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Synthesis and multi-electrochromic properties of asymmetric structure polymers based on carbazole-EDOT and 2, 5–dithienylpyrrole derivatives



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ABSTRACT

Two novel asymmetric structure monomers, 3,6-Bis-(2,3-dihydro-thieno[3,4- b][1,4]dioxin-5-yl)-9-[4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-phenyl]-9H-carbazole (BDTC) and 2,7-Bis-(2,3-dihydro-thieno[3,4-b] [1,4]dioxin-5-yl)-9-[4-(2,5-di-thio phen-2-yl-pyrrol-1-yl)-phenyl]-9H-carbazole (BDDC), were designed and synthesized. Both the monomers could be electropolymerized to form the related polymer films. The electrochemical and electrochromic properties of polymer films were different from that of their homopolymers, which could be attributed to the similar copolymerization effect of asymmetric structure. Different linked positions also led to different features, PBDDC film showed more colors (orange, yellow green, green and blue) than that of PBDTC film (yellow, green and purple blue). However, after the introduction of 2, 2'-Bi(3,4-ethoxylene dioxy thiophene)(BIEDOT), the resulting copolymers exhibited similar electrochromic features(red, brown yellow, green and blue) due to the leading effect of EDOT units. Moreover, all the polymer films displayed fast switching time, reasonable optical contrast and good coloration efficiency, which made them have potential application in electrochromic devices.

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1. Introduction

For the past decades, conjugated polymers have gained many attentions owing to their potential applications in the fields of organic light emitting diodes (OLEDs) [1,2], electrochromic devices (ECDs) [3,4], organic solar cells (OSCs) [5,6] and Li-polymer batteries [7,8]. Especially, as the active layers of ECDs, conjugated polymers possess the advantages of easily turned color-showing via modifying the structure, fast switching time and high coloration efficiency [9–11]. Up to now, many methods including donoracceptor (D-A) effect [12,13], the influence of suspended groups at side chain [14,15] and copolymerization [16,17] have been employed to explore the relationship between structure and performance of the polymer. However, design and synthesis of high performance electrochromic polymer materials are still a challenge. Recently, cross-linked conjugated polymers have attracted researcher's interest due to their better stability and charge transport

ability comparing with the linear molecules. Ma group designed and synthesized a novel poly(3.4-dioxythiophene) derivative (PM-BTE) with soft nano-network structure, which displayed low switching potentials and excellent stability [18]. Zhang group synthesized a novel cross linked polymer (PTPHSNS) connected by conjugated terphenyl groups, which showed fast switching time and excellent color memory behavior [19]. Moreover, Toppare group designed and synthesized a asymmetric structure polymer containing benzotriazole and 2, 5-di(2-thienyl)-1H-pyrrole units, study results indicated that similar copolymerization effect could be achieved [20]. However, the connected groups between the different units of asymmetric structure polymer were hexyl, which ignored the effect of intramolecular charge transfer. With the consideration of the above research results, it is anticipated that cross linked asymmetric structure polymer connected by conjugated groups may hold some unexpected electrochemical and electrochromic properties.

2, 5-dithienylpyrrole derivatives are famous for their low oxidized potential, easy modified structure via N-position of pyrrole units and good electrochemical film-forming ability [21–23]. However, electrochromic properties of resulting polymer film needed to be enhanced by copolymer [24–26]. Fortunately, such



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the deficiency can be made up by similar copolymerization effect of asymmetric structure, so 2, 5-dithienylpyrrole units can be considered as the better choice to construct the asymmetric structure monomer. Moreover, carbazole derivatives possess multi functioned positions, such as 3.6-position, 2.7- position and N-functioned position. And our recent studies indicated that 3.6-position linked carbazole-EDOT derivatives showed good electro-chemical and electrochromic properties via modifying the N-position of carbazole units [27–29]. Other related researches showed that the polymers based on 2.7-position linked carbazole could exhibit lower band gap, which was also benefit for electrochemical and electrochromic properties [30–33]. So it is interesting to integrate 2, 5-dithienylpyrrole units into carbazole-EDOT derivative to gain the asymmetric structure compound and explore its electrochemical and electrochromic properties.

In this manuscript, asymmetric structure monomers based on carbazole-EDOT and 2, 5-dithienylpyrrole connected via p-phenylenediamine structure were designed and synthesized (Scheme 1). Both the monomers can be electropolymerized to form resulting polymer films, the electrochemical and electrochromic properties of polymer films were investigated in detail. Moreover, to further study the effect of increasing EDOT units of the polymer main chain, copolymers with 2, 2'-Bi(3,4-ethoxylene dioxy thiophene)(BIEDOT) were also prepared, whose electrochemical and electrochromic characteristics were studied and compared with those of asymmetric structure polymers.

2. Experimental

2.1. Materials and measurements

3,6-Dibromocarbazole and 2,7-Dibromocarbazole were purchased from Energy Chemical (98%), Tributyl-(3,4-ethoxylenedioxythiophen-2-yl)-stannane were purchased from Suna Tech Inc (95%), PdCl₂ and Pd(OAc)₂ were purchased from Shanghai Macklin Biochemical Co., Ltd, BIEDOT was purchased from Energy Chemical (98%), P^tBu (1.0 M in toluene) were purchased from Aladdin, commercial HPLC grade acetonitrile (ACN, Aladdin, 99.9%) was used without further purification. Toluene was processed with CaH₂ for three days and collected with Molecular sieves (4 Å). Tetrabutyl ammonium perchlorate (TBAP, Zhengzhou Xipaike Chemical Co., Ltd, 98%) was dried at 80 °C in vacuum for 12 h. Anhydrous



Scheme 1. Synthesis route of DTP-Br, DTC, DDC, BDTC and BDDC.

dichloromethane (DCM, 99.9%) was purchased from Aladdin. Other regents were commercial products used as received.

Bruker AVANCE III (Germany) instrument was used to record the ¹H and ¹³C NMR spectra of prepared monomers in CDCl₃. The Mass spectrometry (MS) analysis of the obtained monomers was measured on a GCT Premier spectrometer (Waters, USA). UV–vis spectrophotometer (Lambda 25, Perkin Elmer, USA) was used to investigate the UV–vis spectra of the polymer films. The electrochemical properties were tested on an Autolab PGSTAT302 N electrochemical analyzer (Metrohm, Switzerland). The color images of polymer films were taken by Nikon D90.

2.2. Monomer synthesis

2.2.1. Synthesis of 1-(4-Bromo-phenyl)-2,5-di-thiophen-2-yl-1H-pyrrole(DTP-Br)

1,4-di(2'-thienyl)-1,4-butadione (2 mmol, 0.50 g), 4-Bromoaniline (6 mmol, 1.01 g) and p-toluenesulfonic acid (2 mmol, 0.39 g) were dissolved in anhydrous toluene (50 mL) in a three-neck round-bottomed flask. The reaction mixture was stirred at 90 °C for 48 h under N2 atmosphere. After being cooled to room temperature, toluene was removed under column pressure, then the mixture was extracted with DCM and saturated brine. The organic phase was collected and removed under column pressure. followed processed by column chromatography on silica gel with petroleum: ethyl acetate (20:1) to give a light vellow power (0.52 g)68%). ¹H NMR (500 MHz, CDCl₃) δ: 7.53 (d, 2H), 7.16 (d, 2H), 7.09 (dd, 2H), 6.84 (dd, 2H), 6.54 (d, 2H). 6.52 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ: 137.51, 134.53, 132.38, 131.49, 129.97, 127.02, 124.76, 124.22, 122.95, 110.31. MS (EI) (m/z): calcd for C₁₈H₁₂BrNS₂, 384.96; found, 385.51.

2.2.2. Synthesis of 3,6-Bis-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-9H-carbazole (DTC)

Tributyl-(3,4-ethoxylene-dioxythiophen-2-yl)-stannane (5 mmol, 2.2 g), 3,6-Dibromocarbazole (2.5 mmol, 0.8 g) and PdCl₂ (0.171 mmol, 0.12 g) were dissolved in anhydrous toluene (50 mL) in a 250 mL round bottom flask, then the mixture was degassed and refluxed for 48 h under a nitrogen atmosphere. After being cooled to room temperature, the mixture was washed with saturated salt water and extracted with trichloromethane (TCM). The organic phase was collected and dried with anhydrous MgSO₄, solvent was removed under column pressure and the product was processed by column chromatography on silica gel with petroleum: TCM (10 : 1, by volume) to give a light-yellow power (0.65 g, 58% yield). ¹H NMR (500 MHz, CDCl₃) δ : 8.09 (s, 1H), 7.82 (d, 2H), 7.42 (d, 2H), 6.33 (s, 2H), 4.37 (t, 8H). ¹³C NMR (125 MHz, CDCl₃) δ : 147.39, 141.05, 138.26, 134.19, 130.66, 125.60, 124.18, 123.80, 117.46, 63.57, 63.28, MS (EI): calculated for C₂₄H₁₇NO₄S₂ m/z: 447.06, found m/z: 447.56.

2.2.3. Synthesis of 2,7-Bis-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-9H-carbazole (DDC)

The monomer DDC was prepared according to the above synthesized method.

¹H NMR (500 MHz, CDCl₃) δ: 7.98 (s, 2H), 7.80 (d, 2H), 7.56 (d, 2H), 6.32 (s, 2H), 4.31 (t, 8H). ¹³C NMR (125 MHz, CDCl₃) δ: 142.33, 140.37, 137.91, 130.85, 122.05, 120.30, 118.50, 118.28, 107.96, 97.44, 64.84, 64.52, MS (EI): calculated for $C_{24}H_{17}NO_4S_2$ m/z: 447.06, found m/z: 447.68.

2.2.4. Synthesis of 3,6-Bis-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5yl)-9-[4-(2,5-di- thiophen-2-yl-pyrrol-1-yl)-phenyl]-9H-carbazole (BDTC)

DTP-Br (2 mmol, 0.77 g), DTC (2 mmol, 0.90 g), NaOtBu (2 mmol,

0.2 g) and Pd(OAc)₂ (0.02 g) were dissolved in anhydrous toluene (20 mL) in a three-neck round-bottomed flask, then the mixture was degassed and placed in a nitrogen atmosphere, PtBu (2 mL) was injected with syringe. The mixture was refluxed for 12 h. After cooled to room temperature, the mixture was extracted with DCM and a lot of water, the organic phase was collected and removed under column pressure, and the crude product was processed by column chromatography on silica gel with petroleum: ethyl acetate (10:1) to give a yellow-green power(0.95 g, 63%). ¹H NMR (500 MHz, CDCl₃) δ : 8.45 (s, 2H), 7.81 (d, 2H), 7.61 (d, 2H), 7.54 (d, 2H), 7.43 (d, 2H), 7.15 (t, 2H), 6.92 (d, 2H), 6.72 (d, 2H), 6.60 (s, 2H), 6.31 (d, 2H), 4.37 (t, 4H), 4.30 (t, 4H). ¹³C NMR (125 MHz, CDCl₃) δ : 142.32, 139.73, 137.32, 134.75, 131.65, 130.24, 127.37, 125.91, 124.52, 124.00, 118.43, 118.30, 110.18, 109.85, 96.73, 64.86, 64.59. MS (EI): calculated for C₄₂H₂₈N₂O₄S₄ m/z: 752.09, found m/z: 752.51.

2.2.5. Synthesis of 2,7-Bis-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5yl)-9-[4-(2,5-di- thiophen-2-yl-pyrrol-1-yl)-phenyl]-9H-carbazole (BDDC)

The monomer BDDC was prepared according to the above synthesized method.

¹H NMR (500 MHz, CDCl₃) δ: 8.07 (d, 2H), 7.82 (s, 2H), 7.67 (m, 4H), 7.58 (d, 2H), 7.10 (d, 2H), 6.90 (t, 2H), 6.75 (d, 2H), 6.62 (d, 2H), 6.32 (s, 2H), 4.24 (m, 8H). ¹³C NMR (125 MHz, CDCl₃) δ: 142.33, 141.54, 138.09, 137.14, 134.56, 131.65, 128.01, 136.97, 124.34, 120.43, 118.98, 110.04, 107.01, 97.59, 64.81, 64.47. MS (EI): calculated for $C_{42}H_{28}N_2O_4S_4$ m/z: 752.09, found m/z: 752.87.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis route of the monomers was displayed in Scheme 1, firstly 1,4-di(2'-thienyl)-1,4-butadione was used to prepare DTP-Br by reacting with 4-Bromoaniline through Knorr-Paal reaction [20], and tributyl-(3,4-ethoxylene -dioxythiophen-2-yl)-stannane was used to react with 3,6-Dibromocarbazole and 2,7-Dibromocarbazole by Still coupling reaction to obtain the intermediates DTC and DDC, respectively. Then DTC and DDC reacted with DTP-Br to prepare the desired monomers of BDTC and BDDC by Friedel-Crafts reaction.

¹H NMR, ¹³C NMR, mass spectroscopy (MS) and FT-IR analyses were used to characterize the purity of intermediates and monomers. The NMR and MS spectra of compounds can be seen in Figs. S1–S5 of the supporting information. Fig. 1 shows the FT-IR spectra of DTP-Br, DTC, DDC, BDTC and BDDC. For DTP-Br, the absorption peaks at 698 and 830 cm⁻¹ can be ascribed to the stretching mode of α -H and β -H of thiophene rings [26], the peak at 760 cm⁻¹ are for β -H of pyrrole unit [34], the peaks at 1410 and 1490 cm⁻¹ can be attributed to the bending of C-C of aromatic rings. Comparing the spectrum of DTC and DDC, both the spectra exhibit the characteristic peaks of EDOT groups as follows: 1363 cm⁻¹ (C-C stretching), 1166 and 1070 cm⁻¹(C-O-C stretching) [35]. However, some different absorption peaks (1296 cm^{-1} for DTC, 1328 cm^{-1} for DDC) still exist due to the different substituted positions of carbazole. The spectra of BDTC and BDDC are almost consisted of that of both the asymmetrical sections. According to results of NMR, MS and FT-IR analyses, the pure asymmetrical monomers are synthesized successfully.

3.2. Electrochemical polymerization of the monomers

Cyclic voltammetry (CV) was used to investigate the polymerization process of DTC, DDC, BDTC, BDDC, BDTC/BIEDOT and BDDC/



Fig. 1. The FT-IR spectra of DTP-Br, DTC, DDC, BDTC and BDDC.

BIEDOT in 0.1 M TBAP/ACN-DCM solution at the scan rate of 100 mV/s, and the results were depicted in Fig. 2. As seen from Fig. 2, all the first cycle of CV curves show irreversible redox process (Inset of Fig. 2), which can be attributed to the oxidation of the monomers to form radical-cations [36,37]. For DTC and DDC, the obvious oxidation peaks located at 0.78 and 0.95 V can be observed, the differences can be attributed to the better donor ability of 3. 6positon than 2.7-positon of carbazole [38,39]. After the introduction of DTP unit, BDTC and BDDC exhibit obvious redox peaks at 0.91/0.60 V and 1.01/0.63 V, respectively, which are different from that of DTC, DDC and DTP, indicating that interactions exist between DTP and carbazole-EDOT units. For BDTC/BIEDOT and BDDC/ BIEDOT, the existence of BIEDOT leads to the broad reduction wave between -0.2 and 0.6 V. With the scan cycle increasing, new reversible redox peaks (0.48/0.46 V and 0.89/0.76 V for DTC; 0.43/ 0.29 V and 1.01/0.84 V for DDC; 0.89/0.59 V for BDTC; 0.92/0.63 V for BDDC; 0.58/0.49 V for BDTC/BIEDOT; 0.51/0.36 V for BDDC/ BIEDOT) can be observed thanks to further polymerization of all the



Fig. 2. Continuous CV curves of 2 mM DTC, and 2 mM DDC, 2 mM BDTC, 2 mM BDTC, 2 mM BDTC/2 mM BIEDOT and 2 mM BDDC/2 mM BIEDOT) in the 0.1 M TBAP/ACN:DCM (v:v = 1:1) solution at a scan rate of 100 mV/s (Inset picture: the first cycle of CVs of the compounds).

monomers. Meanwhile, the current intensity of new redox peaks become bigger gradually, indicating that resulting polymer films form on the surface of ITO/glass electrode successfully and the color change of formed polymer films upon the different applied potential can be seen by the naked eye.

3.3. Electrochemical properties of the polymer films

The polymer films were deposited on the surface of ITO/glass work electrode via continued CV sweeps for 16 cycles, then, the films were washed with clear ACN to remove the TBAP and the unreacted monomers. Fig. 3 displays the CV of resulting polymer films in monomer-free 0.1 M TBAP/ACN solution at the scan rate of 100 mV/s. PDTC film shows an oxidation peak at 0.79 V with a reduction peak at 0.59 V, PDDC film exhibits redox peak at 0.75/0.58 V, the different CV curves of PDTC and PDDC film indicate that the distinct electrochemical properties can be obtained via changing linkage positions. After the introduction of DTP and BIE-DOT units, the redox peaks (0.85/0.60 V for PBDTC; 0.86/0.64 V for PBDDC; 0.82/0.47 V for BDTC/BIEDOT; 0.87/0.41 V for BDDC/BIE-DOT) can be observed. The CV curves become similar due to the increase of same units of the conjugated polymer chain. Moreover,

according to the formula [40]: $E_{HOMO} = -(E^{ox}_{onset} vs Ag/AgCl + 4.43)$ eV, the HOMO of PDTC, PDDC, PBDTC, PBDDC, P(BDTC/BIEDOT) and P(BDDC/BIEDOT) calculated are to be -4.56 eV. -4.53 eV. -4.84 eV. -4.86 eV. -4.49 eV and -4.35 eV. respectively, and the other optical and electrochemical parameters can be seen in Table 1. Fig. S6 shows CV of PBDTC, PBDDC, P(BDTC/ BIEDOT) and P(BDDC/BIEDOT) films at different scan rate ranging from 50 to 300 mV/s. As seen from Fig. S6, all the peak current intensity increase with the scan rate increasing, and a linear relationship between them can be observed in the inset of Fig. S6, implying that all the polymer films show good electroactive and well-adhered, and the oxidation-reduction processes are nondiffusional controlled [29].

Long time stability was an important parameter for applications, Fig. 4 exhibits the multiple cycle CV curve of PBDTC, PBDDC, P(BDTC/BIEDOT) and P(BDDC/BIEDOT) films in monomer-free 0.1 M TBAP/ACN solution at the scan rate of 100 mV/s for 500 times cycle. As seen from Figs. 4 and 30% and 28% loss can be observed for PBDTC and PBDDC films, which may be ascribed to the effect of doped and dedoped ion into the polymer chain on the adhered ability of polymer film on the electrode. P(BDTC/BIEDOT) and P(BDDC/BIEDOT) films show higher stability(only 11% and 8% loss,



Fig. 3. CV curves of the PDTC, PDDC, PBDTC, PBDDC, P(BDTC/BIEDOT) and P(BDDC/BIEDOT) films in monomer-free solution of 0.1 M TBAP/ACN a scan rate of 100 mV/s.

able 1
lectrochemical and optical properties of PDTC, PDDC, PBDTC, PBDDC, P(BDTC/BIEDOT) and P(BDDC/BIEDOT) films.

Polymers	E ^{ox} onset V	E _{HOMO} eV	E _{LUMO} eV	$\lambda_{max} \ nm$	λ _{onset} nm	Eg eV
PDTC	0.13	-4.56	-2.07	410	498	2.49
PDDC	0.10	-4.53	-2.27	469	549	2.26
PBDTC	0.41	-4.84	-2.52	420	534	2.32
PBDDC	0.43	-4.86	-2.65	448	561	2.21
P(BDTC/BIEDOT)	0.06	-4.49	-2.60	478	656	1.89
P(BDDC/BIEDOT)	-0.08	-4.35	-2.52	496	678	1.83



Fig. 4. Long time electrochemical stability of PBDTC, PBDTC, PBDTC, PIEDTC/BIEDOT) and P(BDDC/BIEDOT) film in the 0.1 M TBAP/ACN solution at the scanning rate of 100 mV/s.

respectively), which can be attributed to the increase of EDOT units in the conjugated chains [19].

3.4. FT-IR of the polymers films

The chemical structure of PBDTC, PBDDC, P(BDTC/BIEDOT) and P(BDDC/BIEDOT) films were characterized by FT-IR spectra, and the results are shown in Fig. S7. The PBDTC and PBDDC films display almost all the characteristic peaks of BDTC and BDDC, the broader peak at 1080 cm⁻¹ can be attributed to the existence of ClO_4^- of residual TBAP [26]. After the introduction of BIEDOT units, the

intensity of peaks change, for P(BDTC/BIEDOT) and P(BDDC/BIE-DOT) films, the characteristic peaks of PBDTC and PBDDC films can still be observed. However, the characteristic peaks of EDOT units at 1070 and 1360 cm⁻¹ become stronger, which can be ascribed to the increasing content of EDOT groups of the polymer chains. The study results indicate that P(BDTC/BIEDOT) and P(BDDC/BIEDOT) films may be the mixture of their homopolymer or copolymer.

3.5. Surface morphology

SEM was used to investigate the surface morphology of the



Fig. 5. SEM images of the PDTC, PDDC, PBDTC, PBDDC, P(BDTC/BIEDOT) and P(BDDC/BIEDOT) films.

polymer films, which was related with doped ion or electron transfer speed, and the results were shown in Fig. 5. PDTC and PDDC exhibit unsmooth surface with many particles and some aggregates, PBDTC and PBDDC films display smoother surface, but many grains also can be observed, especially for PBDDC films. After the introduction of BIEDOT units, P(BDTC/BIEDOT) exhibits cross-linking network surface, which can be considered to be benefit for the doped ion or electron transfer speed [17]. While the uniform particles on the surface can be found for P(BDDC/BIEDOT) films. Moreover, the thickness of polymer films was test by cross-section SEM, as seen from Fig. S8, the thickness of PBDTC and PBDDC films are found to be 176 nm and 164 nm, respectively, and 198 nm and

204 nm are observed for P(BDTC/BIEDOT) and P(BDDC/BIEDOT) films, the thicker films of copolymer films can be attributed to the effect of BIEDOT units.

3.6. Spectroelectrochemical properities

Spectroelectrochemistry experiments were performed to investigate the doped and undoped changes of polymer film upon different applied potentials via using both electrochemical station and UV–vis spectrophotometer [41]. Fig. 6 exhibits the spectroelectrochemical properities of PDTC, PDDC, PBDTC, PBDDC, P(BDTC/BIEDOT) and P(BDDC/BIEDOT) film. For PDTC and PDDC,



Fig. 6. Spectroelectrochemical spectra changing process for PDTC (a), PDDC (b), PBDDC (c), PBDDC (d), P(BDTC/BIEDOT)(e), P(BDDC/BIEDOT) (f) films upon the different applied potentials in 0.1 M TBAP/ACN solution (Inset picture: photos of the polymer films upon different applied potentials).

the polymer films show the maximum absorption peaks at 410 and 469 nm in the neutral state due to the π - π transitions, according to the onset of their maximum absorption, their band gap are found to be 2.49 and 2.26 eV, respectively. And the absorption features make PDTC and PDDC films reveal yellow-green and reddish orange color at 0.0 V (Inset of Fig. 6a and b). With the applied potential increasing gradually, the intensity of both the maximum absorption peaks at 410 and 469 nm decreases, and new absorption waves around 600 and 1100 nm grow up gradually owing to the formation of polaron and bipolaron [42], the color of PDTC film turns to brown green (0.4 V) and blue purple (0.8 V) (Inset of Fig. 6a), while the color of gray(0.5 V) and deep blue (0.8 V) can be observed for PDDC films(Inset of Fig. 6b).

After the introduction of DTP-Br group, PBDTC and PBDDC films exhibit the maximum absorption peaks at 420 and 448 nm for the neutral state (Fig. 6c and d), their band gaps were calculated to be 2.32 and 2.21 eV, respectively, the differences from these of PDTC and PDDC films can be ascribed to the existence of DTP units in the conjugated chain, and the color of polymer at 0.0 V is found to be light yellow (PBDTC) and orange (PBDDC) (Inset of Fig. 6c and d). As the potentials increase, both the PBDTC and PBDDC films show an absorption wave around 800 nm (0.4–0.9 V), which can be attributed to oxidation of carbazole-phenyl-pyrrole units of polymer, and the color of PBDTC changes to light green (0.8 V) (Inset of Fig. 6c), while yellow green (0.6 V) and green (0.9 V) can be seen for PBDDC film (Inset of Fig. 6d). With the potentials further increasing, the maximum absorption wave move to around 600 nm gradually, meanwhile the absorption wave in near infrared region (around 1100 nm) increase obviously, PBDTC and PBDDC films reveal light purple and blue color, respectively.

The existence of BIEDOT units improves the conjugated ability of polymer, which makes the absorption peaks of P(BDTC/BIEDOT) and P(BDDC/BIEDOT) red shift. As seen from Fig. 6e and f, the maximum absorption peaks at 478 and 496 nm can be observed for P(BDTC/BIEDOT) and P(BDDC/BIEDOT) film at the neutral state, according to our previous study [43], the only one max absorption peak indicates that P(BDTC/BIEDOT) and P(BDDC/BIEDOT) film are the copolymer and not mixture of their homopolymers. And their band gaps are found to be 1.89 and 1.83 eV, respectively, both of them reveal deep red color for the neutral state. Both the polymer films show similar absorption change with the applied potential increasing, the new absorption waves around 800 and 1100 nm appear thanks to the formation of polaron and bipolaron. The color of brown green (0.4 V), green (0.7 V) and blue (0.9 V) are observed for both the polymer films (Inset of Fig. 6e and f), the only difference is that P(BDTC/BIEDOT) shows deep blue at 1.1 V due to the stronger absorption around 600 nm. The rich color showing ability may enlarge the application of the polymer film.

3.7. Electrochromic switching

Optical contrast, switching time and coloration efficiency (CE) of polymer films are three important parameters for their potential applications. Double potential chronoamperometry was performed to explore such properties between the neutral and oxidized state using electrochemical station and UV–vis spectroscopy simultaneously. Fig. 7 shows the switching properties of PBDTC and P(BDTC/BIEDOT) films at different wavelengths with a residence



Fig. 7. Kinetic study performed of PBDTC (a) and P(BDTC/BIEDOT)(c) films monitored at different absorption maxima with the switching time of 10 s; Calculated switching time and applied potential step changes of PBDTC at 617 nm(b) and P(BDTC/BIEDOT) at 1100 nm (d).

Table 2
Electrochromic parameters of PBDTC, PBDDC, P(BDTC/BIEDOT), P(BDDC/BIEDOT) films and other reported polymer films.

Polymers	λ(nm)	△ T(%)	$t_c/t_b(s)$	\triangle_{oD}	Q(mC/cm ²)	$\eta(cm^2/C)$
PBDTC	617	33%	1.20/2.29	0.32	2.13	150
PBDDC	620	27%	0.73/0.76	0.16	1.51	106
P(BDTC/BIEDOT)	1100	38%	1.83/2.67	0.89	1.60	556
P(BDDC/BIEDOT)	1100	39%	1.79/2.71	0.87	1.96	444
P2 [18]	400	22%	1.5	_	-	_
PTPHSNS [19]	630	15%	7.35/5.66	-	-	-
PTPHSNS-EDOT (feed ratio 1:4) [19]	1100 nm	32%	0.84/0.58	_	-	_
Poly(TCT-N) [32]	420	22%	4.3	_	-	264
P(DTP-DPA) [40]	830	24%	2.9/2.8	0.145	1.61	90.06
P(DTP-CPA-DTP) [40]	800	17%	2.3/4.3	0.164	1.73	94.69
PBIEDOT [46]	1050	45.61%	1.07/0.33			159.56

time of 10 s. As seen in Fig. 7a, PBDTC film exhibits 12%, 33% and 32% transmittance change at the wavelengths of 426, 617 and 1100 nm switching between 0.0 V and 1.4 V, however, the transmittance decrease with the cycle time increasing, which is related to the stability of PBDTC film. P(BDTC/BIEDOT) film displays the optical contrast of 24% and 38% at 480 and 1100 nm switching between 0.0 V and 1.2 V(Fig. 7c), and after 300 s cycle, the copolymer films reveal better stability due to the increase of EDOT units of the polymer chain. The transmittance changes of PBDDC and P(BDDC/ BIEDOT) films were calculated to be 27% (620 nm) and 39% (1100 nm), which have been summarized in Table 2. According to the reported works [44], 90% of full-transmittance change is suitable to calculate the response time due to the limitation of our naked eye. The response of PBDTC film at 617 nm is found to be 1.20 s from the bleached state to the colored state (t_c) and 2.29 s from the colored state to the bleached state (t_b) (Fig. 7b). P(BDTC/ BIEDOT) film shows the t_c and t_h as 1.83 and 2.67 s at 1100 nm (Fig. 7d). The response of PBDDC and P(BDDC/BIEDOT) can be seen in Table 2.

The CE of polymer films can be calculated by the equation $(\Delta OD = \log(T_{bleached}/T_{colored}), \eta = \Delta OD/Q)$, where $T_{bleached}$ and $T_{colored}$) are the transmittances of the polymer film for the bleached state and colored state; ΔOD is the optical transmittance change, $Q(mC/cm^2)$ is the injected/ejected charge between bleached and colored states [45]. As seen in Table 2, the CE of PBDTC, PBDDC, P(BDTC/BIEDOT) and P(BDDC/BIEDOT) films are found to be 150, 106, 556 and 444 cm²/C, which are a little higher than 2, 5–dithienylpyrrole derivatives (P(DTP-DPA) and P(DTP-CPA-DTP) [40]).

4. Conclusion

Two new asymmetric structure monomers based on carbazole-EDOT and 2, 5–dithienylpyrrole were synthesized successfully, their polymer films could be obtained on the surface of the ITO/ glass electrode by electropolymerization. Both the polymer films showed multi-electrochromic properties. Moreover, the copolymers with BIEDOT were also prepared, they not only showed well-defined electrochemical properties and better stability, but also possessed milti-electrochromism(red, brown yellow, green and blue color at different applied potentials) and outstanding coloration efficiency(556 and 444 cm²/C).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.electacta.2019.03.050.

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