

Covering the More Visible Region by Electrochemical Copolymerization of Carbazole and Benzothiadiazole Based Donor-Acceptor Type Monomers

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Abstract An electrochromic copolymer film of 2-(3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-yl)-7-(3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-8-yl)-9*H*-carbazole (**M1**) and 4,7-bis(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**M2**) was prepared *via* electrochemical technique. The copolymerization was performed with one to one monomer feed ratio. Electrochemical and optical properties of the resulting copolymer film (**P3**) and the homopolymer films of **M1** and **M2** (**P1** and **P2**) were investigated by using cyclic voltammetry and UV-Vis spectrometry techniques, and the corresponding results were compared. Incorporation of **M1** and **M2** into copolymer matrix was clearly observed on the resulting cyclic voltammograms and UV-Vis spectra. **P3** covered the visible regions coming from both **P1** and **P2**, and exhibited a neutral state darker color than those of homopolymers. **P3** film was found to have a multichromic behavior, appearing as brown in its neutral state while changing its color upon oxidation to dark-gray (at about 0.3 V), to blue (at about 0.6 V) and finally to grayish cyan (beyond 0.9 V), with a corresponding optical band gap of 1.65 eV.

Keywords Electrochemical polymerization; Copolymer; Electrochromic polymers

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INTRODUCTION

Electrochromic polymers have gained more attention in past three decades, which are special types of organic materials able to change their colors upon applied potentials. Moreover, the potential difference needed for electrochromism is relatively low and depends on the structure of the polymers. Conjugation in the main chain can be extended by making structural modifications, and the resulting electrochromic polymer can change its color upon lower voltages. Since the corresponding color change is reversible, electrochromic polymers have been used in various applications such as smart windows,^[1,2] car rear views,^[3] displays,^[4–7] biosensors^[8] and many other electrochromic or optoelectronic devices.^[9–17]

During the structure-property studies of conjugated systems, donor-acceptor approach has been found as the most suitable way for structural modification.^[18,19] Combining different donor and acceptor units in the polymer chain creates a special type of copolymer and allows to alter the electrochemical and optical properties of the resulting polymers such as optical band gap, switching time, neutral and oxidized state colors and even solubility.^[20–23]

Another way of structural modification is copolymerization of different donor-acceptor type monomers, in which the incorporation of both molecules can be observed. Copolymerization can be achieved either chemically^[24,25] or electrochemically by using at least two comonomers with different monomer feed ratios in the same solvent. On the other hand, electrochemical copolymerization is an easy and a fast way to synthesize a well adhered copolymer film on an electrode surface and investigate the electro-optical behaviors of the resulting copolymer film. There are various studies about the electrochemical synthesis and characterization of different copolymers *via* electrochemical techniques in the literature.^[26–32]

In this study, a new electrochromic copolymer was synthesized *via* electrochemical techniques using two donor-acceptor type monomers with one to one monomer feed ratio: 2-(3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-yl)-7-(3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-8-yl)-9*H*-carbazole (**M1**) and 4,7-bis(thiophen-2-yl)benzo[*c*]-[1,2,5]thiadiazole (**M2**). The electrochemical and optical characterization of homopolymers, **P1** and **P2**, were previously reported by our group in separate studies.^[33,34] These monomers were selected due to their different optical absorption bands: **M1** and **M2** show the maximum optical absorption at 355 and 445 nm, respectively. When **M1** and **M2** are copolymerized, it is expected that the

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resulting copolymer will have a broader absorption band and exhibit a darker color in its neutral state by covering more visible region as investigated. All the electrochemical and optical results were depicted and discussed.

EXPERIMENTAL

M1 was already synthesized as previously reported and directly used.^[33] **M2** was used as received (Derthon Chemicals). All the other chemicals were purchased from Sigma Aldrich and used without any purification. Tetrabutylammonium tetrafluoroborate (TBABF₄, 0.1 mol/L) in acetonitrile (ACN)/dichloromethane (DCM) was used as an electrolytic medium for polymerizations. ACN and DCM were distilled and purged with nitrogen prior to use. Monomer behaviors and polymer stability were investigated by using Pt disc as working electrode (versus Ag/AgCl reference electrode). Monomers and comonomers were successfully electropolymerized *via* potentiodynamic methods on indium tin oxide (ITO) glass working electrode (versus Ag wire) for electro-optical studies. Spectroelectrochemical measurements were conducted in ACN containing 0.1 mol/L TBABF₄, using a Carry 60 model UV-Vis spectrometer combined with Gamry PCI4/300 potentiostat-galvanostat. ITO (Delta Tech. 8-12, 0.7 cm × 5 cm) coated glass, Pt wire, and Ag wire were used as working, counter, and pseudo reference electrodes, respectively, in spectroelectrochemical studies. Monomer solutions with the same concentration were used, and the cyclic voltammetry was applied for 5 repetitive cycling for all of the electropolymerizations, with the contact area of 1.7 cm² (2.4 cm ×

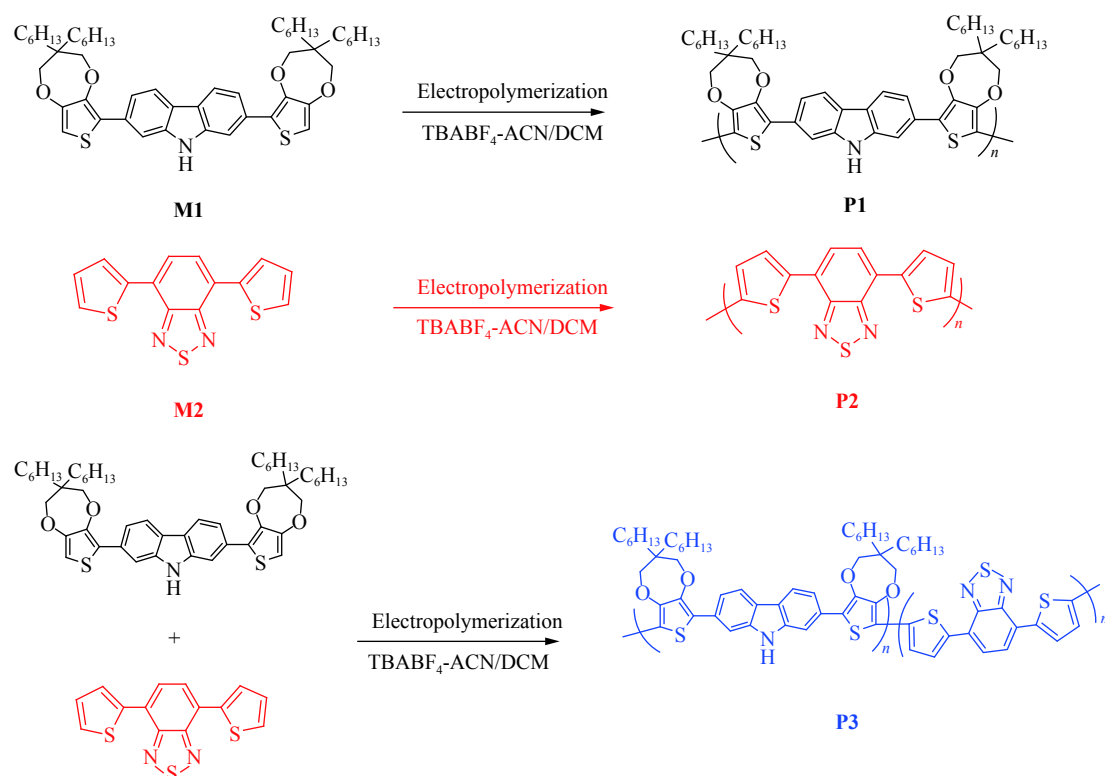
0.7 cm) between the electrolyte and ITO glass working electrode during the cyclic voltammetry tests. Fluorescence emission measurements were conducted on a Varian Cary eclipse fluorescence spectrophotometer.

RESULTS AND DISCUSSION

The molecular structures of the monomers (**M1** and **M2**) and the corresponding copolymerization route are demonstrated in Scheme 1.

In order to examine the electrochemical behaviors, CVs of **M1**, **M2** and one to one (0.015 mol/L-0.015 mol/L) concentrated comonomer mixture (**M3**) were collected in 0.1 mol/L TBABF₄-ACN/DCM (10/1 *V/V*) electrolyte solution. As shown in Fig. 1, the oxidation onset potential ($E_{\text{ox-onset}}$) of **M1** was observed at 0.82 V, having a corresponding oxidation maximum (E_{ox}) at 1.02 V. $E_{\text{ox-onset}}$ and E_{ox} values were recorded at 1.15 and 1.25 V for **M2**, respectively. On the other hand, the first oxidation onset potential of **M3** was measured at 0.83 V with the maximum of the corresponding oxidation peak at 1.12 V, which is probably coming from **M1**. Then **M3** continued to further oxidize by giving a second oxidation peak with the maximum at 1.26 V ($E_{\text{ox-onset}} = 0.93$ V), possibly affected by **M2**.

UV-Vis and emission spectra of the monomers were measured in DCM in order to reveal the optical behavior of the monomers **M1** and **M2** (Fig. 2). The maximum of the electronic absorptions bands of **M1** and **M2** in the visible region appeared at 364 and 445 nm, respectively. Emission spectra of **M1** and **M2** were also measured in DCM, and the resulting spectra are depicted in Fig. 2 (dashed lines). **M1**



Scheme 1 Molecular structures of **M1** and **M2** and the electropolymerization routes

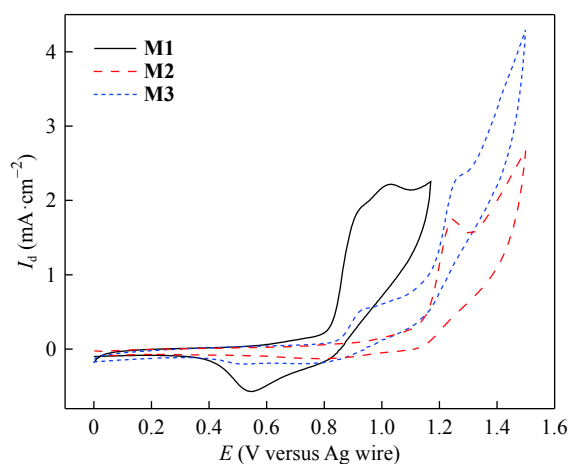


Fig. 1 Cyclic voltammograms of **M1**, **M2**, and the comonomer mixture **M3** (on Pt disc working electrode) in $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBABF₄-ACN/DCM electrolyte solution (at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$) (**M1** was scanned between 0.0 and 1.2 V; **M2** and **M3** were scanned between 0.0 and 1.5 V.)

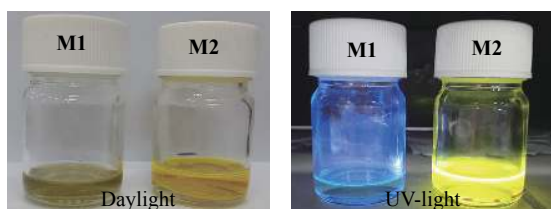
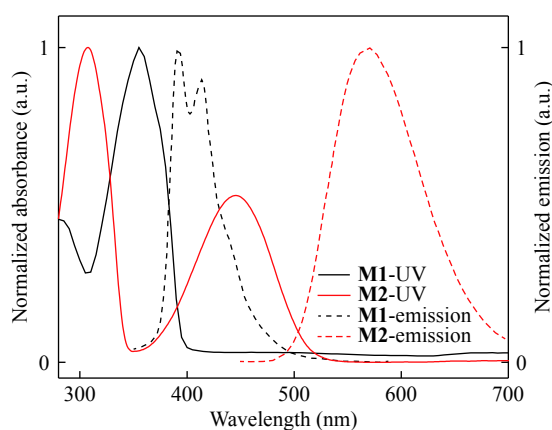


Fig. 2 UV-Vis and emission spectra of **M1** and **M2**, in DCM. Photographs: The colors of the monomer solutions under daylight and under UV light.

gave its emission band with two maxima at 392 and 415 nm (excited at 340 nm). The maximum of the emission spectrum of **M2** was observed at 568 nm (excited at 430 nm). Larger Stoke's shift (122 nm) was observed in **M2** comparing to that of **M1** (about 30 nm), which might indicate the easier intramolecular charge transfer at excited state between donor and acceptor units of **M2**.^[35] A relatively weak donor-acceptor interaction between 3,4-propylenedioxythiophene (PRODOT) and carbazole units may be attributed to the resulting smaller Stoke's shift observed in **M1**.

After determining the electrochemical and optical behaviors of monomers, the electroactive polymer films of **M1**,

M2, and **M3** were prepared on ITO-glass working electrode by performing 5 repetitive cycling in $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBABF₄-ACN/DCM electrolyte solution. CVs during polymerizations were collected and are shown in Fig. 3. During electropolymerizations, the increasing current intensities for homopolymerizations (Figs. 3a and 3b) and copolymerization (Fig. 3c) at each successive scan indicated the polymer formation on the working electrode surface. As shown in Fig. 3, the polymerization behaviors of **M1**, **M2**, and **M3** were observed to be different. After the electropolymerizations were completed, the resulting polymer films (homopolymer of **M1**, **P1**; homopolymer of **M2**, **P2**; and copolymer, **P3**) were washed in ACN to remove the monomeric-oligomeric species from the electrode surface and taken into $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBABF₄-ACN electrolyte solution without monomer. Fig. 3(d) shows the CVs of the resulting polymer films. As shown in Fig. 3(d), the onset oxidation potential for the oxidation of **P3** appeared at 0.57 V, which is found to be positioned between **P1** ($E_{\text{ox-onset}} = 0.47 \text{ V}$) and **P2** ($E_{\text{ox-onset}} = 0.74 \text{ V}$). It can be concluded that the copolymer matrix is affected from the properties of both polymers, which proves the copolymer formation. The same behavior can be observed in the current intensities of the corresponding CVs of the polymers. The copolymer film exhibited lower current intensity compared to **P1** and higher to **P2**, indicating the incorporation of **P1** and **P2** into the copolymer matrix.

UV-Vis spectra of **P1**, **P2**, and **P3** were measured in the monomer-free electrolyte solution of $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBABF₄-ACN, and the combined spectra are shown in Fig. 4. It can be seen that the optical absorption spectrum of **P3** covers the region of the homopolymers, resulting in a broader optical absorption band. The absorption maxima of **P1** and **P2** were found to be at 446 and 563 nm, respectively. For **P3**, on the other hand, the optical absorption band showed two maxima at 459 and 563 nm, which is due to incorporation of **M1** and **M2** into copolymer matrix.

The electro-optical properties of **P1**, **P2**, and **P3** were investigated by monitoring the changes in their electronic absorption spectra as a function of applied potential and the results are depicted in Fig. 5. During the electrochemical oxidations of polymer films on ITO glass working electrode, the intensity of the $\pi \rightarrow \pi^*$ transition band for each polymer decreased, which is accompanied by the appearance of a newly intensifying bands (at about 620 nm for **P1**, 800 nm for **P2**, and 680 nm for **P3**), indicating the formation of charge carriers or polarons (Fig. 5). With further oxidation, a new band beyond 1000 nm was also noted for each polymer most probably due to the formation of bipolarons.^[36] For the copolymer **P3**, the intensity of the first absorption band decreased at first due to the earlier oxidation potential coming from **P1**, and then the intensity of the second absorption band decreased after 0.6 V, which might be the effect of **P2** in the copolymer matrix. Furthermore, two isosbestic points at 510 and 620 nm were detected for **P3**; the former might be considered as the oxidation of **P1** while the latter might be due to oxidation of **P2**. These electrochromic polymers also exhibited color changes owing to the changes in their electronic absorption spectra. **P1** film was observed as yellow in

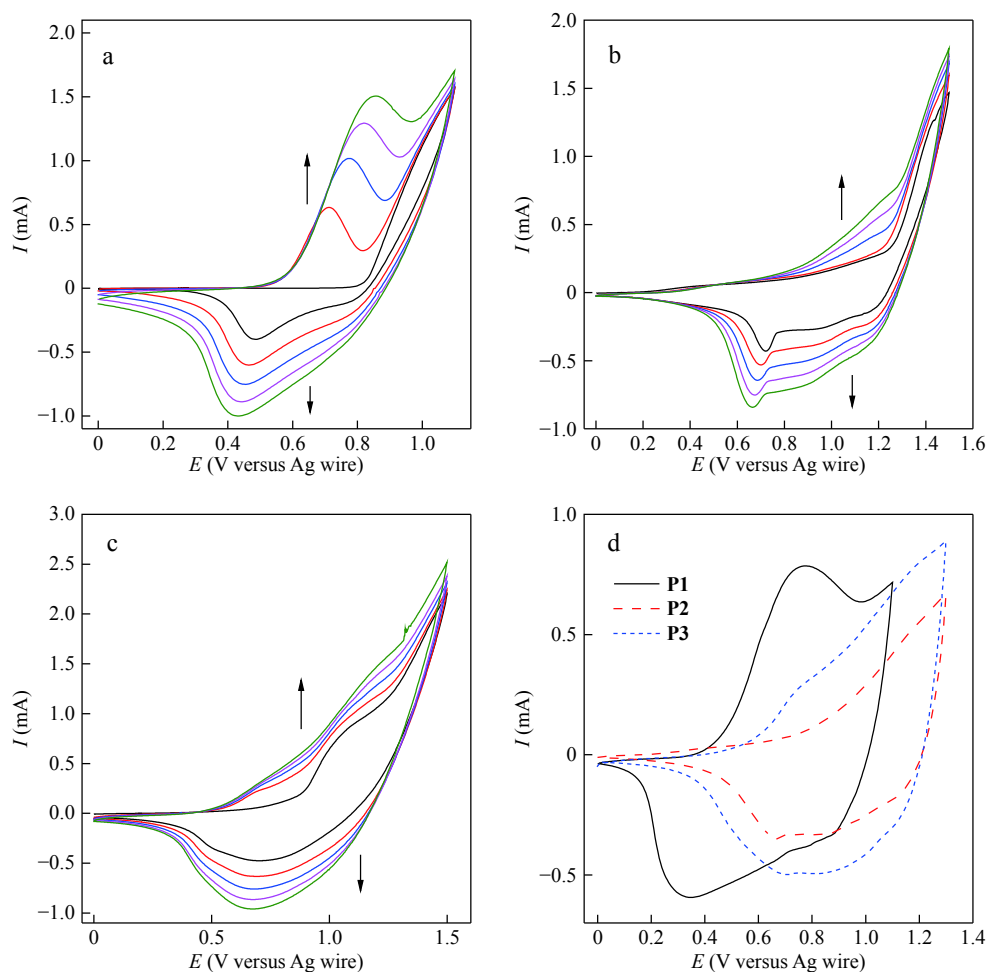


Fig. 3 Cyclic voltammograms of (a) **M1**, (b) **M2**, and (c) **M3** during the electropolymerization on ITO-glass working electrode with applying the potentials between 0.0 and 1.1 V for **M1**, 0.0 and 1.5 V for **M2**, and 0.0 and 1.5 V for **M3** (in $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBABF₄-ACN/DCM, at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$); (d) Cyclic voltammograms of the resulting polymers (**P1**, **P2**, and **P3**), collected in $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBABF₄-ACN, at a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$.

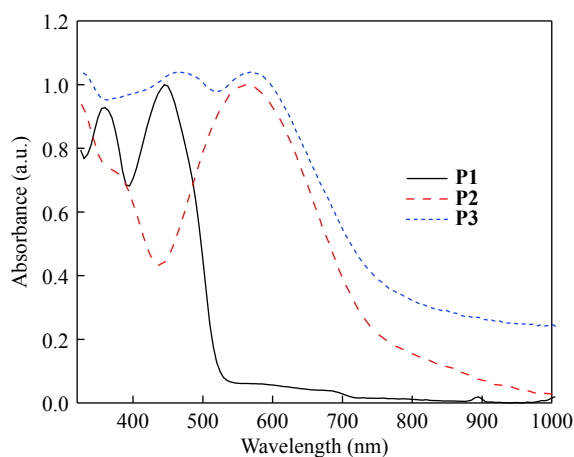


Fig. 4 UV-Vis spectra of **P1**, **P2**, and **P3** on ITO-glass working electrode, measured in $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBABF₄-ACN electrolyte solution

its neutral state. During oxidation, this color began to turn blue in its fully oxidized state. On the other hand, **P2** revealed pale magenta color in its neutral state and became cy-

an in the oxidized state. The copolymer, **P3**, on the other hand, exhibited multichromic behavior: brown in its neutral form, and turned to dark gray (at about 0.3 V), then blue (at about 0.6 V), and finally grayish cyan (beyond 0.9 V) upon oxidation (see the photographs in Fig. 5).

Optical band gap values (E_g) were also elucidated from the commencement of the low energy end at $\pi\rightarrow\pi^*$ transition bands of the polymer films. E_g values were found to be 2.36 eV for **P1** and 1.65 eV for **P2** and **P3**, indicating the existence of both polymer behaviors in the copolymer matrix. As mentioned before, the optical absorption band of **P3** was found to be broader than those of **P1** and **P2**, which might be due to the incorporation of both structures into copolymer matrix. Moreover, **P3** can be oxidized earlier than **P2**, while keeping its optical band gap the same as **P2**. The electrochemical and optical properties of the polymers are also summarized in Table 1.

For an electrochromic polymer, it is important to reveal some other properties such as switching times (t_{ox} and t_{red}), percent transmittance (T%), and coloration efficiency (CE), in order to provide the suitability of the material in the elec-

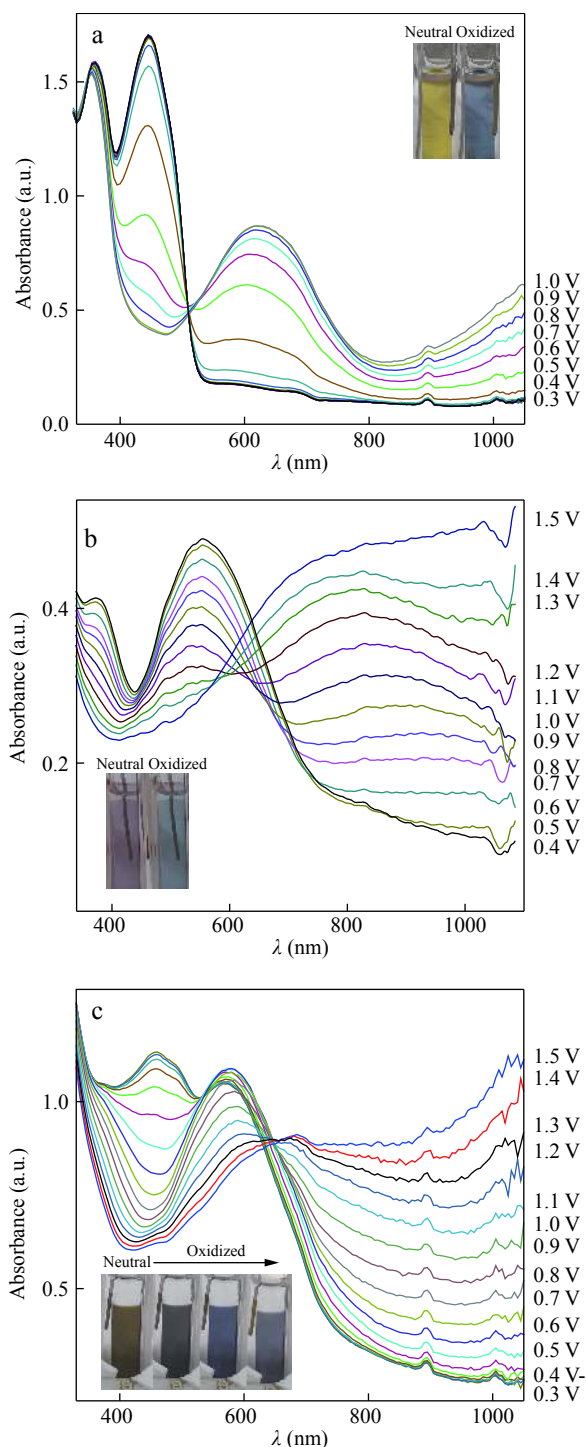


Fig. 5 UV-Vis spectra of (a) **P1**, (b) **P2**, and (c) **P3** on ITO-glass working electrode during a slow oxidation process (scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$) in $0.1 \text{ mol} \cdot \text{L}^{-1}$ TBABF₄-ACN monomer-free electrolyte solution. (Applied potential ranges: **P1**: 0.0–1.0 V; **P2**: 0.0–1.5 V; **P3**: 0–1.5 V. The spectra between 0.0 and 0.3 V may not be seen in the figures due to overlapping.) Photographs: The colors of the corresponding polymer films in their neutral and oxidized states.

trochromic applications. Therefore, kinetic studies were performed to elucidate these properties. The polymer films were subjected to square wave input of corresponding potentials and the visible transmittance was monitored as a function of time. All kinetic results were given at 95% of the full contrast, as human eye is most sensitive. Switching times of the polymer films were elucidated from the obtained transmittance data given in Fig. 6, by measuring the time for the 5th cycles of coloring and bleaching of the polymer films at their specific wavelengths, for 10 s switchings.^[37] For **P1**, t_{ox} and t_{red} values were calculated as 1.4 and 0.8 s, respectively. For **P2**, t_{ox} was calculated as 2.5 s and t_{red} was found to be 0.5 s, indicating a fast reduction of **P2**. On the other hand, t_{ox} and t_{red} values for **P3** were found to be 2.6 and 1.4 s, respectively. It can be concluded that the copolymerization of **M1** and **M2** resulted in a slower oxidation and longer reduction time than that of **P1** and **P2**. This may be due to the value of applied potential on **P3** film during the doping process. **P1** film reached its fully oxidized state at about 1.0 V, while the oxidation of **P2** can be achieved at about 1.3 V. When they were combined in the same chain, the maximum amount of potential was applied in order to see all the color changes in copolymer film. The consecutive oxidations coming from **P1** and **P2** may cause a retardation on **P3**. Moreover, the carbazole and benzothiadiazole acceptor units might have possessed their specific charge transfer abilities in the copolymer matrix.^[33,34]

The percent transmittance values were obtained from the kinetic measurements depicted in Fig. 6. **P1** revealed 34 T% and 12 T% at 446 and 624 nm, respectively (Fig. 6a). For **P2**, T% value was measured as 17 T% at 563 nm and 25 T% at 818 nm (Fig. 6b). **P3** exhibited 13 T%, 10 T%, and 15 T% at the respective wavelengths of 455, 560, and 690 nm (Fig. 6c). Since **P3** had broader optical absorption band, it exhibited darker colors in its neutral and oxidized states compared with **P1** and **P2**, which resulted in a decrease in its percent transmittance change. As shown in Fig. 6(c), the copolymer film was further switched in 10, 5, 3, 2, and 1 s intervals, in order to see the transmittance lost with increasing switching rates. 10 T% loss was observed in 5 s switching and 30 T% loss in 1 s switching intervals. Since the oxidation time of **P3** was greater than 1 s, it was expected that **P3** could be exhausted in subsecond switching rates.

Coloration efficiency (CE) expresses the relationship between the optical absorbance change and charge/discharge density required for a full switch at a specific wavelength, which was calculated by the following equation:^[38]

$$CE = \frac{\Delta OD}{Q_d}, \Delta OD = \lg\left(\frac{T_{\text{bleached}}}{T_{\text{colored}}}\right) \quad (1)$$

where Q_d is injected-ejected charge per cm^2 between neutral and oxidized states, $(T_{\text{colored}}/T_{\text{bleached}})$ is the ratio of

Table 1 Electrochemical and optical properties of the polymer films

Polymer	λ_{max} (nm)	$E_{\text{ox-onset}}$ (V)	$E_{\text{g(optical)}}$ (eV)	CE ($\text{cm}^2 \cdot \text{C}^{-1}$)	Neutral to oxidized colors	$t_{\text{ox}}/t_{\text{red}}$ (s)	Percent transmittance (T%)
P1	446	0.47	2.36	468	Yellow to blue	1.4/0.8	34 at 446 nm
P2	563	0.74	1.65	136	Pale magenta to cyan	2.5/0.5	17 at 563 nm
P3	459/569	0.57	1.65	107	Brown to/gray/blue/grayish-cyan	2.6/1.4	13 at 455 nm

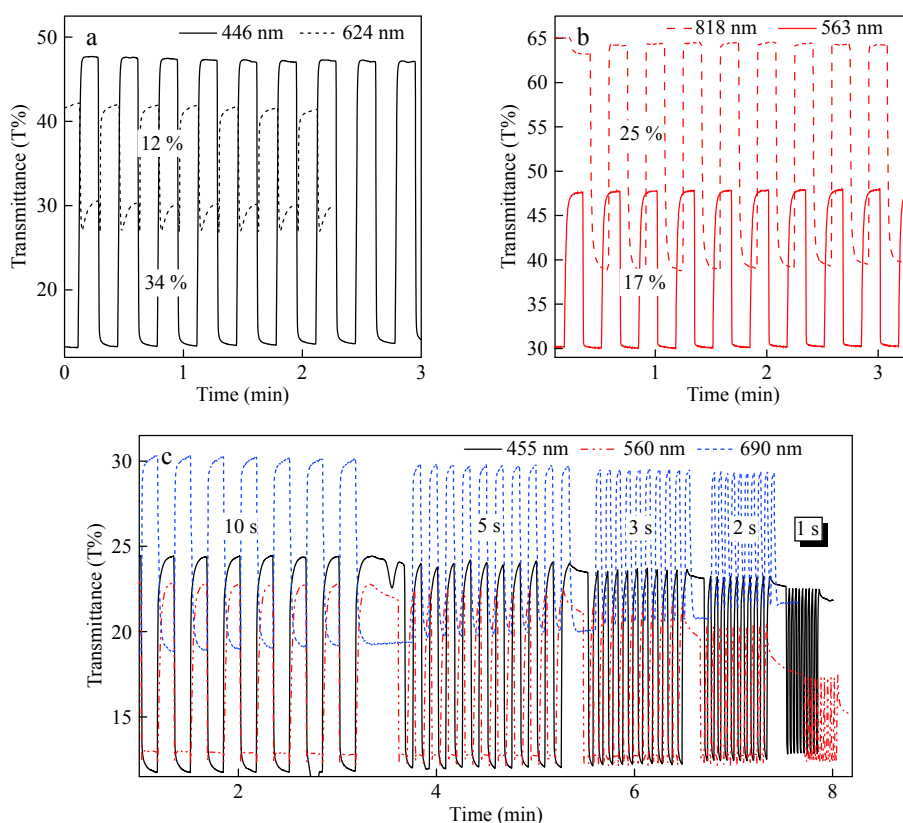


Fig. 6 Kinetic studies performed on the polymer films, measured at (a) 446 and 624 nm for **P1** (The applied potentials are -0.1 and 1.1 V with 10 s intervals), (b) 563 and 818 nm for **P2** (The applied potentials are -0.1 and 1.3 V with 10 s intervals), (c) 455, 560, and 690 nm for **P3** (The applied potentials are -0.1 and 1.3 V with 10, 5, 3, 2, and 1 s intervals for **P3**).

transmittances in the oxidized and neutral states, ΔOD is the optical density of the polymer film.

CE values of **P1**, **P2** and **P3** were calculated as 468, 136, and $107 \text{ cm}^2 \cdot \text{C}^{-1}$, indicating a decrease in coloration ability for copolymer compared with **P1** when the unit charge is injected-ejected between neutral and oxidized states. This can be concluded as the effect of **P2** in the copolymer structure. All other kinetic results are summarized in Table 1.

Electrochemical stability of an electrochromic polymer is also an important property for the electrochromic device applications, indicating the electroactivity of the polymer upon many switchings. Electrochemical stability of **P1**, **P2**, and **P3** films on Pt disc electrode was investigated *via* square wave potential technique. The polymer films were oxidized and reduced repeatedly at 0.0 and 0.9 V for **P1**, and at 0.0 and 1.2 V for **P2** and **P3**, respectively, with 5 s intervals. The CVs before and after 200 switching are given in Fig. 7. Although no remarkable anodic or cathodic peak current loss was observed for **P1**, 0.03 V right-shift in oxidation was detected. For **P2**, 28% anodic and only 1% cathodic loss were observed. For the copolymer, **P3**, 0.2 V of initial oxidation delay occurred in its first oxidation peak. For the second oxidation peak of **P3**, no shift but 27% anodic current loss was observed. As a result, the polymer films retained their electroactivity upon 200 switches. **P1** was found to be the most electrochemically stable upon many switchings. **P3**, on the

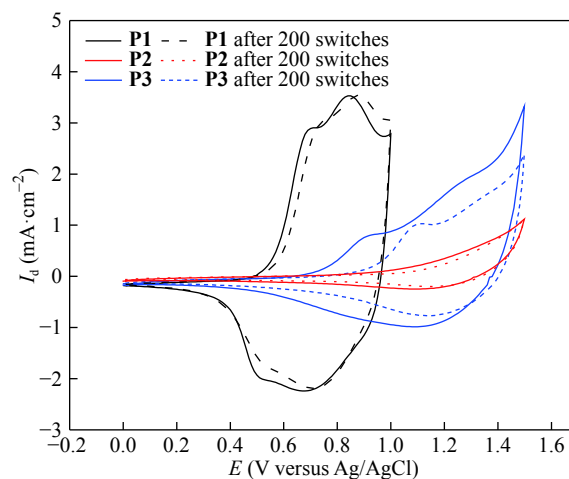


Fig. 7 Cyclic voltammograms of **P1**, **P2**, and **P3** films on Pt disc working electrode at a scan rate of $100 \text{ mV} \cdot \text{s}^{-1}$ in $0.1 \text{ mol} \cdot \text{L}^{-1}$ TBABF₄-ACN before and after 200 switches

other hand, was observed to be exhausted in consecutive redox processes, but still electroactive.

CONCLUSIONS

An electrochromic copolymer synthesis was achieved with two donor-acceptor-donor type conjugated monomers *via* electrochemical technique. **M1** bears carbazole as an

acceptor and dihexylated 3,4-propylenedioxy as a donor. On the other hand, **M2** includes benzothiadiazole as an acceptor and thiophene as a donor unit. **M1** provides a stronger donor and **M2** contributes the stronger acceptor units. The effect of the combination of these units in the same polymer chain was investigated in terms of electrochemical and optical properties. The optical absorption spectrum of the resulting copolymer covered both visible regions absorbed by its corresponding homopolymers. The optical band gap of the copolymer film was found as 1.65 eV, while those of homopolymers were measured as 2.36 eV (**P1**) and 1.65 eV (**P2**). Moreover, the copolymer film exhibited a multi-chromatic behavior and changed its neutral brown color to gray (at about 0.3 V) and then blue (at about 0.6 V) upon oxidation, and finally turned to cyan (beyond 1.0 V) upon further oxidation. Since it has two oxidation region during doping, the copolymer film could not turn to cyan color (the second oxidation region beyond 1.0 V) in reasonable times. As a result, the copolymer film can be a good candidate for electrochromic applications with a narrow band gap, low oxidation potential and exhibiting various colors upon different voltages.

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REFERENCES

- Pennisi, A.; Simone, F.; Barletta, G.; Di Marco, G.; Lanza, L. Preliminary test of a large electrochromic window. *Electrochim. Acta* **1999**, *44*, 3237–3243.
- Rauh, R. Electrochromic windows: an overview. *Electrochim. Acta* **1999**, *44*, 3165–3176.
- Mortimer, R. G. Electrochromic materials. *Chem. Soc. Rev.* **1997**, *26*, 147–156.
- Argun, A. A.; Aubert, P. H.; Thompson, B. C.; Schwendeman, I.; Gaupp, C. L.; Hwang, J.; Pinto, N. J.; Tanner, D. B.; MacDiarmid, A. G.; Reynolds, J. R. Multicolored electrochromism in polymers: structures and devices. *Chem. Mater.* **2004**, *16*, 4401–4412.
- Mortimer, R. J.; Dyer, A. L.; Reynolds, J. R. Electrochromic organic and polymeric materials for display applications. *Displays* **2006**, *27*, 2–18.
- Bradley, D. D. C. Conjugated polymer electroluminescence. *Synth. Met.* **1993**, *54*, 401–415.
- Kelly, F. M.; Meunier, L.; Cochrane, C.; Koncar, V. Polyaniline: application as solid state electrochromic in a flexible textile display. *Displays* **2013**, *34*, 1–7.
- Lee, K.; Povlich, L. K.; Kim, J. Recent advances in fluorescent and colorimetric conjugated polymer-based biosensors. *Analyst* **2010**, *135*, 2179–2189.
- Dance, Z. E. X.; Ahrens, M. J.; Vega, A. M.; Ricks, A. B.; McCamant, D. W.; Ratner, M. A.; Wasielewski, M. R. Direct observation of the preference of hole transfer over electron transfer for radical ion pair recombination in donor-bridge-acceptor molecules. *J. Am. Chem. Soc.* **2008**, *130*, 830–832.
- Sonmez, G.; Sonmez, H. B.; Shen, C. K. F.; Jost, R. W.; Rubin, Y.; Wudl, F. A processable green polymeric electrochromic. *Macromolecules* **2005**, *38*, 669–675.
- Zhou, H.; Yang, L.; Stuart, A. C.; Price, S. C.; Liu, S.; You, W. Development of fluorinated benzothiadiazole as a structural unit for a polymer solar cell of 7% efficiency. *Angew. Chem.* **2011**, *50*, 2885–2998.
- Song, S.; Jin, Y.; Kim, S. H.; Shim, J. Y.; Son, S.; Kim, I.; Lee, K.; Suh, H. Synthesis and characterization of polyfluorenevinylene with cyano group and carbazole unit. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 6540–6551.
- Froehlich, J. D.; Young, R.; Nakamura, T.; Ohmori, Y.; Li, S.; Mochizuk, A. Synthesis of multi-functional POSS emitters for OLED applications. *Chem. Mater.* **2007**, *19*, 4991–4997.
- Usta, H.; Facchetti, A.; Marks, T. J. Air-stable, solution-processable *n*-channel and bipolar semiconductors for thin-film transistors based on the indenofluorenebis(dicyanovinylene) core. *J. Am. Chem. Soc.* **2008**, *130*, 8580–8581.
- Yang, C.; Kim, J. Y.; Cho, S.; Lee, J. K.; Heeger, A. J.; Wudl, F. Functionalized methanofullerenes used as *n*-type materials in bulk-heterojunction polymer solar cells and in field-effect transistors. *J. Am. Chem. Soc.* **2008**, *130*, 6444–6450.
- Malitesta, C.; Losito, I.; Zamboni, P. G. Molecularly imprinted electrochromic polymers: New materials for biomimetic sensors. *Anal. Chem.* **1999**, *71*, 1366–1370.
- John, R.; Spencer, M.; Wallace, G. G.; Smyth, M. R. Development of a polypyrrole-based human serum albumin sensor. *Anal. Chim. Acta* **1991**, *249*, 381–385.
- Duan, C.; Huang, F.; Cao, Y. Recent development of push-pull conjugated polymers for bulk-heterojunction photovoltaics: Rational design and fine tailoring of molecular structures. *J. Mater. Chem.* **2012**, *22*, 10416–10434.
- Zhou, H.; Yang, L.; You, W. Rational design of high performance conjugated polymers for organic solar cells. *Macromolecules* **2012**, *45*, 607–632.
- Durmus, A.; Gunbas, G.; Camurlu, P.; Toppare, L. A neutral state green polymer with a superior transmissive light blue oxidized state. *Chem. Commun.* **2007**, 3246–3248.
- Durmus, A.; Gunbas, G.; Toppare, L. New, highly stable electrochromic polymers from 3,4-ethylenedioxythiophene—bis-substituted quinoxalines toward green polymeric materials. *Chem. Mater.* **2007**, *19*, 6247–6251.
- Mei, J.; Bao, Z. Side chain engineering in solution processable conjugated polymers. *Chem. Mater.* **2014**, *26*, 604–615.
- Kularatne, R. S.; Magurudeniya, H. D.; Sista, P.; Biewer, M. C.; Stefan, M. C. Donor-acceptor semiconducting polymers for organic solar cells. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 743–768.
- Hardeman, T.; Koeckelberghs, G. Synthesis of conjugated polymers by combining different coupling reactions. *Polym. Chem.* **2017**, *8*, 3999–4004.
- Xie, R.; Chen, Z.; Zhang, G.; Huang, Y.; Ying, L.; Huang, F.; Cao, Y. Synthesis and characterization of *p*-conjugated copolymers based on alkyltriazolyl substituted benzodithiophene. *New J. Chem.* **2016**, *40*, 4727–4734.
- Akbayrak, M.; Cansu-Ergun, E. G.; Onal, A. M. Synthesis and electro-optical properties of a new copolymer based on EDOT

- and carbazole. *Des. Monomers Polym.* **2016**, *19*, 679–687.
- 27 Nie, G.; Qu, L.; Xu, J.; Zhang, S. Electrosyntheses and characterizations of a new soluble conducting copolymer of 5-cyanoindole and 3,4-ethylenedioxythiophene. *Electrochim. Acta* **2008**, *53*, 8351–8358.
- 28 Aydın, A.; Kaya, I. Syntheses and characterization of yellow and green light emitting novel polymers containing carbazole and electroactive moieties. *Electrochim. Acta* **2012**, *65*, 105–114.
- 29 Aydın, A.; Kaya, I. Syntheses of novel copolymers containing carbazole and their electrochromic properties. *J. Electroanal. Chem.* **2013**, *691*, 1–12.
- 30 Ates, M.; Uludag, N. Carbazole derivative synthesis and their electropolymerization. *J. Solid State Electrochem.* **2016**, *20*, 2599–2612.
- 31 Carbas, B. B. Novel electrochromic copolymers based on 3-3'-dibromo-2-2'bithiophene and 3,4-ethylenedioxythiophene. *Polymer* **2017**, *113*, 180–186.
- 32 Zhou, W.; Xu, J.; Wei, Z.; Pu, S. Electrochemical copolymerization of dibenzofuran and 3-methylthiophene in boron trifluoride diethyl etherate. *Chinese J. Polym. Sci.* **2008**, *26*, 81–90.
- 33 Cansu-Ergun, E. G.; Onal, A. M. Carbazole based electrochromic polymers bearing ethylenedioxy and propylenedioxy scaffolds. *J. Electroanal. Chem.* **2018**, *815*, 158–165.
- 34 Cansu-Ergun, E. G.; Akbayrak, M.; Akdag, A.; Onal, A. M. Effect of thiophene units on the properties of donor-acceptor type monomers and polymers bearing thiophene-benzothiadiazole-scaffolds. *J. Electrochem. Soc.* **2016**, *163*, 153–158.
- 35 Zhao, H. P.; Tao, X. T.; Wang, F. Z.; Ren, Y.; Sun, X. Q.; Yang, J. X.; Yan, Y. X.; Zou, D. C.; Zhao, X.; Jiang, M. H. Structure and electronic properties of triphenylamine-substituted indolo[3,2-*b*]carbazole derivatives as hole-transporting materials for organic light-emitting diodes. *Chem. Phys. Lett.* **2007**, *439*, 132–137.
- 36 Bakalis, J.; Cook, A. R.; Asaoka, S.; Forster, M.; Scherf, U.; Miller, J. R. Polarons, compressed polarons, and bipolarons in conjugated polymers. *J. Phys. Chem. C* **2014**, *118*, 114–125.
- 37 Kumar, A.; Welsh, D. M.; Morvant, M. C.; Piroux, F.; Abboud, K. A.; Reynolds, J. R. Conducting poly(3,4-alkylenedioxythiophene) derivatives as fast electrochromics with high contrast ratios. *Chem. Mater.* **1998**, *10*, 896–902.
- 38 Beaujuge, P. M.; Reynolds, J. R. Color Control in *p*-conjugated organic polymers for use in electrochromic devices. *Chem. Rev.* **2010**, *110*, 268–320.