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Copolymerization of Azobenzene-bearing Monomer and 3,4-Ethylenedioxythiophene (EDOT): Improved Electrochemical Performance for Electrochromic Device Applications

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Abstract In this study, novel electrochromic copolymers of 3,4-ethylenedioxythiophene (EDOT) and (*E*)-1,2-bis(2-fluoro-4-(4-hexylthiophen-2-yl)phenyl)diazene (M1) with different monomer feed ratios were designed and synthesized electrochemically. Electrochemical and spectro-electrochemical characterizations were performed using voltammetry and UV-Vis-NIR spectrophotometry techniques to test the applicability of copolymers for electrochromic applications. In terms of electrochemical behaviors, addition of an electron-rich EDOT unit into the azobenzene-containing copolymer increased the electron density on the polymer chain and afforded copolymers with very low oxidation potentials at around 0.30 V. While the homopolymers (P1 and PEDOT) exhibited neutral state absorptions centered at 510 and 583 nm, EDOT-bearing copolymers showed red shifted absorptions compared to those of P1 with narrower optical band gaps. In addition, the poor optical contrast and switching times of azobenzene-bearing homopolymer were significantly improved with EDOT addition into the copolymer chain. As a result of the promising electrochromic and kinetic preperties, CoP1.5-bearing single layer electrochromic device that works between purple and light greenish blue colors was constructed and characterized.

Keywords Azobenzene; EDOT; Copolymerization; Electrochromic device

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INTRODUCTION

New generation materials have aroused great interest over the last decades due to their potential applicability in the next generation electronics such as electrochromic devices (ECDs),[1,2] solar cells,[3,4] light emitting diodes,[5] and biosensors.[6,7] For the advanced applications, low cost, good conductivity, electrochemical reversibility, and adjustable band gaps are crucial parameters that should be arranged carefully.[8] Conjugated polymers (CPs) are good candidates for a variety of technological applications. Among the above-mentioned applications, ECDs belong to one of the most popular and widely studied fields and CPs as next generation materials are mostly used in this field due to their promising behaviors, namely, easy structural modifications, fast switching times, high coloration efficiency, and high optical contrasts.[9–11]

Many exhaustive studies in this fascinating field proved that bandgap has tremendous effect on the physicochemical and electrochromic properties of CPs. In literature, donor-acceptor (D-A) approach is a commonly preferred technique in order to modify the optoelectronic characters.[12,13] Furthermore, the desired physicochemical and electrochromic properties of conjugated polymers can be achieved by copolymerization technique or insertion of different units into the polymer backbone. Although copolymerization can be performed *via* either chemical or electrochemical techniques, well-adhered multifunctional polymer films could be fabricated more easily and faster *via* electrochemical copolymerization, which makes it a widely used technique.[14] During electrocopolymerization, at least two comonomers with different monomer feed ratios were mixed in the same solvent to obtain the copolymers. In order to synthesize multipurpose new generation polymers, the comonomers should be selected carefully.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most popular polythiophene-derivative conjugated polymers and widely used in the research for copolymerization due to its fascinating properties such as low band gap at around 1.6 eV, high stability, good conductivity, low oxidation potential, transparent oxidized state, biocompatibility, and easy synthesis.[15,16] Given these certain advantages, many reports have indicated that EDOT is a good candidate for a variety of electrochromic studies.[17–19]

Another interesting and fascinating group is azobenzene with its desired properties such as bright color, good stability, low flammability, and reversible photoisomerization.[20,21] Thanks to these advantages, azobenzene is widely used in polymerization, photochemical applications, optoelectronic

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devices, and optical data storage devices.[22–24] In 2016, Tang and coworkers synthesized the azobenzene-bearing electrochromic materials and reported that azobenzene-bridged neutral-neutral electrochromic materials exhibited fast response, high coloration efficiency, and the maximum percent transmittance.[21] Yigit *et al*. used azobenzene group as a chromophore unit to functionalize the electrochromic polymers and also compared it with coumarine and fluorescein units in the study.[25] Furthermore, Apaydin *et al*. synthesized and reported the novel conjugated polymers which combined azobenzene and thiophene derivatives on the polymer main chain for electrochromic applications. The resulting polymers exhibited multichromic behaviors, whereas their poor electrochromic and kinetic properties prevented their usage for ECD applications. These polymers had stability problems and their kinetic studies were only reported for the first cycle.[24] In this work, the azobenzene-bearing polymers reported before[24] were copolymerized with EDOT for ECD applications.

Herein, we designed and synthesized (*E*)-1,2-bis(2-fluoro-4-(4-hexylthiophen-2-yl)phenyl)diazene) (M1) and EDOT comprising novel copolymers CoP1.5, CoP1.10, and CoP1.15 with the different monomer feed ratios (M1:EDOT equal to 1:5, 1:10, and 1:15), respectively. Copolymerization of the azobenzene-bearing monomer with EDOT unit improved the electrochemical and electrochromic behaviors significantly. The resulting copolymers showed very low oxidation potentials at around 0.3 V, multichromic behaviors with red shifted absorption, and lower optical band gap values compared to those of P1. Finally, as a result of the promising kinetic properties with 43% optical contrast values in the visible region, ECD was constructed with CoP1.5 and characterized in terms of electrochromic and optical behaviors.

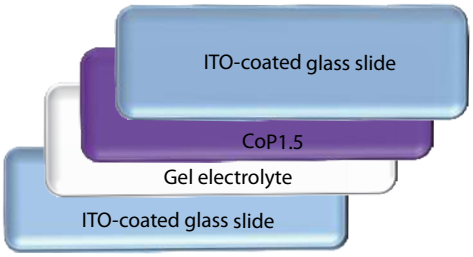
EXPERIMENTAL

Materials and Equipments

(*E*)-1,2-bis(2-fluoro-4-(4-hexylthiophen-2-yl)phenyl)diazene (M1) was already synthesized as previously reported and directly used.[24] EDOT was used as received (Sigma-Aldrich). All the other chemicals were purchased from Sigma Aldrich and used without any purification. Electrochemical studies were performed in a three-electrode cell consisting of an indium tin oxide (ITO)-coated glass slide as the working electrode (WE), platinum wire as the counter electrode (CE), and Ag wire as the reference electrode (RE) using a Gamry Reference 600 Potentiostat in 0.1 mol/L tetrabutylammonium hexafluorophosphate ($TBAPF_6$), acetonitrile (ACN)/dichloromethane (DCM) electrolytic medium. The band energies (HOMO-LUMO energy levels) were calculated relative to the vacuum level taking the value of standard hydrogen electrode (SHE) as −4.75 eV versus vacuum. To perform the spectroelectrochemical studies, Jasco V 750 UV-Vis-NIR spectrophotometer was combined with Solatron potentiostat-galvanostat. Spectroelectrochemical measurements were performed in a three-electrode system, namely, ITO coated glass, Pt wire, and Ag wire, as WE, CE, and pseudo RE, respectively.

Construction of Electrochromic Device (ECD)

Due to the promising electrochromic behaviors, CoP1.5 with a monomer feed ratio (M1:EDOT, 1:5) was used for ECD applications. CoP1.5 was electrochemically coated onto the ITO-coated glass and the ECD was constructed by arranging an electrochromic polymer coated ITO and pristine ITO facing each other in sandwich form. The ITO electrodes were separated by a gel electrolyte which was prepared according to literature. A schematic representation of the CoP1.5-based electrochromic device is illustrated in Scheme 1.[26,27]



Scheme 1 Schematic representation of the CoP1.5 based ECD.

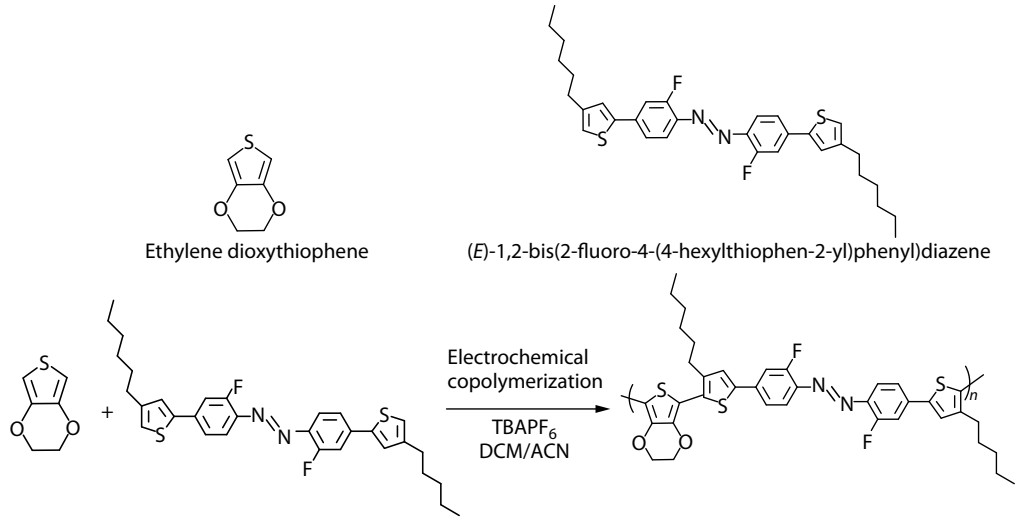
RESULTS AND DISCUSSION

Electrochemical Studies

Cyclic voltammetry (CV) is a very beneficial and widely used technique for both electropolymerization and electroactivity determination of the compounds due to its certain simplicity and advantages. In addition to electrochemical polymerization, HOMO-LUMO energy levels and redox potentials could be determined *via* CV. Due to the above-mentioned advantages, in this study all electrochemical homopolymerizations and copolymerizations were conducted *via* CV in a 0.1 mol/L $TBAPF_6$ DCM/ACN (5/95, *V*/*V*) solution at a scan rate of 100 mV/s (Scheme 2). This study aims at improving the electrochemical and electrochromic behaviors of azobenzene-comprising polymer (P1). For that purpose, initially homopolymers (P1 and PEDOT) and then copolymers (CoP1.5, CoP1.10, CoP1.15 (with a monomer feed ratio (M1:EDOT) of 1:5, 1:10, and 1:15)) were synthezied *via* CV and corresponding voltamograms are reported in Figs. 1 and 2.

During electropolymerizations, formations of irreversible monomer oxidations were observed in the first cycle, and new reversible redox couples emerged with increasing current intensities, which suggested the formation of electroactive homopolymer and copolymer films on ITO electrodes. Then, CVs of electrochemically synthesized polymers were recorded in a monomer-free solution to observe the doping properties with corresponding oxidation potentials and HOMO-LUMO energy levels which are crucial to characterizing the polymers for various applications. Both homopolymers (P1 and PEDOT) and copolymers (CoP1.5, CoP1.10, CoP1.15) exhibited p-type doping property with reversible oxidation potentials at 1.12 and 0.30 V for P1 and PEDOT at 0.22, 0.24, and 0.20 V for CoP1.5, CoP1.10, and CoP1.15, respectively (Table 1). As seen, insertion of EDOT unit into the azobenzene-bearing copolymer chain resulted in copolymers with very low oxidation potentials. The mentioned potentials were calculated from the first oxidation peaks of CVs, while all copolymers exhibited two more oxidation peaks at higher potentials, which can be attributed to the insertion of azobenzene-based monomer into the polymer chains.

Another important parameter for electrochemical characterization is HOMO energy level, which can be calculated from



Scheme 2 Structures of monomers and their electrochemical copolymerization in a 0.1 mol/L $TBAPF_6$ DCM/ACN (5/95, *V*/*V*) solution.

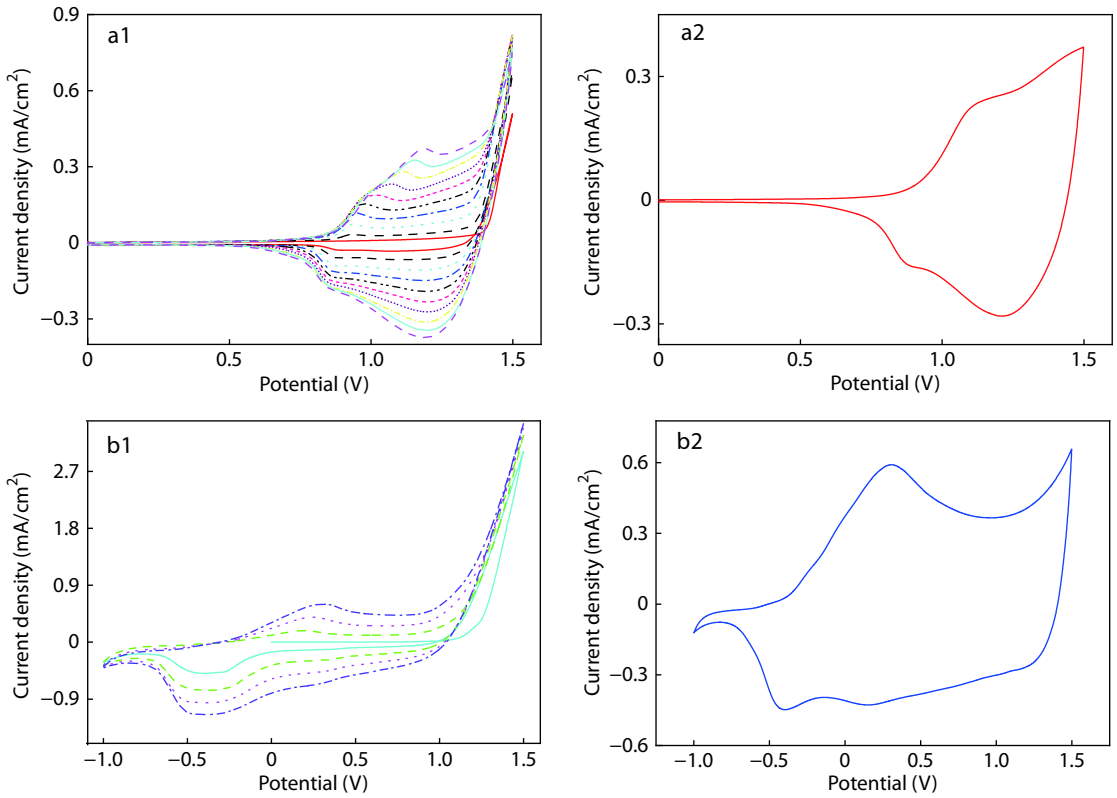


Fig. 1 Cyclic voltammograms of (a1) P1 and (b1) PEDOT during electropolymerization, and (a2, b2) single scan cyclic voltammograms of homopolymers.

CVs. HOMO energy levels of both homopolymers and copolymers were calculated from the onsets of the corresponding oxidation potentials (E^{ox}_{onset}) and reported as –5.66, –4.37, –4.34, –4.67, and –4.31 eV for P1, PEDOT, CoP1.5, CoP1.10, and CoP1.15, respectively. HOMO energy levels were calculated with Eq. (1) and all electrochemical results are collected in Table 1.

$$E_{HOMO} = -\left(4.75\ \text{eV} + E^{ox}_{onset}\right)$$

As seen in Fig. 3, while azobenzene-comprising polymer (P1) exhibited higher oxidation potential at around 1.00 V, incorporation of electron-rich EDOT unit into the polymer chain with different monomer feed ratios increased the electron density on the polymer chain and resulted in copolymers with very low oxidation potentials between 0.20 and 0.30 V.

Spectroelectrochemical Characterizations

The copolymer films were also investigated in terms of their

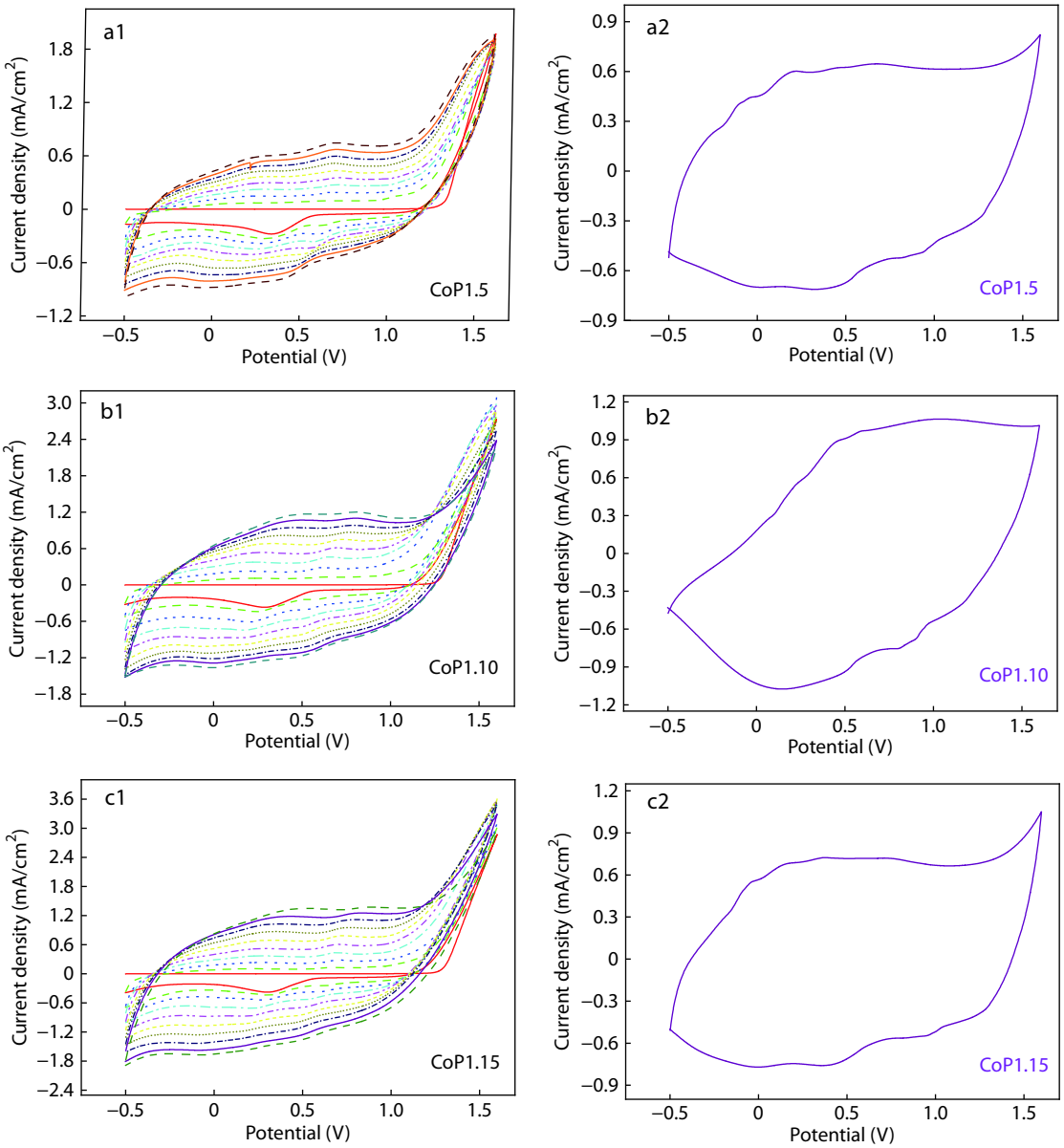


Fig. 2 Cyclic voltammograms of (a1) CoP1.5, (b1) CoP1.10, and (c1) CoP1.15 during the electropolymerization in 0.1 mol/L $TBAPF_6$ DCM/ACN (5/95, *V/V*) solution, and (a2, b2, c2) single scan CVs of the copolymers in a monomer-free medium.

Table 1 Summary of electrochemical and spectroelectrochemical properties of PBT, PP3CA, and corresponding copolymers.

	Monomer feed ratio (M1:EDOT)	$E_{p\text{-doping}}$ (V)	E^{ox}_{onset} (V)	E_{HOMO} (eV)	λ_{max} (nm)	λ_{max}^{onset} (nm)	E_g^{op} (eV)
Polymer (P1)	1:0	1.12	0.91	−5.66	510	700	1.77
PEDOT	0:1	0.30	−0.38	−4.37	583	813	1.53
CoP1.5	1:5	0.22	−0.41	−4.34	565	772	1.61
CoP1.10	1:10	0.24	−0.08	−4.67	579	836	1.48
CoP1.15	1:15	0.20	−0.44	−4.31	595	757	1.64

optical changes upon stepwise doping and the electrochromic properties to learn their applicability in different fields such as electrochromic devices. For further characterization, the copolymers were obtained on ITO working electrode surface *via* CV in 0.1 mol/L DCM/ACN (5/95, *V/V*)-$TBAPF_6$ solvent-electrolyte couple, and spectroelectrochemical analyses were performed using 0.1 mol/L $TBAPF_6$ as the supporting electrolyte in ACN.

Before stepwise oxidation, constant potentials at −0.5 V were applied to all polymer-films to record the true neutral film absorptions *via* removing any trapped charge or ion. After all polymer-coated films were reduced to their neutral states, stepwise oxidation was performed between −0.5 and 0.8 V. Neutral state absorption maxima (λ_{max}) and optical band gap (E_g) of the resulting copolymers are crucial for fur-

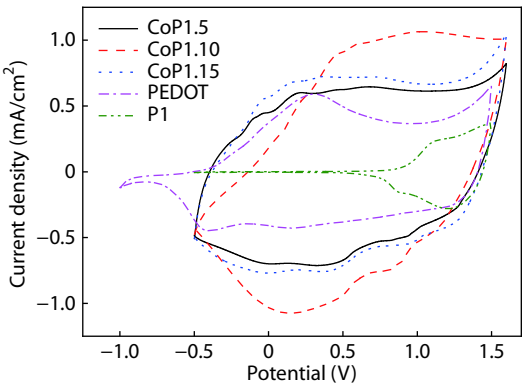


Fig. 3 Single scan cyclic voltammograms for PEDOT, P1, and electrochemically synthesized copolymers of CoP1.5, CoP1.10, and CoP1.15.

ther characterization and can be calculated from spectroelectrochemical analyses. λ_{max} can be defined as the wavelength at which the polymer has π-π^* transition, and they was observed at 565 nm for CoP1.5, 579 nm for CoP1.10, and 595 nm for CoP1.15. The optical band gap (E_g^{op}) values were elucidated from the onset of the neutral state absorptions as 1.61 eV for CoP1.5, 1.48 eV for CoP1.10, and 1.64 eV for CoP1.15.

When electrochemically synthesized azobenzene- and EDOT-bearing copolymers were compared with homopolymers (P1 and PEDOT) in terms of optical behaviors, the effect of electron-rich EDOT unit on the λ_{max} and E_g values can be apparently seen in Table 1. The corresponding λ_{max} values were calculated as 510 nm for P1 and 583 nm for PEDOT with 1.77 and 1.53 eV optical band gaps. As seen, increasing the EDOT amount in monomer feed ratio from 1:5 to 1:15 (M1: EDOT) resulted in a significantly red-shifted neutral state ab-

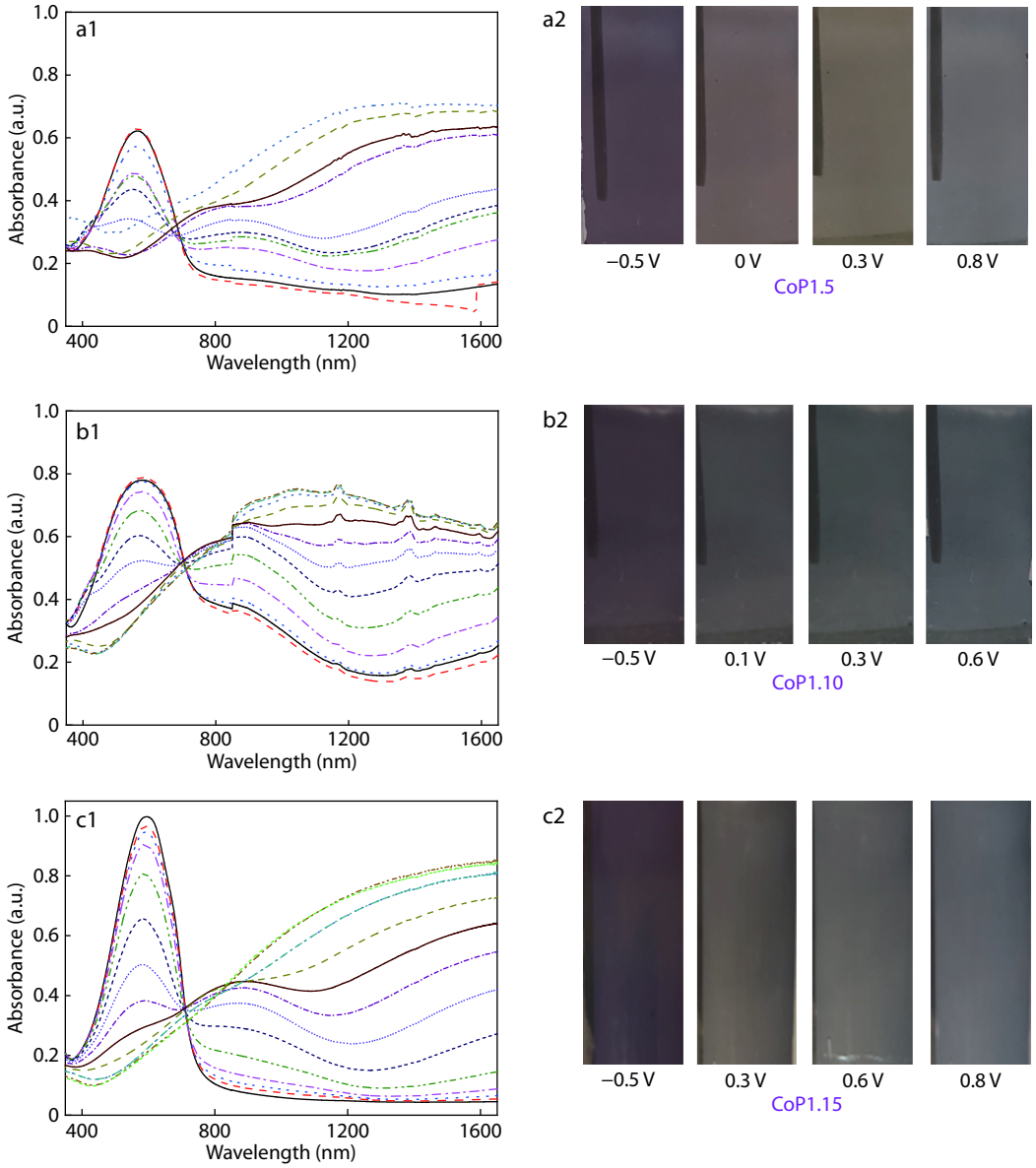


Fig. 4 Spectroelectrochemical studies of (a1) CoP1.5, (b1) CoP1.10, and (c1) CoP1.15 in 0.1 mol/L ACN/TBAPF$_6$ solvent-electrolyte couple and (a2, b2, c2) corresponding colors at neutral/oxidized states with intermediate colors.

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sorption with lower band gap values.

During stepwise oxidation of copolymer films, the intensity of neutral state absorption of each copolymer depleted, which is accompanied by the formation of newly generated bands at around 800 and 1200 nm that indicated the formation of charge carriers, *i.e.*, polarons and bipolarons (Fig. 4).

Furthermore, the photographs of the copolymer films were recorded at different applied potentials for colorimetric determination (Fig. 4). While azobenzene-comprising homopolymer P1 exhibited red color in the neutral state,[24] insertion of EDOT unit resulted in a significantly red-shifted absorption with purple-colored copolymers in neutral state. As seen in Fig. 4, all copolymers had multichromic behavior and they exhibited different tones of purple in the neutral state with blue-colored oxidized states. In addition, while CoP1.5 showed red and brown colors in the intermediate states, CoP1.10 and CoP1.15 had different tones of gray and green as intermediate colors.

Kinetic Studies

Given these promising electrochemical and optical behaviors of

Table 2 Summary of kinetic studies for copolymers.

	Optical contrast (ΔT%)	Wavelength (nm)	Switching time (s)
CoP1.5	43	565	2.4
	56	1550	2.2
CoP1.10	41	580	1.9
	62	1250	2.8
CoP1.15	38	595	2.0
	54	1600	3.1

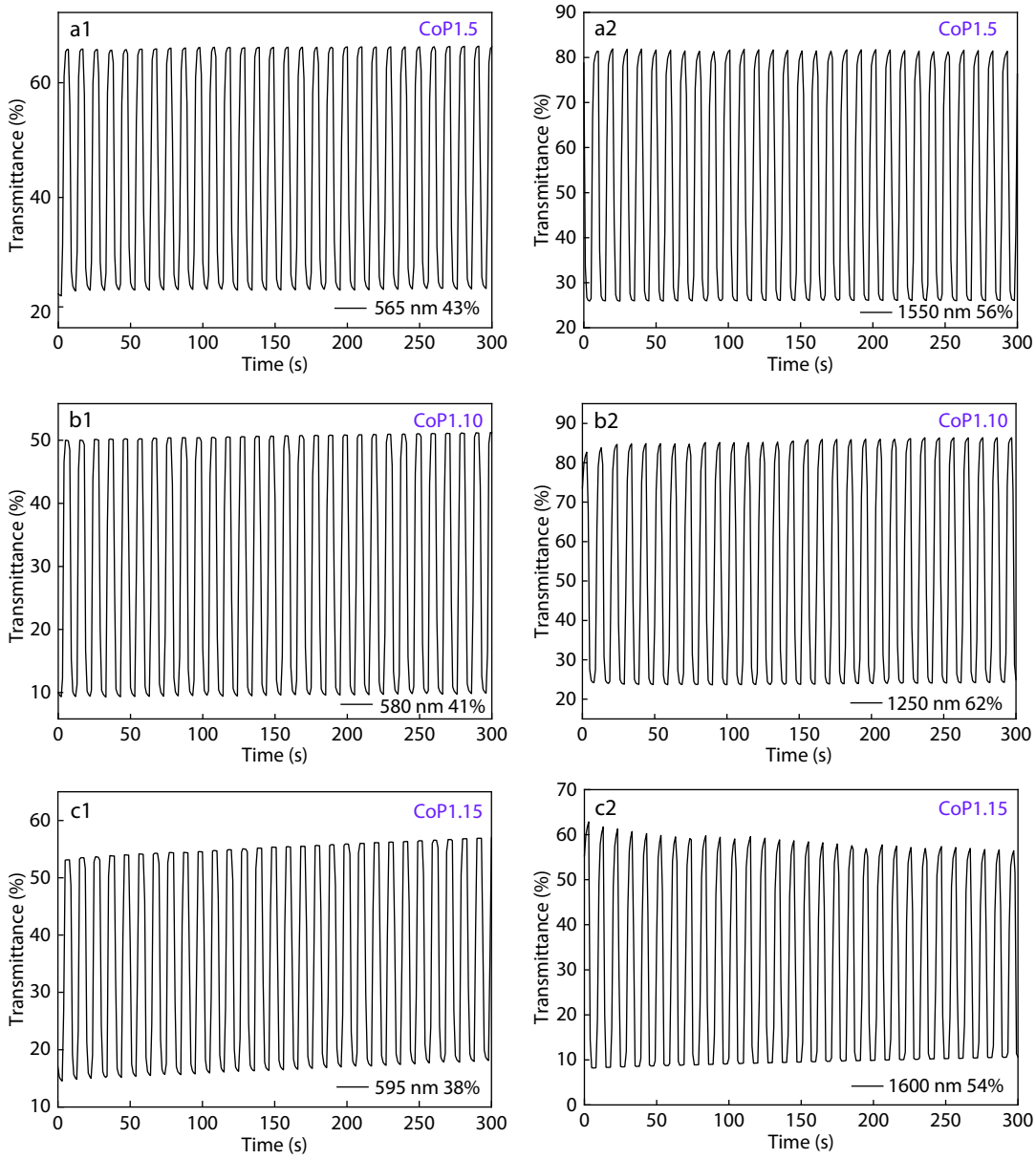

Fig. 5 Optical transmittance changes for CoP1.5 at (a1) 565 nm and (a2) 1550 nm, CoP1.5 at (b1) 580 nm and (b2) 1250 nm, and CoP1.15 at (c1) 595 nm and (c2) 1600 nm in 0.1 mol/L ACN/TBAPF$_6$ solution.

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azobenzene- and EDOT-bearing copolymers, we decided to use them for ECD applications so their kinetic studies were performed to investigate optical contrast and switching time values in the Vis and NIR regions. In order to investigate the switching time and optical contrast values, a square-wave potential method was used by applying –0.5 and 0.8 V potentials with 5 s intervals at λ_{max} values determined from spectroelectrochemical studies as 565 nm/1550 nm for CoP1.5, 580 nm/1250 nm for CoP1.10, and 595 nm/1600 nm for CoP1.15.

While the change in percent transmittance between the two extreme states (neutral and oxidized states) is named as optical contrast, switching time defines the time required for one full switch between two mentioned states of polymers under an external potential. These parameters, which are vital for electrochromic applications, can be calculated from kinetic studies. As summarized in Table 2 and depicted in Fig. 5, while CoP1.5 showed 43% (at 565 nm) and 56% (at 1550 nm) transmittance changes, CoP1.10 revealed 41% (at 580 nm) and 62% (at 1250 nm) transmittance changes, and finally CoP1.15 exhibited 38% (at 595 nm) and 54% (at 1600 nm) optical contrast values upon doping/de-doping processes. Corresponding switching time was calculated at the above mentioned wavelengths as 2.4 and 2.2 s for CoP1.5, 1.9 and 2.8 s for CoP1.10, and 2.0 and 3.1 s for CoP1.15 in the visible and NIR regions.

Kinetic studies strongly supported the argument discussed in the previous parts. As explained before, insertion of EDOT comonomer into the copolymer unit increased the electron density in azobene-based copolymer chain with red-shifted absorption. It is noteworthy to mention that, in the previous study reported by Apaydin *et al.*, the kinetic studies could not be performed for azobenzene- and thiophene-bearing polymers due to the stability problem. In this study, the optical contrast values of azobenzene-derivative copolymers were enhanced significantly with improved stability *via* insertion of EDOT unit into the copolymer chains.[24]

The stability of an electrochromic polymer is a desired property for future applications in commercial electrochro-

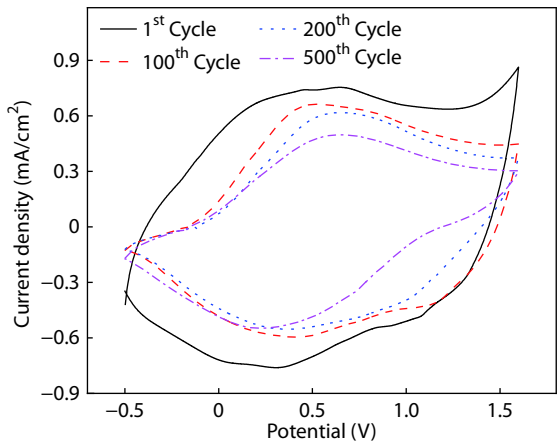

Fig. 6 Stability test of CoP1.5 in 0.1 mol/L $TBAPF_6$/ACN solvent electrocrolyte couple at 100 mV/s.

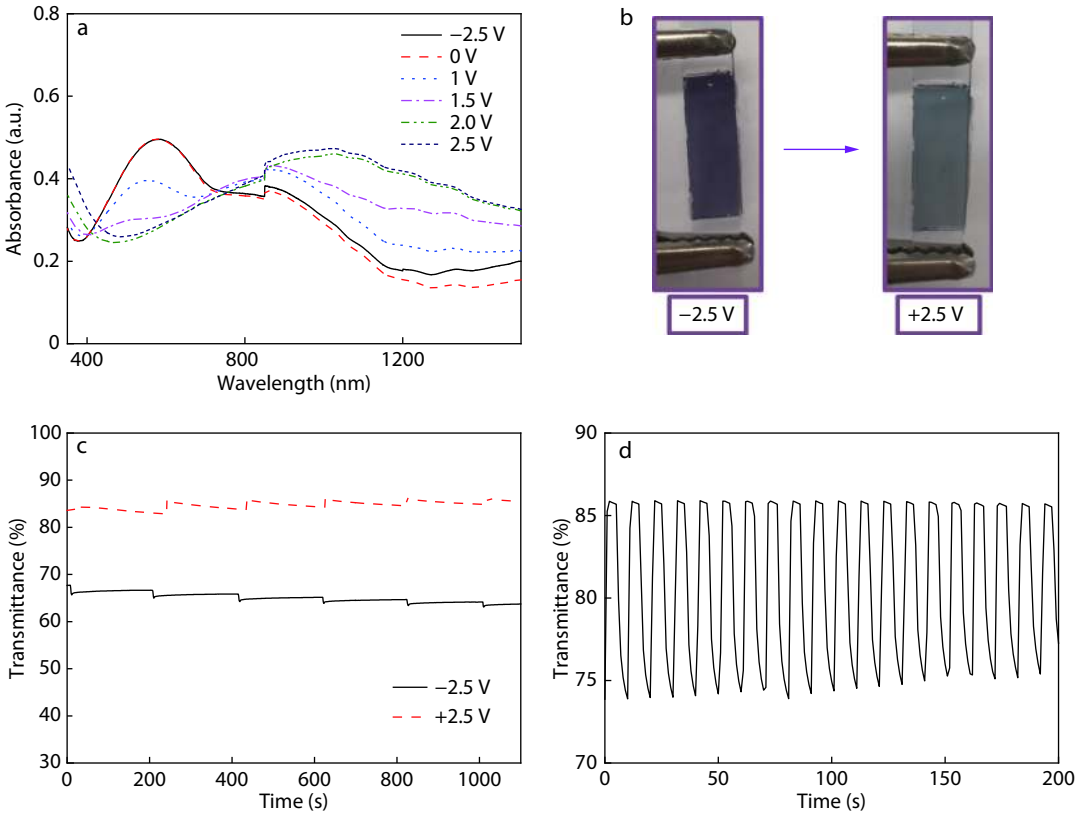

Fig. 7 (a) Spectroelectrochemistry of CoP1.5-based ECD at applied potentials between −2.5 and +2.5 V; (b) Colors of ECD at the two extreme states; (c) Open-circuit memory of ECD at 585 nm; (d) Electrochromic transmittance changes during redox switching of ECD.

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mic devices (ECD) such as smart windows. In order to investigate the stability of azobenzene- and EDOT-bearing copolymer, the polymer was switched between fully oxidized and fully neutral states (−0.5 and 1.5 V) *via* CV. As seen in Fig. 6, CV was recorded in the 100th, 200th, and 500th cycles. The polymer retained 69% of its activity between the 100th and 500th cycles, showing that CoP1.5 had sufficient stability to be a good candidate for a variety of applications such as ECD.

ECD Fabrication and Characterization

As a result of promising electrochemical, electrochromic, and optical behaviors of CoP1.5, herein, the prototype solid state single layer electrochromic device with ITO/CoP1.5/gel electrolyte/ITO device configuration was fabricated and its device properties were examined. Azobenzene- and EDOT-bearing CoP1.5 with 1:5 (M1:EDOT) monomer feed ratio was used as the anodically electrochromic material for ECD construction. The copolymer was electrochemically synthesized on ITO-coated glass electrode as described before and a CoP1.5-based electrochromic device was set up in a sandwich configuration in the presence of gel electrolyte which allowed the electron transfer.

The optoelectronic and electrochromic characterizations of the CoP1.5-based ECD were conducted using a UV-Vis spectrophotometer combined with potentiostat. The electronic absorption spectra, colors between two extreme states, results for open circuit memory, and kinetic studies are reported in Fig. 7.

Incrementally increasing potentials were applied between −2.5 and 2.5 V for spectroelectrochemical characterization and electronic absorption spectra were recorded. As seen in Fig. 7, CoP1.5-based ECD changed between purple and light greenish blue similar to the recorded colors for CoP1.5 films in ACN solution in the neutral and oxidized states. Electronic absorption spectra also proved the colors reported. While ECD exhibited the neutral state absorption centered at 585 nm (at −2.5 V) resulting in purple color, in the oxidized state (at 2.5 V) the neutral state absorption depleated, and new asorption between 600 and 700 nm with small intensity was observed, which led to the light greenish blue color.

Then, as reported in Fig. 7(d), kinetic studies were performed to investigate the optical contrast values of the CoP1.5-based ECD. During the optical contrast determination, double potential step pulses (−2.5 and 2.5 V) were applied within each 5 s and ECD showed 12% and 11% optical contrast values initially and at 200 s with 9% optical contrast loss.

Finally, another crucial parameter of an ECD, namely open-circuit memory of resulting devices, was investigated. This parameter is related to the energy consumption of ECD and can be measured with the time at which the device sustains its color under open circuit conditions.[28,29] Open-circuit memory experiments were performed *via* applying 1 s pulse to the ECD at the two extreme states (+2.5 or −2.5 V) for 200 s at 585 nm (the neutral state absorption maxima of ECD) and simultaneously, percent transmittance was recorded under open-circuit conditions. As seen, the ECD exhibited no significant transmittance change upon time at +2.5 V, and at −2.5 V after open-circuit conditions (200 s) the transmittance decreased from 68% to 63%; the device worked with 7% transmittance loss, which is very low and difficult to detect with naked eye.

CONCLUSIONS

In conclusion, three novel low oxidation potential azobenzene- and EDOT-bearing copolymers were designed, electrochemically copolymerized, and characterized *via* electrochemical and spectroelectrochemical methods. Due to the superior electrochromic and kinetic properties, CoP1.5-based single layer ECD was constructed and characterized. The electrochemically synthesized copolymers (CoP1.5, CoP1.10, CoP1.15) showed superior optical and electrical properties due to increased electron density on the copolymer chain, which caused very low oxidation potentials at around 0.3 V. While the homopolymers P1 and PEDOT showed absorptions at 510 nm and 583 nm, increasing the EDOT amount in the monomer feed ratio from 1:5 to 1:15 (P1:PEDOT) resulted in a significantly red-shifted neutral state absorptions as 565, 579, and 595 nm with lower optical band gap values as 1.61, 1.48, and 1.64 eV. As a result of the red-shifted absorption *via* EDOT insertion into the structure, all copolymers had multichromic behaviors with different tones of purple-colors in the neutral states and blue-colored oxidized states. In terms of kinetic studies, the significant improvements were observed *via* copolymerization. In the previous studies the kinetic parameters could not be calculated for azobenzene- and thiophene-bearing polymers due to the stability problem, whereas CoP1.5 exhibited 43% optical contrast in visible region (at 565 nm) with moderate stability. Finally, CoP1.5 was used for ECD construction, and the single layered device was characterized in terms of electrochemical and spectroelectrochemical features. Resulting ECD worked between −2.5 and +2.5 V and exhibited purple and light greenish blue colors at the two extreme states (neutral and oxidized) with 12% optical contrast.

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