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ARTICLE

Substituent and Heteroatom Effects on the Electrochromic Properties of Similar Systems

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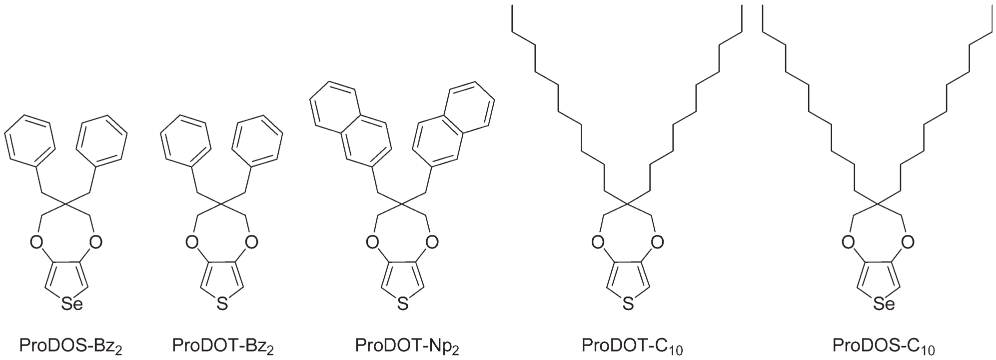
ABSTRACT: Electrochromic polymers called poly(3,4-dihydro-3,3-bis ((naphthalen-1-yl)methyl)-2H-thieno[3,4-b][1,4]dioxepine) (PProDOT-Np_2), poly(3,3-dibenzyl-3,4-dihydro-2H-selenopheno [3,4-b][1,4]dioxepine), and poly(3,3-dibenzyl-3,4-dihydro-2H-thieno [3,4-b][1,4]dioxepine) were synthesized electrochemically and the effect of substituents and heteroatoms on the electrochromic properties were investigated for the similar systems. All polymers show electrochromism from a colored state when neutralized to transmissive when oxidized. Although, increasing bulky size (PProDOT-Np_2) causes lower coloration efficiency (CE) as well as lower optical contrast, the replacement of S atom by Se atom resulted in a lower band gap polymer with a higher CE than its thiophene analog. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 615–621, 2012

KEYWORDS: conducting polymers; conjugated polymers; electrochemistry; electrochromism; polyselenophenes; 3,4-propylenedioxyselenophenes; ProDOS; redox polymers

INTRODUCTION Electrochromism is defined as a visible color change under external applied potentials, which is one of the most important properties of conjugated polymers and thanks to easy synthesis and tunable intrinsic properties (i.e., electrical and optical), a lot of distinct and saturated colors like blue,[1–3] green,[3–7] and black[8–10] were reported in the neutral state. These features make them promising candidates for displays,[11] smart windows,[12,13] electrochromic devices,[14–16] mirrors,[17,18] and camouflage materials.[19–21] Among organic electrochromic polymers, polythiophenes and their alkylenedioxythiophene derivatives[22] have attracted considerable interest because of their multicolor changes in the same structure, long cycle life, high optical contrast ratio, film forming properties as well as fast switching time, and low operation voltage, when compared to inorganic materials and other polymers. The optical and electrical properties of organic electrochromic polymers are very crucial in determining their use. Therefore, it is very important to control the optical and electrical properties of the conjugated polymers and there have been extensive research on this issue. Reynolds and coworkers[23] reported the effect of ring size and substituent on electrochromic properties. They conjectured that increasing the bridge size and rigidity of substituents on 3,4-alkylenedoxythiophene-based polymers causes higher optical contrast ratio ($\Delta\%T$), as the interchain separation improves the charge/discharge ability of the counter anion during doping process. On the basis of foregoing results, Kumar and coworkers[24] reported a new electrochrome based on dibenzyl substituted poly(3,4-propylenedioxythiophene) (PProDOT-Bz_2) with 89% at $\lambda_{\max} = 632$ nm (no information was given about polymer thickness) of the highest optical contrast reported to date. Because of the inspiration of the results and the solubility problem, different aromatic and alkyl analogs were synthesized by the same group[25] and unfortunately, all optical contrast values were found to be lower than 89%. Interestingly, in the same study, the optical contrast of PProDOT-Bz_2 was given as 76%, which caused some questions in mind about the optical contrast of PProDOT-Bz_2. On the other hand, Bendikov and coworkers recently reported a novel electrochrome based on 3,4-ethylenedioxyselenophene. When compared to poly(3,4-ethylenedioxythiophene), the replacement of S atom by Se atom results in a lower band gap polymer (PEDOS, poly(3,4-ethylenedioxythiophene), 1.4 eV) with lower oxidation potential (1.4 V vs. Ag/AgCl) and somewhat higher stability (it retained almost 83% of its electroactivity after 5000 cycles).[26] Unexpectedly, monohexyl substituted PEDOS (poly(3,4-propylenedioxyselenophene)) polymer was reported as the second polymer bearing the highest optical contrast (89%) at 763 nm.[27] It can be easily concluded that the kind of heteroatom in the same system significantly affects the intrinsic properties of the obtained polymer. Under the light of these findings, recently, we reported blue to

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Chemical structures of aryl and alkyl substituted ProDOT and ProDOS monomers: ProDOS-Bz$_2$, ProDOT-Bz$_2$, ProDOT-Np$_2$, 3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (ProDOT-C$_{10}$), and ProDOS-C$_{10}$.

highly transmissive soluble electrochromes based on dialkyl substituted poly(3,4-propylenedioxyselenophene)s (PProDOSs).[2,28] Although the contrast ratios of the polymers are less than their thiophene analogs, they have lower band gaps, higher coloration efficiencies, and higher redox stabilities.

Inspired by the results, in this study, we try to investigate systematically the effect of substituents and heteroatoms on the electrochromic properties in the similar systems. To achieve this aim, a series of substituted PProDOS- and poly(3,4-propylenedioxythiophene) (PProDOT)-based electrochromes were polymerized electrochemically (Scheme 1).

RESULTS AND DISCUSSION

From the viewpoint of device and high performance display applications, spectroelectrochemical properties of the electrochromes should be manifested using the changes in electronic absorption spectra under a voltage pulse. Therefore, UV–vis spectra of poly(3,3-dibenzyl-3,4-dihydro-2H-selenopheno[3,4-b][1,4]dioxepine) (PProDOS-Bz$_2$), PProDOT-Bz$_2$, and poly (3,4-dihydro-3,3-bis((naphthalen-1-yl)methyl)-2H-thieno[3,4-b][1,4]dioxepine) (PProDOT-Np$_2$) films electrodeposited on indium-tin oxide (ITO) glass were monitored in an electrolyte solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) in acetonitrile (ACN).

As shown in Figure 1, especially neutral PProDOS-Bz$_2$ and PProDOT-Bz$_2$ films have similar optical spectra bearing some vibronic coupling indicating highly regular polymer backbones[25] or various conjugation lengths within the polymer structure.[29] The band gap (E_g) values were calculated from the onset of the lowest energy end of the π–π^* transitions and found to be as 1.62 eV for PProDOS-Bz$_2$, 1.86 eV for PProDOT-Bz$_2$, and 1.85 eV for PProDOT-Np$_2$ (Table 1). As shown in Table 1, the polymer films based on ProDOS monomers distinctly have lower band gaps and also, it can be concluded that there is no any appreciable change in the band gap value by changing substituents.

As expected from an electrochromic polymer, during oxidation, π–π^* transition bands start to disappear and a concomitant increase in near infrared region is observed due to the formation of charge carriers. On further oxidation, π–π^* transition bands completely diminished and the polymer films exhibited different colors. PProDOS derivatives exhibit pure blue color due to the absence of absorbance between 400 and 500 nm when neutralized and are transparent when oxidized, whereas PProDOT derivatives, except for PProDOT-Np$_2$, have dark blue/violet color in their neutral states and are transparent in their oxidized states. PProDOT-Np$_2$ shows a color change from purple to transmissive during p-doping.

The transmittance change of the polymer films were monitored at their absorption maxima for potential steps of 10 s (square-wave potential steps of 10 s) and the change in percent transmittance, $\Delta T\%$, (optical contrast) was calculated between colored and bleached states (Table 1). Although the optical contrast value of PProDOT-Bz$_2$ is lower than reported in the literature (89% at 632 nm),[24] it is in well agreement with the value reported by Kumar and his coworkers[25] in their second publication (PProDOT-Bz$_2$; 18 mC/cm^2) as 78% at 634 nm elsewhere.

PProDOT-Bz$_2$ (10.28 mC/cm^2) has 75% of optical contrast and this value decreases to 67% when the S atom was replaced by Se atom (PProDOS-Bz$_2$; 14.80 mC/cm^2) (Fig. 2 and Table 1). In this study, we replaced benzyl groups in ProDOT-Bz$_2$ with naphtyl groups to increase the interchain separation in its polymer, PProDOT-Np$_2$, for easier dopant ion transport, which is expected to give higher optical contrast as it was previously reported by Kumar and his coworkers.[24] Unfortunately, the increasing rigid and bulky substituent on ProDOT-based polymers gave lower optical contrast as 63% when compared to PProDOT-Bz$_2$. An inspection of Table 1 reveals that almost the same optical contrast value (73%) can be obtained using flexible alkyl chains, PProDOT-C$_{10}$ (poly(3,3-didecyl-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxephine), instead of bulky groups. As a result, it can be safely concluded that it is not necessary to use bulky substituent to increase the optical contrast value, as flexible alkyl chains can also do the same job with additional advantage of bringing solubility.

Also, among the polymer films, PProDOS-Bz$_2$ film exhibited the largest coloration efficiency (CE, at 95% of the full contrast) as 992 cm^2/C, and it can be concluded that PProDOS derivatives with rigid bulky groups or flexible alkyl chains have generally larger CE values when compared to PProDOT derivatives.

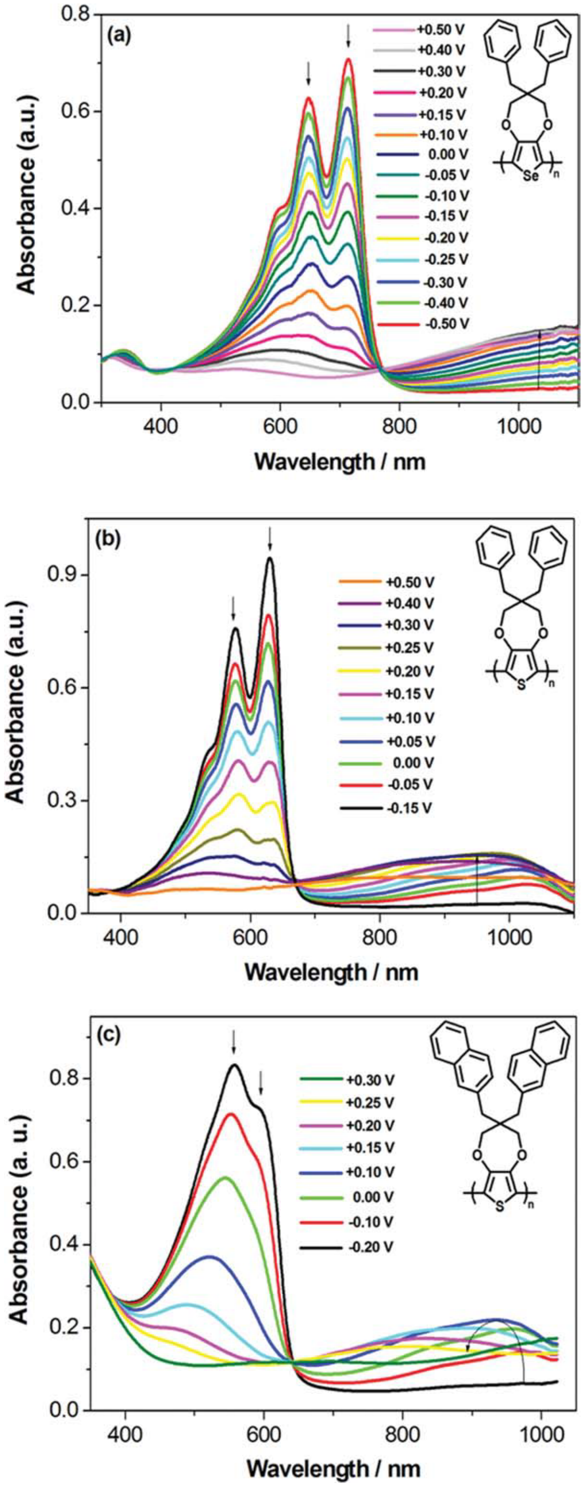


FIGURE 1 Optical absorption spectra of (a) PProDOS-Bz_2, (b) PProDOT-Bz_2, and (c) PProDOT-Np_2 on ITO in 0.1 M TBAH/ACN at various applied potentials.

The appearance of the new redox couples indicates the formation of the new products on the electrode surface and these redox couples were intensified after each successive scan, which indicates both an increasing thickness and the formation of electroactive polymer films, namely PProDOS-Bz_2, PProDOT-Bz_2, and PProDOT-Np_2 (Fig. 3).

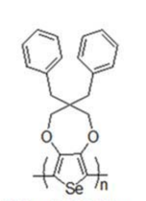
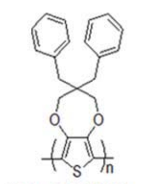
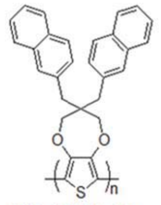
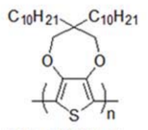
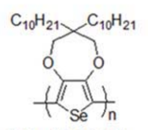
Redox behaviors of the polymers were investigated in the monomer free electrolyte solution containing 0.1 TBAH and ACN. During anodic scan reversible redox couples were observed and the currents of these couples increase linearly as a function of scan rate, indicating the well-adhered polymeric film on the electrode surface and nondiffusional redox process (Supporting Information, Fig. S5).

All polymers have a robust structure under ambient conditions, as they retain their electroactivity after thousands of switching between their redox states via a square wave potential method. Stability of the polymers was controlled via cyclic voltammetry. As shown in Figure 4, ProDOS-Bz_2, ProDOT-Bz_2, and ProDOT-Np_2 retain 89%, 67%, and 63% of their electroactivities, respectively, after 5000 switchings (Fig. 4). On the other hand, poly(3,3-didecyl-3,4-dihydro-2H-selenopheno[3,4-b][1,4]dioxepine) (PProDOS-C_{10}) exhibited the highest electrochemical stability with 97% of its electroactivity after 5000 switchings, whereas PProDOT-C_{10} retains 68% of its electroactivity after 5000 switchings. In the light of these findings, one can conclude that the polymer films based on ProDOS units are exceptionally more stable than their ProDOT analogs under ambient conditions.

EXPERIMENTAL

All chemicals were purchased from Aldrich Chemical and used as received unless otherwise noted. TBAH (0.1 M) dissolved in distilled dichloromethane (DCM, under CaH_2 and N_2 atmosphere) was used as an electrolyte solution. Platinum disc (0.02 cm^2) and platinum wire electrodes were used as working electrode and counter electrode, respectively. A Ag/AgCl electrode in 3 M NaCl (aq) solution was used as a reference electrode. The polymer films were obtained both by repetitive cycling and constant potential electrolysis. After electropolymerization, the working electrode was washed with DCM to remove the nonpolymerized monomers and then the film was transferred into 0.1 M TBAH/DCM electrolyte solution. *In situ* optical properties were investigated using an ITO (Delta. Tech. 8–12 Ω, 0.7 × 5 cm^2) electrode in a UV cuvette. A platinum wire and Ag wire electrodes were used as counter electrode and pseudoreference electrode, respectively. The polymer films coated on ITO had been switched between the neutral and oxidized states several times to break-in the polymer films before electrochemical and electro-optical analysis were applied. Electroanalytical measurements were performed using a Gamry PCI4/300 potentiostat–galvanostat and the electro-optical spectra were monitored on a Hewlett–Packard 8453A diode array spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer and chemical shifts were given relative to tetramethylsilane as the internal standard. FTIR spectra were recorded on Nicolet 510 FTIR with attenuated total reflectance. Photographs of the polymer film were taken using a Canon (PowerShot A75) digital camera. Colorimetric

TABLE 1 Electrochemical and Optical Properties of PProDOS and PProDOT Derivatives

Polymers		 PProDOS-Bz$_2$		 PProDOT-Bz$_2$		 PProDOT-Np$_2$		 PProDOT-C$_{10}$		 PProDOS-C$_{10}$	
E^{onset}_{mon} (V)		1.37		1.42		1.40		1.55		1.39	
$E^{ox}_{p,1/2}$ (V)		0.28		0.41		0.14		0.35		0.35	
Stability (After 5000 switching)		89		67		63		68		97	
Δ%T		67% at 645 nm		75% at 630 nm		64% at 630 nm		73% at 622 nm		56% at 636 nm	
CE(cm^2 /C)		992		551		337		306		328	
E$_g$		1.62		1.86		1.85		1.82		1.58	
λ$_{max}$		645, 710		575, 630		559, 630		571, 622		636,697	
Colors		Neut	Ox	Neut	Ox	Neut	Ox	Neut	Ox	Neut	Ox
	From Picture										
	From L*a*b* values										
L*		57.32	91.74	38.32	90.85	66.54	89.01	54.88	84.40	73.72	91.80
a*		-13.21	-6.20	23.23	-1.83	21.22	0.88	7.51	0.40	-11.81	-1.49
b*		-42.74	-0.45	-59.29	0.91	-22.29	-1.16	-31.27	2.54	-20.23	3.80

measurements were recorded on Specord S600 (standard illuminator D65, field of width 10° observer) and color space was given by the International Commission of Illumination with luminance (*L**), hue (*a**), and intensity (*b**). Platinum cobalt DIN ISO 621, iodine DIN EN 1557, and Gardner DIN ISO 6430 are the references of colorimetric measurements.

Synthesis of 3,3-Dibenzyl-3,4-dihydro-2H-selenopheno[3,4-b][1,4]dioxepine

Like ProDOT-Np$_2$, synthesis of ProDOS-Bz$_2$ was done by the standard transetherification reaction between 3,4-dimethoxyselenophene[26] (5) and 2,2-dibenzylpropane-1,3-diol[24] (6) as shown in Scheme 2. To an argon degassed solution of 3,4-dimethoxyselenophene (200 mg, 1.05 mmol) and 2,2-dibenzylpropane-1,3-diol (537 mg, 2.1 mmol) in 40 mL dry toluene, *p*-toluenesulfonic acid (PTSA, 20 mg, 0.105 mmol) were added. The mixture was heated under reflux during 24 h. After cooling to room temperature, the solvent was removed under reduced pressure. Using the solvent ratio of 2 hexane:1 DCM, the crude product was purified via column chromatography to give ProDOT-Bz$_2$ as a light pink solid with 40% yield (see Supporting Information, Figs. S1 and S2).

^{1}H NMR (400 MHz, CDCl$_3$, δ(ppm)): 7.23–7.10 (m, 10H,Ar H), 6.9 (s, 2H,Ar H), 3.75 (s, 4H), 2.77 (s, 4H); ^{13}C NMR (100 MHz,CDCl$_3$, δ(ppm)): 151.4, 136.65, 130.7, 128.2, 126.5, 109.1, 45.2, 39.7.

Synthesis of 2-((Naphthalen-2-yl)methyl)-2-((naphthalen-3-yl)methyl)propane-1,3-diol (3)

Na (0.46 g; 20.08 mmol) was added in 30 mL ethanol and mixed up to all Na was dissolved. Then, 1 g (6.18 mmol) diethyl malonate (1) was added to this solution and reaction mixture was heated. After the observation of the reflux, 5.2 g

(22.56 mmol) of 2-(bromomethyl)naphthalene was added and the mixture was heated under reflux during 24 h. Ethanol was removed under reduced pressure, cold water was added and extracted with cold ether. The crude mixture was chromatographed on silica gel by eluting with ethyl acetate: hexane (1:20, v/v) to diethyl 2-((naphthalen-2-yl)methyl)-2-((naphthalen-3-yl)methyl)malonate (2) as a white solid with a 39% yield (Scheme 3). Then, 1.07 g of 2-((naphthalen-2-yl)methyl)-2-((naphthalen-3-yl)methyl)malonate (2) was dissolved in 100 mL THF (tetrahydrofuran) and 175 mg (4.3 mmol) lithium aluminum hydride was added to this solution under inert atmosphere. The mixture was heated under

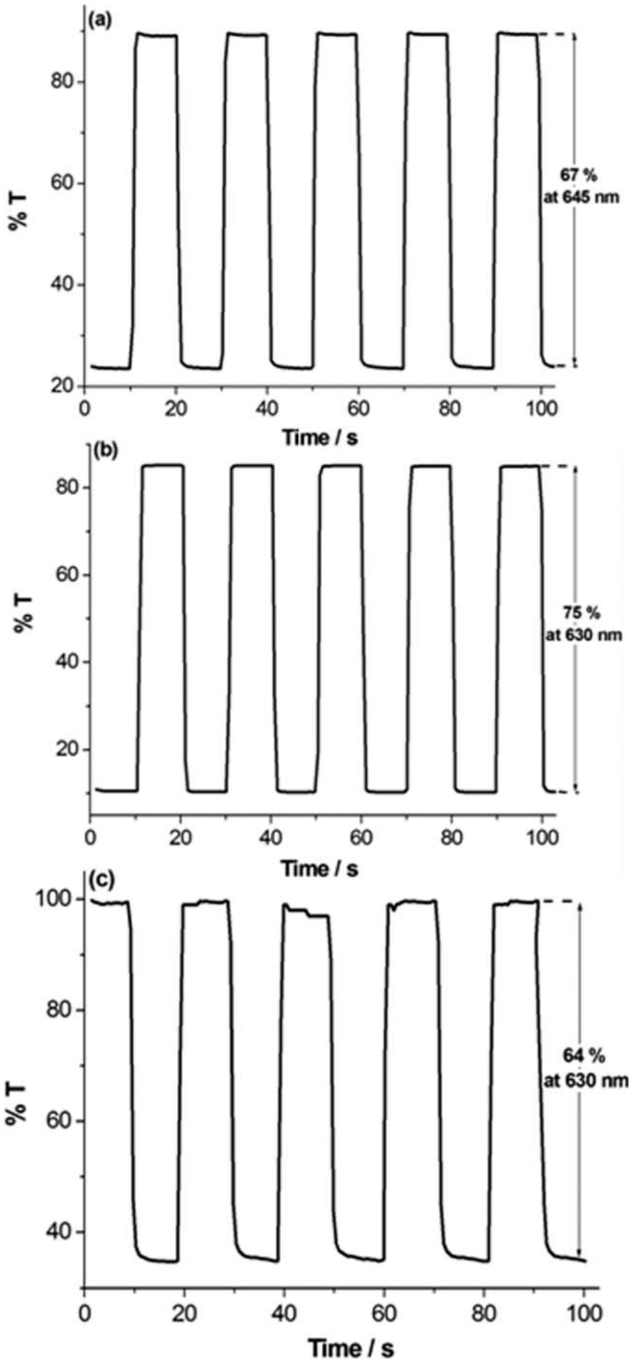


FIGURE 2 Chronoabsoptometry experiments for (a) PProDOS-Bz_2, (b) PProDOT-Bz_2, and (c) PProDOT-Np_2 films on ITO in 0.1 M TBAH/ACN when the polymers switched between redox states.

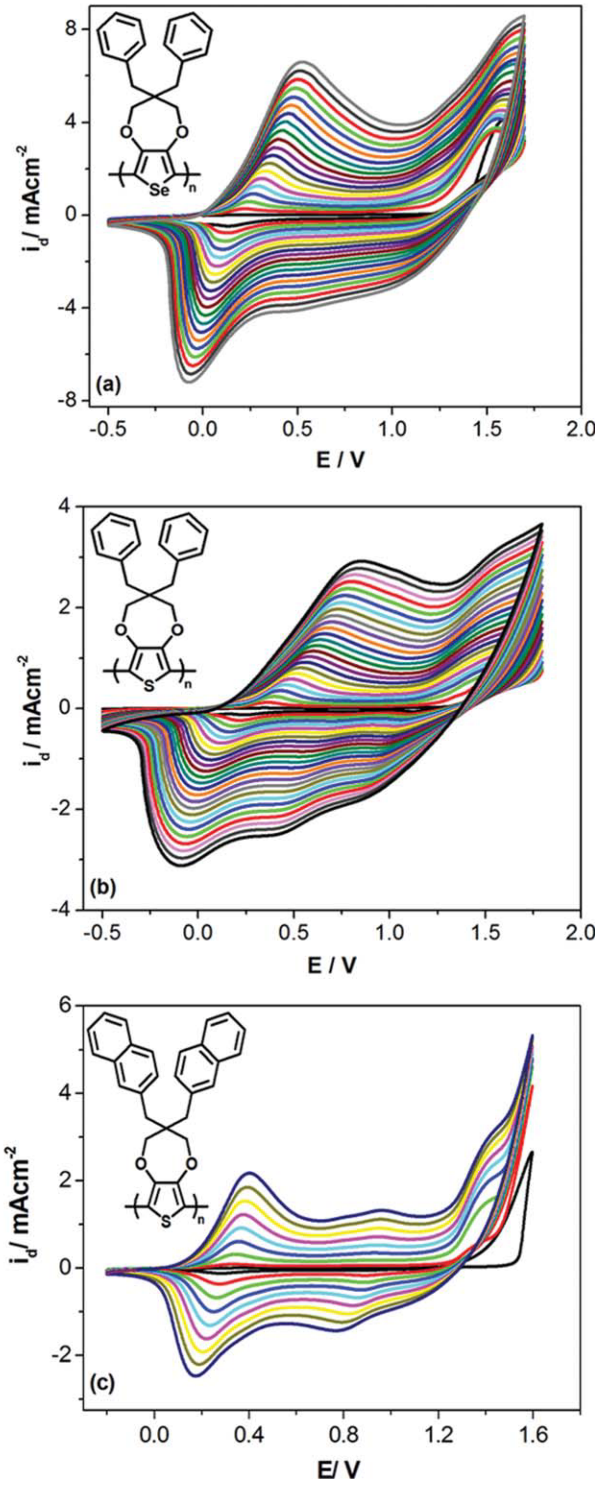


FIGURE 3 Electropolymerization of 1.0×10^{-2} M (a) ProDOS-Bz_2, (b) ProDOT- Bz_2, and (c) ProDOT-Np_2 in 0.1 M TBAH/DCM at a scan rate of 100 mV/s versus Ag/AgCl.

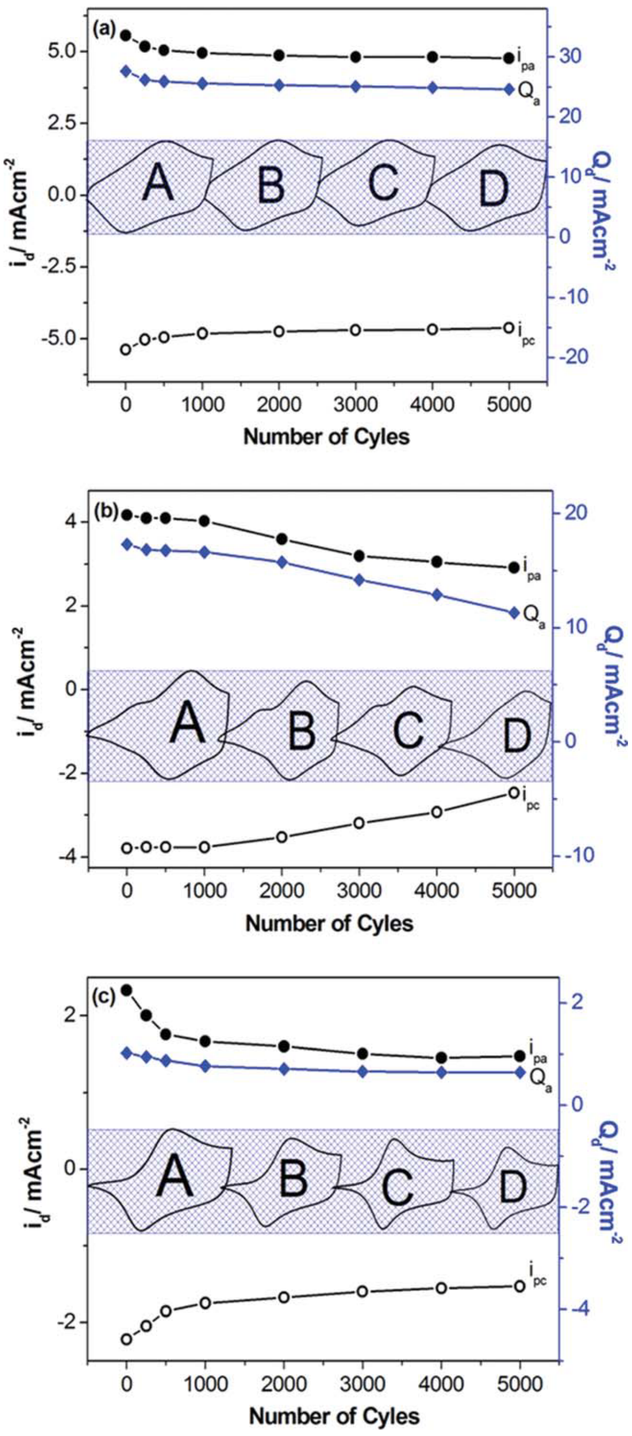


FIGURE 4 Electrochemical stability of PProDOS-Bz$_2$, PProDOT-Bz$_2$, and PProDOT-Np$_2$ after 5000 switching by a square wave potential method with a 2 s interval at each redox state. i_{pa}: Anodic peak current, i_{pc}: cathodic peak current, and Q_a: anodic charge deposited (calculation of stabilities had been done according to Q_a values).

reflux during 14 h. THF was removed under reduced pressure, water was added and extracted with ether. The crude product was used without further purifications. **2**: ^{1}H NMR (400 MHz, CDCl$_3$, δ(ppm)): 7.3–7.8 (m, 14H,Ar H), 4.13 (q, 4H, $J = 7.2$ Hz), 3.44 (s, 4H), 1.26 (m, 6H); ^{13}C NMR (100 MHz,CDCl$_3$, δ(ppm)): 171.12, 134.02, 133.40, 132.52, 129.19, 128.36, 127.79, 127.72, 127.66, 126.09, 125.75, 61.42, 60.44, 39.61, 13.96.

3: ^{1}H NMR (400 MHz, CDCl$_3$, δ(ppm)): 7.84–7.27 (m, 14H,Ar H), 3.67 (s, 2H), 2.97 (s, 2H), 1.43 (br, 2H).

Synthesis of 3,4-Dihydro-3,3-bis((naphthalen-1-yl) methyl)-2H-thieno[3,4-b][1,4]dioxepine

The ProDOT-Np$_2$ was synthesized by the standard transetherification reaction between 3,4-dimethoxythiophene (4) and 2,2-dinapthyllpropane-1,3-diol (3) as shown in Scheme 2. To an argon degassed solution of 3,4-dimethoxythiophene (182 mg, 1.25 mmol); 2,2-dinapthyllpropane-1,3-diol (890 mg, 2.5 mmol) and PTSA (24 mg, 0.125 mmol) were mixed in dry toluene (50 mL) and the mixture was heated under reflux during 24 h. After cooling to room temperature, the solvent was removed under reduced pressure. The crude product was purified via column chromatography using the solvent ratio of 3 hexane:1 DCM to give ProDOS-C$_{10}$ as yellow viscous liquid in 55% yield (see Supporting Information, Figs. S3 and S4).

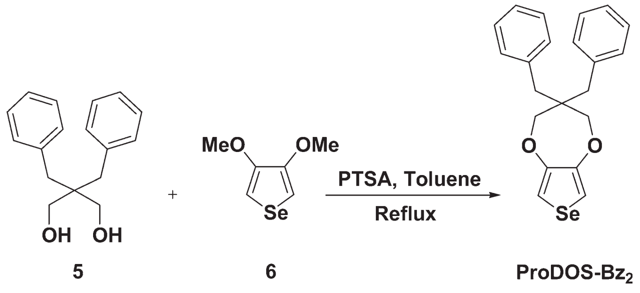
^{1}H NMR (400 MHz, CDCl$_3$, δ(ppm)): 7.38–7.73 (m, 10H,Ar H), 6.45 (s, 2H,Ar H), 3.89 (s, 4H), 2.99 (s, 4H); ^{13}C NMR (100 MHz,CDCl$_3$, δ(ppm)): 152.1, 135.8, 132.1, 133.4, 129.6, 127.8, 125.8, 125.2, 106.4, 105.2, 46.7, 41.2.

The rest of the monomers were synthesized in the same manner and we ended up with five different monomers, as shown in Scheme 1.

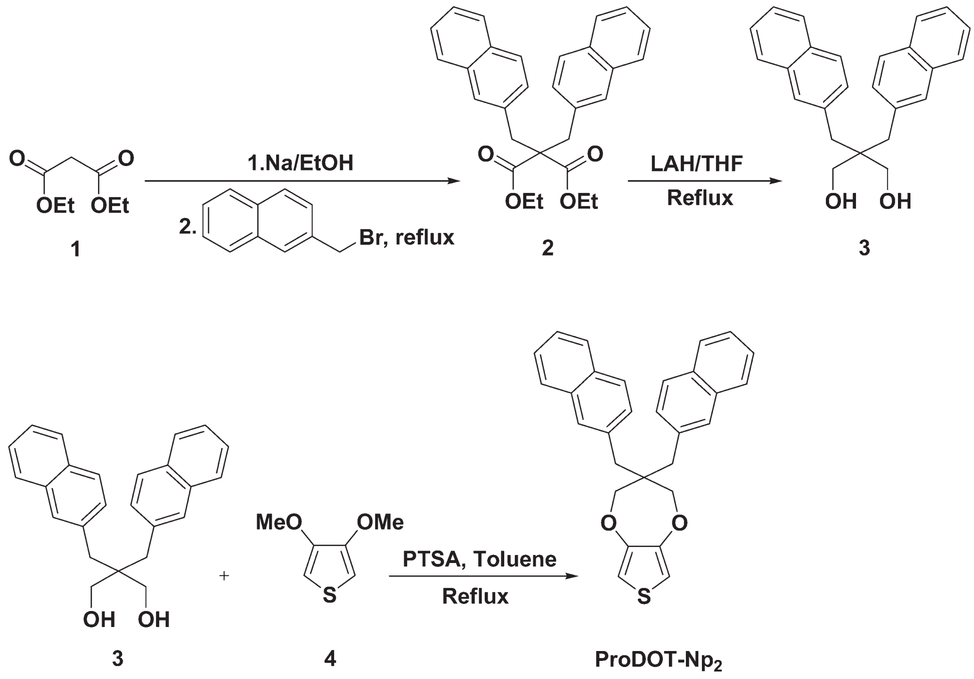
CONCLUSIONS

In this study, different derivatives of 3,4-propylenedioxythiophene/selenophene having different substituent groups were synthesized electrochemically and the effect of substituents and heteroatoms on the electrochromic and optical properties were investigated. The results of chronoabsoptometry experiments indicated that increasing the bulkiness of the substituent does not increase the optical contrast of the obtained polymer.

Therefore, instead of using bulky substituents, flexible alkyl substituents can also be used. Thus, using flexible alkyl groups will not only increase the optical contrast value but also will enhance the solubility of corresponding polymer.



SCHEME 2 Synthesis of dibenzyl propylenedioxyselenophene, ProDOS-Bz$_2$.



SCHEME 3 Synthesis of dinapthyl propylenedioxythiophene, ProDOT-Np$_2$.

The crucial point to mention is that the two different contrast values, 89% and 78%, for ProDOT-Bz$_2$ were reported in the literature.[24,25] However, from our repetitive experiments a contrast values of 75% was obtained for ProDOT-Bz$_2$. Although this value is lower than the formerly reported one,[24] it is almost similar with the latter one.[25]

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