

Carbazole based electrochromic polymers with benzoazole units: Effect of heteroatom variation on electrochromic performance

C. Doyranlı^{1,2}, F. Baycan Koyuncu^{1,2*}

¹Department of Chemistry, Faculty of Sciences and Arts, Çanakkale Onsekiz Mart University, 17020 Çanakkale, Turkey

²Polymeric Materials Research Laboratory, Çanakkale Onsekiz Mart University, 17020 Çanakkale, Turkey

Received 26 February 2016; accepted in revised form 5 April 2016

Abstract. A series of carbazole-based polymers were synthesized via Suzuki polymerization between N-(2-ethylhexyl)carbazole-3,6-bis(ethyleneboronate) (**Cbz**) and dibromobenzoazole unit. Three different polymers, **PCBN**, **PCBS** and **PCBSe** were obtained from 4,7-dibromo-2-hexyl-2H-benzotriazole (**BN**), 4,7-dibromo-2,1,3-benzothiadiazole- (**BS**) and 4,7-dibromo-2,1,3-benzoselenadiazole (**BSe**), respectively. It is observed that, the variation of heteroatoms (N,S and Se) on the benzoazole unit have most important effect on electro-optic properties of the **PCBX** polymers. Neutral state color of the polymer films and their electrochromic performances are also influenced. Among the synthesized polymers, the **PCBS** bearing 2,1,3-benzothiadiazole as acceptor units has a broad absorption and 50% of ΔT in the near-IR regime at the oxidized state. This property of **PCBS** is a great advantage for near-IR electrochromic applications.

Keywords: polymer synthesis, molecular engineering, electrochromic polymers, carbazole, benzotriazole, benzothiadiazole

1. Introduction

For 20 years, the donor-acceptor electrochromic polymers have been intensively studied owing to their respectable properties such as their tunable band gaps, and also electrochemical and optical properties. A reversible and visual color change called as electrochromism is obtained by the reversible redox behavior of the electroactive polymers. Electron-donor and electron-withdrawing parts are attached on the same polymer backbone of the donor-acceptor systems [1]. HOMO–LUMO energy levels of these systems are recognized exactly due to their dual electrochemical properties. These polymers have also an important charge transfer band in the neutral state to apply on the photovoltaic and electroluminescent devices. They also can be used in electrochromic materials to fabricate smart windows [2, 3], switchable mirrors [4, 5] and camouflage materials [6, 7].

Carbazole is one of the widely used donor moieties in the donor-acceptor systems as it can be functionalized at different positions such as (3,6) [8], (2,7) [9] or N-positions [10]. It is also an efficient blue emissive polymer in the organic light emitting diodes [11]. Owing to their effective carrier transport properties, carbazole based polymers can form relatively stable cations (polarons) and dications (bipolarons) when applying positive potential or doping agent [12]. Because of these superior properties, these polymers can be used in electrochromic materials, light emitting diodes, electrophotography and as photovoltaic constituents [9, 13–15]. Nevertheless, organic optoelectronic applications of poly-3,6-carbazoles are limited because of both poor conjugation within the polymer backbone and also not obtaining high molecular weights. Therefore, poly-3,6-carbazoles are still used as host materials because of

*Corresponding author, e-mail: fatmabaycan@hotmail.com
© BME-PT

their high ability of hole transporting [16–18]. Besides, these polymers demonstrate remarkable electrochromic properties due to the conjugation broken on the carbazyl nitrogen. One of the exciting multi-color polymer frameworks based on the 3,6-linked carbazole moiety was proposed by Reynolds and coworkers [18–20]. These polymers can form radical cations that are separated from each other owing to the broken conjugation on the polymer backbone. When applying higher potentials on the polymer, radical dications (bipolarons) are formed in the polymer system via removing another electron. For these reasons, electrochromic materials containing poly(3,6)carbazole derivatives have multielectrochromic behavior due to their distinct oxidation property in the anodic regime [21, 22].

To understand the effect of heteroatom variation both on electro-optic properties of polymers and also on their electrochromic performance, we synthesized a series of donor-acceptor polymers based on N-(2-ethylhexyl)carbazole-3,6-bis(ethyleneboronate) (**Cbz**) and dibromobenzazole unit (**BX**) with different heteroatoms (N, S and Se) named as poly(4,7-(N-hexylbenzotriazole)-3,6-(N-(2-ethylhexyl)carbazole) (**PCBN**), poly(4,7-(2,1,3-benzothiadiazole)-3,6-(N-(2-ethylhexyl)carbazole) (**PCBS**) and poly(4,7-(2,1,3-benzoselenadiazole)-3,6-(N-(2-ethylhexyl)carbazole) (**PCBSe**). The band gap of polymers and also the neutral state color of the films can be tuned by attaching a heteroatom on the acceptor moiety, changing nitrogen to sulfur or selenium. Further, owing to multi step redox behavior at the anodic regime, various colors were obtained on the polymer films upon applied potentials. Among the **PCBX** polymers, **PCBS** has a broad absorption and 50% of ΔT in the near-IR regime at the oxidized state. Owing to this property, **PCBS** can be a good candidate to use for near-IR electrochromic applications.

2. Experimental section

2.1. Materials

Compounds were procured from Aldrich. The initial compounds (**Cbz**, **BN**, **BS** and **BSe**) were prepared and characterized according to the literature [23].

2.2. Instrumentation

Fourier transform infrared spectra (FT-IR) were recorded on a Perkin Elmer FT-IR Spectrum One spec-

trometer by using an attenuated total reflectance (ATR) module (4000–650 cm^{-1}). $^1\text{H-NMR}$ spectra were recorded on a Bruker Advance DPX-400 at 25 °C in deuterated chloroform solutions with tetramethylsilane (TMS) as internal standard. Electrochemical analyses were performed by Biologic SP50 potentiostat–galvanostat system with a platinum disk (0.02 cm^2) as working electrode (WE), Ag wire as reference electrode (RE) and Pt wire as counter electrode (CE). UV-vis absorption spectra were recorded by an Analytic Jena Speedcord S-600 diode-array spectrophotometer. The optical band gaps (E_g) of polymers were found from their absorption onsets [24]. The emission spectra measurements were taken by a PTI QM1 fluorescence spectrophotometer. Spectro-electrochemical measurements were carried out to consider absorption spectra of polymer films under applied potential. The color coordinates are determined by three characteristics; luminance (L), hue (a), and saturation (b) in Commission Internationale de l'Éclairage (CIE) system [25]. To determine these characteristics, Analytic Jena UV-vis spectrophotometer containing a chromameter module was used. GPC analysis of the polymers was performed with Agilent 1260 HPLC instrument. This system consists of an Agilent 1200 series pump, three Waters Styragel HR columns (guard, 4, 3) and a BI-DNDC differential refractometer (Brookhaven Instruments Corporation, 620 nm) with a THF flow rate of 1 mL/min. Polystyrene was used as calibration standard. Surface morphologies were investigated by Nanosurf Naio AFM.

2.3. Synthesis of PCBX polymers

The polymers were synthesized via Suzuki polymerization reaction between 2-ethylhexyl-9H-carbazole-3,6-diboronic acid bis(1,3-propanediol) ester and dibromo benzoazole-based heterocycles. Benzoazole-dibromide (1 mol) and 2-ethylhexyl-9H-carbazole-3,6-diboronic acid bis(1,3-propanediol) ester (1 mol) were added into potassium carbonate solution (K_2CO_3 , 2M in H_2O) and 20 mL toluene. Then, $\text{Pd}(\text{PPh}_3)_4$ (5 mol%) was added to flask. The mixture was heated to 110 °C and refluxed for 16 h under N_2 . For ending the reaction benzeneboronic acid (0.122 mol) was added and refluxed about 3 h and then bromobenzene (0.122 mol) was also put into flask and stirred for 3 h, too. Lastly, the mixture was cooled and then

filtered. After that, it poured into methyl alcohol. The crude product was filtered again and dried. Soxhlet extraction was achieved with methyl alcohol and then CHCl_3 for the last purification.

PCBN (Yield 78%; yellow powder): FTIR [cm^{-1}]: 3094 (C–H aromatic); 2957, 2931, 2856 (C–H aliphatic); 1615 (C=N); 1595, 1530 (C=C aromatic); 1443 (C–N); $^1\text{H-NMR}$ (CHCl_3 -d): δ ppm, 8.84–7.17 (m, 8H, C–H aromatic); 4.81 (m, 2H, $-\text{NCH}_2-$, triazole); 4.52 (m, 2H, $-\text{NCH}_2-$, carbazole); 2.17–1.33 (m, 17H, C–H aliphatic); 0.91 (m, 9H, $-\text{CH}_3$).

PCBS (Yield 86%; orange powder): FTIR [cm^{-1}]: 3086 (C–H aromatic); 2954, 2929, 2850 (C–H aliphatic); 1612 (C=N); 1578, 1524 (C=C aromatic); 1441 (C–N); $^1\text{H-NMR}$ (CHCl_3 -d): δ ppm, 8.82–7.48 (m, 8H, C–H aromatic); 4.29 (m, 2H, $-\text{NCH}_2-$); 2.19–1.38 (m, 9H, C–H aliphatic); 0.91 (m, 6H, $-\text{CH}_3$).

PCBSe (Yield 82%; red powder): FTIR [cm^{-1}]: 3084 (C–H aromatic); 2950, 2925, 2796 (C–H aliphatic); 1610 (C=N); 1574, 1522 (C=C aromatic); 1440 (C–N); $^1\text{H-NMR}$ (CHCl_3 -d): δ ppm, 8.71–7.16 (m, 8H, C–H aromatic); 4.29 (m, 2H, $-\text{NCH}_2-$); 2.15–1.39 (m, 9H, C–H aliphatic); 0.91 (m, 6H, $-\text{CH}_3$).

3. Results and discussion

3.1. Synthesis of PCBX polymers

Cbz, BN, BS and BSe were synthesized according to procedures from the literature [23]. Syntheses of the polymers (PCBN, PCBS and PCBSe) were achieved by Suzuki reaction between Cbz-donor and BX-acceptors respectively (Figure 1). FTIR and $^1\text{H-NMR}$ analysis were used to prove the formation of the PCBX polymers. Noteworthy, spectral properties variations were detected for initial and the final compounds. According to $^1\text{H-NMR}$ spectra of polymers,

carbazole and benzazole aromatic proton signals were observed 8.84–7.16 ppm. Because of the electron-acceptor effect of carbazyl nitrogen, N– CH_2 aliphatic group signal was detected at higher ppm, (4.52 ppm for PCBN – 4.29 ppm for PCBS and PCBSe) than that of other aliphatic protons (Figure 2). The similar situation was also observed in the benzotriazole's N– CH_2 aliphatic signal (4.81 ppm).

GPC was used for the investigation of polydispersity index (PDI) and molecular weight of the polymers. According to GPC measurements, degree of polymerization of PCBX polymers was found to be 7, 6 and 4 respectively (Table 1). The results obtained indicate that these molecules are oligomers. Because of the presence of an alkyl chain on the benzotriazole moiety, the molecular weight of PCBN higher than that of the other polymers.

3.2. Optical properties of PCBX polymers

The optic characterization of PCBX polymers were achieved by UV-Vis and Fluorescence spectroscopy. Owing to π - π^* transitions arising from the conjugation of the polymer main chain, PCBX polymers showed absorption bands at about 300 nm. Besides, because of the interaction of carbazole-donor and benzazole-acceptor at the conjugated polymer system, a typical charge transport band was obtained at 360 nm for PCBN, at 440 nm for PCBS and at 475 nm for PCBSe, respectively (Figure 2a). Finally,

Table 1. Molecular weights of PCBN, PCBS and PCBSe

Polymer	M_n [Da]	M_w [Da]	PDI
PCBN	3339	4768	1.42
PCBS	2516	3632	1.44
PCBSe	1626	2031	1.24

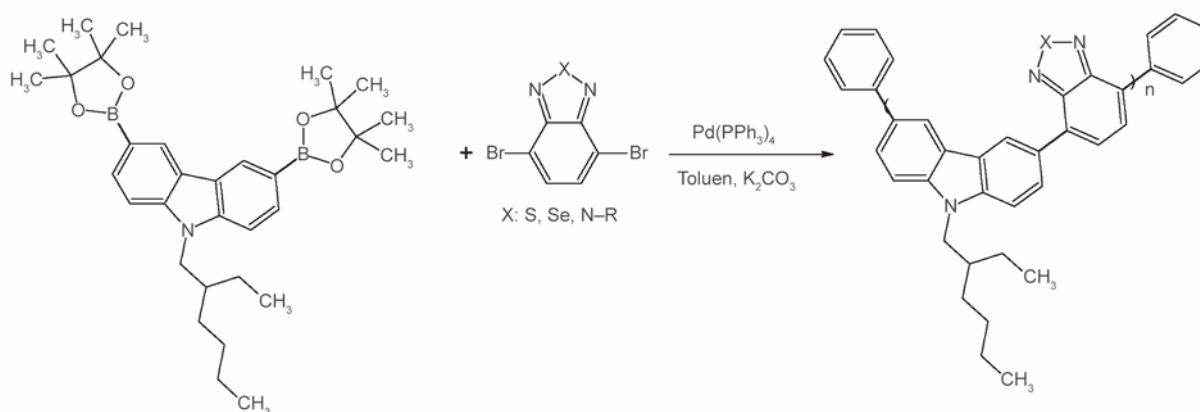


Figure 1. Synthetic route for PCBX polymers

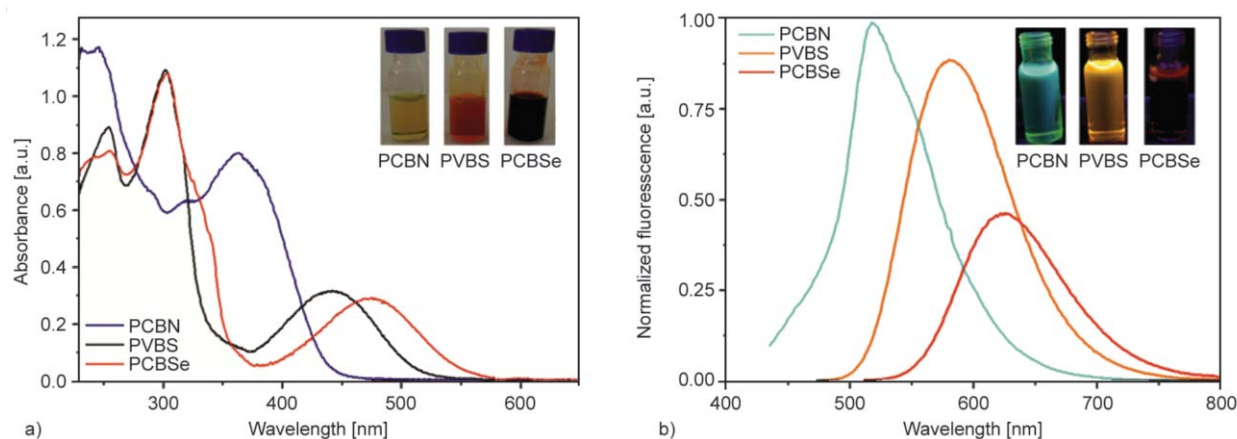


Figure 2. Absorption (a) and fluorescence (b) spectra of PCBX polymers in CH_2Cl_2 solution

the optical band gaps were found to be 2.80 eV for **PCBN** (at 442 nm), 2.42 eV for **PCBS** (at 513 nm) and 2.18 eV for **PCBS** (at 569 nm) respectively. According to this result, there is about 127 nm bathochromic shift from **PCBN** to **PCBS**. On the other hand, similar results were observed in the fluorescence measurements. Upon **PCBXs** excited from absorption maxima of their charge transfer band ($\lambda_{\text{max}} = 360$ nm for **PCBN**, $\lambda_{\text{max}} = 440$ nm for **PCBS**, and $\lambda_{\text{max}} = 475$ nm for **PCBS**) strong emission bands were obtained at 440, 580, and 623 nm with Stokes' shifts of 157, 140, and 148 nm, respectively (Figure 2b). The emission colors of the polymer solutions were diverse as cyan, orange and red, respectively. Finally, absorption and fluorescence behavior could be arranged by the substitution of different heteroatoms on the benzazole acceptor moiety to carbazole donor unit.

3.3. Electrochemical properties of PCBX polymers

To understand the redox behaviors of **PCBX** polymers, cyclic voltammetry (CV) technique was used. **PCBN**, **PCBS** and **PCBS** have a great difference

in their redox properties obtained from the CV voltammograms which are shown in Figure 3. The electron-deficient character of the heteroatom on the benzazole moiety strongly affected the reduction potentials of the polymers in the cathodic regime. **PCBN**, **PCBS** and **PCBS** polymers have an irreversible reduction peak at -1.65 , -1.50 and -1.42 V, respectively. According to these results, changing the electron-deficient unit of the polymer significantly altered the reduction potential of the polymers. Thus, LUMO levels responded differently and consequently **PCBS** has a lower band gap value compared with **PCBS** and **PCBN** because of the stronger electron-withdrawing character of benzoselenadiazole moiety [26–28]. On the other hand, semi reversible oxidation peaks were found at $E_{\text{p,a}}^{\text{ox}} = 1.35$ V, $E_{\text{p,c}}^{\text{ox}} = 1.01$ V and $E_{\text{p,1/2}}^{\text{ox}} = 1.18$ V for **PCBN**; $E_{\text{p,a}}^{\text{ox}} = 1.26$ V, $E_{\text{p,c}}^{\text{ox}} = 0.98$ V and $E_{\text{p,1/2}}^{\text{ox}} = 1.12$ V for **PCBS**, $E_{\text{p,a}}^{\text{ox}} = 1.58$ V, $E_{\text{p,c}}^{\text{ox}} = 1.05$ V and $E_{\text{p,1/2}}^{\text{ox}} = 1.32$ V for **PCBS** in the anodic region. According to Table 2, it can be deduced that electrochemical and optical behaviors of the polymers were significantly affected by varying the heteroatom on the acceptor moiety attached to the carbazole-donor main chain.

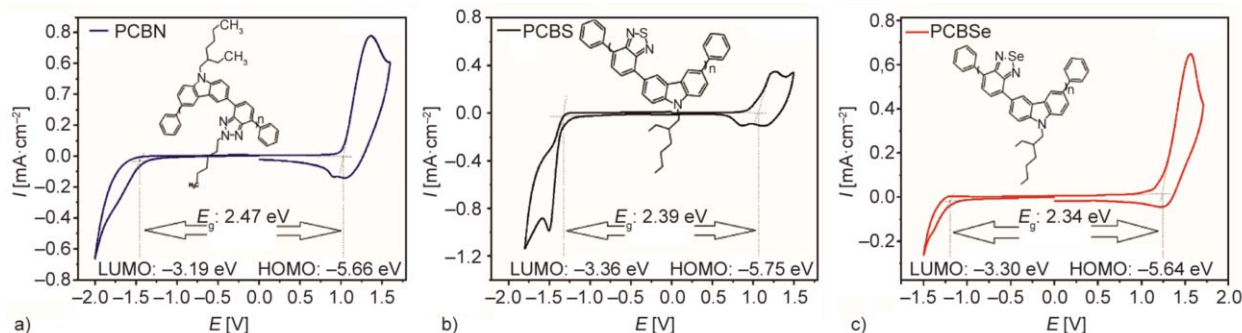


Figure 3. Redox behavior of PCBN (a) PCBS (b) and PCBS (c) in 0.1 M $\text{TBAPF}_6/\text{CH}_2\text{Cl}_2$ electrolyte solution at scan rate 100 mV/s, vs. Ag wire

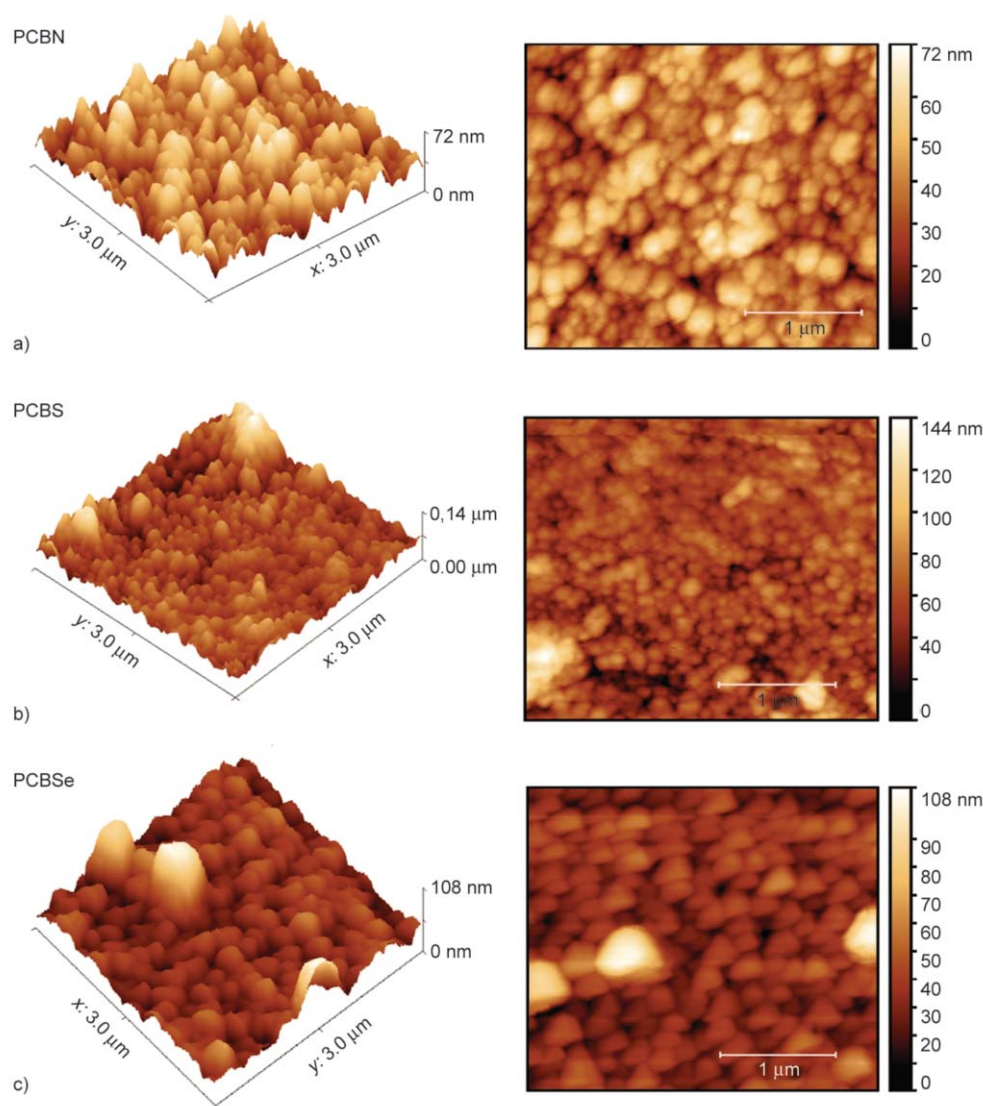
Table 2. HOMO-LUMO, electrochemical and optical band gaps (E_g) of PCBX polymers

Polymer	HOMO [eV]	LUMO [eV]	Optical E_g [eV]	Electrochemical E_g [eV]
PCBN	-5.66	-3.19	2.80	2.47
PCBS	-5.75	-3.36	2.42	2.39
PCBSe	-5.64	-3.30	2.18	2.34

3.4. Surface morphologies

Morphology of **PCBN**, **PCBS** and **PCBSe** film surfaces was examined by atomic force microscopy (AFM) (Figure 4). Polymer solutions were obtained from 20 mg/mL of PCBX in CHCl_3 . PCBX polymer films were prepared by using spin-casting method on ITO substrates at 2000 rpm for 60 s from the polymer solutions. While the thickness of the films were calculated as 96, 168 and 190 nm, for **PCBN**, **PCBS** and **PCBSe** respectively, the RMS (root mean sur-

face) roughness of polymers are found to be 10.38, 18.87 and 25.45 nm. The AFM image of the PCBS and PCBSe exhibit conglomerate non-uniform structure and the roughness of these polymer films are high. Besides, PCBN has a longer side alkyl chain on the benzotriazole acceptor moiety. Because of this, solvation is promoted by increasing the length of the alkyl chain. As a result of increasing the solubility and also expansion of π conjugation along the polymer backbone, a uniform surface could be obtained. Consequently, better polymer thin films could be obtained by decreasing the roughness [29, 30]. As known in the literature [31–33] during electrochromic switching, the electrolyte ions are injected/ejected to the polymer film surface. Because of the feature, the electrochromic performance of the PCBX polymer was affected by the polymer film surface roughness.

**Figure 4.** AFM image of PCBN (a), PCBS (b) and PCBSe (c) onto ITO/glass surface

3.5. Spectroelectrochemical properties of PCBX polymers

Spectroelectrochemical investigation of **PCBN**, **PCBS** and **PCBSe** films was carried out via Diode-array UV-Vis spectrophotometer. While oxidation of **PCBN** film (0–1.2 V), an absorption band at 360 nm corresponds to valence band-conduction band ($\pi \rightarrow \pi^*$ transition) started to decrease and another band intensified at 550 nm. This new absorption band pointed out the formation of polaron on the carbazole based polymer chain and thus light yellow neutral state color of the film (L: 78.7; a: –13.5; b: 47.8) converted to green (L: 71.5; a: –27.5; b: 56.9). Additionally, upon applied higher potentials (1.2–1.8 V), another new band was observed in the near-IR region (at 860 nm) as a result of the formation of a bipolaron. Consequently, the color of the **PCBN** polymer film turned into red (L: 39.01; a: 4.98; b: 4.54) at fully oxidized state (Figure 5).

Anodic scan of **PCBS** (0 to 1.8 V) (Figure 6), the charge transfer band at 455 nm decreased, and two new absorption bands were started to form at 600 nm (0–1.4 V) and 825 nm (1.4–1.8 V) (Figure 5). Moreover, formation of polaron and bipolaron on the **PCBS** polymer backbone was verified by the intensification of the broad band in the visible and near-IR regime (Figure 5). While the orange color of the film at neutral state (L: 69.57; a: 5.66; b: 56.67) changed to blue (L: 24.9; a: 3.6; b: –28.7) and then black (L: 39.08; a: –0.4; b: –1.25) upon the applied positive potential (Figure 6).

Further, red color **PCBSe** polymer film (L: 42.6; a: 28.6; b: 32.6) was exhibited a maximum absorption band at 475 nm (λ_{\max} , the charge transfer band) at the neutral state. During to anodic scan (Figure 7), in-

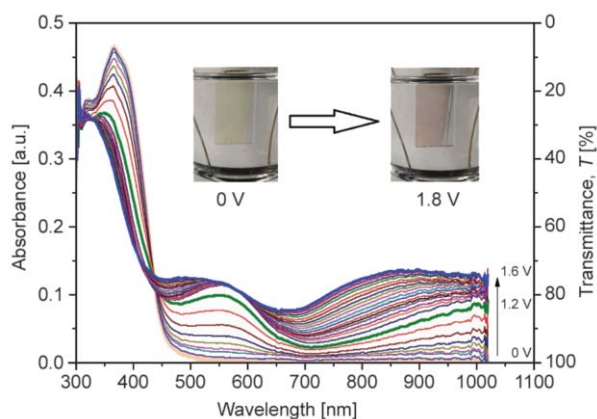


Figure 5. Color changes and spectroelectrochemistry of PCBN film on ITO in the anodic region

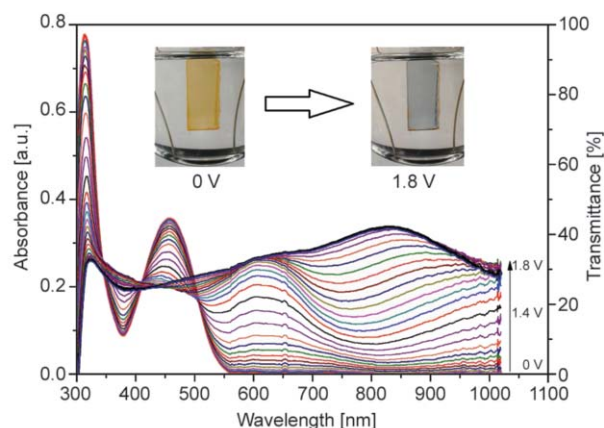


Figure 6. Color changes and spectroelectrochemistry of PCBS film on ITO in the anodic region

tensity of $\pi \rightarrow \pi^*$ transition and charge transfer bands were decreased. On the other hand, new absorption bands at about 650 nm (0–1.4 V) and 800 nm (1.4–1.8 V) started to be intensified depending on the formation of polarons and bipolarons, respectively (Figure 7). Hence, above 700 nm (the Near-IR region) was intensely absorbed by the **PCBSe** polymer film at fully oxidized state. According to these results, the red polymer film converted to oily green (L: 34.5; a: –11.7; b: 16.5), and dark blue (L: 29.6; a: –2.98; b: –11.7), respectively (Figure 7).

Kinetic performance of **PCBX** polymers was carried out by the square-wave voltammetry which observes the difference of transmittance at the point of absorption maxima against to time while applying voltage between redox states of polymers with a residence time of 10 s (Figure 7). The percentage transmittance change ($\Delta T\%$) of **PCBX** polymers was investigated between 0–1.8 V with switching time of 10 s. As a result of these measurements, $\Delta T\%$ was found to be 21% for **PCBN** at 860 nm, 45% for **PCBS** at 825 nm

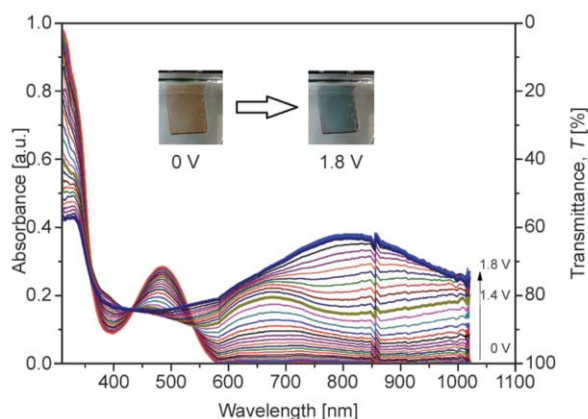


Figure 7. Color changes and spectroelectrochemistry of PCBSe film on ITO in the anodic region

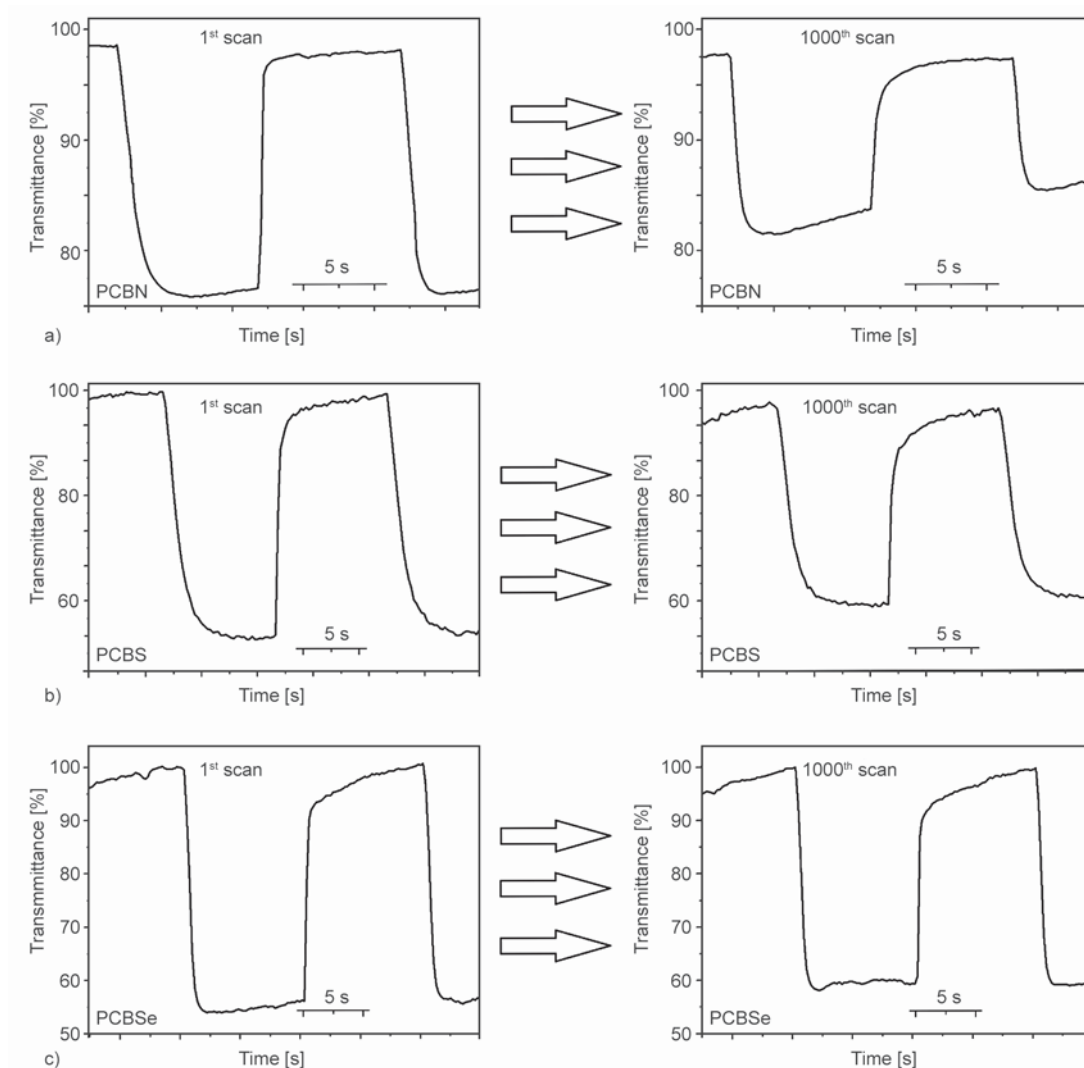


Figure 8. Stability test of polymers. [Optical difference watched at 860 nm for PCBN (a), 825 nm for PCBS (b) and 800 nm for PCBSe between 0 and 1.8 V (c)]

and 41% for **PCBN** at 800 nm respectively (Figure 8).

Optical activity is one of the most significant parameter to determine the electrochromic performance of the polymer films [34]. While **PCBN** has 62% of the optical activity, **PCBS** and **PCBSe** have 84% and 86% of the optical activity after 1000 cycles, respectively. The reduction and oxidation response times were also determined. The values were found to be 4.8 and 1.2 s for **PCBN**, 2.4 and 6.1 s for **PCBS**, and 1.8 and 2.4 s for **PCBSe** respectively.

Another important parameter is coloration efficiency (CE) for the electrochromic applications. CE was determined via the equation: $CE = \Delta OD / Q_d$ and $\Delta OD = \log(T_{\text{bleached}} / T_{\text{colored}})$ [where T_{bleached} is transmittance at neutral state, T_{colored} is transmittance at oxidized

state and Q_d is Injected/ejected charge between redox states] [25]. According to this equation, CE values of **PCBN**, **PCBS** and **PCBSe** were determined as 93, 178 and 154 $\text{cm}^2 \cdot \text{C}^{-1}$ respectively. As it can be clearly observed, CE values of **PCBS** and **PCBSe** are approximately two times greater than that of **PCBN**. Considering all data, electrochromic performance of the polymers was significantly affected by the type of heteroatom on the benzoazole acceptor moiety. Finally, **PCBN**, **PCBS** and **PCBSe** polymer films exhibited multi-electrochromic behavior, reasonable response time and optical contrast. Furthermore, **PCBS** has a broad absorption band in both the visible and near-IR regime at its oxidized state. Consequently, it could be a good candidate to use a visible and near-IR filter in various applications.

4. Conclusions

In this work, a series of carbazole based electrochromic polymers with benzazole moiety as electron-acceptor were synthesized and characterized. Besides, the heteroatom variation effects on the analogous electrochromic polymers were also investigated. The polymer thin films of PCBX were obtaining by using spin-casting metod. They have several colors presented for the neutral and polaronic species, owing to multiple redox behavior of carbazole moiety at their oxidized state. The neutral state color of PCBX polymers were yellow, orange and red, respectively. On the other hand, the color of the films converted to red, black and dark blue at fully oxidized state, respectively. In conclusion, electrochromic polymers **PCBN**, **PCBS** and **PCBSe** exhibit medium band gaps (2.47, 2.39 and 2.34 eV) and reasonable electrochromic performance (optical activity, coloration efficiency and oxidation/reduction times).

Acknowledgements

The authors would like thank Çanakkale Onsekiz Mart University for financial support (Project Number: 2015/56).

References

- [1] Shirota Y.: Organic materials for electronic and optoelectronic devices. *Journal of Materials Chemistry*, **10**, 1–25 (2000).
DOI: [10.1039/a908130e](https://doi.org/10.1039/a908130e)
- [2] Niklasson G. A., Granqvist C. G.: Electrochromics for smart windows: Thin films of tungsten oxide and nickel oxide, and devices based on these. *Journal of Materials Chemistry*, **17**, 127–156 (2007).
DOI: [10.1039/b612174h](https://doi.org/10.1039/b612174h)
- [3] Granqvist C. G., Azens A., Hjelm A., Kullman L., Niklasson G. A., Rönnow D., Mattsson M. S., Veszelei M., Vaivars G.: Recent advances in electrochromics for smart windows applications. *Solar Energy*, **63**, 199–216 (1998).
DOI: [10.1016/S0038-092X\(98\)00074-7](https://doi.org/10.1016/S0038-092X(98)00074-7)
- [4] Mortimer R. J.: Electrochromic materials. *Chemical Society Reviews*, **26**, 147–156 (1997).
DOI: [10.1039/cs9972600147](https://doi.org/10.1039/cs9972600147)
- [5] Rosseinsky D. R., Mortimer R. J.: Electrochromic systems and the prospects for devices. *Advanced Materials*, **13**, 783–793 (2001).
DOI: [10.1002/1521-4095\(200106\)13:11<783::AID-ADMA783>3.0.CO;2-D](https://doi.org/10.1002/1521-4095(200106)13:11<783::AID-ADMA783>3.0.CO;2-D)
- [6] Chandrasekhar P., Zay B., Birur G. C., Rawal S., Piereson E. A., Kauder L., Swanson T.: Large, switchable electrochromism in the visible through far-infrared in conducting polymer devices. *Advanced Functional Materials*, **12**, 95–103 (2002).
DOI: [10.1002/1616-3028\(20020201\)12:2<95::AID-ADFM95>3.3.CO;2-E](https://doi.org/10.1002/1616-3028(20020201)12:2<95::AID-ADFM95>3.3.CO;2-E)
- [7] Beaupré S., Breton A.-C., Dumas J., Leclerc M.: Multi-colored electrochromic cells based on poly(2,7-carbazole) derivatives for adaptive camouflage. *Chemistry of Materials*, **21**, 1504–1513 (2009).
DOI: [10.1021/cm802941e](https://doi.org/10.1021/cm802941e)
- [8] Zhang Z.-B., Fujiki M., Tang H.-Z., Motonaga M., Torimitsu K.: The first high molecular weight poly(*N*-alkyl-3,6-carbazole)s. *Macromolecules*, **35**, 1988–1990 (2002).
DOI: [10.1021/ma011911b](https://doi.org/10.1021/ma011911b)
- [9] Blouin N., Michaud A., Gendron D., Wakim S., Blair E., Neagu-Plesu R., Belletête M., Durocher G., Tao Y., Leclerc M.: Toward a rational design of poly(2,7-carbazole) derivatives for solar cells. *Journal of the American Chemical Society*, **130**, 732–742 (2008).
DOI: [10.1021/ja0771989](https://doi.org/10.1021/ja0771989)
- [10] Watanabe T., Ueda S., Inuki S., Oishi S., Fujii N., Ohno H.: One-pot synthesis of carbazoles by palladium-catalyzed *N*-arylation and oxidative coupling. *Chemical Communications*, **43**, 4516–4518 (2007).
DOI: [10.1039/b707899d](https://doi.org/10.1039/b707899d)
- [11] Thomas K. R. J., Lin J. T., Tao Y.-T., Ko C.-W.: Light-emitting carbazole derivatives: Potential electroluminescent materials. *Journal of the American Chemical Society*, **123**, 9404–9411 (2001).
DOI: [10.1021/ja010819s](https://doi.org/10.1021/ja010819s)
- [12] Pomerantz Z., Zaban A., Ghosh S., Lellouche J.-P., Garcia-Belmonte G., Bisquet J.: Capacitance, spectroelectrochemistry and conductivity of polarons and bipolarons in a polydicarbazole based conducting polymer. *Journal of Electroanalytical Chemistry*, **614**, 49–60 (2008).
DOI: [10.1016/j.jelechem.2007.11.005](https://doi.org/10.1016/j.jelechem.2007.11.005)
- [13] Liou G.-S., Hsiao S.-H., Huang N.-K., Yang Y.-L.: Synthesis, photophysical, and electrochromic characterization of wholly aromatic polyamide blue-light-emitting materials. *Macromolecules*, **39**, 5337–5346 (2006).
DOI: [10.1021/ma0608469](https://doi.org/10.1021/ma0608469)
- [14] Akcelrud L.: Electroluminescent polymers. *Progress in Polymer Science*, **28**, 875–962 (2003).
DOI: [10.1016/S0079-6700\(02\)00140-5](https://doi.org/10.1016/S0079-6700(02)00140-5)
- [15] Getautis V., Daskeviciene M., Malinauskas T., Gaidelis V., Jankauskas V., Tokarski Z.: Cross-linkable hydrazone-containing molecular glasses for electrophotography. *Synthetic Metals*, **155**, 599–605 (2005).
DOI: [10.1016/j.synthmet.2005.09.039](https://doi.org/10.1016/j.synthmet.2005.09.039)

- [16] Brunner K., van Dijken A., Börner H., Bastiaansen J. J. A. M., Kikken N. M. M., Langeveld B. M. W.: Carbazole compounds as host materials for triplet emitters in organic light-emitting diodes: Tuning the HOMO level without influencing the triplet energy in small molecules. *Journal of the American Chemical Society*, **126**, 6035–6042 (2004). DOI: [10.1021/ja049883a](https://doi.org/10.1021/ja049883a)
- [17] Tsai M-H., Lin H-W., Su H-C., Ke T-H., Wu C-C., Fang F-C., Liao Y-L., Wong K-T., Wu C-I.: Highly efficient organic blue electrophosphorescent devices based on 3,6-bis(triphenylsilyl)carbazole as the host material. *Advanced Materials*, **18**, 1216–1220 (2006). DOI: [10.1002/adma.200502283](https://doi.org/10.1002/adma.200502283)
- [18] Cirpan A., Argun A. A., Grenier C. R. G., Reeves B. D., Reynolds J. R.: Electrochromic devices based on soluble and processable dioxithiophene polymers. *Journal of Materials Chemistry*, **13**, 2422–2428 (2003). DOI: [10.1039/b306365h](https://doi.org/10.1039/b306365h)
- [19] Witker D., Reynolds J. R.: Soluble variable color carbazole-containing electrochromic polymers. *Macromolecules*, **38**, 7636–7644 (2005). DOI: [10.1021/ma050805x](https://doi.org/10.1021/ma050805x)
- [20] Schwendeman I., Hickman R., Sönmez G., Schottland P., Zong K., Welsh D., Reynolds J. R.: Enhanced contrast dual polymer electrochromic devices. *Chemistry of Materials*, **14**, 3118–3122 (2002). DOI: [10.1021/cm020050y](https://doi.org/10.1021/cm020050y)
- [21] Wang H-M., Hsiao S-H., Liou G-S., Sun C-H.: Synthesis, photoluminescence, and electrochromism of polyamides containing (3,6-di-*tert*-butylcarbazol-9-yl)triphenylamine units. *Journal of Polymer Science Part A: Polymer Chemistry*, **48**, 4775–4789 (2010). DOI: [10.1002/pola.24269](https://doi.org/10.1002/pola.24269)
- [22] Koyuncu F. B., Koyuncu S., Ozdemir E.: A novel donor–acceptor polymeric electrochromic material containing carbazole and 1,8-naphthalimide as subunit. *Electrochimica Acta*, **55**, 4935–4941 (2010). DOI: [10.1016/j.electacta.2010.03.094](https://doi.org/10.1016/j.electacta.2010.03.094)
- [23] Icli M., Pamuk M., Algi F., Önal A. M., Cihaner A.: Donor–acceptor polymer electrochromes with tunable colors and performance. *Chemistry of Materials*, **22**, 4034–4044 (2010). DOI: [10.1021/cm100805g](https://doi.org/10.1021/cm100805g)
- [24] Patil A. O., Heeger A. J., Wudl F.: Optical properties of conducting polymers. *Chemical Reviews*, **88**, 183–200 (1988). DOI: [10.1021/cr00083a009](https://doi.org/10.1021/cr00083a009)
- [25] Thompson B. C., Schottland P., Sonmez G., Reynolds J. R.: *In situ* colorimetric analysis of electrochromic polymer films and devices. *Synthetic Metals*, **119**, 333–334 (2001). DOI: [10.1016/S0379-6779\(00\)00863-8](https://doi.org/10.1016/S0379-6779(00)00863-8)
- [26] Das S., Pati P. B., Zade S. S.: Cyclopenta[*c*]thiophene-based D–A conjugated copolymers: Effect of heteroatoms (S, Se, and N) of benzazole acceptors on the properties of polymers. *Macromolecules*, **45**, 5410–5417 (2012). DOI: [10.1021/ma3006697](https://doi.org/10.1021/ma3006697)
- [27] Shen P., Bin H., Zhang Y., Li Y.: Synthesis and optoelectronic properties of new D–A copolymers based on fluorinated benzothiadiazole and benzoselenadiazole. *Polymer Chemistry*, **5**, 567–577 (2014). DOI: [10.1039/C3PY00968H](https://doi.org/10.1039/C3PY00968H)
- [28] Baran D., Oktem G., Celebi S., Toppare L.: Neutral-state green conjugated polymers from pyrrole bis-substituted benzothiadiazole and benzoselenadiazole for electrochromic devices. *Macromolecular Chemistry and Physics*, **212**, 799–805 (2011). DOI: [10.1002/macp.201000744](https://doi.org/10.1002/macp.201000744)
- [29] Zhang Q., Cirpan A., Russell T. P., Emrick T.: Donor–acceptor poly(thiophene-*block*-perylene diimide) copolymers: Synthesis and solar cell fabrication. *Macromolecules*, **42**, 1079–1082 (2009). DOI: [10.1021/ma801504e](https://doi.org/10.1021/ma801504e)
- [30] Li Z., Zhang Y., Tsang S-W., Du J., Zhou J., Tao Y., Ding J.: Alkyl side chain impact on the charge transport and photovoltaic properties of benzodithiophene and diketopyrrolopyrrole-based copolymers. *Journal of Physical Chemistry C*, **115**, 18002–18009 (2011). DOI: [10.1021/jp202996p](https://doi.org/10.1021/jp202996p)
- [31] Poverenov E., Li M., Bitler A., Bendikov M.: Major effect of electropolymerization solvent on morphology and electrochromic properties of PEDOT films. *Chemistry of Materials*, **22**, 4019–4025 (2010). DOI: [10.1021/cm100561d](https://doi.org/10.1021/cm100561d)
- [32] Mortimer R. J., Graham K. R., Grenier C. R. G., Reynolds J. R.: Influence of the film thickness and morphology on the colorimetric properties of spray-coated electrochromic disubstituted 3,4-propylenedioxithiophene polymers. *ACS Applied Materials and Interfaces*, **10**, 2269–2276 (2009). DOI: [10.1021/am900431z](https://doi.org/10.1021/am900431z)
- [33] Neo W. T., Shi Z., Cho C. M., Chua S-J., Xu J.: Effects of chemical composition, film thickness, and morphology on the electrochromic properties of donor–acceptor conjugated copolymers based on diketopyrrolopyrrole. *ChemPlusChem*, **80**, 1298–1305 (2015). DOI: [10.1002/cplu.201500182](https://doi.org/10.1002/cplu.201500182)
- [34] Cihaner A., Algi F.: A processable rainbow mimic fluorescent polymer and its unprecedented coloration efficiency in electrochromic device. *Electrochimica Acta*, **53**, 2574–2578 (2008). DOI: [10.1016/j.electacta.2007.10.030](https://doi.org/10.1016/j.electacta.2007.10.030)