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Electrochromic polymers electrochemically polymerized from 2, 5–dithienylpyrrole (DTP) with different triarylamine units: Synthesis, characterization and optoelectrochemical properties

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ABSTRACT

A series of polymers, consisting both 2, 5-dithienylpyrrole (DTP) and different triarylamine units were synthesized by electrochemical oxidative polymerization. The structures of the monomers, including N-(4-(2,5-di(thiophen-2- yl) –1H-pyrrol-1-yl)phenyl)-N-Phenyl Naphthalene-2-amine (DTP-PNA), 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-N,N-diphenylaniline (DTP-DPA), 4-(tert-butyl)-N-(4-(tert-butyl)phenyl)-N-(4-(2,5-di(thiophen-2-yl)-1H –pyrrol-1-yl)phenyl) aniline (DTP-TBPA), 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-N-(4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)phenyl)-N-(p-tolyl)aniline (DTP-PTA-DTP), and N-(4-(9H-carbazol-9-yl)phenyl)-4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-N-(4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)phenyl)aniline (DTP-CPA-DTP) were elucidated by FT-IR, ^{1}H NMR, ^{13}C NMR, Mass spectra (MS) and the performance and morphology of resulting polymers (P(DTP-PNA), P(DTP-DPA), P(DTP-TBPA), P(DTP-PTA-DTP), and P(DTP-CPA-DTP)) were determined by cyclic voltammetry (CV), ultra-visible-near infrared (UV–Vis–NIR) spectrophotometer, and scanning electron microscopy (SEM), respectively. The polymers exhibit good reversible multicolor in the visible and NIR region (original yellowish to dusty blue until violet occurred), with better coloration efficiency (CE), fast response time.

1. Introduction

At present, electrochromic (EC) polymers, which exhibit reversible absorption spectral changes by changing the applied potentials, have attained much prominence [1,2–8]. They are used widely in our daily life, such as smart windows, optical displays and e-paper due to their high optical contrast, stable oxidation states, excellent switching reproducibility and flexibility [9]. Organic conjugated polymers have been generally considered as one of the most prospective intelligent materials, such as polythiophene, polypyrrole, polyaniline and polycarbazole, owing to their good conductivity, photochemical and electrochromic properties compared with inorganic and small organic compounds [10].

As has been stated earlier, polythiophene and polypyrrole derivatives have the great optoelectrochemical performance [11,12]. The advantages of them are the lower energy gap, better conductivity, good stability, photochemical properties, electrochromic properties and film-forming properties, which make them suitable to design the electrochromic devices, sensors and solar cells [13]. The polythiophene and polypyrrole can be obtained chemically or electrochemically, however, the potential which is used to oxidize the thiophene monomer, meanwhile, often leads to overoxidation of the polymer itself, because the oxidation potential is a little higher and reaches the potentials of the polythiophene selfoxidation. This is known as the “polythiophene paradox” [14]. Similar problem occurred with polypyrrole. Although we can prevent the paradox from reducing the oxidation potentials, the performances will degrade at the same time. In order to avoid this phenomenon and improve the performances of the polymer, the dimers and trimers with two or more hetero-aromatic rings, such as dithiophene, trithiophene and thienylpyrrole, having lower oxidized potential without destroying their

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optical and mechanical performance, have been selected as monomers for electropolymerization [15].

From previous article, Ferraris and Skiles [16] obtained the 2,5-bis(2-thienyl)-1H-pyrrole polymer (PSNS) by the direct polymerization of thiophene and pyrrole derivative (SNS) in 1987 firstly. From that moment on, many researchers have synthesized a series of different polymer of 2,5-bis(2-thienyl)-1H-pyrrole, and discussed their physical and chemical properties [17,18–20]. And furthermore, from beginning of 2000, Enric Brillas has begun to study their electrochemical performance. Later on, Chane Ching [21], L. Toppare [22,23] and A. Cihaner [24–27] synthesized a large number of polymers and studied their photoelectrochemical properties in detail. For example, Toppare proved that the new conducting polymers of 1-(4-nitrophenyl)-2,5-di (2-thienyl) −1H-pyrrole can be used as the immobilization matrices for invertase. In A. Cihaner's research, a series of polymers of 1-(1-naphthyl)-2,5-di(thiophen-2-yl)-1H-pyrrole,1-(2-naphthyl)-2,5-di(thiophen-2-yl)-1H-pyrrole,1-(9H-fluoren-2-yl)−2,5-di(thiophen-2-yl)-1H-pyrrole and 1-(benzo-15-crown-5)-2,5-di(thiophen-2-yl)- 1H-pyrrole were synthesized by electrochemical polymerization, which exhibited multielectrochromic behavior (yellow, green, blue and violet).

On the other hand, Liou and Hsiao's groups have been making efforts on the triarylamine compounds [28], which attracted much interest as EC materials because of their relative high mobilities and low ionization potentials [29]. Especially, Hsiao's group has done some electropolymerization of poly(amide-triarylamine)s containing triptycene units, which exhibit reversible electrochemical oxidation process, higher coloration efficiency and stronger color changes [30]. In addition, You's group synthesized poly-DTP-Ph-TPA by electropolymerization, which proved the polymer has the high contrast and a very short response time [31]. In J. S. Zhao's group, they obtained a kind of polymer based on 4,4'-di(N-carbazoyl)biphenyl and 2, 2'-bithiophene units by electropolymerization in 2011 [32]. What's more, J. K. Xu's et. al designed and synthesized the various length polyether chains bridged thiophene (T-E-T) and 2,2-bithiophene (BT-E-BT) groups [33].

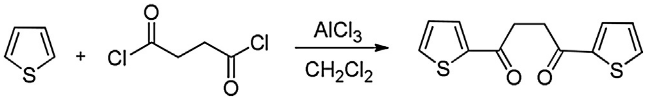
Compared with the traditional method, named chemical routes to obtain the electrochromic (EC) polymer, electrochemical polymerization has several advantages, such as it saves the time for coating the film [34], requires only a small quantity of monomer to synthesize the polymer [35], can control the thickness of the films [36] and provides mild experimental conditions at room temperature [37].

However, up to now, there is not intensive and systematical research on the effect of different triarylamine substituted group on the photoelectrochemical properties. Thus, in this study, we synthesized successfully five new monomers, which containing 2, 5-dithienylpyrrole (DTP) and different aromatic amines groups. Then, the polymer films were prepared on the conductive substrates directly by electrochemical oxidative polymerization. Finally, we researched the properties of the different triarylamine substituted group on 2,5-bis(2-thienyl)-1H-pyrrole based polymer and discussed the performance effect of different triarylamine units. These polymers have the both advantages of the monomers. Meanwhile, 2, 5-dithienylpyrrole derivatives could be widely used in the optoelectronic field due to their good environmental stability and electrical chemical properties [38].

2. Experimental

2.1. Materials

Thiophene, succinyl chloride, aluminum chloride and p-toluenesulfonic acid (PTSA) were supplied from TCI Co. The starting material, 1, 4-di(thiophen-2-yl)butane-1,4-dione was prepared from Paal-Knorr reaction by the method proposed in the literature [39,40] (Scheme 1), and N-(naphthalen-2-yl)-N-phenylbenzene-1,4-diamine (TPA-1), N,N-diphenylbenzene-1,4-diamine (TPA-2), N,N-bis(4-(tert-butyl)phenyl)benzene-1,4-diamine (TPA-3), N-(4-aminophenyl)-N-(p-tolyl)benzene-1,4-diamine (TPA-4) and N-(4-(9H-carbazol-9-yl)phenyl)-N- (4-aminophenyl)benzene-1,4-diamine (TPA-5) were synthesized according to the method similarly described in the literature [41]. Dichloromethane, toluene, and dimethyl sulfoxide (DMSO) were purified by distillation over calcium hydride. All the other reagents and solvents were analytical grade and without further purification. Flash column chromatography purification was carried out on silica gel (200–300 mesh).



Scheme 1. Synthesis route of 1, 4-di(thiophen-2-yl)butane-1,4-dione.

2.2. Synthesis of N-(4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)phenyl)-N-Phenyl Naphthalene-2-amine (DTP-PNA)

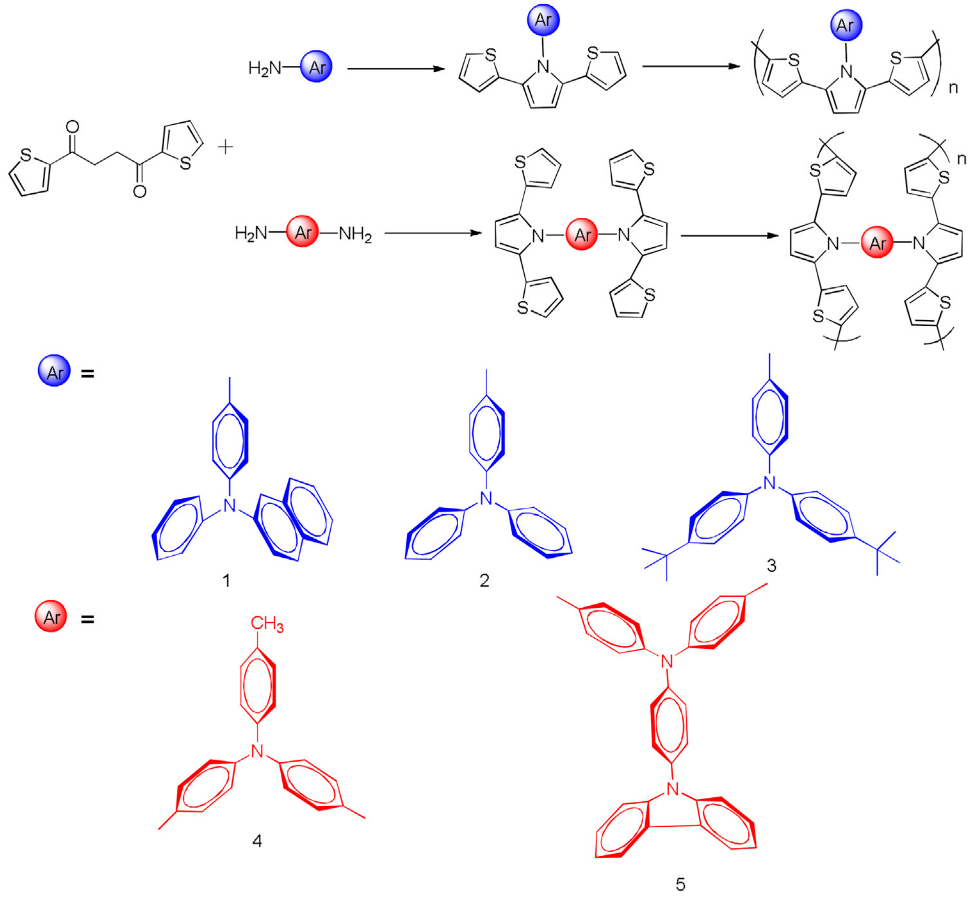
A three-neck round-bottomed flask equipped with a Dean-stark trap, a nitrogen inlet and a reflux condenser was charged with 0.25 g (1.00 mmol) compound 1, 0.3105 g (1.00 mmol) TPA-1, 0.0264 g (0.14 mmol) PTSA, and 80 ml toluene. The reaction mixture was stirred and refluxed for 3 days under N_2 atmosphere. After cooling to room temperature, evaporation of the toluene, adding enough CH_2Cl_2 to dissolve solid, then undissolved solid was separated under reduced pressure, evaporation of the filtrate, followed by flash column chromatography (SiO_2 column, elution with dichloromethane) afforded the crude compound. Finally, the desired product was obtained as yellow solid followed by flash column chromatography (SiO_2 column, elution with dichloromethane and petroleum ether). Other compounds 4-(2,5-di (thiophen-2-yl)-1H-pyrrol-1-yl)-N,N-diphenylaniline (DTP-DPA), 4-(tert- butyl)-N-(4-(tert-butyl)phenyl)-N-(4-(2,5-di(thiophen-2-yl)-1H−pyrrol-1-yl)phenyl) aniline (DTP-TBPA), 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-N-(4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)phenyl)-N-(p-tolyl)aniline (DTP-PTA-DTP), N-(4-(9H-carbazol-9-yl)phenyl)-4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-N-(4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)phenyl)aniline (DTP-CPA-DTP) were prepared by an analogous procedure. The synthetic route of the monomers and polymers are shown in Scheme 2.

2.3. DTP-PNA

FTIR: (KBr, ν/cm^{-1}): 3044, 844, 820, 760, 694; ^{1}H NMR: (DMSO-d$_6$, 400 MHz): 7.90 (d, 1 H), 7.85 (d, 1 H), 7.71 (d, 1 H), 7.49 (m, 2 H), 7.45 (m, 1 H), 7.43 (m, 1 H), 7.40 (m, 2 H),7.36 (s, 2 H), 7.30 (d, 1 H), 7.23 (d, 1 H), 7.16(d, 1 H), 7.08 (d, 2 H), 6.96(m, 1 H), 6.82 (d, 2 H), 6.17 (d, 2 H); ^{13}C-NMR (DMSO-d$_6$, 100 MHz): 145.7, 143.3, 142.7, 140.5, 139.9, 138.6, 138.1, 135.9, 134.8, 134.6, 133.7, 132.1, 130.8, 129.8, 129.3, 128.4, 127.8, 127.1, 126.7, 126.6, 125.3, 125.2, 124.7; MS (EI) (m/z): [M]$^+$ calcd for $C_{34}H_{24}N_2S_2$, 524.0; found, 524.07.

2.4. DTP-DPA

FTIR: (KBr, ν/cm^{-1}): 3050, 841, 826, 760, 732, 694; ^{1}H NMR: (DMSO-d$_6$, 400 MHz): 7.34 (d, 2 H), 7.21 (d, 2 H), 7.11 (m, 2 H), 7.09 (m, 2 H), 7.01 (t, 2 H), 6.93 (d, 2 H), 6.80 (d, 4 H), 6.56 (d, 2 H); ^{13}C-NMR (DMSO-d$_6$, 100 MHz): 148.7, 147.6, 135.4, 131.9, 131.1, 130.5,



Scheme 2. Synthesis routes of DTP-PNA, DTP-DPA, DTP-TBPA, DTP-PTA-DTP, DTP-CPA-DTP and P(DTP-PNA), P(DTP-DPA), P(DTP-TBPA), P(DTP-PTA-DTP), P(DTP-CPA-DTP).

129.7, 127.1, 125.3, 124.3, 124.0, 123.7, 122.9; MS (EI) (m/z): $[M]^+$ calcd for $C_{30}H_{22}N_2S_2$, 474.0; found, 474.08.

2.5. DTP-TBPA

FTIR: (KBr, ν/cm^{-1}): 3051, 844, 830, 755, 730; ^{1}H NMR: (DMSO-d$_6$, 400 MHz): 7.38 (d, 2 H), 7.33 (d, 2 H), 7.18 (d, 2 H), 7.04 (m, 2 H), 6.95 (d, 4 H), 6.93 (d, 2H), 6.80 (m, 4H), 6.56 (d, 2H), 1.27(s, 18H); ^{13}C-NMR (DMSO-d$_6$, 100 MHz): 148.9, 146.5, 144.5, 135.3, 131.1, 130.5, 127.2, 126.3, 124.5, 123.9, 121.9, 109.2, 34.4, 31.5; MS (EI) (m/z): $[M]^+$ calcd for $C_{38}H_{38}N_2S_2$, 586.0; found, 586.2.

2.6. DTP-PTA-DTP

FTIR: (KBr, ν/cm^{-1}): 3101, 859, 787, 631; ^{1}H NMR: (DMSO-d$_6$,400 MHz): 7.33(d, 4H), 7.30(q, 4H), 7.28(d, 4H), 7.25(d, 4H), 7.12 (d, 4H), 6.93(q, 2H), 6.80(d, 4H), 6.57 (d, 4H), 2.30(s, 3H); ^{13}C-NMR (DMSO-d$_6$, 100 MHz): 148.1, 143.7, 134.5, 132.6, 131.8, 131.1, 130.4, 127.7, 126.9, 125.2, 124.4, 123.6, 122.5, 109.5, 20.9; MS (EI) (m/z): $[M]^+$ calcd for $C_{43}H_{31}N_3S_4$, 717.0; found, 717.2.

2.7. DTP-CPA-DTP

FTIR: (KBr, ν/cm^{-1}): 2963, 1505, 802, 750, 688; ^{1}H NMR: (DMSO-d$_6$, 400 MHz): 8.27(d, 4H), 7.76(d, 2H), 7.64(d, 4H), 7.48(d, 4H) 7.42(d,2H), 7.40(s,2H), 7.38(d, 4H), 7.32(s, 2H), 6.96(t, 2H), 6.86 (d, 4H), 6.64 (d, 4H); ^{13}C-NMR (DMSO-d$_6$, 100 MHz):140.6, 138.4, 137.3, 135.0, 131.7, 130.4, 127.6, 127.0, 126.2, 124.7, 124.4, 123.8, 120.4, 110.3, 109.6; MS (EI) (m/z): $[M]^+$ calcd for $C_{54}H_{36}N_4S_4$, 868.0, found, 868.1.

2.8. Electrochemical polymerization

Electrochemical polymerization of the DTP-TPAs were accomplished via potential dynamic method in a compartment cell furnished with Pt electrode, ITO working electrode, reference electrode, in the presence of 0.10 mol/L TBAP (tetrabutylammonium perchlorate) of the CH_2Cl_2, 2×10^{-3}mol/L monomer of the CH_2Cl_2. The electrodes coated with the polymer were rinsed with CH_2Cl_2 in order to get rid of the salts and unreacted monomer.

2.9. Instrument

The obtained compounds were characterized by the following techniques: FT-IR spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AC–400 MHz and AC–100 MHz spectrometer using DMSO-d$_6$ as solvent. Mass Spectra (MS) was performed on a Finnigan LC–MS/MS system (Thermo Electron, San Jose, CA, USA).

The cyclic voltammogram (CV) was conducted on a CH Instruments 660A electrochemical analyzer with the use of a three-electrode cell at the different scan rate with a 0.1 mol/L $LiClO_4$ as the supporting electrolyte under nitrogen atmosphere in dried acetonitrile (CH_3CN). Geometry optimizations were carried out using the B3LYP functional as implemented in Gaussian 98 program.

For the electrochromic investigations, the films were deposited on an ITO-coated glass substrate by electrochemical polymerization, and a home-made electrochemical cell was built from a commercial UV–vis cuvette. The cell was placed in the optical path of the sample light beam in a UV–vis spectrophotometer, which allowed us to acquire electronic absorption spectra under potential control in a 0.1 mol/L $LiClO_4/CH_3CN$.

Colorimetry measurements were performed by using Conica Minolta CS-200 chromameter with viewing geometry as recommended by Commision Internationale de I'Eclairage (CIE). According to the CIE system, the color is made up of three aspects: luminance (L), hue (a), and saturation (b). These values (L; a; b) were measured at the neural, intermediate and fully oxidized state of the electrochromic polymer on the ITO/glass surface.

SEM measurement was carried out on a S4800 instrument with accelerating potentials of 2 kV, and the samples were sputtered with Pt prior to observation.

3. Results and Discussion

3.1. Synthesis and Characterization

In this study, we devoted our efforts to synthesize a series of 2, 5-dithienylpyrrole derivative monomers and obtain polymer films by electrochemical polymerization. The monomers were prepared in two steps mainly (Scheme 1). The starting reagent 1, 4-di(2-thienyl)-1, 4-butanedione and five kinds of TPAs compounds were synthesized according to the previously reported work. Then the monomers were prepared by the condensation reaction, Knorr-Paal reaction, between compound 1 (1, 4-di(2-thienyl)-1, 4-butanedione) and TPAs in presence of PTSA enough as the catalyst in toluene, and yellow crude products were obtained. Finally, the polymer films were fabricated via electrochemical polymerization. And structural identification of these compounds was elucidated by using FT-IR, ^{1}H NMR, ^{13}C NMR, MS techniques after each reaction.

After condensation reaction, molecular structures of the monomers (DTP-TPAs) were also identified by FT-IR, ^{1}H NMR spectra, ^{13}C NMR spectra and MS (Seen in Supporting Information Figs. S1–S5). On the one hand, in the FT-IR of DTP-PNA, we can observe three peaks at 820 cm^{-1}, 760 cm^{-1} and 621 cm^{-1}, which attribute to β/β'-hydrogens of thiophene rings, β-hydrogens of pyrrole ring and α-hydrogens of thiophene rings respectively [42]. Compared with DTP-PNA, the P(DTP-TPA)'s peak at 621 cm^{-1} disappears but the other peaks still exist. On the other hand, in the ^{1}H NMR spectra, the characteristic amine band which was attributed to TPA disappeared by the accomplishment of the synthesis of DTP-TPAs. The tall singlet signal at 6.58 ppm belongs to the protons (H-4) on the pyrrole unit of these DTP-TPAs monomers. Taking DTP-DPA for example, the integrals of the proton (H-4) and the other protons are 0.10 and 1.00, respectively, which are consistent with the theoretical values. In conclusion, these results indicate that the presence of thiophene and pyrrole rings in the polymer structure.

3.2. Electrochemical polymerization of the DTP-TPAs

The P(DTP-TPA)s coated on ITO electrodes were obtained by the electrochemical polymerization of DTP-TPA in 0.1 mol/L TBAP dissolved in CH_2Cl_2 solutions at the room temperature. The scan potentials were added between 0.0 V and 1.5 V at the rate of 50 mV/s. As seen in the first cycle (Fig. 1 Scheme 1 and S6), the monomer oxidation peak appeared at 1.10 V, 1.12 V, 1.05 V, 0.86 V and 0.94 V, respectively, which resulted from 2, 5-dithienylpyrrole (DTP) group[43]. However, it was a little different from the previous report, perhaps due to the TPA unit inserting the monomer, which influencing the potential. During the second scan, a couple of new reversible redoxidation peaks were observed for different monomers at 0.72V/0.82V, 0.87 V/0.70V, 0.90 V/0.84V, 1.01V/0.62V, and 0.77 V/0.46V respectively, which contribute to the oxidation of the monomers gradually. Meanwhile, the current intensity of this reversible peak became higher and higher after each successive cycle, which clearly indicated the electroactive polymer was deposited on the ITO/glass surface successfully. After the polymerization, the deposited films were washed with CH_2Cl_2 for several times to wash off the inorganic salts and the unreacted monomers.

3.3. Electrochemical properties of the P(DTP-TPA)s

Electrochemical properties of P(DTP-TPA)s were investigated via cyclic voltammetry (CV) (Fig. 2). In the cyclic voltammetry of P(DTP-PNA), peaks at 0.91 V and 1.36 V were observed as the oxidation process while 0.85 V and 1.22 V were the reduction peaks. As shown in the inset of Fig. 2, a linear relationship was showed between the peak current and the scan rate, signifying this polymerization was a reversible and non-diffusional redox process and the electroactive polymer films were well-adhered, which was proving that the process of the oxidation-reduction reaction was due to the electronic gain and loss. Other polymers' cyclic voltammetry at different scan rate were given in Supporting Information Fig. S7. The cyclic voltammetrys curves of the monomers were given in Supporting Information Fig. S8 and

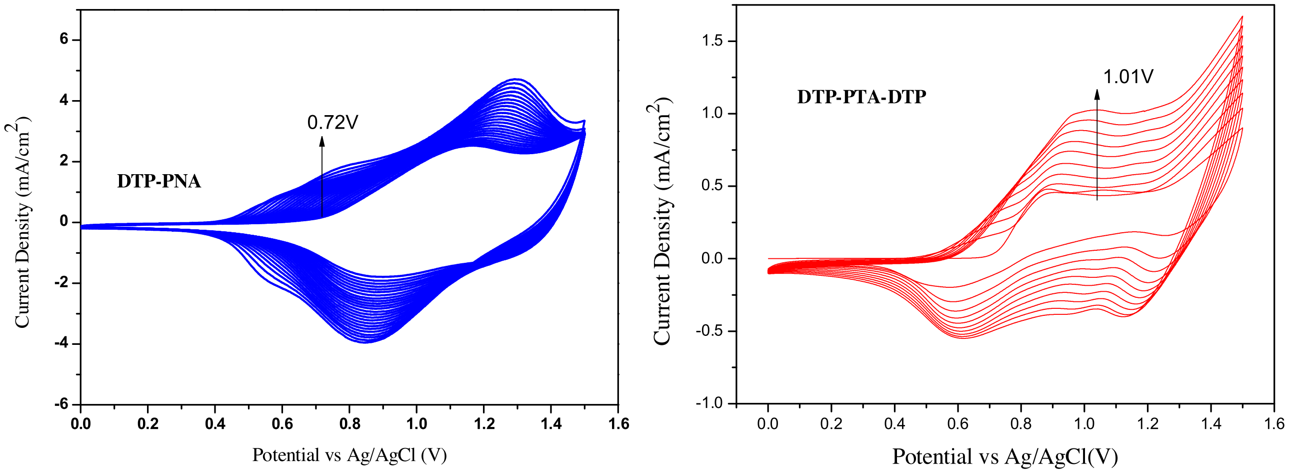


Fig. 1. Electrochemical polymerization of DTP-PNA and DTP-PTA-DTP in 0.1 mol/L $TBAP/CH_2Cl_2$ via repetitive cycling at a scan rate 50 mV/s.

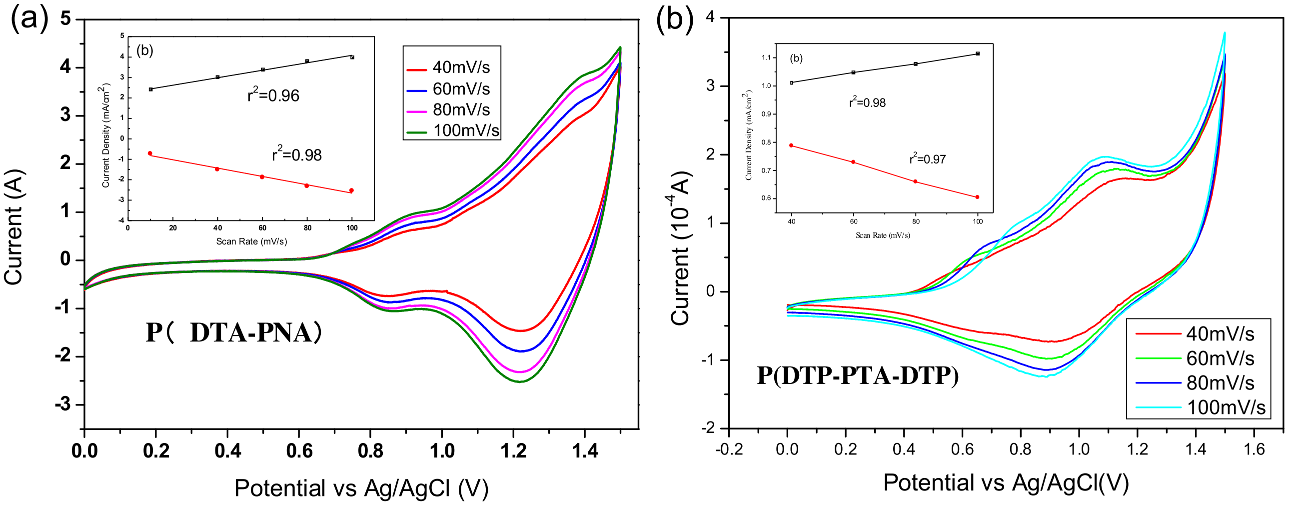


Fig. 2. (a) Electrochemical oxidation process behavior of P(DTP-PNA) and P(DTP-PTA-DTP) film at different scan rates (b) anodic and cathodic current peaks as a function of scan rate in 0.1 mol/L $LiClO_4/CH_3CN$.

Fig. 3 showed the CV of the polymers. During the scan, we can see the polymers exhibit different oxidation peaks compared with the monomers. The first oxidation peaks of the polymer P(DTP-TPA)s are at 0.91 V, 0.85 V, 0.65 V, 0.67 V, 0.62 V respectively, which are ascribed to the radical cation (TPA^+) formation which are similar to the reported TPA derivatives [44]. The peak appeared at 1.36 V, 1.34 V, 1.20, 0.97 V, 1.00 V respectively, maybe occur from DTP unit [31]. All these observation are proved that the polymers are synthesized successfully.

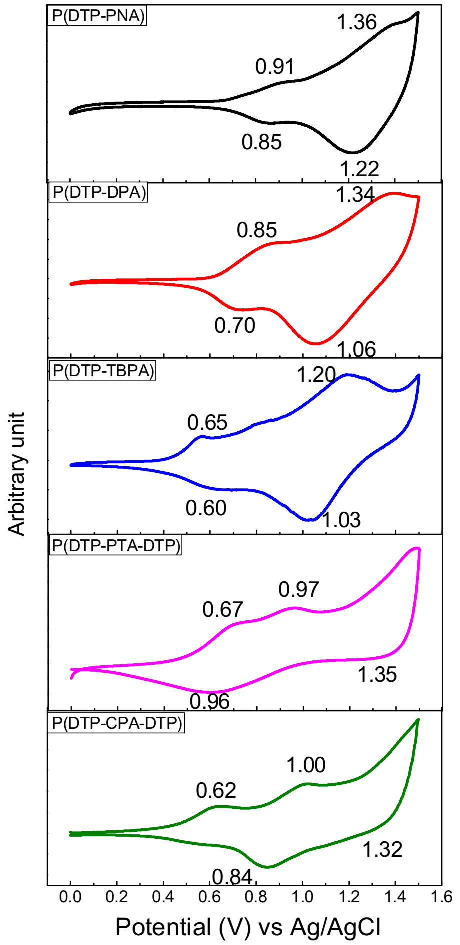


Fig. 3. Cyclic voltammetry curves for P(DTP-TPA)s in 0.1 mol/L $LiClO_4/CH_3CN$ at a scan rate of 50 mV/ s.

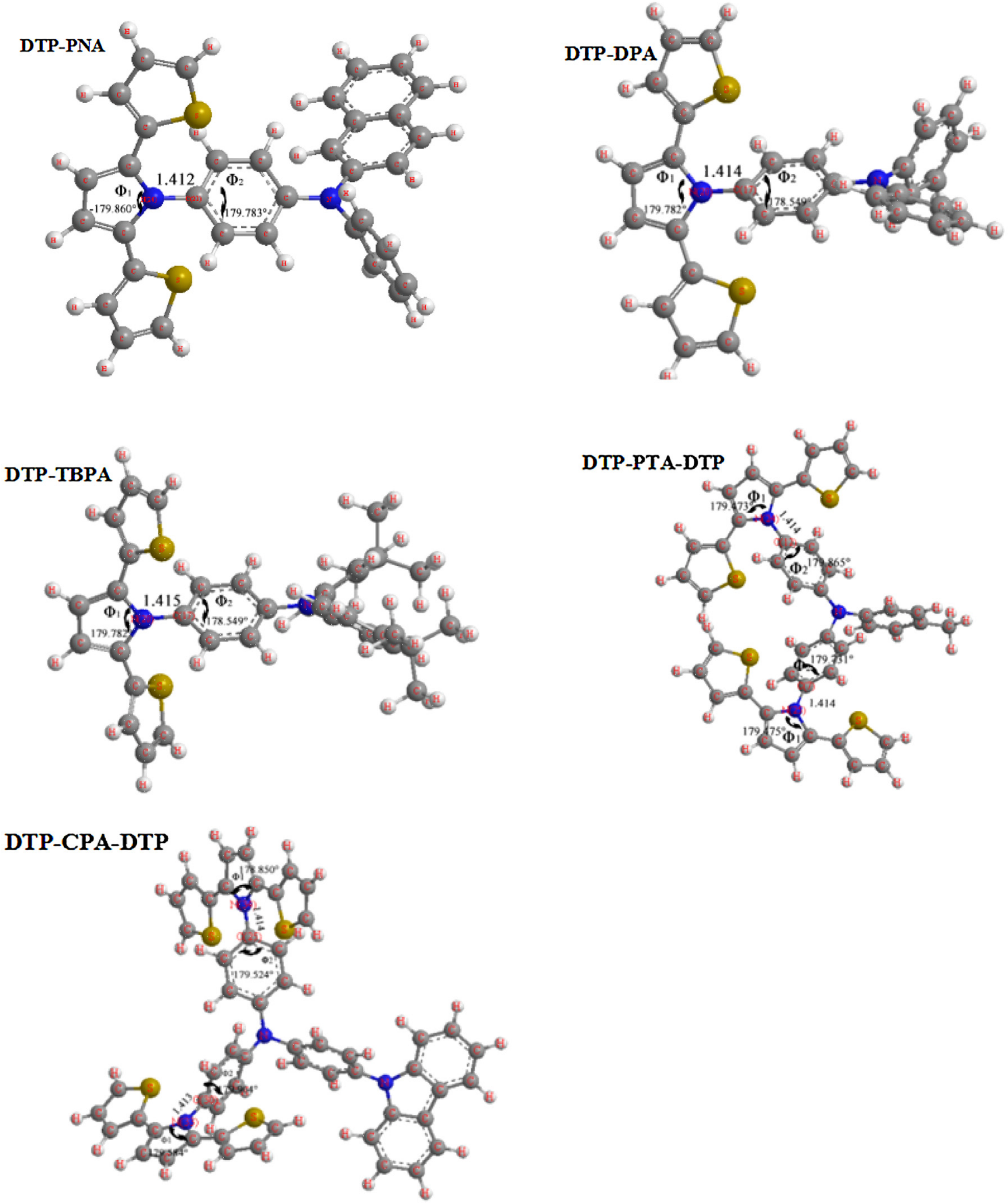
3.4. Geometry and electronic structure of P(DTP-TPA)s

In order to obtain deeper insight into the polymer structure-property relationships, the ground-state geometry optimizations and the energy levels of P(DTP-TPA)s were carried out by using density functional theory at the B3LYP/6-31G level.

The average C=N bond lengths between the pyrrole ring and phenylene ring in DTP-PNA, DTP-DPA, DTP-TBPA, DTP-PTA-DTP and DTP-CPA-DTP are 1.412 nm, 1.414 nm, 1.415 nm, 1.414 nm and 1.413 nm (1.414 nm), respectively, and the torsional angles (Φ) between the C=N linkage and adjacent phenylene or pyrrole ring are in the range of $178°-180°$(Fig. 4 and Table S1), which suggest that they are nearly in one planar conformation.

To better understand the evolution of the oxidation and reduction potentials, we studied the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the polymers via cyclic voltammetry (CV) method. The E_{HOMO} and the optical band gap (E_g) were calculated from E_{onset} and λ_{onset} (Table 1) [45]. In order to obtain the accurate redox potential, we use $E_{Fc/Fc+} = -4.80$ eV as reference electrode, which has been calibrated already. We know the $E_{1/2(Fc/Fc+vsAg/AgCl)} = 0.37$ V via cyclic voltammetry of (F_c/F_c^+). Then the E_{HOMO}, E_{LUMO} and E_g were summarized in Table 1. The results showed that the TPA derivatives had an important influence on regulating the electronic structure of the 2, 5 –dithienylpyrrole derivatives. The lower potentials they are, the easier electron goes into the polymer films from ITO.

On the other hand, E_{HOMO} represents the supply electronic capability while E_{LUMO} is relating to acceptance electronic power. In HOMO state, the electron cloud is completely distributed in 2, 5 –dithienylpyrrole part, which in favor of higher hole mobility (Fig. 5). However, in LUMO state, electron cloud is mainly distributed in TPA unit which can reduce E_g effectively. The lone pair electron of N in the TPA core unit would couple with π electron strongly, resulting effective density distribution in the molecule during the charge transfer. From Table 1, we can know the theoretical data are basically consistent with the experimental data. In experimental data, $E_{(P(DTP-DPA))} > E_{(P(DTP-PNA))} > E_{(P(DTP-TBPA))} >$


DTP-PNA

DTP-DPA

DTP-TBPA

DTP-PTA-DTP

DTP-CPA-DTP

Fig. 4. Optimized geometries of the DTP-TPAs.

Table 1
Optical and electrochemical properties of the polymers.

Polymers	λ_{max} nm	λ_{onset}[a] nm	E_{onset}^{ox}[b] eV	E_{HOMO}[c] eV	E_{LOMO}[d] eV	E_g[e] eV	E_g^{quntum}[f] eV
P(DTP-PNA)	328	477	0.67	−6.10	−3.50	2.60	3.64
P(DTP-DPA)	326	476	0.62	−5.05	−2.44	2.61	3.67
P(DTP-TBAP)	325	484	0.45	−4.88	−2.32	2.56	3.96
P(DTP-PTA-DTP)	453	545	0.50	−4.93	−2.66	2.27	2.41
P(DTP-CPA-DTP)	448	560	0.46	−4.89	−2.68	2.21	2.67

[a] λ_{onset}: the absorption starting wavelength.

[b] $E_{ox/onset(Fc/Fc+vsAg/AgCl)} = 0.37$ V.

[c] based on formula (1) $E_{HOMO} = -(E_{onset}^{ox}$ vs Ag/AgCl + 4.43) eV.

[d] based on formula (2) $E_{LUMO} = E_{HOMO} + E_g$.

[e] based on formula (3) $E_g = 1240/\lambda_{onset}$.

[f] E_{quntum}: values of theoretical calculation.

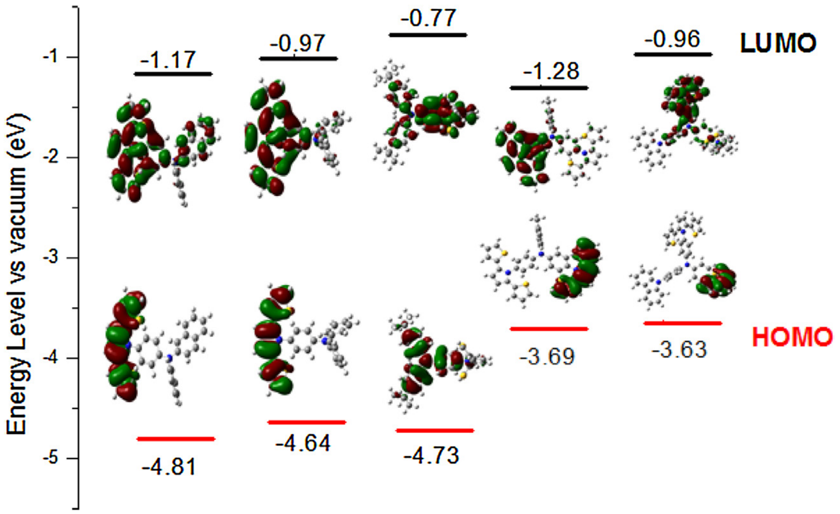


Fig. 5. Pictorial representations of the electron density in the frontier molecular orbitals of repetition units.

$E_{(P(DTP\text{-}PTA\text{-}DTP))} > E_{(P(DTP\text{-}CPA\text{-}DTP))}$. However, in theoretical data, $E_{(P(DTP\text{-}TBPA))} > E_{(P(DTP\text{-}DPA))} > E_{(P(DTP\text{-}PNA))} > E_{(P(DTP\text{-}CPA\text{-}DTP))} > E_{(P(DTP\text{-}PTA\text{-}DTP))}$. The slight deviation may be owing to the influence of the adjacent benzene ring. Moreover, theoretical data only resulted from the monomer, not long polymer chain. In fact, the solvent and electrolyte also play an important effect on the result.

3.5. Spectroelectrochemical properities

Spectroelectrochemical measurements were conducted by UV–Vis–NIR spectrophotometer upon incrementally changing the applied potential (from 0.0 V to 1.5 V) of the polymer films. The optical behavior as well as electronic structure of the polymers can be explained. Taking P(DTP-PNA) for example (Fig. 6), the polymer film is yellow at neutral state in the visible region and transparent in the NIR regions, which has a strong band at 321 nm and 397 nm. The absorptions were accounted for the π-π^* and n-π^* transitions of the DTP backbones and the TPA subunits [46]. But the absorption of 321 nm intensity decreased sharply when the potentials grew up, meanwhile, the absorption at 397 nm gradually increased. Also, the absorption at 816 nm and 1313 nm gradually increased with the potentials growing up, and the color of the film became from yellow (L:65; a:-5; b:23) to dusty blue (L:61; a:-22; b:-16) to violet (L:65; a:-4; b:-9), which is according with the view that conjugated polymers are promising materials for electrochromic applications. However, the absorption of P(DTP-PTA-DTP) at 453 nm decreased gradually when the applied potentials increased, and two new bands which appeared at 755 nm and 1181 nm increased. Other electronic absorption spectra changing process are given in Supporting Information Fig. S9. From Fig. 7, we can know the mechanism of the electron transfer of the P(DTP-TPA)s.

Colorimetric analysis is used to evaluate the color changes of electrochromic material. The measurements were performed by Commission Internationale de L'Eclairage (CIE) system. According to CIE system, the color is made up of three aspects: luminance (L), hue (a), saturation (b) [47], which representing the brightness of the materials, how red versus green and how yellow versus blue, respectively. In other words, this means the higher of the L, a, b, the brighter of the materials, the redder of the materials and the more yellow of the materials. These color and corresponding L, a, b values are shown in Table S2 in Supporting Information.

Response time, one of the most important characteristics of electrochromic materials, is the time needed to perform a switching between the neutral and oxidized states of the materials [48], which was measured by UV–Vis–NIR spectroscopy at fixed

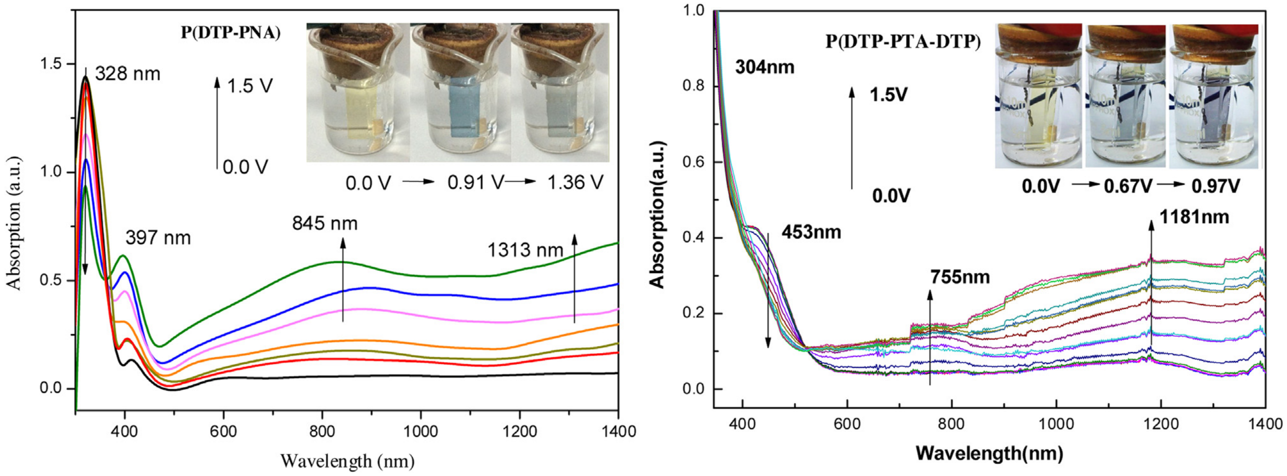


Fig. 6. Electronic absorption spectra changing process for P(DTP-PNA) and P(DTP-PTA-DTP) in 0.1 mol/L $LiClO_4/CH_3CN$ solution (insets are the photos of changing color).

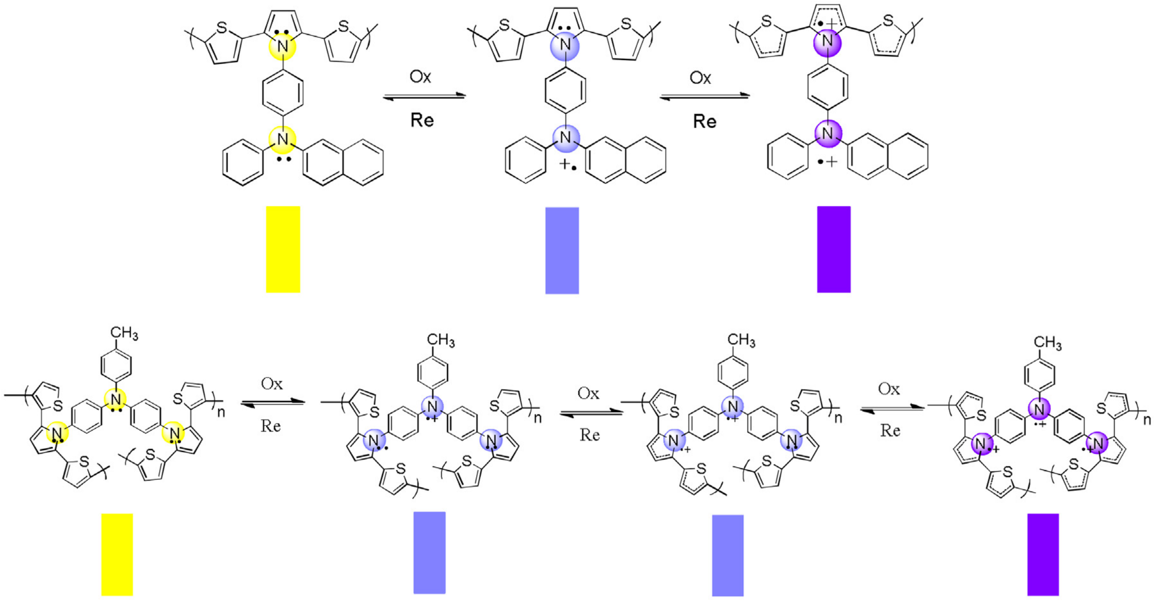


Fig. 7. The proposed electrochromism mechanization of P(DTP-PNA) and P(DTP-PTA-DTP).

wavelength from 0.0 V to 1.0 V. The response is found to be 2.9 s from the neutral to the oxidized state and 2.8 s from the oxidized to the reduced state of P(DTP-PNA) in 816 nm at Fig. 8(a). The coloration time is different from fading time, which may be owing to dispersion dynamics of ionic resulting from the different surface images of the oxidation-reduction process. At Fig. 8(b), we find that the current density of PDTP-PNA keeps stable in 100 s from 0.0 V to 1.0 V, which indicating that P(DTP-PNA) has stable electrochromic properties. P(DTP-PNA), P(DTP-DPA), P(DTP-TBPA), P(DTP-PTA-DTP) and P(DTP-CPA-DTP) films have a high optical contrast, which are attributed to the introduction of triarylamine units into the polymer backbone, but the P(DTP-PNA), P(DTP-DPA) and P(DTP-TBPA) are more faster than P(DTP-PTA-DTP) and P(DTP-CPA-DTP), which may be attribute to their more smaller steric hindrance. Other P(DTP-TPA)s have a similar explanation.

The coloration efficiency (CE) is another important characteristic for the electrochromic materials. CE can be calculated using the equations given below [49]

$$\delta_{OD} = \lg(T_b/T_c) \quad (1)$$

$$\eta = \delta_{OD}/Q \quad (2)$$

where T_b and T_c denote the transmittances of the film before and after colorations, respectively. δ_{OD} is the change of the optical density, which is proportional to the amount of created color centers. η denotes the coloration efficiency (CE). Q (mC/cm^2) is the amount of injected charge per unit sample area. ΔT(%) is the percentage transmittance change. As a result, the calculating data shows the CEs of the P(DTP-TPA)s are 75.72 cm^2/C, 90.06 cm^2/C, 102.4 cm^2/C, 83.55 cm^2/C, 94.69 cm^2/C, respectively (Table 2). At the same time, the ΔT(%) of the polymers are 23%, 24%, 13%, 19% and 17%, respectively. It indicates that the materials have not relative high CEs but have a relative high color changing velocity.

3.6. Surface Morphology

The morphology and stacking mode of the polymer have a very important influence on their properties, such as electron transfer speed, stability and so on. So the morphologies of film surface of the P(DTP-TPA)s were investigated specially by SEM. The surface morphologies of the polymer films were shown in Fig. 9, which were deposited on ITO electrodes via electrochemical polymerization. The closer the distance of movement of ion is, the faster of the ion transfers, and the more efficiency of electrochromic gets. From Fig. 9, we can see the polymer films are composed of many well-distributed microspheres. When the images are enlarged, as the inset in Fig. 9, the particles diameter is estimated as approximately 300–1000 nm. The larger surface area of the particles is in favor of increasing the area of the electrolyte solution contacting to the polymers surface, then facilitating the ion carriers transferring freely passing in out the films.

4. Conclusions

In summary, a series of polymers based on 2,5–dithienylpyrrole (DTP) and triarylamine units (TAA) with excellent optical transmittance change were successfully designed and synthesized. Spectroelectrochemical as well as electrochemical properties were used for the structural characterication. The polymers P(DTP-PNA), P(DTP-DPA) and P(DTP-TBPA) with single branched DTP unit have a better performance than P(DTP-PTA-DTP), P(DTP-CPA-DTP) containing double branched DTP unit, which may be due to the steric hindrance of the latter two is larger than the first three, so the properties of the P(DTP-PTA-DTP) and P(DTP-CPA-DTP) need further improvement. Meanwhile by SEM, we can see all films surface are regular, which are in favor of the carrier's input and output in polymer structure, and have a potential application on the device. Also, an obvious color change was observed from a yellow neutral to dusty blue and violet. These prominent features make P(DTP-TPA)s have many applications in the feature, such as light-emitting, hole-transporting materials, electrochromic materials and memory device application.

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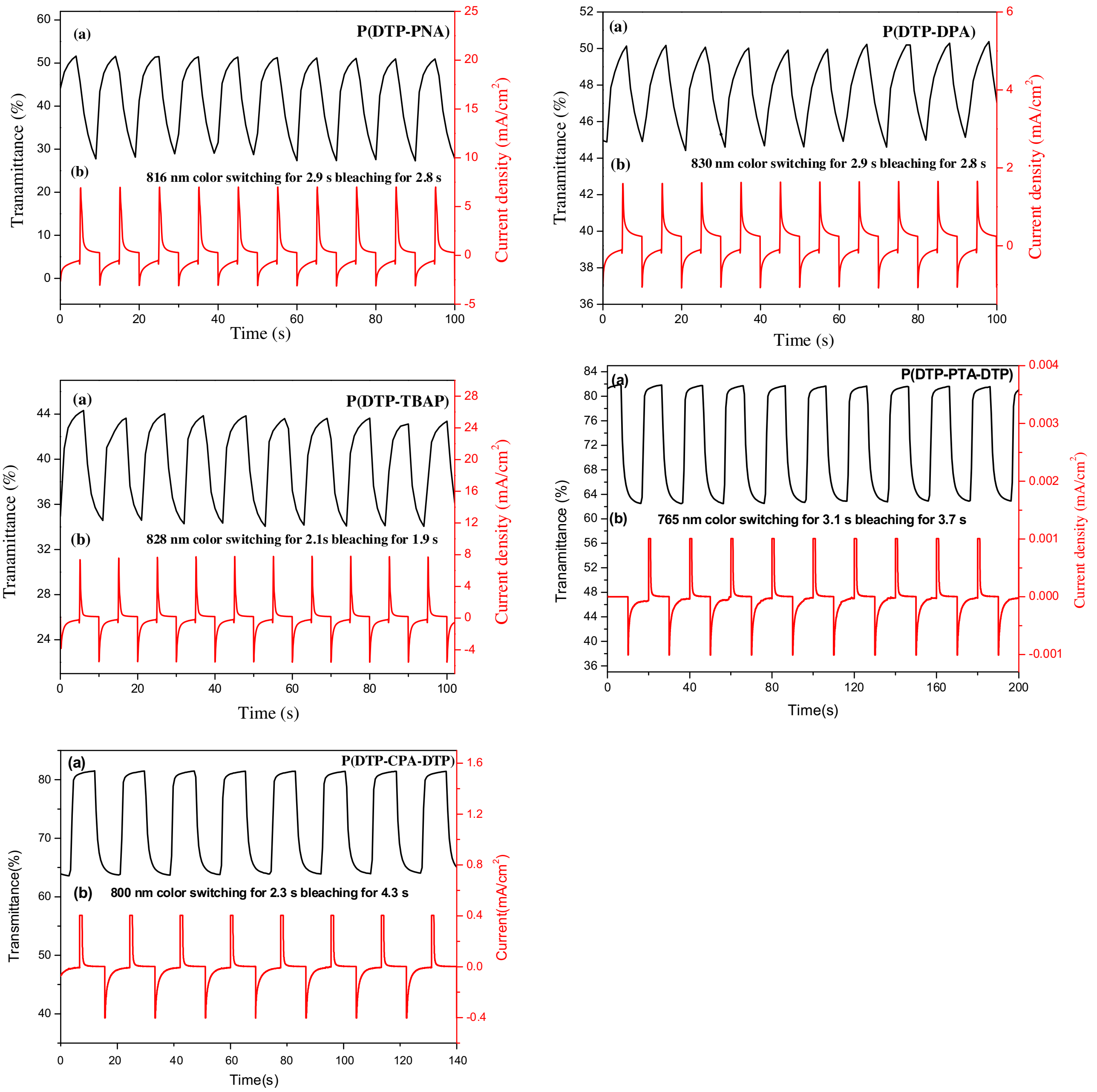

Fig. 8. Optical switching procedures: (a) potential step transmittance of P(DTP-TPA)s by applying a potential step (0.0-1.0 V); (b) Current consumption of P(DTP-TPA)s.

Table 2
Optical and Electrochemical Data Collected for Coloration Efficiency Measurements of P(DTP-TPA)s.

Polymers	$\lambda_{(nm)}$[a]	δ_{OD}[b]	Q(mC/cm^2)[c]	η(cm^2/C)[d]	ΔT(%)[e]
P(DTP-PNA)	816	0.1310	1.730	75.72	23
P(DTP-DPA)	830	0.1450	1.610	90.06	24
P(DTP-TBAP)	828	0.1280	1.250	102.4	13
P(DTP-PTA-DTP)	765	0.0715	0.856	83.55	19
P(DTP-CPA-DTP)	800	0.1641	1.733	94.69	17

[a] The given wavelength where the date were determined.
[b] Optical density change at the given wavelength.
[c] Injected charge, determined from the in situ experiments.
[d] Coloration efficiency is derived from the Eq. (2).
[e] The percentage transmittance changes.

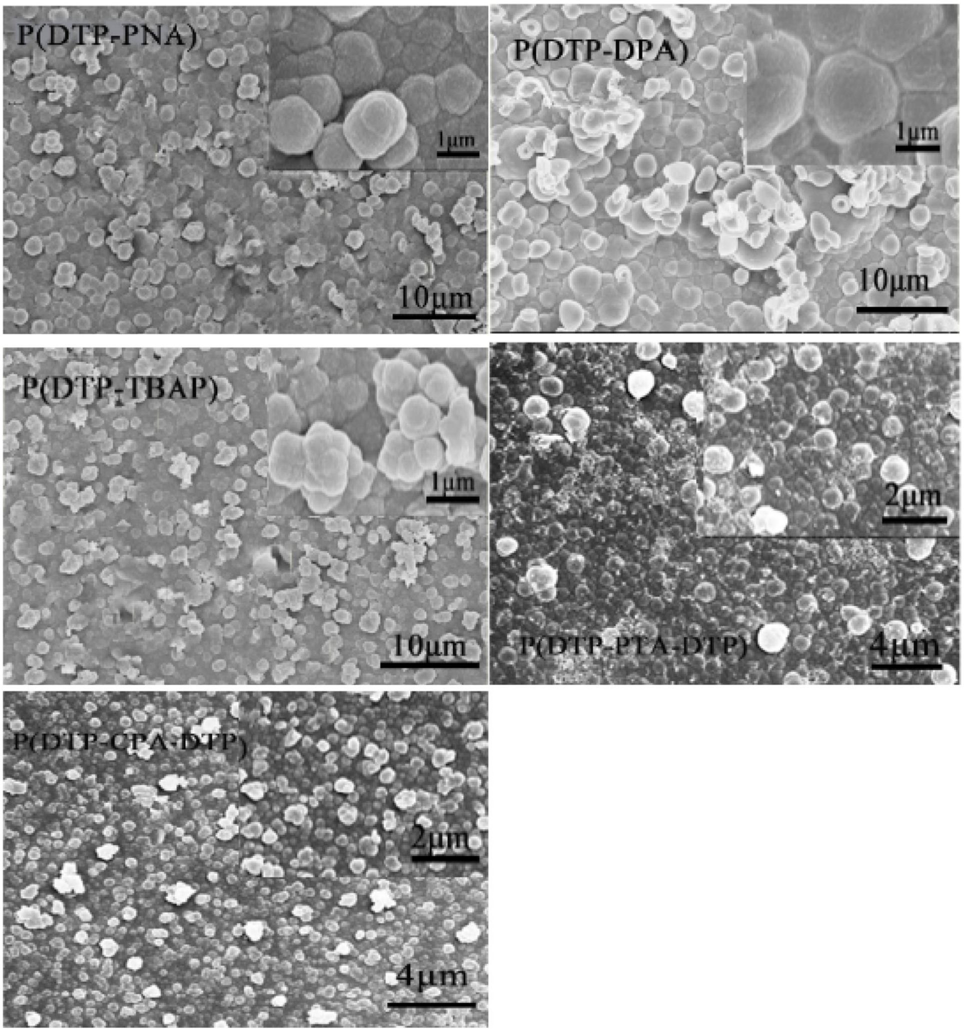

Fig. 9. SEM image of P(DTP-TPA)s deposited on ITO electrodes via electrochemical polymerization method.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2017.01.071.

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