemical polymerizations of M1 and EDOT and single scans for P1 and PEDOT are shown in Fig. 1. During the copolymer design, to investigate the effect of EDOT on the electrochemical and electrochromic properties of carbazole comprising polymer (P1), the amount of EDOT comonomer was changed from 1:3 to 1:5 as the feed ratio. Hence, initially homopolymers (P1 and PEDOT) and then copolymers (CoP1.3, CoP1.5) were synthesized and reported in Figs. 1 and 2. As mentioned before, some vital calculations could be performed from CV, herein monomer and polymer oxidation potentials (E_{m}^{ox} , $E_{\text{p-doping}}$, $E_{\text{p-dedoping}}$) with corresponding HOMO/LUMO energy levels were calculated for both copolymers (CoP1.3 and CoP1.5) and summarized in Table 1. Both CoP1.3 and CoP1.5 exhibited p-type doping property with reversible oxidation potentials reported at 0.23 V/0.93 V for CoP1.3 and 0.30 V/0.98 V for CoP1.5 with 0.08 V/0.58 V and -0.08 V/0.47 V p-type dedoping potentials, respectively. Another important parameter for conjugated polymers which affect their applicability in different fields are the HOMO and LUMO energy levels that can be calculated from single scan CVs. As reported in Table 1, HOMO energy levels were calculated from the onsets of the corresponding oxidation potentials for both copolymers as -4.18 eV for CoP1.3 and -4.24 eV for CoP 1.5 by using the Eq. (1).

$$\text{HOMO} = -(4.75 + E_{\text{doping}}^{\text{onset}}) \quad (1)$$

Scan rate studies were performed in order to test the dependency of doping-dedoping process on scan rates. For that purpose, single scan CVs were recorded at six different scan rates (50, 100 150, 200, 250, 300 mV/s) in 0.1 M $\text{NaClO}_4\text{-LiClO}_4/\text{ACN}$ solution and current density vs scan rate graphs were drawn from voltammograms. As shown in Fig. 3, there is a direct relationship between the current density and scan rate for both copolymers (CoP1.3 and CoP1.5) which shows us that the formation of well adhered copolymer films on ITO electrode. In addition, another significant point about this linear relationship is that the doping-dedoping processes (redox processes) are non-diffusion controlled for both copolymers (CoP1.3 and CoP1.5).

3.2. Spectroelectrochemical properties

After electrochemical copolymerization and characterization of CoP1.3 and CoP1.5, optical and spectroelectrochemical properties of resulting copolymers were investigated via UV-vis-NIR spectrophotometer in combination with potentiostat. For spectroelectrochemical studies, polymer coated ITO electrodes were prepared as described before and washed with ACN, then studies were performed in 0.1 M NaClO₄-LiClO₄ / ACN solution between -0.5 V and 1.0 V. Before stepwise oxidation, neutral state absorptions were recorded at -0.5 V constant potentials for both copolymers and UV-vis-NIR spectrophotometers were recorded upon stepwise oxidation.

Another important parameter for conjugated polymers is λ_{\max} which is a wavelength where maximum absorbance is obtained. λ_{\max} values were determined from the neutral state absorptions as 575 nm and 594 nm for CoP1.3 and CoP1.5, respectively. Then, from the slope of the neutral state absorptions, $\lambda_{\max}^{\text{onset}}$ values were determined as 1029 nm and 1051 nm for CoP1.3 and CoP1.5 (Fig. 4). The $\lambda_{\max}^{\text{onset}}$ values are used to calculate the optical band gap that is an important characteristic property of the resulting copolymers especially for their organic solar cell applications. E_g^{op} values were calculated as 1.21 eV and 1.18 eV for CoP1.3, CoP1.5 respectively. Band gap is the difference between the HOMO and LUMO energy levels, since both copolymers exhibited only p-type doping property, LUMO values were calculated from the difference between optical band gap and HOMO energy level as -2.97 eV for CoP1.3 and -3.06 eV for CoP1.5. During spectroelectrochemical studies, upon stepwise oxidation while the absorption in the visible region depleted new absorption bands arose due to the formation of charge carriers. Upon stepwise oxidation while the neutral state absorptions which also called as $\pi \rightarrow \pi^*$ transitions were depleting, a new transitions at around 1000 nm and 1200 nm originates due to the formation of charge carrier bands. The corresponding charge carriers were called as polaronic and bipolaronic states. Potentials beyond 0 V enhanced the formation of polaron and bipolaron bands signified by the broad transitions around 1000 nm and 1200 nm. The copolymerization also affected polaronic and bipolaronic charge carriers reported at around 640 nm and 1100 nm for the homopolymer of 3,6-dithienylcarbazole [46]. As mentioned before copolymerization of 3,6-dithienylcarbazole with EDOT increased the electroactivity of resulting polymers with lower oxidation potentials and higher effective conjugation length which resulted red shifted absorption and lower optical band gap in the electronic absorption spectra. As expected, copolymerization also resulted in red shifted polaronic and bipolaronic charge carriers. As summarized in Table 2, these values were found as 1050 nm/1240 nm for CoP1.3 and 975 nm/1170 nm for CoP1.5.

3.3. Colorimetry studies

Both CoP1.3 and CoP1.5 exhibited multichromic behavior with different colors in their neutral and oxidized states. Colorimetry studies were conducted to give details of these colors in a more scientific way. During the colorimetry studies photographs of the polymers were recorded and illustrated in Table 3 with the corresponding L, a, b values according to CIE (Commission Internationale de l'Eclairage) coordinates which were used to identify the colors of the materials. In this coordinate system, the color scale is determined with the help of some parameter namely L, a and b that represent each color with a single point. In order to define the colors in this coordinate system, 'L' indicates the brightness of the color, 'a' represents the colors between red and green and 'b' represents the colors between yellow and blue. These values are used in many areas of the world for color control, such as plastics, materials, textiles, paints and so on [48]. While both copolymers (CoP1.3 and CoP1.5) exhibited different tones purple colors in the neutral states, the colors turned to blue colors upon applied potentials. Also with the applied potential the L values are increasing and the color has become brighter. When 1.3 V is applied, negative b values confirm

the blue colors for both copolymers.

3.4. Electrochromic contrast and switching studies

Electrochromic contrast and switching studies were performed to determine the optical contrast and switching time values in the visible and NIR regions for both copolymers at three different wavelengths. Both CoP1.3 and CoP1.5 were synthesized electrochemically on ITO electrode as described before and kinetic studies were performed in 0.1 M NaClO₄-LiClO₄/ACN electrolyte/solvent system via UV-vis-NIR spectrophotometer combined with potentiostat. In order to investigate the switching time and optical contrast values, a square-wave potential method was used and oxidation/reduction potentials were applied with 5 s intervals at corresponding λ_{\max} values. As depicted in Fig. 5, percent transmittance versus time graphs were recorded at 555 nm, 1050 nm, 1240 nm for CoP1.3 and 565 nm, 975 nm, 1170 nm for CoP1.5 and the calculated optical contrasts and switching times were reported in Table 4. The change in percent transmittance between the neutral and oxidized states is named as the optical contrast and switching time defines the time required for one full switch between these two extreme states (neutral and oxidized states). These parameters, which are very important for electrochromic applications were determined from Fig. 5. Optical contrast values were calculated and reported as 31 % (at 555 nm), 55 % (at 1050 nm) and 38 % (at 1240 nm) for CoP1.3 and 34 % (at 565 nm), 25 % (at 975 nm) and 45 % (at 1170 nm) for CoP1.5. Switching times during oxidation processes were calculated as 2.5 s, 1.7 s, 1.9 s for CoP1.3 and 1.9 s, 1.8 s, 2.7 s for CoP1.5. On the other hand, switching times during reduction processes were found as 3.5 s, 2.4 s, 2.6 s for CoP1.3 and 1.9 s, 2.2 s, 2.7 s for CoP1.5 at the corresponding wavelengths.

3.5. Comparison of electrochemical, spectroelectrochemical and kinetic properties of copolymers (CoP1.3 and CoP1.5) with the homopolymer (P1)

As mentioned before carbazole comprising polymers could be used for a variety of applications such as; photoconductors and charge-transporting materials, however their blue shifted absorption in the visible region, higher band gaps and higher redox potentials negatively affected their electrochromic performances.³⁵ In literature, copolymerization of these units with other well performed electrochromic materials provides significant improvements in electrochemical, electrochromic and kinetic properties. In the light of these knowledge, the copolymerization of M1 and EDOT was performed with two different comonomer feed ratios (1:3 and 1:5) to obtain CoP1.3 and CoP1.5 electrochemically. The electrochemical and electrochromic properties of both copolymers were compared in Table 5 with those of homopolymer (P1) to illustrate the improvements clearly.

As seen in Table 5, addition of EDOT unit into copolymer backbone resulted the obvious improvements in electrochemical, optical, electrochromic and kinetic properties. While P1 had higher oxidation potential at around 0.6 V, after incorporation of electron-rich EDOT unit into the copolymer chain, very low oxidation potentials at 0.23 V for CoP1.3 and 0.3 V for CoP1.5 were recorded. Furthermore, as a result of spectroelectrochemical studies, the improvements on the λ_{\max} and E_g values were depicted in Table 5. While carbazole comprising homopolymer (P1) could only absorbed the part of the visible region with 370/415 nm λ_{\max} values and 1.93 eV optical band gap, insertion of EDOT satisfied the full visible absorbing copolymers with 575 nm, 594 nm λ_{\max} and 1.21 eV, 1.18 eV E_g values, respectively. In other words, electro copolymerization of M1 with EDOT resulted in red-shifted neutral state absorption with lower optical band gap values. The resulting copolymers not only absorbed the full visible region and also both absorbed the part of NIR region with 1050 nm $\lambda_{\max}^{\text{onset}}$ values which resulted grayish purple colored copolymers in the neutral state while the homopolymer exhibited greenish yellow color in the neutral state. Finally, kinetic studies strongly supported the previous results

and discussions, while P1 had 6% and 22 % optical contrast values in the visible region and NIR region, the optical contrasts were recorded as 31 % and 38 % for CoP1.3 and 34 % and 45 % for CoP1.5. As seen, the significant improvements were satisfied in terms of all above-mentioned properties via copolymerization with EDOT which make CoP1.3 and CoP1.5 good candidates for variety of applications.

As a further characterization, coloration efficiency values (CE) of the resulting copolymers were calculated from transmittance and electrochemical charge data with the following equation.

$$\eta = \Delta OD/Q_d = \log [T_{ox}/T_{neut}]/Q_d$$

In this equation, Q_d is electrochemical charge, T_{ox} and T_{neut} are the transmittance values at the oxidized/neutral states. A high CE proves the easier optical modulation per inserted charge. Resulting coloration efficiencies were calculated as $158 \text{ cm}^2 \text{ C}^{-1}$ (555 nm), $324 \text{ cm}^2 \text{ C}^{-1}$ (1050 nm), $219 \text{ cm}^2 \text{ C}^{-1}$ (1240 nm) for CoP1.3 and $185 \text{ cm}^2 \text{ C}^{-1}$ (565 nm), $91.2 \text{ cm}^2 \text{ C}^{-1}$ (975 nm), $203 \text{ cm}^2 \text{ C}^{-1}$ (1170 nm) for CoP1.5.

4. Conclusions

3,4-Ethylenedioxythiophene (EDOT) and a carbazole comprising monomer (M1) were used to synthesize novel electrochromic copolymers with different monomer feed ratios. The electrochemical and spectroelectrochemical characterizations of this intensified copolymers were performed with CV and UV-vis-NIR spectrophotometer. Carbazole containing monomer (M1) and EDOT were used in two different comonomer feed ratios, (1: 3 and 1: 5) in order to investigate the effect of increasing EDOT amount on electrochemical and electrochromic behaviors. The addition of electron-rich EDOT unit into the copolymer chain affected the electrochemical properties significantly by changing the electron density of the polymer. Both copolymers exhibited p-type doping property with reversible oxidation potentials reported at 0.23 V/0.93 V for CoP1.3 and 0.30 V/0.98 V for CoP1.5. Band gap values were calculated as 1.21 eV for CoP1.3 and 1.18 eV for CoP1.5. As a result of the high EDOT quantity in the structure, the value of the band gap for CoP1.5 is lower than the other. Both CoP1.3 and CoP1.5 exhibited multichromic behavior with different colors in the neutral and oxidized states. While both copolymers (CoP1.3 and CoP1.5) exhibited a purple color in the neutral states, they turned blue upon applied potentials. Finally, optical contrast values were calculated and reported as 31 % (at 555 nm), 55 % (at 1050 nm) and 38 % (at 1240 nm) for CoP1.3 and 34 % (at 565 nm), 25 % (at 975 nm) and 45 % (at 1170 nm) for CoP1.5. As mentioned before, CoP1.5 exhibited the higher optical contrast and lower switching time values compared to those of CoP1.3, due to the higher EDOT content in the resulting copolymer. Furthermore, addition of EDOT unit into copolymer backbone resulted the obvious improvements in electrochemical, optical, electrochromic and kinetic properties which make the copolymers good candidates for electrochromic applications.

Authorship contributions

Please indicate the specific contributions made by each author (list the authors' initials followed by their surnames, e.g., Y.L. Cheung). The name of each author must appear at least once in each of the three categories below.

CRedit authorship contribution statement

S.O. Hacıoğlu: Design of study, writing-review&editing. **L. Toppare:** Supervision. **I. Kalay:** writing-original draft. **D. Yiğit:** Design of study, writing-review&editing. **T. Depci:** Formal analysis. **M. Güllü:** Methodology, review&editing.

Declaration of Competing Interest

None.

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