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Graphical Abstract

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Abstract

A series of phenantrene centered donor-acceptor type electroactive 3,4-ethlenedioxythiophene (EDOT) monomers (EP-X) containing N, S and Se heteroatom on the bezophenantra-X-diazole acceptor unit have been synthesized by Stille coupling reaction. These monomers were electrochemically polymerized by potentiodynamic method to obtain electrochromic polymer films. Spectro-electrochemical properties were also investigated by UV-vis absorption connected with the cyclic voltammetry measurements. The polymer films exhibited a remarkable trend of visible color (yellow, orange, red) at the neutral state due to changing the central acceptor moiety. These polymer films have multielectrochromic properties by means moderately changing the of absobance/transmitance at the visible regime upon applied positive potentials. The donor-acceptor interaction at the neutral state correlated by DFT calculations was also supported by the interesting trend in the colors of these polymers. Finally, the electrochromic performance of EP-X polymer films represented a high redox stability, reasonable contrast ratio, coloration efficiency and response times.

Keywords: Electrochromic polymers, Phenantrene, EDOT

1. Introduction

Electrochromism is one of the important properties of the electroactive materials that can be defined as reversible and visible change in color of such materials under an externally applied potential.[1] Studies and interest on the electrochromic materials have been increasing due to their potential applications, such as information storage, [2] electrochromic displays, [3] optical switch, [4] smart windows[5, 6], antiglare mirrors [7, 8] and camouflage materials[9, 10]. Despite the fact that the first studies about electrochromic materials started with the inorganic semiconductors (e.g. metal oxide materials) [11, 12]. Recently organic semiconductors have been more popular than the inorganic ones due to their some superior features such as low driving voltage, high coloration efficiency and low cost [13]. The main advantage of organic materials in electrochromic technology are simple and inexpensive in the solution processing thin film formation[14, 15]. Another advantage is the observation of different colors in these materials between their redox steps under applied potentials [16, 17]. Among organic electrochromic materials, conjugated polymers have superior characteristics due to their excellent color efficiency[18], fast color change capacity[19], observation of many colors in same material [20] and the ability to adjust band gap values by modifying chemical structure of the material [21]. Although many studies are realized with electrochromic polymers, their commercialization has not been widespread yet. Long term stability is the main problem of the polymeric electrochromic materials like other polymers that use in the such applications [22]. Planar structures like perylene [23, 24], phenantrene [25], xanthene [26] and pyrene[27, 28] are good candidates to improve the stability of thin film based organic electrochromic devices due to rigidity and strong π -stacking interactions on the film surface. These type polymers were also used in the other optoelectronic applications such as organic field effect transistors (OFETs)[29], organic light-emitting diodes (OLEDs)[30] and organic photovoltaic devices (OPVs)[31].

Poly(3,4-ethylenedioxithiophene) (PEDOT) and its derivatives are widely used in electrochromic materials due to low oxidation potential and good film forming ability [32, 33]. PEDOT derivatives is the one of the most important member of the neutral state blue electrochromic materials. Another important property of PEDOT derivatives is high transmissivity at the oxidized state[34]. These properties provide that PEDOT and its derivatives are very interesting members for electrochromic application to complete the RGB main color space [35, 36]. Furthermore, in order to complete CMYK color space, PEDOT based donor-acceptor polymers are generally used in the literature[37].

Herein, a series of planar phenantra-X-diazole centered donor acceptor monomer with EDOT moiety were synthesized. Furthermore, optical, electrochemical properties and also electrochromic performance were compared according to differentiated acceptor center moieties. The stepwise red shift was observed both absorbance and photoluminescence of the donor-acceptor monomers by changing the acceptor ability. Because of this property, the neutral state color on the thin film surface was varied from yellow to red. All polymer films have multielectrochromic behaviors in order to intensify the new band in the visible regime upon applied positive potential. Cihaner et al. was also synthesized EDOT-benzothiadiazole based donor acceptor polymer to investigate the donor-acceptor interaction effect on the electrochromic performance [21]. In this work, the center planarity of the donor-acceptor electrochromic polymers is expanded for the first time by using phenantrene center unit instead of phenylene. Kinetic study reveals that all electrochromic EP-X polymer films are very stable against the applied sequential potential between oxidized and reduced state.

2. Experimental

2.1. Materials

All chemicals supplied from Aldrich and TCI Chemical Co. were used without further purification. Phenantrene centered EDOT electroactive monomers were prepared according to synthetic route on the Scheme 1. Synthetic procedures of initial compounds, M1-4 were given in the Supporting Information.



a) NH₂OH.HCl,pyridine/ethyl alcohol, 130 C, 3 h; b) Pd/C,ethyl alcohol, 110 °C, 3 h; c) for M3-N---i)Acetic acid, NaNO₂, ii) methanol,potassium tertbutoxide, 60 °C, 12 h; for M3-S: S₂Cl₂, DMF, 2 h, r.t.; for M3- Se: SeO₂, Ethyl Alcohol, 80 °C, 2 h. d) NIS, H₂SO₄, r.t., 2 h; e) Pd(PPh₃)₄, Toluene, 110 °C, 5 h;

Scheme 1. Synthetic route to EP-X monomers

2.2. Synthesis of 5,10-bis(3,4-ethylenedioxythienyl)phenantro[9,10-c][1,2,5]-X-azole (EP-X) monomers

M4-X (0.5 mmol), 2-(tri-n-butylstannyl)-3,4-ethylenedioxythiophene (0,7 g, 1.5 mmol) and 15 mL toluene were added in a 100 ml flask and stirred under argon atmosphere, for 30 min. After adding the Pd(PPh₃)₄ (5 mol %) as a catalyst, the reaction mixture was refluxed at 110°C for 24 h. Finally, the reaction mixture was cooled and precipitated in 500 mL of ethanol. Column chromatography [silica gel, CHCl₃:Hexane (1:1)] was carried out for the final purification. The pure yellow product (EP-X) was obtained and then dried at 40 °C in vacuum oven.



EP-X, X: -N- C_6H_5 , S, Se

EP-N; (yellow powder; 0,19 g; yield:37%); ¹H-NMR (CDCl₃): δ ppm, 6.04 (a,2H, H_{aa}'); 8.03 (d, 2H, H_{bb}'); 7.5 (d, 2H, H_{cc}'); 8.84 (d, 2H, H_{dd}'), 4,26 (t, H_{ee}', 2H), 4.66 (t, 4H, -CH₂-); 2.44 (m, 8H, -CH₂-); 1.61 (m, 4H, -CH₂); 1.25 (m, 8H, -C₂H₄-); 0.88 (t, 6H, -CH₃).

EP-S; (yellow powder; 0,20 g; Yield:45%); ¹H-NMR (CDCl₃): δ ppm, 6.04 (d, 2H, H_{aa}'); 7.95 (d, 2H, H_{bb}'); 7.61 (d, 2H, H_{cc}'), 8.71(d, 2H, H_{dd}'), 4.25 (t, 2H, H_{ee}'), 4.26 (t, 2H, H_{ff}').

EP-Se; (yellow powder; 0,25 g; Yield:52%); ¹H-NMR (CDCl₃): 6.04 (d,2H, H_{aa}'); 8.14 (d, 2H, H_{bb}'); 7.42 (d, 2H, H_{cc}'), 8.76 (d, 2H, H_{dd}'), 4.25 (t, 2H, H_{ee}'), 4.30 (t, 2H, H_{ff}').

2.3. Instrumentation

FT-IR spectra were measured by a Perkin Elmer FT-IR Spectrum Two by using an ATR attachment (4000-650 cm⁻¹). ¹H-NMR (Bruker Avance DPX-400) data were recorded at 25 °C by using TMS as internal standard and CHCl₃-d as solvent. CH Instruments 617D electrochemical workstation was used in the cyclic voltammetry and chronoamperometry measurements. The electrochemical cell consists of platinum disk (0.02 cm²) as a working electrode (WE), a Pt wire as counter electrode (CE), a Ag wire as reference electrode (RE) immersed in 0.1 M TBAPF₆ in CH₂Cl₂ as the supporting electrolyte. All measurements were carried out under argon atmosphere. Oxidation and reduction potential onsets of EP-X monomers and polymers calibrated to the ferrocene redox couple $E^{o}(Fc/Fc+) = +0.41$ V were used for the calculation HOMO-LUMO energy levels, and the potentials. Analytic Jena Speedcord S-600 diode-array spectrophotometer was used in the UV-Vis absorption and spectro-electrochemical measurements. The optical band gap (E_g) of EP-X monomers and polymers were calculated from their absorption edges. The spectro-electrochemical cell consist of a quartz cuvette, an Ag wire as RE, Pt wire counter electrode as CE and ITO/glass as transparent WE. These measurements were carried out in 0.1 M TBAPF₆ as supporting electrolyte in acetonitrile (ACN). Colorimetry measurements were carried out by using the same spectrophotometer which consisted of a chromameter module (standard illuminator D65, field of with 10° observer) with viewing geometry as recommended by CIE. According to the CIE color measurements system, the color is obtained of three attributes; luminance (L), hue (a), and saturation (b). Platinum cobalt DIN ISO 621, iodine DIN EN 1557, and Gardner DIN ISO 6430 are the references of colorimetric measurement [38]. These parameters were measured for the neutral and oxidized states of the polymers on the ITO/glass surface. To investigate surface morphology of the EP-X polymer films, a Nanosurf Naio-AFM were used at room temperature and ambient condition., the non-contact mode was used in this system to obtain phase and topographic images. The system was covered by acoustic chamber to avoid electromagnetic noises.

2.4. Electrochemical polymerization of EP-X monomers

Electrochemical polymerization of EP-X monomers were carried out by using potentiodynamic method. During the electrochemicaly coating process, the peak currents intensified after each cycle between the redox potentials of the EP-X monomers. Finally, prepared polymer films on the ITO/glass surface were rinsed with ACN to remove the electrolyte salts.



Fig. 1. Repeated potential scans of EP-X monomers (a: EP-N; b: EP-S; c: EP-Se) in 0.1 M TBAHF₆ in CH₂Cl₂, scan rate 100 mV/s.

3. Results and discussion

3.1. Synthesis and Characterization

Electroactive EP-X monomers were synthesized in 5 steps (Scheme 1). First, 9,10-N,N'dihydroxyphenanthrene-9,10-diimine (M1) was prepared by the condensation reaction between hydroxylamine hydrochloride and Phenantroquinone in ethanol-pyridine mixture. This compound was reduced to its diamine derivative by using Pd/C as reducing agent in ethanol. Then, five membered ring closing reactions were performed by using S, Se and N-hegzyl based reagents. After that, synthesized phenantra-X-diazole compounds was iodinated by using N-iodosuccinimide. Finaly, synthesis of EP-X electroactive monomers were achieved by Stille-coupling reaction between Tributyl(2,3-dihydrothieno[3,4][1,4]dioxin-5-yl)stannane and diiodo-phenantra-X-dizole compounds in presence of Pd(PPh₃)₄ as a catalyst. Then, chemical structure of initial compounds and EP-X monomers were clarified by ¹H NMR.

3.2. Optical properties

The optical characterization of EP-X monomers were carried out by using UV-Vis absorption and fluorescence spectroscopy techniques. Absorption spectra of EP-X monomers represented a characteristic peak at $\lambda_{max} = 350$ nm attributed to π - π * transition of the conjugated system (Fig. 2a). Weak charge transfer bands occurred at 375-450 nm, due to the basic electronic interaction between EDOT donor and the phenantra-X-diazole-acceptor moieties. The reason for the weak charge transfer bands was partially blocked the intramolecular electron localization of the phenantra-X-diazole acceptor unit to the phenantra-X-diazole acceptor unit. On the other hand, as the acceptor character increased from EP-N to EP-Se, the charge transfer bands were shifted to the red region. Therefore, the optical band gap values

calculated from the absorption onset were found to be 3.10 eV for EP-N, 2.75 eV for EP-S and 2.69 eV for EP-Se, respectively.

Similar effects were observed in UV-Vis absorption spectra of polymer films obtained by electrochemical polymerization method (Fig. 2b). When compared to the EP-X monomers, a red shift was observed in all spectra as a result of the increase of π - π^* conjugation in the main chain after polymerization process. The optical band gap values were calculated as 2.33 eV for poly(EP-N), 1.92 eV for poly(EP-S) and 1.87 eV for poly(EP-Se) like monomeric structures.

On the other hand, the photoluminescence properties of EP-X electroactive molecules were investigated by excitation at the maximum wavelength of the lowest energy absorption peak (Fig. 2c). Like the absorption bands, the photoluminescence of EP-X linearly red shifted due to the exchange of heteroatoms on the center of the phenantrene connected to the EDOT donor moiety. The emission colors changed as blue, cyan and yellow upon varying the central acceptor unit.

10



Figure 2. UV-vis absorption spectra of EP-X monomers in CH_2Cl_2 (a), EP-X polymer films on ITO/glass surface (b) and photoluminescence spectra of EP-X monomers in CH_2Cl_2 .

3.3. Electrochemical properties

The cyclic voltammograms of the EP-X monomers and corresponding polymers were measured in the ACN electrolyte solution on the platinum disk WE surface (Fig 3 and 4). The EP-X polymers were electrochemically coated onto the platinum disk electrode surface, while the monomers were coated as drop casting process from the CH_2Cl_2 solution. Due to the presence of the different electron-acceptor phenantra-X-diazole moieties, the reduction peaks were shifted positively upon changing the center atom from N-C₆H₅, S to Se, respectively. Obtained results clearly showed that

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the center heteroatom on the phenantra-X-diazole derivative was directly effective the electrochemical reduction potentials for all molecules. According to these results, the LUMO levels obtained from the reduction potential onsets were calculated as 2.84 eV for EP-N, 2.91 eV for EP-S and 2.98 eV for EP-Se, respectively (Table 1). On the other hand, it was observed that the oxidation potential did not change too much due to electron localization on the phenantrene center containing triple condensed phenylene moieties. The HOMO levels was calculated from the oxidation onsets was found as about 5.3 eV for all molecules.



Figure 3. Redox behavior of EP-N (a) EP-S (b) and EP-Se (c) in 0.1 M TBAPF₆/CH₂Cl₂ electrolyte solution at scan rate 100 mV/s, vs. Ag wire

The same redox behaviors were observed for the EP-X polymers. Because of increasing conjugation on the polymer backbone, the oxidation peak was observed as reversible and shifted positively upon compared to the corresponding monomers. The HOMO level of poly(EP-N) was observed higher than the other polymers. This might be happened due to having higher conjugation degree of pol(EP-N) containing extra hexyl side chain. On the other hand, the band gap calculated from the HOMO and LUMO levels was reduced from the 2.25 eV to 1.98 eV when changing the heteroatom on the phenantra-X-diazole unit.



Figure 4. Redox behavior of EP-N (a) EP-S (b) and EP-Se (c) in 0.1 M TBAPF₆/ACN electrolyte solution at scan rate 100 mV/s, vs. Ag wire

Molecule	Oxidation Potantial (V)	Reduction Potantial (V)	HOMO (eV)	LUMO (eV)	Optical Band Gap (eV)	Electrochem. Band Gap (eV)
EP-N	$E^{ox}_{m,a} = 1.13$	$E^{red}_{m,c} = -1.58$	-5.29	-2.84	3.1	2.45
EP-S	$E^{ox}_{m,a} = 1.05$	$E^{red}_{m1,c} = -1.74$	-5.29	-2.91	2.75	2.38
EP-Se	$E^{ox}_{m,a} = 1.30$	$E^{\frac{red}{m,a}} = -1.34$	-5.31	-2.98	2.69	2.33
	$E^{m,c}_{m,c} = 1.07$	$E^{m,c}_{m,c} = -1.26$				
poly(EP-N)	$E^{p,a} = 1.11$	E ^{p,a} = -1.78	-4.87	-2.62	2.33	2.25
	$E^{p,c} = 1.04$	$E^{p,c} = -1.55$	K	>		
poly(EP-S)	$E^{p,a} = 1.18$	$E^{p,a} = -1.58$	-5.03	-2.99	1.92	2.04
poly(EP-Se)	$E^{px} = 0.75$	$E^{p,c} = -1.30$	-5.04	-3.06	1.87	1.98
	$E^{ox} = 1.23$	E^{red} = -1.13				
		- 115				

Table 1. Optical and Electrochemical Values of EP-X monomers and corresponding polymers

3.4. DFT calculations

Theoretical HOMO-LUMO charge distribution of the EP-X electroactive molecules were carried out by using DFT calculations. The calculations were performed by Spartan10 program at the parameters of B3LYP and $6-31 + G^*$ basis set. It was clearly seen that all molecules were very flat due to planar structure of the phenantrene center. The planar structures of the electroactive molecules could positively affect the film forming property during the electrochemically coating process on the WE surface. As a result of this approach, high-performance and highly stable

polymer films could be obtained in the optoelectronic applications [25, 27, 39, 40]. According to DFT calculations, the charges at HOMO orbital were localized on the EDOT-Phenanthene main chain as electron donor moieties. On the other hand, the charges orbital were delocalized on the electron-accepting phenantro-X-diazole subunit at LUMO. Due to weak acceptor property of the triazole moiety, the charge on the EP-N could not much transfer to the acceptor unit when compared to EP-S and EP-Se. The weak charge transfer band at UV-Vis absorption of EP-N also supported this situation. Moreover, all theoretical calculated HOMO-LUMO orbitals were compatible for the experimental values from the UV-Vis and CV measurements.



Table 2. Molecular orbital diagrams and the HOMO-LUMO levels of EP-X electroactive molecules.

3.4. Surface properties

Surface characterization of electrochemically coated EP-X polymer films was performed by atomic force microscopy (AFM). The thicknesses of EP-X polymer films coated under the same conditions were arranged between 104 nm and 186 nm (Table 3). The roughness was very low according to electrochemically coated polymer films in the literature [41, 42]. This was probably due to self-

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assembly behavior of the planar phenantrene center on the polymer repeating unit[25]. In addition, EP-N polymer film roughness was partially higher than the other EP-X polymers due to consisting of side alkyl chain on the triazole unit on the polymer backbone. On the other hand, EP-N polymer film has smaller particles than that of other EP-X polymer films because of the long alkyl chain partly prevent packing by creating a steric hindrance in the three dimensional plane among the polymer chains. Therefore, EP-Se polymer film has large and non-uniform crystalline domains when compared the other EP-X polymer films (Fig 5).



Figure 5. AFM images of a) poly(EP-N), b) poly(EP-S) and c) poly(EP-Se)films; i) height image, ii) phase image, and iii) topography image.

Polymer film	Thickness (nm)	Roughness(RMS)(nm)	Average particle diameter (nm)
Poly(EP-N)	174	9.08	124
Poly(EP-S)	142	6.76	316
Poly(EP-Se)	146	8.31	188

Table 3. Surface properties of EP-X polymer films obtained from AFM measurements

3.6. Electrochromic properties

Electrochromic properties of EP-X polymer films were investigated by spectro-electrochemical measurements in 0.1M TBAPF₆-ACN electrolyte. The EP-N polymer film color was yellow because of having a weak shoulder absorption band connected with the π - π transition band at the visible regime until 500 nm. When scanned between its redox potentials (0-1.8V), the new band was intensified the 550 nm and the yellow color (L*:97.7; a: -2.24; b: 24.9) of the film was converted to purple (L*: 76.1; a: 11.2; b: -5.5). On the other hand, the same trend was observed for the EP-S and EP-Se polymer films. As mentioned in the optical properties section, the neutral state absorption band was bathochromically shifted upon changing the acceptor unit on the EP-X polymer structure. For EP-S polymer film, the orange color of the film (L*:86.1; a: 14.3; b: 28.4) was converted to dark purple (L*:71.8; a: 9.8; b: -9.9) when observed a new band centered at about 600 nm at the oxidized state (1.6V). Due to having phenantra-selenadiazole as a stronger acceptor moiety, the sharp charge transfer absorption band at the neutral state was observed. When applied positive potentials between 0-1.6V, the new band was seen at about 600 nm like EP-S polymer and the red coloured polymer film at the neutral state (L*:74.6; a: 26.7; b: 13.3) turned into violet (L*:67.8; a: 13.7; b: -20.4). Consequently, all EP-X polymer films had multielectrochromic behavior due to dramatically changing their absorption behavior at the visible regime when applied positive potential.



Figure 6. UV-Vis spectrum and the color changes during the applied potential of poly(EP-X) films on ITO/glass surface in 0.1 M TBAPF₆/ACN.

The electrochromic performances of EP-X polymer films were determined by applying a chronoamperometry technique (Fig. 7). When the polymer films were analyzed with the changes in transmittance (increments or decrements of the absorption band with respect to time) while switching the potential step wisely between the neutral and oxidized states with a residence time of 10 s. According to these measurements, it has been determined that all EP-X polymer film maintain the optical activity of above 95% after 5000 cycle (Table 4, Fig 7 and Fig. S1-3). Thin film morphology is an important issue for organic optoelectronic device performance [39]. AFM results also revealed that EP-X polymer thin films had uniform structure and low roughness degree

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according to electrochemical coating process due to self-organization property of phenantrene center by strong π - π interaction at the solid state. Cihaner et al synthesized a series of benzo-X-diazole---EDOT based electroactive structures for electrochromic applications [21]. When our work was compared to that work, blue shifts were detected at the neutral state absorption bands and also colors after the planarity was increased on the electroactive monomer center by attached phenantrene moiety instead of phenylene. In our previous paper, the planar center effect on the electrochromic performance was also investigated [25]. It was concluded that the planar center moiety on the electroactive structure had a great impact especially on the electrochemical also electrochromic stability of the polymers. Finally, the coloration efficiency values calculated for the EP-N polymers (214 cm² C⁻¹) were found to be about three times higher than the EP-S (62 cm² C⁻¹, and EP-Se (58 cm² C⁻¹) (Table 4). These values were very low except for EP-N when compared to the literature [21]. EP-N has an extra alky chain on the triazole acceptor center and the electrolyte dopant ions can more move in and out of the space between polymer chains owing to steric hindrance of the alkyl chain of the electrochromic material during redox switching.



Figure 7. Electronic absorption spectra for poly(EP-N) at 545 nm (a), poly(EP-S) at 650 nm (b) and poly(EP-Se) at 650 nm (c) films in anodic regime between their redox potentials in a monomer-free 0.1 M $TBAPF_{6}/ACN$ solution.

Molecule	Optical contrast change wavelength (nm)	Optical contrast change (AT%)	Responce Time (s)	Optical activity after 5000 cycles (%)	Coloration Efficiency (cm²/C)
poly(EP-N)	545	ΔT: 48% T _{neut} .: 95% T _{oxi} .: 47%	Oxidation 2.4 s Reduction 1.7 s	%97	214
poly(EP-S)	650	ΔT: % 18 T _{neut.} : %99 T _{oxi.} : %81	Oxidation 1.8 s Reduction 0,7 s	%96	62
poly(EP-Se)	650	ΔT: % 17 T _{neut.} : %96 T _{oxi.} : %79	Oxidation 1.2 s Reduction 1.0 s	%98	58

Tablo 4. Electrochromic Parameters for EP-X polymer films

4. Conclusion

Herein for the first time we reported a series of phenantrene centered donor acceptor electroactive monomers substituted with two EDOT unit by Stile coupling reaction. Then EP-X monomers were electrochemically polymerized onto transparent ITO/glass surface to give very stable electrochromic polymer films against to applied potential. Optical and electrochemical properties of EP-X monomers and corresponding polymers were greatly influenced by changing central heteroatom on the phenantra-X-diazoleacceptor unit. Besides, AFM results revealed that the polymer particles have uniform structure thus well-organized polymer films could be obtained owing to self-organization property of the planar phenantrene centers. Multielectrochromic behavior could be obtained by the changing the absorbance/transmittance at the visible regime upon applied positive potentials. Moreover, it was concluded that the planar center moiety was greatly affected on the electrochromic stability performance of the electroactive polymer films.

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Highlights

► We report a series of phenantrene centered donor-acceptor type electroactive polymer for electrochromic applications

► A remarkable trend of visible color (yellow, orange, red) at the neutral state can be obtained by changing the central acceptor moiety

► It is observed that planar center unit is greatly affected on the electrochromic stability performance of the electroactive polymer films.

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