

Multi-electrochromic 2,7-linked Polycarbazole Derivative and Its Application in Electrochromic Devices

Lingqian Kong^{1,2}, Zhong Wang³, Jinsheng Zhao^{4,*}, Jianzhong, Xu^{1,*}

¹ College of Chemistry and Environmental Science, Hebei University, Baoding, 071002, P. R. China

² Dongchang College, Liaocheng University, Liaocheng, 252059, P. R. China

³ Liaocheng Hospital., Liaocheng, Shandong Province, 252000, P. R. China.

⁴ Shandong Key Laboratory of Chemical Energy-storage and Novel Cell Technology, Liaocheng University, Liaocheng 252059, P. R. China.

*E-mail: j.s.zhao@163.com (j.s.zhao); xjz8112@sina.com (j.z.xu)

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Two 2,7-linked carbazole derivatives, 2,7-bis(2-thiophene)-N-methylcarbazole (BTC) and 2,7-bis(2,3,4-ethylenedioxythiophene)-N-methylcarbazole (BEC), were successfully synthesized and electropolymerized. The electrochemical and optical investigations indicated that the two monomers and their resulting polymers (PBTC and PBEC) showed excellent polymerization and redox activity, and substitution with EDOT units resulted in a decrease in the monomer and polymer oxidation potentials, narrowing of the electronic band gap relative to the corresponding thiophene substituted 2,7-carbazoles. Spectroelectrochemical study revealed that both of the polymers had interesting electrochromic properties and displayed multi-electrochromic behaviors as well as good switching properties. The electrochromic properties of the two polymers are dependent on the selective of substituents attached at the 2,7-positions of N-methylcarbazole. Moreover, dual-type electrochromic devices (ECDs) consisting of PBTC (or PBEC) and PEDOT layers were also fabricated and characterized in detail. It was found that both of the ECDs displayed good electrochromic performances, such as reasonable optical contrast, fast response time and excellent redox stability.

Keywords: Poly(2,7-carbazole); Conjugated polymer; Spectroelectrochemistry; Electrochromic device.

1. INTRODUCTION

Electrochromism can be defined as the reversible change in optical properties of a material resulting from electrochemically induced redox states [1,2]. Electrochromic materials have recently received a great deal of attention for their technological application as smart windows that control the

sun radiation in buildings and cars, rear-view mirrors for cars, and display devices as well as from the stand point of scientific interest [3]. Both inorganic and organic materials have been used as EC materials. Although inorganic systems are now in practical use, organic systems have advantages over inorganic systems in several ways such as driving at low voltage, coloration over a wide range, color distinction, and multicoloration, etc [4]. For instance, conducting polymers (CPs) with carbon and heteroatom frameworks have attracted more and more attention in the last three decades due to their ease of chemical and electrochemical synthesis, redox stability, processability and multichromism [5]. These properties of CPs can be tuned by functionalization of the electroactive monomer structure before polymerization and association of the conducting polymer with other materials, such as main-chain and pendant-group structural modification and copolymerization as well as the use of blends and composites.

As a class of electroactive polymers, carbazole-containing polymers have been widely investigated owing to their attractive and practical opto-electrochemical properties. Generally, the disadvantages existing in the directly polymerization of carbazole are that it requires a high potential for oxidation, and the polymerization proceeds rather sluggishly [6]. To solve these problems, there have been many reports about preparing multi-ring electropolymerizable monomers with electron-rich heterocycles at the terminal polymerization sites of carbazole. When electron-donating substituents are incorporated on monomers to be oxidatively polymerized, large decreases are observed in the oxidation potential because of the extended conjugation of the monomer, allowing mild polymerization conditions to be used [7], and the electroactive polymers exhibit a wide range of properties. To date, many reports have focused on poly(3,6-carbazole)s to investigate their interesting semiconductive, electrochromic and luminescence properties [6,8–11]. On the contrary, there are only a little reports about 2,7-carbazole based polymers due to the fact that the 3 and 6 positions are more easily electrophilic-substituted by heterocycles to afford reactive monomers than the 2,7-positions. While, it should be noted that poly(2,7-carbazole)s were found to have more extended effective conjugation lengths than poly(3,6-carbazole)s [12–14] due to their poly(*p*-phenylene)-like structure. More interestingly, several approaches have been proposed for the preparation of 2,7-carbazole based optoelectronic materials in recent years. For instance, a series of *N*-alkylated-2,7-di(2-heterocycle)carbazoles were synthesized and electropolymerized to obtain electroactive films of poly(2,7-carbazole) with low band gaps and significant electrochromic behaviors as reported by Kawabata et al [15]. In addition, Koyuncu et al. reported the electropolymerization of a new 2,7-carbazole derivative 9-(4-nitrophenyl)-2,7-di-2-thienyl-9H-carbazole to give stable, electroactive and electrochromic materials [16]. To date, electrochemical polymerization of 2,7-di(2-thienyl)carbazole monomers have been reported [17]. However, to the best of our knowledge, there is still no a thorough study on the electrochromic switching properties and electrochromic devices of bis(2-thienyl)- and bis(2-(3,4-ethylene-dioxythiophene))-substituted poly(*N*-methyl-2,7-carbazole)s.

Herein, in this study, *N*-methyl-2,7-di(2-heterocycle)carbazole monomers were synthesized by introducing thiophene or 3,4-ethylenedioxythiophene (EDOT) units at 2,6-positions of *N*-methylcarbazole and electrochemically polymerized to form their polymers. The spectroelectrochemical and electrochromic properties of the resultant polymers were studied in detail. It is interesting to find that the polymer films exhibit multichromic behaviors with excellent switching

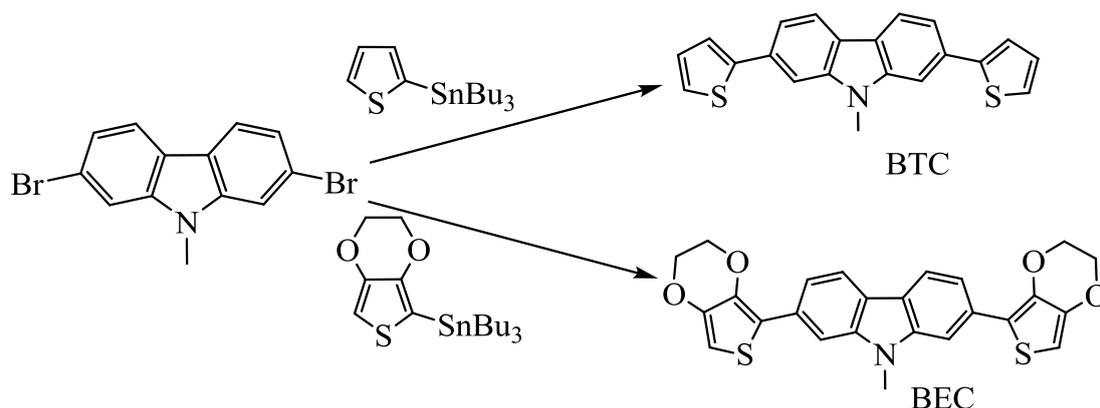
ability. In addition, dual type electrochromic devices (ECDs) utilizing the corresponding polymers and PEDOT were also constructed and characterized in detail.

2. EXPERIMENTAL DETAILS

2.1. Materials

2,7-Dibromocarbazole, thiophene and 3,4-ethylenedioxythiophene (EDOT, 98%) were all purchased from Aldrich Chemical and used as received. Commercial high-performance liquid chromatography grade acetonitrile (ACN, Tedia Company, INC. USA), dichloromethane (DCM, Sinopharm Chemical Reagent CO., Ltd., China), poly(methyl methacrylate) (PMMA, Shanghai Chemical Reagent Company), propylene carbonate (PC, Shanghai Chemical Reagent Company), tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , Shanghai Chemical Reagent Company) and lithium perchlorate (LiClO_4 , Shanghai Chemical Reagent Company, 99.9%) were used directly without further purification. Sodium perchlorate (NaClO_4 , Shanghai Chemical Reagent Company, 98%) was dried in vacuum at 60 °C for 24 hours before use. Other reagents were all used as received without further treatment. Indium-tin-oxide-coated (ITO) glass (sheet resistance : $< 10 \Omega \square^{-1}$, purchased from Shenzhen CSG Display Technologies, China) was washed with ethanol, acetone and deionized water successively under ultrasonic, and then dried by N_2 flow.

2.2. Synthesis of 2,7-bis(2-thiophene)-N-methylcarbazole (BTC) and 2,7-bis(2-3,4-ethylenedioxythiophene)-N-methylcarbazole (BEC)



Scheme 1. Synthetic routes of the monomers BTC and BEC

The BTC and BEC monomers were synthesized by Stille cross coupling reaction as shown in Scheme 1. Thiophene and 3,4-ethylenedioxythiophene was converted to its stannyl derivative by treating it with $n\text{-BuLi}$ and SnBu_3Cl . A Stille coupling reaction between 2,7-dibromocarbazole and 2-tributylstannyl-thiophene (or 2-tributylstannyl-3,4-ethylenedioxythiophene) in the presence of CuI , 18-crown-6 and K_2CO_3 gave the compound BTC and BEC. The purified product was a white crystal for

BTC and a pale green for BEC. ^1H Nuclear magnetic resonance (^1H NMR) verified the structure of the monomers. BTC (CDCl_3 , 400 MHz, ppm): δ = 8.034 (d, 2H, Cz), 7.601 (s, 2H, Cz), 7.532 (d, 2H, Cz), 7.433 (d, 2H, Th), 7.309 (d, 2H, Th), 7.143 (t, 2H, Th), 3.921 (s, 3H, N- CH_3). BEC (CDCl_3 , 400 MHz, ppm): δ = 8.010 (d, 2H, Cz), 7.744 (d, 2H, Cz), 7.587 (d, 2H, Cz), 6.334 (s, 2H, Th), 4.369 (m, 8H, O- CH_2 - CH_2 -O), 3.897 (s, 3H, N- CH_3).

2.3. Instrumentation

^1H NMR spectroscopy studies were carried out on a Varian AMX 400 spectrometer and tetramethylsilane was used as the internal standard for ^1H NMR. UV-vis spectra were carried out on a Shimadzu UV-2550 spectrophotometer. Digital photographs of the polymer films were taken by a Canon Power Shot A3000 IS digital camera.

2.4. Electrochemistry

Electrochemical synthesis and experiments were performed in a one-compartment cell with a CHI 760 C Electrochemical Analyzer under computer control, employing a platinum wire with a diameter of 0.5 mm as working electrode, a platinum ring as counter electrode, and a silver wire (Ag wire) as pseudo reference electrode. The working and counter electrodes for cyclic voltammetric (CV) experiments were placed 0.5 cm apart during the experiments. All electrochemical polymerization and CV tests were taken in ACN/DCM (1:1, by volume) solution containing 0.2 M NaClO_4 as a supporting electrolyte. The pseudo reference electrode was calibrated externally using a 5 mM solution of ferrocene (Fc/Fc^+) in the electrolyte ($E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.25$ V vs. Ag wire in ACN/DCM (1:1, by volume) solution containing 0.2 M NaClO_4 and all the potentials mentioned follow were vs. the Ag wire electrode. The half-wave potential ($E_{1/2}$) of Fc/Fc^+ measured in ACN/DCM (1:1, by volume) solution containing 0.2 M NaClO_4 was 0.28 V vs. SCE. Thus, the potential of Ag wire was assumed to be 0.03 V vs. SCE. All of the electrochemical experiments were carried out at room temperature under nitrogen atmosphere.

2.5. Spectroelectrochemistry

Spectroelectrochemical data were recorded on Perkin-Elmer Lambda 900 UV-vis-near-infrared spectrophotometer connected to a computer. A three-electrode cell assembly was used where the working electrode was an ITO glass, the counter electrode was a stainless steel wire, and an Ag wire was used as pseudo reference electrode. The polymer films for spectroelectrochemistry were prepared by potentiostatically deposition on ITO electrode (the active area: 0.8 cm \times 2.1 cm). The measurements were carried out in ACN/DCM (1:1, by volume) solution containing 0.2 M NaClO_4 .

2.6. Preparation of the gel electrolyte

A gel electrolyte based on PMMA (MW: 350,000) and LiClO₄ was plasticized with PC to form a highly transparent and conductive gel. ACN was also included as a high vapor pressure solvent to allow an easy mixing of the gel components. The composition of the casting solution by weight ratio of ACN:PC:PMMA:LiClO₄ is 70:20:7:3. The gel electrolyte was used for construction of the polymer electrochromic device cell [18].

2.7. Construction of ECDs

ECDs were constructed using two complementary polymers, PBTC (or PBEC) as the anodically coloring material and PEDOT as the cathodically coloring material. All of the polymeric films were electrodeposited onto the ITO-coated glasses (the active area: 1.8×2.0 cm²) at 1.1 V for PBTC, 0.8 V for PBEC and 1.4 V for PEDOT, respectively. Before sealing the ECDs, the anodically coloring film PBTC (or PBEC) was fully reduced and the cathodically coloring film PEDOT was fully oxidized. Then the ECDs was built by arranging the two polymeric films (one reduced, the other oxidized) facing each other separated by a gel electrolyte.

3. RESULTS AND DISCUSSION

3.1. Electrochemical polymerization and characterization

3.1.1 Electrochemical polymerization

The electrochemical behavior of carbazole based monomers BTC and BEC were investigated by cyclic voltammetry technique. Cyclic voltammogram (CV) is a very useful method which is used for investigate the electroactivity of monomer. It also gives evidence on the reversibility of the electron transfer reactions during the electropolymerization. Electrochemical polymerization of the monomers were carried out in ACN/DCM (1:1, by volume) solution containing 0.005 M BTC or BEC monomer and 0.2 M NaClO₄ via CV at a scan rate of 100 mV s⁻¹.

As shown in Fig. 1a, the CV curves of BTC exhibited a monomer oxidation peak at 1.2 V at the first cycle. And the onset oxidation potential ($E_{\text{onset, m}}$) of BTC was calculated to be 0.99 V. As the CV scan continued, an electroactive polymer film quickly grew on the surface of working electrode (WE) revealing a new reversible redox process between 0.5 and 0.9 V with an accompanying increase in the current intensity. Compared with BTC, BEC showed a lower monomer oxidation peak at 0.7 V accompanied with a broad redox wave located at 0.3~0.5 V (Fig. 1b). The $E_{\text{onset, m}}$ of BEC was found to be 0.63 V, which is more easily oxidized than BTC. For monomer BEC, the presence of electron-donating ethylene-dioxy bridge on EDOT units lowers the oxidation potential compared to that of thiophene substituted monomer BTC. As the cyclic scan proceeded, intensities of anodic and cathodic currents of the polymer films gradually increased, indicating the presence of a conductive polymer on the electrode.

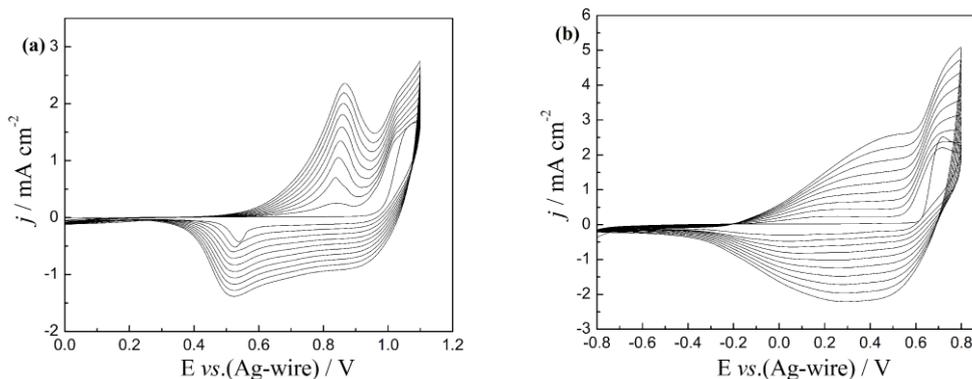


Figure 1. Cyclic voltammogram curves of 0.005 M BTC (a) and 0.005 M BEC (b) in ACN/DCM (1:1, by volume) containing 0.2 M NaClO_4 solution at a scan rate of 100 mV s^{-1} , respectively.

3.1.2. Electrochemistry behavior of the polymeric films

Electrochemistry behaviors of the polymeric film PBTC and PBEC were carried out in monomer-free solution of 0.2 M $\text{NaClO}_4/\text{ACN}/\text{DCM}$ via CV at different scan rates. As seen from Fig. 2, the oxidation potentials of polymers were observed as reversible and at lower potential compared with corresponding monomers due to the extended conjugation in the polymers backbone. The CVs of the PBTC film presented a reversible redox process between 0.8 and 0.5 V (Fig. 2a). While, the PBEC film exhibited a more negative redox couple at 0.4~0.5 V (Fig. 2b) as compared to PBTC. Moreover, the onset oxidation potential (E_{onset}) of PBTC (0.50 V) shifts anodically by 40 mV relative to that of PBEC, which is consistent with the presence of the ethylene-dioxy bridge in the latter case, making it electron richer and easily oxidized. As depicted in the insets of Fig. 2, linear relationships between scan rates and current intensities indicated that the two polymers were electroactive and well adhered on the electrode surface and the electrochemical processes were not diffusion limited [19].

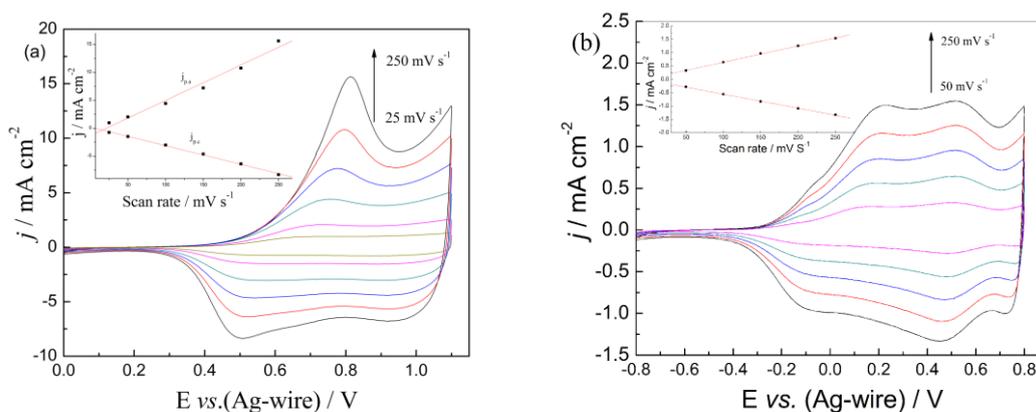


Figure 2. CV curves of the PBTC (a) and PBEC (b) film at different scan rates between 25 mV s^{-1} and 250 mV s^{-1} , respectively. The insets: Scan rate dependence of the anodic (j_{pa}) and cathodic (j_{pc}) peak current densities graphs.

3.1.3 Optical Properties

The UV–visible absorption spectra of the monomers BTC and BEC in CH_2Cl_2 and their dedoped polymer films PBTC and PBEC in solid state on an indium-tin-oxide (ITO) electrode are illustrated in Fig. 3. Monomer BTC features the absorption maximum (λ_{max}) of 353 nm with a weak shoulder at 371 nm, while BEC displays the bathochromically shifted λ_{max} of 365 nm with a distinct shoulder at 380 nm (Fig. 3). This indicates that molecule BEC possessed more conjugation length than BTC due to the electron-donating property of the ethylene-dioxy groups. Additionally, the optical band gaps ($E_{\text{g,opt}}$) of BTC and BEC were found to be 2.31 and 2.26 eV, respectively, which were determined from the absorption onsets (λ_{onset}) by using the equation: $E_{\text{g,opt}} = 1240/\lambda_{\text{onset}}$. Generally, substituting an electron donating moiety into the polymer backbone has the tendency to increase its HOMO energy level, resulting in a decreased band gap. On the other hand, the polymers PBTC and PBEC have maximum absorptions at 399 and 475 nm (a shoulder at around 525 nm for PBEC), and the absorption onsets at 537 and 580 nm, corresponding to band gaps of 2.31 and 2.14 eV, respectively (inset, Fig. 3). The observed red-shift of absorption bands in polymers (PBTC and PBEC) with respect to corresponding monomers (BTC and BEC) indicates that longer conjugated sequences in the polymer backbone π – π^* conjugation is extended.

The UV–vis absorption data of the present monomers BTC and BEC and their polymers PBTC and PBEC are summarized in Table 1 together with the corresponding data for the structurally related monomers (e.g. 9-Ethyl-2,7-di(2-thienyl)carbazole (DTCz2) [20], 9-Ethyl-3,6-di(2-thienyl)carbazole (3,6DTCz2) [20], N-Butyl-2,7-di(2-thienyl)carbazole (DTCz4) [15], N-Butyl-2,7-di(2-(3,4-ethylenedioxy)thienyl)carbazole (DECz4) [15], N-Methyl-3,6-di(2-(3,4-ethylenedioxy)thienyl)carbazole (3,6-BEC) [21]) and their polymers (e.g. PDTCz4, PDECz4, P(3,6-BEC)) for comparison. Compared to PBTC, the 2,7-di(thienyl)-N-alkylated monomers (e.g. DTCz2, DTCz4) show the same absorption maxima (λ_{max}) at 353 nm and shoulders at around 370 nm as well as slightly longer absorption onsets (393~395 nm), corresponding to band gaps of 3.15~3.13 eV (Table 1). A same case was found for 2,7-diEDOT-linked monomers (e.g. BEC and DECz4). While, 3,6-di(thienyl)-N-alkylated monomer 3,6-DTCz2 exhibits blue-shifted maximum absorption at 314 nm and higher band gap of 3.22 eV compared to the 2,7-di(thienyl)-N-alkylated monomers, indicating that 2,7-linked carbazoles have a more extended effective conjugation length than 3,6-linked carbazoles [22]. On the other hand, bisEDOT substituted poly(2,7-carbazole)s (PBEC and PDECz4) exhibits longer absorption maxima and lower band gaps relative to bithiophene substituted poly(2,7-carbazole)s (PBTC and PDTCz4) indicating the presence of longer conjugated sequences in the former polymer backbones. In addition, compared to bisEDOT substituted poly(2,7-carbazole) PBEC, bisEDOT derived poly(3,6-carbazole) P(3,6-BEC) shows significantly blue-shifted absorption maximum (424 nm) and increased band gap (2.5 eV), indicating the shorter effective conjugation length along the main chains of 3,6-carbazole-derived polymers compared to that of 2,7-carbazole-derived polymers due to conjugation breaks induced by 3,6-carbazole units [23].

The energies of frontier molecular orbitals (HOMO and LUMO) derived from the electrochemical and optical data are also listed in Table 1. The energy of the HOMO levels of the monomers and polymers were calculated by using the formula $E_{\text{HOMO}} = -e(E_{\text{onset}} + 4.4)$ (E_{onset} vs. SCE)

and LUMO energy levels (E_{LUMO}) of them were calculated by the subtraction of the optical band gap from the HOMO levels [24]. As depicted in Table 1, the HOMO levels of the polymer PBTC and PBEC were calculated as -4.93 and -4.89 eV, respectively, which are higher than that of the monomer BTC (-5.42 eV) and BEC (-5.06 eV).

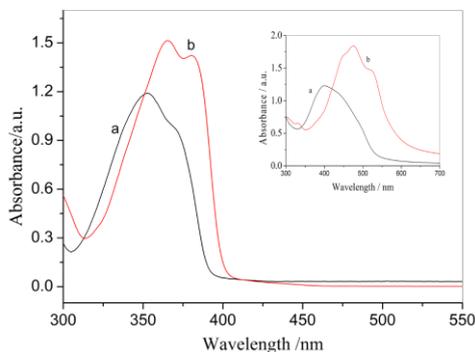


Figure 3. UV-vis spectra of BTC (a) and BEC (b) dissolved in CH_2Cl_2 . Inset: absorption spectra of PBTC (a) and PBEC (b) deposited on ITO electrode in the neutral state.

Table 1. Onset oxidation potential (E_{onset}), HOMO and LUMO energy levels, maximum absorption wavelength (λ_{max}), absorption onset (λ_{onset}) and optical band gap ($E_{\text{g,opt}}$) of BTC, BEC, PBTC, PBEC and structurally related monomers (e.g. DTCz2, 3,6-DTCz2, DTCz4, DECz4, 3,6-BEC) and their polymers (e.g. PDTCz4, PDECz4, P(3,6-BEC)) for comparison.

| Compounds | E_{onset} (V) ^a | HOMO (eV) ^b | LUMO (eV) ^c | $\lambda_{\text{max}}/\lambda_{\text{onset}}$ (nm) | $E_{\text{g,opt}}$ (eV) ^d |
|--------------------------|-------------------------------------|------------------------|------------------------|--|--------------------------------------|
| BTC | 0.99 | -5.42 | -2.25 | 353, 371/391 | 3.17 |
| DTCz2 ^[20] | — | -5.44 | -1.66 | 353, 370/395 | 3.13 |
| DTCz4 ^[15] | — | -5.37 | -2.22 | 353, 370/393 | 3.15 |
| 3,6DTCz2 ^[20] | — | -5.34 | -1.21 | 314, 345/385 | 3.22 |
| BEC | 0.63 | -5.06 | -1.95 | 365, 380/398 | 3.11 |
| DECz4 ^[15] | — | -5.14 | -2.15 | 365, 380/400 | 2.99 |
| PBTC | 0.50 | -4.93 | -2.62 | 399/537 | 2.31 |
| PDTCz4 ^[15] | — | -4.97 | -2.67 | 428/— | 2.3 |
| PBEC | 0.46 | -4.89 | -2.75 | 475, 525/580 | 2.14 |
| PDECz4 ^[15] | — | -4.33 | -2.23 | 483/— | 2.1 |
| P3,6-BEC ^[21] | — | — | — | 424/496 | 2.5 |

^aAll potentials vs. (Ag-wire).

^bHOMO = $-e(E_{\text{onset}} + 4.4)$ (E_{onset} vs. SCE).

^cLUMO = HOMO $- E_{\text{g,opt}}$.

^d $E_{\text{g,opt}} = 1240/\lambda_{\text{onset}}$.

Additionally, the electron donating ability of the EDOT unite made the EDOT substituted poly(carbazole)s (e.g. PBEC, PDECz4) with higher HOMO energy levels compared to the

corresponding thiophene substituted poly(carbazole)s (e.g. PBTC, PDTCz4). Both of PBTC and PBEC have comparable energy levels when compared with the structurally related 2,7- or 3,6-linked poly(carbazole)s as listed in Table 1. As a result of the data in Table 1, optical and electrochemical properties of the molecules were greatly influenced by the electro-donating ability of heterocycles and alkyls as subunits in the structure. Moreover, the data seem to indicate that PBTC and poly PBEC can be considered as materials suitable for the optoelectronic device applications for their comparable HOMO/LUMO levels.

3.2. Electrochromic properties of PBTC and PBEC films

3.2.1. Spectroelectrochemical properties of PBTC and PBEC films

Spectroelectrochemistry is a useful method to obtain information about the electronic structure of polymers. The spectroelectrochemical behaviors of the PBTC and PBEC films were examined through spectral measurements in a 0.2 M NaClO₄/ACN/DCM solution at different potentials. Fig. 4 shows the changes in the absorption spectra of PBTC (a) and PBEC (b) films at various applied potentials. As seen in Fig. 4a, the absorption spectra of neutral form of the PBTC film exhibit absorption bands at 399 nm due to the π - π^* transition. Upon progressive oxidation of the PBTC film, the intensity of the π - π^* transition bands decreased while two new absorption bands at around 550 nm and longer than 800 nm wavelengths increased dramatically, corresponding to the formation of polaronic and bipolaronic bands.

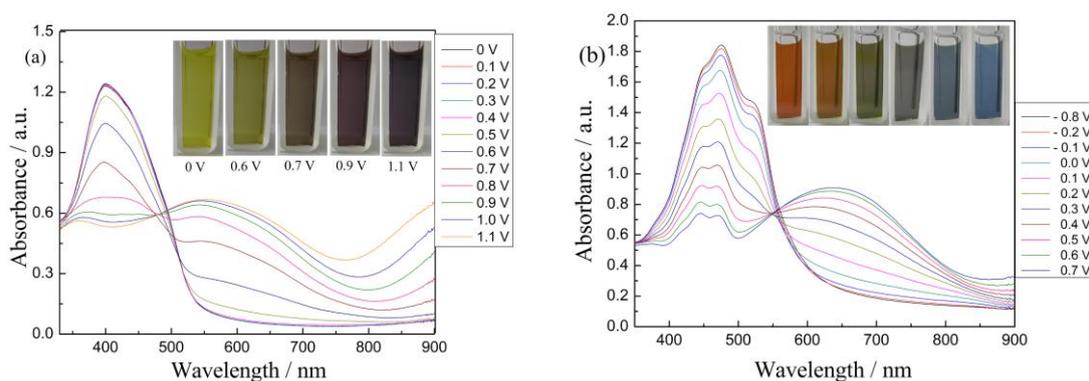


Figure 4. Spectroelectrochemical spectra of PBTC (a) and PBEC (b) with applied potentials between reduced state and oxidized state in ACN/DCM (1:1, by volume) containing 0.2 M NaClO₄. The insets show the various colors at different potentials.

As a result of these variations in the absorption spectra of PBTC, the color of the polymer changes from yellow in the neutral state to gray, violet and bluish violet upon doping (Fig. 4a, inset). In the case of PBEC, the film exhibits a π - π^* transition at 475 nm at the dedoped state while two charge carrier bands located at around 650 nm and longer than 900 nm were intensified upon oxidation (Fig. 4b). The PBEC film displays distinct color transition with six different colors from reddish brown

to blue (Fig. 4a, inset), indicating its multichromic property relative to the PBTC film. As a result, the presence of a number of electroactive groups in the structure causes the molecule to have different oxidation levels, making it to be a multielectrochromic material [25]. Furthermore, stable color changes were observed for both of the polymer films. The excellent electrochromic abilities of the resulting polymers are desired for their applications in electrochromic devices.

3.2.2. Electrochromic switching of PBTC and PBEC films in solution

It is important that polymers can switch rapidly and exhibit a noteworthy color change for electrochromic applications. For this purpose, double potential step chronoamperometry technique was used to investigate the switching ability of PBTC and PBEC films between its neutral and full doped state (Fig. 5a). As seen in Fig. 5a, the dynamic electrochromic experiment for PBTC was carried out at the potential switched between 0 and 1.1 V with regular interval of 5 s at 400 nm and 550 nm, respectively. One important characteristic is the optical contrast (ΔT %), which can be defined as the transmittance difference between the redox states. The optical contrast of PBTC was found to be 15.44% and 28.78% at 400 and 550 nm, respectively. Response time, one of the most important characteristics of electrochromic materials, is the necessary time for 95% of the full optical switch (after which the naked eye could not sense the color change) [26]. The optical response time of PBTC from the reduced to the oxidized state was found to be 3.4 s at 400 nm, 1.2 s at 550 nm. The electrochromic switching response of PBEC was also carried out between -0.8 V and 0.7 V at 475 and 645 nm (Fig.5b). The optical contrast of PBEC at 475 and 645 nm are calculated to be 25.75% and 33.91%, which are higher than that of PBTC. The response time of PBEC film was found to be 2.9 s and 1.3 s at 475 and 645 nm, respectively, which are slightly faster compare to PBTC film. Besides, another important characteristic of the electrochromic materials is color efficiency (CE), which can be calculated by using the equations $CE = \Delta OD / \Delta Q$ and $\Delta OD = \log(T_b / T_c)$, where ΔQ is the injected/ejected charge between neutral and oxidized states, T_b and T_c are the transmittance in the neutral and oxidized states, respectively [27]. The CE values of the films were calculated to be 118 $\text{cm}^2 \text{C}^{-1}$ for PBTC and 319 $\text{cm}^2 \text{C}^{-1}$ for PBEC, respectively. Obviously, the CE of PBEC film is almost three times greater than that of PBTC, indicating that the PBEC film has a dramatic coloration ability when unit charge was injected/ejected between neutral and oxidized states.

The electrochromic switching data of PBTC and PBEC film are tabulated in Table 2 together with structurally related poly(9-phenyl-2,7-di-2-thienyl-9H-carbazole) poly(TCT) and poly(9-(4-nitrophenyl)-2,7-di-2-thienyl-9H-carbazole) poly(TCT-N) [16] films for comparison. In the visible region (e.g. 420 nm), the poly(TCT) and poly(TCT-N) exhibit lower optical contrast (8% and 22%, respectively) as compared to PBTC and PBEC. While in the near-infrared (NIR) region (e.g. 1000 nm), the poly(TCT) and poly(TCT-N) show higher optical contrast of 55%~57% relative to PBTC and PBEC. In addition, the response time of poly(TCT) and poly(TCT-N) in the NIR region are 1.8 and 4.3 s, respectively, which are slower than that of PBTC and PBEC. Due to the structural similarity between PBTC and poly(TCT), they show similar colors at the reduced state as well as similar coloration efficiencies. Especially, EDOT derivatized PBEC has much greater coloration efficiency

than that of thiophene-based PBTC, poly(TCT) and poly(TCT-N) due to the existence of ethylene-dioxy groups. Consideration of the good electrochromic performance of polymers mentioned above, such 2,7-substituted poly(carbazole)s, especially EDOT derivatized PBEC, could be a promising electrochromic material.

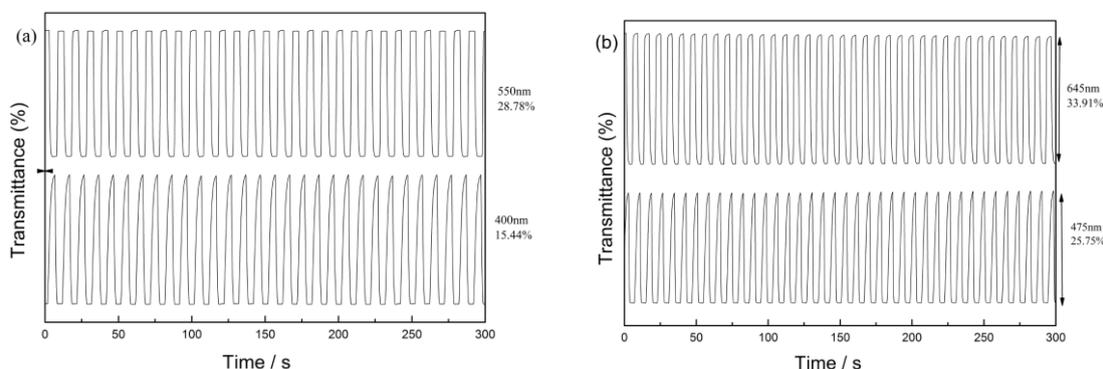


Figure 5. Electrochromic switching, optical response for PBTC (a) and PBEC (b) films monitored at specific wavelength between neutral and oxidized state with a same residence time of 5 s.

Table 2. Electrochromic switching properties of PBTC, P(TCT), P(TCT-N) and PBEC

| Materials | Optical contrast ($\Delta T\%$) | Response time (s) | Color efficiency ($\text{cm}^2 \text{C}^{-1}$) | Color |
|-----------------------------|-----------------------------------|-------------------|--|----------------------|
| PBTC | 15.44% (400 nm) | 3.6 (400 nm) | 118 | Yellow (red.) |
| poly(TCT) ^[16] | 28.78% (550 nm) | 1.5 (550 nm) | - | Bluish violet (ox.) |
| | 8% (420nm) | - | 126 | Yellow (red.) |
| poly(TCT-N) ^[16] | 55% (1000 nm) | 1.8 (1000 nm) | - | Dark gray (ox.) |
| | 22% (420 nm) | - | 264 | Orange (red.) |
| PBEC | 57% (1000 nm) | 4.3 (1000 nm) | - | Dark blue (ox.) |
| | 25.75% (475 nm) | 2.9 (475 nm) | 319 | Reddish brown (red.) |
| | 33.91% (645 nm) | 1.3 (645 nm) | - | Blue (ox.) |

red. ~ reduced state.

ox. ~ oxidized state.

3.3. Spectroelectrochemistry of electrochromic devices (ECDs)

3.3.1. Spectroelectrochemical properties of ECDs

The dual type ECD consisting of the polymer (PBTC or PEDOT) film and PEDOT film was constructed and its spectroelectrochemical behaviors were also studied (Fig. 6a and b). Fig. 6a shows the spectroelectrochemistry result of PBTC/PEDOT ECD between -0.8 V and 1.5 V . At -0.8 V , the device reveals a maximum electronic absorption at 395 nm where the color of the device is green. The green color is attributed to the absorption of reduced PBTC ($\pi-\pi^*$ transition), since PEDOT is in its

oxidized form (highly transparent). As the applied potential increased, the PBTC layer starts to be oxidized while PEDOT layer is reduced, which lead to a new absorption at 600 nm due to the reduced state of PEDOT (Fig. 6a), and the dominated color of the device is blue at 1.7 V. On the other hand, the spectroelectrochemistry of the PBEC/PEDOT ECD was also recorded between -0.8 V and 1.5 V. As depicted in Fig. 6b, the distinct optical changes between the reduced and oxidized state were observed for PBEC/PEDOT ECD, leading to a reversible color change between grayish violet and blue. It can be anticipated that the above two ECDs with interesting colors will have promising applications.

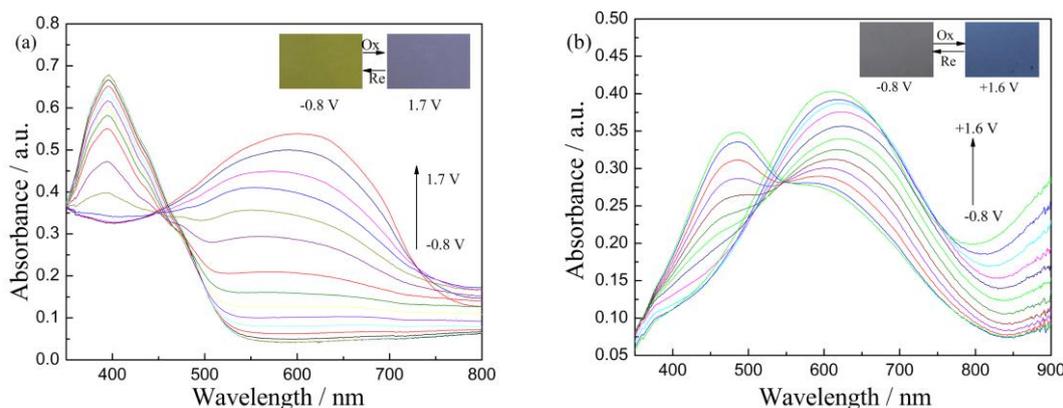


Figure 6. Spectroelectrochemical spectra and the colors of PBTC/PEDOT (a) and PBEC/PEDOT (b) devices at various applied potentials.

3.3.2. Switching of ECDs

Kinetic studies were also done to test the response time of the electrochromic devices (ECDs). Between -0.8 and 1.7 V inputs with a regular time interval of 4 s, the optical response of PBTC/PEDOT device at 400 nm and 580 nm was illustrated in Fig. 7a. The optical contrast (ΔT %) and response time of PBTC/PEDOT device were calculated as 6.33% and 1.2 s at 400 nm, 26.27% and 1.3 s at 580 nm, respectively. On the other hand, the switching property of PBEC/PEDOT device was also tested (Fig. 7b). PBEC/PEDOT device exhibited optical contrast of 11.99% (470 nm) and 20.10% (616 nm), and response time of 0.4 s (470 nm) and 0.5 s (616 nm). It was obvious that the use of PBEC film as the anodic coloring layer can dramatically quicken the response time of ECDs when compared with PBTC-based ECDs. In addition, the coloration efficiency (CE) of them were measured as 120 cm^2 C^{-1} for PBTC and 399 cm^2 C^{-1} for PBEC, respectively. Compared with poly[3,6-bis(2-(3,4-ethylenedioxythiophene))-N-methylcarbazole]/PEDOT (PBEDOT-NCH₃Cz/PEDOT) device reported by Reynolds et al. [28], the PBEC/PEDOT device has competitive response time and coloration efficiency, which is very suitable for electrochromic device application.

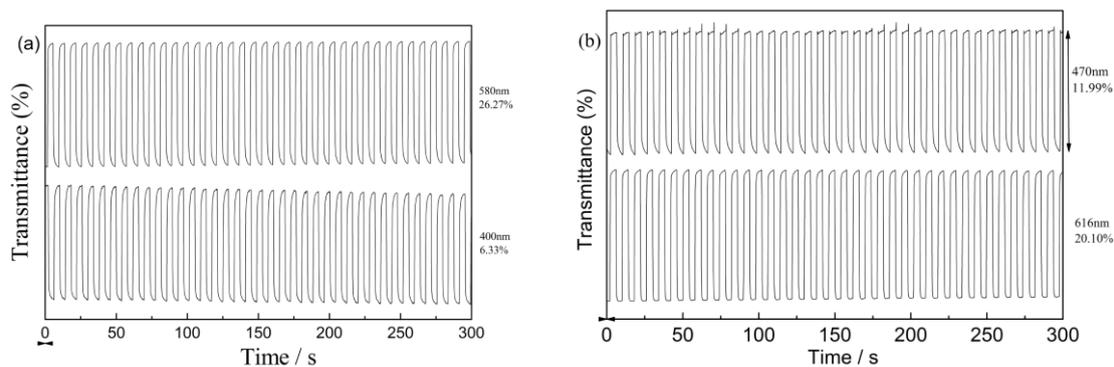


Figure 7. Electrochromic switching, optical response for PBTC/PEDOT (a) device and PBEC/PEDOT at specific wavelengths by applying potentials between the neutral state and the oxidized state with a residence time of 4 s.

3.3.3. Open circuit memory of ECDs

The optical memory in electrochromic devices is an important parameter since it is directly related to its application and energy consumption during the use of ECDs [17]. The optical spectra for PBTC/PEDOT device was monitored at 600 nm as a function of time at -0.8 and 1.8 V by applying the potential for 1 s for each 200 s time interval (Fig. 8). As depicted in Fig. 8, at the reduced state, the device shows a true permanent memory effect since there is almost no transmittance change under applied potential or open circuit conditions. In blue colored state device is rather less stable in terms of color persistence, however this matter can be overcome by application of current pulses to freshen the fully colored states. The same phenomena were also found for procedure PBEC/PEDOT device (data was not shown), which exhibited a good optical memory.

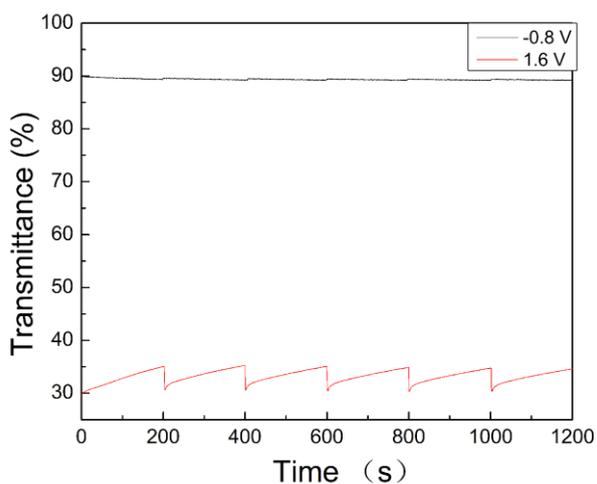


Figure 8. Open circuit stability of the PBTC/PEDOT device monitored at 600 nm.

3.3.4. Stability of ECDs

The stability of the ECD for long-term switching between oxidized and neutral states is important for practical applications. The PBTC/PEDOT device was tested by cyclic voltammetry of the applied potential between -0.8 and 1.7 V with 500 mV s^{-1} to evaluate the stability of the device (Fig. 9). The above observation of the ability to switch between oxidized and reduced states of the ECD. After 500 cycles, 92% of its electroactivity was retained and there was no obvious decrease of activity between 500 cycles and 1000 cycles, which indicating that this device has satisfactory redox stability. On the other hand, the stability measurement of PBEC/PEDOT device was also recorded by cyclic voltammetry. 94% of its electroactivity was retained after 1000 cycles for PBEC/PEDOT device. As a result, both of the two ECDs possess exceptional redox stability.

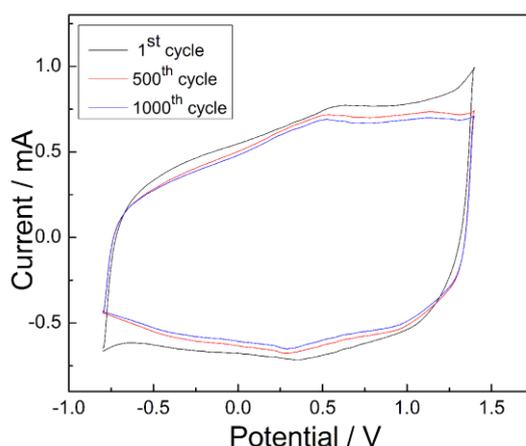


Figure 9. Cyclic voltammogram of PBTC/PEDOT device as a function of repeated with a scan rate of 500 mV s^{-1} .

4. CONCLUSION

In this report, two 2,7-heteroaromatic carbazole monomers (BTC and BEC) were synthesized and electropolymerized. The optical and electrochemical properties of monomers and the corresponding polymers (PBTC and PBEC) were found to be influenced by the selection of the heterocycle substituent (thiophene or EDOT). For instance, the bisEDOT derived poly(carbazole) (PBEC) was easily to be oxidized and exhibited lower band gap (2.14 eV) compared to bithiophene derived polymer (PBTC). Spectroelectrochemistry study revealed that both of the polymers displayed excellent multi-electrochromic properties. Dual type ECDs based on the two polymers and PEDOT were constructed and characterized. Electrochromic switching study showed that both of the devices exhibited reasonable optical contrast and faster response time was observed for PBEC/PEDOT device relative to PBTC/PEDOT device. Additionally, the two devices showed satisfactory optical memory and excellent redox stability. Consideration of these good features above, both of the polymers can be candidate for potential application in electrochromic devices.

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