

A Conjugated Copolymer Bearing Imidazolium-based Ionic Liquid: Electrochemical Synthesis and Electrochromic Properties

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Electronic Supplementary Information

Abstract An imidazolium-based ionic liquid (IL) modified triphenylamine derivative, namely 1-(4-((4-(diphenylamino)benzoyl)oxy)butyl)-3-methyl imidazole tetrafluoroborate (TPAC₆IL-BF₄), was designed and synthesized, and further applied with 3,4-ethylene dioxythiophene (EDOT) to prepare conjugated copolymer P(EDOT:TPAC₆IL-BF₄) via electrochemical polymerization. The cyclic voltammetry curves show that the copolymer P(EDOT:TPAC₆IL-BF₄) possesses two pairs of redox peaks, which should be ascribed to the redox behaviors of EDOT and triphenylamine. The ultraviolet-visible (UV-Vis) absorption spectrum of P(EDOT:TPAC₆IL-BF₄) exhibits one maximum absorption peak at 580 nm and a small shoulder characteristic peak at 385 nm under neutral state which are assigned to π - π^* conjugated structure of EDOT and triphenylamine. After being applied at the positive voltage, the copolymer color changes from dark blue to light blue, which is close to the color of poly(3,4-ethylenedioxythiophene) (PEDOT). Surprisingly, the copolymer P(EDOT:TPAC₆IL-BF₄) shows shorter switching time of 0.37 s, 0.30 s at 580 nm and 0.38 s, 0.45 s at 1100 nm compared with PEDOT. It is more intriguing that the copolymer P(EDOT:TPAC₆IL-BF₄) exhibits electrochromism even in free supporting electrolyte. The results confirm that the existence of imidazolium-based ionic liquid has an improvement on the ion diffusion properties and the switching time of conjugated polymer, which may provide a potential direction for the preparation of high-performance electrochromic materials.

Keywords Electrochromism; Copolymer; Ionic liquid; Electropolymerization; Fast switching

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INTRODUCTION

Electrochromic (EC) materials have gradually received more attention and become a promising research field for various potential applications, such as smart windows, anti-glare rear-view mirrors, displays and memory devices.^[1–4] Conjugated polymers have gained popularity owing to their good processability, diverse colors, high coloration efficiency and especially facile structural modification.^[5–8] However, the relatively long switching time still limits their practical applications, especially for display device.^[9] Generally, the change of the π -electron characteristics of the polymers during redox reactions will cause the occurrence of electrochromism. And reversible insertion/extraction of ions happens simultaneously, which has significant influence on the switching time.^[10] Thus, the design and synthesis of novel conjugated polymers with superior electrochromic properties are still urgent for the requirement of commercial applications.

Of the EC polymers, PEDOT and its derivatives possess outstanding properties including low oxidation potential, nar-

row band gap and stable doped (oxidized) state, and thus have been widely studied and extensively used in electrochromic-supercapacitor devices.^[11–17] It is an effective method for achieving desirable properties via adjusting the polymer backbone of PEDOT, including main chain and pendant group structural modification. Otero *et al.* designed and synthesized a cross-linked PEDOT derivative with fine electrochromic properties.^[18] Hu *et al.*, Zhao *et al.*, Xu *et al.* and Niu *et al.* also reported series of EC polymers based on EDOT through the modification of main chain, which exhibited multichromism or tunable electrochromism.^[19–22] However, only few literatures were related to the synthesis of PEDOT derivatives through pendant group structural modification aiming to achieve fast switching property.

Ionic liquids consisting of inorganic anions and stable organic cations are commonly used as a conductive medium for the electrolyte system owing to their high ionic conductivity and wide electrochemical window.^[23–25] Ouyang *et al.* indicated that a poly(4,4',4"-tris[4-(2-bithienyl)-phenyl]amine) (PT-BTPA) film prepared on the ionic liquid-functionalized indium tin oxide (ITO) electrode exhibited shorter switching time compared with the neat PTBTPA film.^[26] In our recent work, a novel polytriphenylamine derivative was designed and pre-

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pared by introducing ionic liquid unit at the side chain, which further demonstrated better ion diffusion character and shorter switching time.^[27] In addition, copolymerization as a general synthetic method is a promising strategy to obtain materials with better properties than those of respective homopolymers.^[28] Thus, it is anticipated that copolymer films based on EDOT and the monomer with pendent ion liquids would exhibit short switching time. Besides, electropolymerization is a common method for preparing functional polymer films. The polymer film can be obtained directly on the surface of the electrode *via* electropolymerization and its structure and morphology can be well controlled by changing the electropolymerization parameters.

In this work, a new imidazolium-based ionic liquid modified triphenylamine derivative, namely 1-(4-((4-(diphenylamino)benzoyl)oxy)butyl)-3-methylimidazole tetrafluoroborate (TPAC₆IL-BF₄), was successfully synthesized through the ester group and the alkyl chain at the *para* position of triphenylamine. Then, the copolymer P(EDOT:TPAC₆IL-BF₄) was prepared *via* electrochemical copolymerization of TPAC₆IL-BF₄ and EDOT. PEDOT film was also obtained and investigated as a reference. Their chemical structures and morphologies were characterized by ¹H nuclear magnetic resonance spectroscopy (¹H-NMR), mass spectrometry (MS) and scanning electron microscopy (SEM). The electrochemical, electrochromic properties and ion diffusion characters were investigated systematically. In addition, the electrochromic behavior of the copolymer P(EDOT:TPAC₆IL-BF₄) in free supporting electrolyte solution was studied to verify the significant influence of the pendent ionic liquid on the switching time.

EXPERIMENTAL

Materials

Diphenylamine, 4-fluorobenzonitrile, sodium hydride, bis(triphenylphosphine)palladium(II) dichloride, *N*-bromosuccinimide (NBS), sodium hydroxide, 4-dimethylaminopyridine (4-DMAP), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI), 6-bromo-1-hexanol, 1-methylimidazole, silver tetrafluoroborate, tetrabutylammonium perchlorate (TBAP) and EDOT were purchased from Aladdin and used as received. Commercial HPLC grade acetonitrile (ACN, 99%) and dichloromethane (DCM, 99%) were purchased from Aladdin. Indium tin oxide (ITO) glass substrates (Kaivo Optoelectronic Technology Co., Ltd.) were cleaned by ultrasonic in a series of solvents including sodium hydroxide solution, distilled water, ethanol, acetone and methylbenzene for 15 min, respectively.

Characterization

¹H-NMR spectra of all these synthesized compounds were recorded by Bruker AVANCE III instrument (Bruker, Switzerland). Mass spectra (MS) were recorded by AXIMA-CFRTM plus instrument. Electrochemical polymerizations of EDOT and the mixture of EDOT and TPAC₆IL-BF₄ were performed by a CHI660E electrochemical analyzer (Chen Hua, China). Surface morphologies of the polymer films were observed by the FEI Nova Nano (FEI, USA). Thickness measurements of polymer films were performed by the DEKTAK-XK step profiler (Bruker, Germany). UV-Vis absorption spectra, spectroelectrochemical analysis, optical contrast and switching time were characterized by the Shimadzu UV-1800 spectrophotometer (Shimadzu, Japan) com-

bined with CHI660E electrochemical analyzer. The electrochemical impedance spectroscopy (EIS) was carried out from 0.01 Hz to 1 MHz by CHI660E electrochemical analyzer.

Synthesis of Monomers

Synthesis of 4-(diphenylamino) benzonitrile (1)

Sodium hydride (1.50 g) and diphenylamine (5.11 g) were firstly dissolved in *N,N*-dimethylformamide (DMF) (40 mL). Then, 4-fluorobenzonitrile (4.49 g) was added to the above solution. The reaction was performed under nitrogen atmosphere for 12 h at 110 °C. The resulting solution was extracted with DCM and saturated salt solution several times, then dried by anhydrous MgSO₄. The solvent was evaporated off and the solid residue was purified by column chromatography to afford white powder with 58.2% (4.75 g) yield. ¹H-NMR (500 MHz, CDCl₃, δ , ppm): 7.43 (t, 2H), 7.35 (d, 4H), 7.18 (d, 2H), 7.16 (t, 4H), 6.97 (d, 2H); MS (EI): *m/z*: 271.1.

Synthesis of 4-(diphenylamino) benzoic acid (2)

1 (1.43 g) was dissolved in ethanol (40 mL) and 25% NaOH solution (40 mL). The reaction was performed for 14 h at 80 °C. The resulting solution was added with 3 mol·L⁻¹ HCl (90 mL) and yellow powder was separated out. After filtrated by vacuum filtration and washed by distilled water, the product was then dried in vacuum for 24 h at 60 °C and afforded with a yield of 88.9% (1.36 g). ¹H-NMR (500 MHz, CDCl₃, δ , ppm): 7.91 (m, 2H), 7.34 (m, 4H), 7.16 (d, 6H), 7.00 (d, 2H); MS (EI): *m/z* (%): 290.1.

Synthesis of 6-bromohexyl 4-(diphenylamino) benzoate (3)

2 (0.64 g), 4-DMAP (0.14 g), EDCI (1.27 g) and 6-bromo-hexanol (0.60 g) were dissolved in DCM (25 mL). The reaction was performed for 15 h at 30 °C. The resulting solution was extracted with DCM and saturated salt solution several times and dried by anhydrous MgSO₄. The solvent was evaporated off and the solid residue was purified by column chromatography to afford yellow viscous liquid with 87.8% (0.87 g) yield. ¹H-NMR (500 MHz, CDCl₃, δ , ppm): 7.85 (m, 2H), 7.32 (m, 4H), 7.13 (d, 6H), 6.98 (d, 2H), 4.30 (t, 2H), 3.43 (t, 2H), 1.90 (m, 2H), 1.77 (m, 2H), 1.47 (m, 4H); MS (EI): *m/z* (%): 453.3.

Synthesis of 1-(6-(4-diphenylamino) benzoyl) oxyhexyl)-3-methylimidazole bromide (4)

3 (506.2 mg) and 1-methylimidazole (83.3 mg) were dissolved in ACN (15 mL). The reaction was performed for 32 h at 70 °C. ACN in the resulting solution was evaporated off and ice ethyl acetate was added dropwise into the solution. The viscous liquid was kept and washed with ice ethyl acetate for several times. It was dried in vacuum for 24 h at 60 °C and yellow viscous liquid was obtained with 86.3% (465.4 mg) yield. ¹H-NMR (500 MHz, DMSO-*d*₆, δ , ppm): 9.13 (s, 1H), 7.80 (d, 1H), 7.78 (d, 2H), 7.71 (d, 1H), 7.40 (m, 4H), 7.18 (d, 2H), 7.14 (d, 4H), 6.89 (d, 2H), 4.24 (t, 2H), 4.16 (t, 2H), 3.84 (s, 3H), 1.80 (m, 2H), 1.67 (m, 2H), 1.41 (m, 2H), 1.29 (m, 2H); MS (EI): *m/z* (%): 535.1.

Synthesis of 1-(6-(4-diphenylamino) benzoyl) oxyhexyl)-3-methylimidazole tetrafluoroborate (TPAC₆IL-BF₄)

Monomer **4** (224.3 mg) and silver tetrafluoroborate (108 mg) were dissolved in methanol (20 mL). The reaction was performed without light for 3 h at room temperature. In order to prevent silver salt from decomposition in the light, the resulting solution was filtrated in the dark and the orange-yellow solution was kept. The solvent was evaporated off to afford yellow powder with 77.9% (177.0 mg) yield. ¹H-NMR (500 MHz, DMSO,

δ , ppm): 9.13 (s, 1H), 7.80 (d, 1H), 7.78 (d, 2H), 7.71 (d, 1H), 7.40 (m, 4H), 7.18 (d, 2H), 7.14 (d, 4H), 6.89 (d, 2H), 4.24 (t, 2H), 4.16 (t, 2H), 3.84 (s, 3H), 1.80 (m, 2H), 1.67 (m, 2H), 1.41 (m, 2H), 1.29 (m, 2H); MS (EI): m/z (%): 535.1. The synthesis routes to TPAC₆IL-BF₄ are given in Scheme 1.

Electrochemical Synthesis of Polymers

The copolymer P(EDOT:TPAC₆IL-BF₄) was prepared *via* cyclic voltammetry polymerization between -0.8 and 1.6 V at a scan rate of $0.2 \text{ V}\cdot\text{s}^{-1}$ (the number of cycle was controlled at 5) in conventional three-electrode system with an ITO-coated glass substrate as working electrode, a platinum sheet as auxiliary electrode and a Ag/AgCl electrode as reference electrode. The electrochemical polymerization route to P(EDOT:TPAC₆IL-BF₄) is given in Scheme 2. The electrolyte solution for copolymerization contains $4 \text{ mmol}\cdot\text{L}^{-1}$ EDOT, $1 \text{ mmol}\cdot\text{L}^{-1}$ TPAC₆IL-BF₄ and $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBAP in DCM/ACN solution (3/7, V/V). As a reference, PEDOT was also prepared *via* cyclic voltammetry polymerization containing $4 \text{ mmol}\cdot\text{L}^{-1}$ EDOT and $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBAP in DCM/ACN solutions (3/7, V/V) with the same electropolymerization parameters. The electrochemical measurements, spectroelectrochemical experiments, optical contrast and switching time measurements of polymer films were performed in $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBAP/ACN solution.

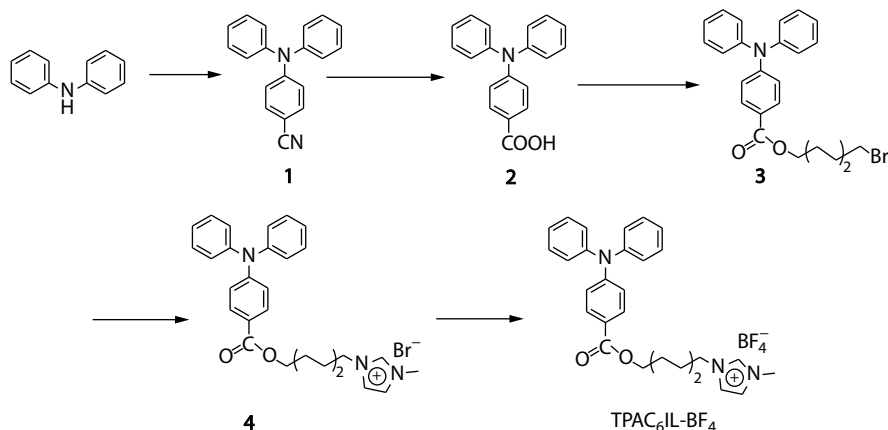
RESULTS AND DISCUSSION

Electrochemical Polymerization

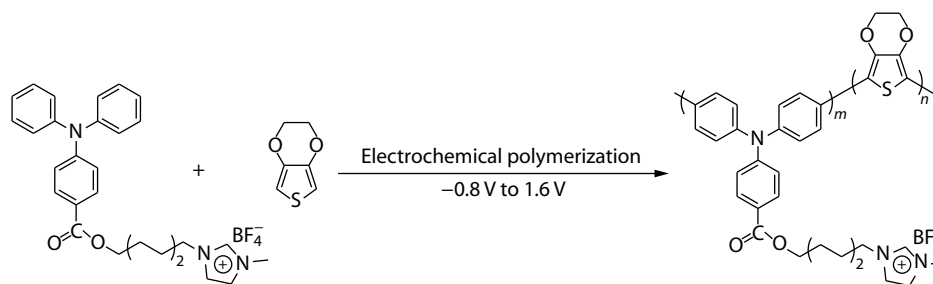
The polarization curves of $1 \text{ mmol}\cdot\text{L}^{-1}$ TPAC₆IL-BF₄, $4 \text{ mmol}\cdot\text{L}^{-1}$ EDOT, as well as the mixture of $1 \text{ mmol}\cdot\text{L}^{-1}$ TPAC₆IL-BF₄ and $4 \text{ mmol}\cdot\text{L}^{-1}$ EDOT in DCM/ACN solution (3/7, V/V) containing $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBAP at a scan rate of $0.02 \text{ V}\cdot\text{s}^{-1}$ when using the

glassy carbon electrode as the working electrode are shown in Fig. 1(a). The onset oxidation potentials of TPAC₆IL-BF₄ and EDOT are 1.01 and 1.26 V, respectively. The polarization curve of the mixture of TPAC₆IL-BF₄ and EDOT shows a combination of those of their individual monomers, which contains the one of TPAC₆IL-BF₄ at the potential lower than 1.2 V that belongs to the oxidation of the triphenylamine (TPA) group and the one of EDOT at higher potential. The small difference of the onset oxidation potential implies that the electrochemical copolymerization is readily to be achieved.^[29]

The cyclic voltammetry curves of $1 \text{ mmol}\cdot\text{L}^{-1}$ TPAC₆IL-BF₄, $4 \text{ mmol}\cdot\text{L}^{-1}$ EDOT, and the mixture of $1 \text{ mmol}\cdot\text{L}^{-1}$ TPAC₆IL-BF₄ and $4 \text{ mmol}\cdot\text{L}^{-1}$ EDOT were carried out from -0.8 V to 1.6 V when using the ITO glass as the working electrode (in Fig. S1 in the electronic supplementary information, ESI). TPAC₆IL-BF₄ exhibits a pair of redox peaks at 1.26 and 1.08 V at the first cycle, but the peak current does not increase with the increase of scan cycles, indicating that polymerization reaction does not happen due to the formation of TPB²⁺.^[30] EDOT shows an irreversible reduction peak at around -0.54 V at the first cycle, then a pair of reversible redox peaks at 0.11 and -0.54 V emerge and the peak current gradually increases as the subsequent scan cycles increases, indicating the formation of electroactive polymer. Compared with EDOT, the mixture of EDOT and TPAC₆IL-BF₄ presents a pair of redox peaks located at 1.28 and 1.09 V belonging to TPAC₆IL-BF₄ and an irreversible reduction peak at -0.51 V belonging to EDOT. The increment of these peak currents with the successive cycles implies the formation of copolymer well deposited on the electrode owing to the cross-linking between EDOT and triphenylamine units.



Scheme 1 Synthesis routes to monomer TPAC₆IL-BF₄.



Scheme 2 Electrochemical synthesis route to P(EDOT:TPAC₆IL-BF₄).

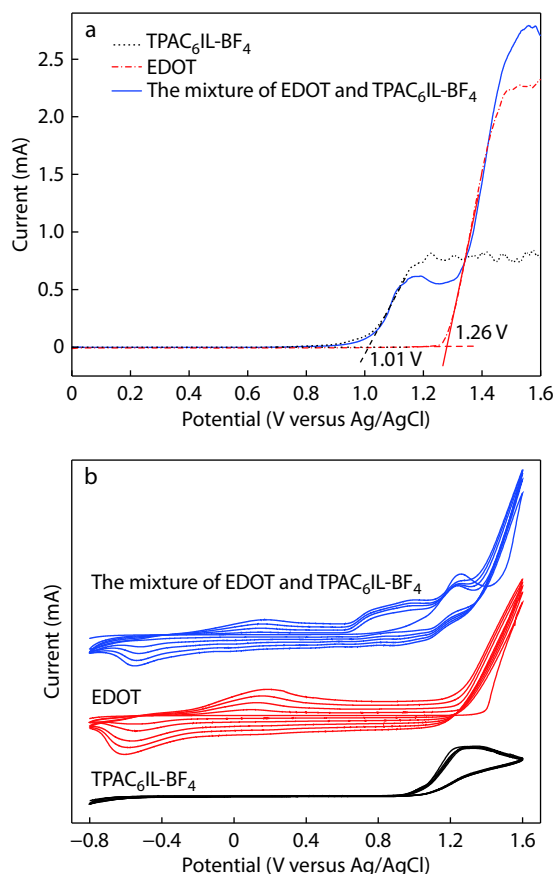


Fig. 1 (a) Polarization curves and (b) cyclic voltammograms of TPAC₆IL-BF₄ (1 mmol·L⁻¹), EDOT (4 mmol·L⁻¹), the mixture of EDOT and TPAC₆IL-BF₄ (1 and 4 mmol·L⁻¹) in DCM/ACN solution (3/7, V/V) containing 0.1 mol·L⁻¹ TBAP.

Electrochemistry

Fig. 2 shows the cyclic voltammograms of P(EDOT:TPAC₆IL-BF₄) and PEDOT films in 0.1 mol·L⁻¹ TBAP/ACN solution. PEDOT shows a pair of redox peaks at around 0.18 and -0.52 V, while the copolymer P(EDOT:TPAC₆IL-BF₄) exhibits two pairs of redox peaks. The peaks located at 0.17 and -0.49 V belong to the EDOT group and the other peaks located at 1.13 and 0.99 V belong to the TPA group. This electrochemical behavior further proves the formation of copolymer instead of the mixture of individual homopolymers because the homopolymerization reaction of TPAC₆IL-BF₄ does not happen.

Morphology Characterization

The surface morphologies of P(EDOT:TPAC₆IL-BF₄) and PEDOT films were characterized by SEM. As shown in Fig. 3, it is clear that PEDOT film exhibits a flocculent structure with many pores, while the copolymer P(EDOT:TPAC₆IL-BF₄) film presents flocculent morphology with much looser structure. The phenomenon may be because long alkyl chain and imidazolium-based ionic liquid from TPAC₆IL-BF₄ make the aggregation much looser between different polymer molecules during the formation of copolymer film. It is supposed that much looser flocculent structure of the copolymer film may be beneficial to ion diffusion. In order to better compare the electrochromic properties, it is very important to control the film thickness

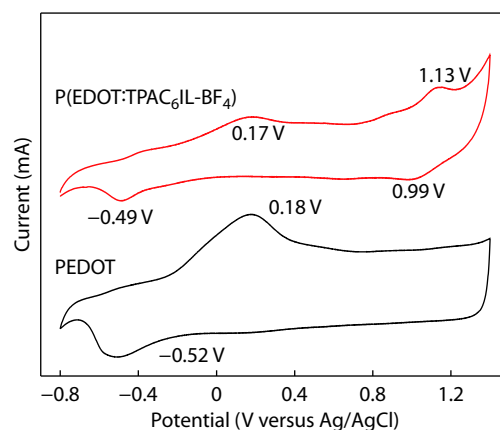


Fig. 2 Cyclic voltammograms of P(EDOT:TPAC₆IL-BF₄) and PEDOT in a 0.1 mol·L⁻¹ TBAP/ACN solution at a scan rate of 0.1 V·s⁻¹.

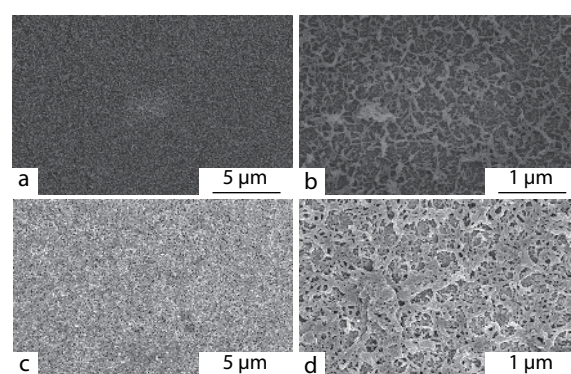


Fig. 3 SEM images of (a, b) P(EDOT:TPAC₆IL-BF₄) and (c, d) PEDOT at (a, c) low and (b, d) high resolutions.

through changing the electropolymerization parameters. Thus, the film thicknesses of P(EDOT:TPAC₆IL-BF₄) and PEDOT films are about 50 nm as measured by DEKTA-KK step profiler, and the thickness data is shown in Fig. S2 and Table S1 (in ESI).

Spectroelectrochemistry

Spectroelectrochemical analysis is a powerful way to investigate the optical switches and changes upon potential change, which provides the insights into the electronic structure of the conjugated polymers.^[31,32] The absorption spectra of P(EDOT:TPAC₆IL-BF₄) and PEDOT films are shown in Fig. 4. The maximum absorption characteristic peak of the PEDOT film is located at 620 nm, which should be attributed to the π - π^* conjugated structure of the main chain. The absorption intensity gradually decreases with the increase of the applied potential and a new absorption peak emerges at 1100 nm, which is mainly due to the generation of polaron and bipolaron, accompanied with the color changes from dark blue to light blue. As for P(EDOT:TPAC₆IL-BF₄), the maximum characteristic peak at neutral state is blue shifted to around 580 nm with a small peak located at 385 nm, which should be ascribed to the π - π^* transitions of the EDOT and TPA moieties of the main chain. However, the absorption peak located at 385 nm is very weak, which may result from the smaller ratio of TPAC₆IL-BF₄ in the copolymer structure during the electrochemical copolymerization. Similarly, the maximum absorption intensity gradually decreases with the increase of the applied potential

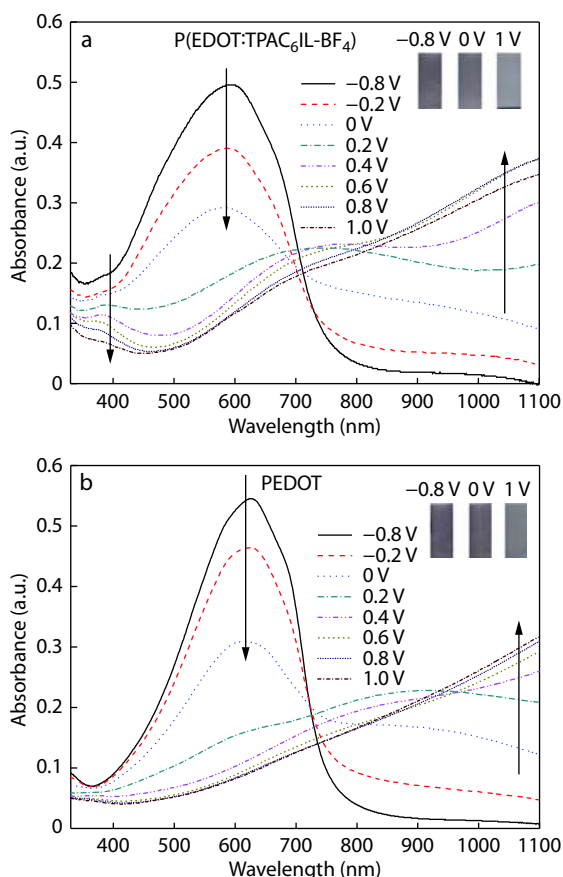


Fig. 4 Spectroelectrochemistry and color changes of (a) P(EDOT:TPAC₆IL-BF₄) and (b) PEDOT films in 0.1 mol·L⁻¹ TBAP/ACN solution.

and a new absorption peak emerges at 1100 nm, which is mainly due to the generation of polaron and bipolaron, accompanied with the color changes from dark blue to light blue. It implies that the introduction of imidazolium-based ionic liquid has little influence on the color changes of the copolymer compared to PEDOT.

Electrochromic Properties

Kinetic studies were carried out to elucidate the electrochromic properties (including optical contrast and switching time) for conjugated polymer films. The transmittance changes as a function of time were monitored at their corresponding absorption wavelength under a repeated stepping potential between 0 and 1.2 V with a residence of 5 s. As shown in Fig. 5, the copolymer P(EDOT:TPAC₆IL-BF₄) shows high optical contrasts of 35% (580 nm) and 44% (1100 nm), while the optical contrasts of the PEDOT film at 620 and 1100 nm are measured as 44% and 50%, respectively. In addition, the copolymer P(EDOT:TPAC₆IL-BF₄) also shows a small optical contrast of 7.5% at 385 nm (as shown in Fig. S3 in ESI). It can be found that P(EDOT:TPAC₆IL-BF₄) possesses a relatively similar optical contrast to that of PEDOT in the visible and near infrared regions.

The switching time is viewed as the time required to reach 95% of the full switch of the transmittance changes. Fig. 6 reveals the switching time of P(EDOT:TPAC₆IL-BF₄) and PEDOT films at different wavelengths. The oxidation time and reduc-

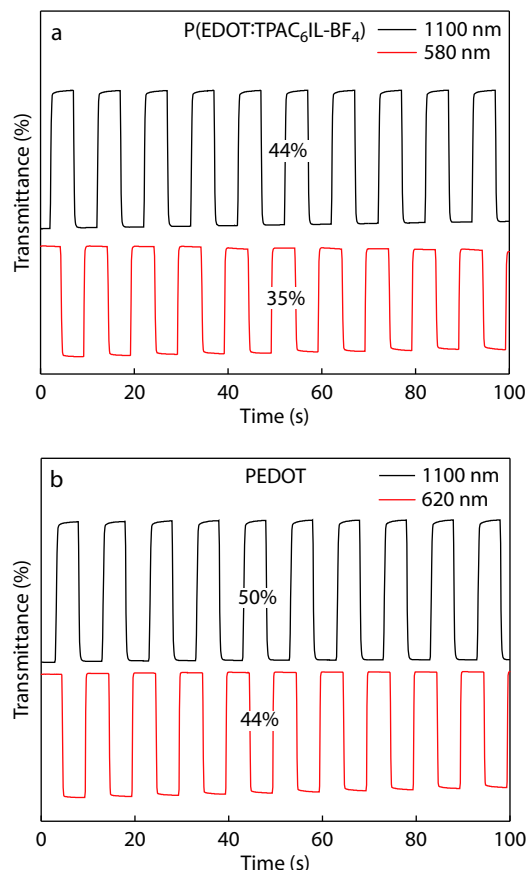


Fig. 5 Optical contrast of (a) P(EDOT:TPAC₆IL-BF₄) at 580 and 1100 nm and (b) PEDOT at 620 and 1100 nm in 0.1 mol·L⁻¹ TBAP/ACN solution between 0 and 1.2 V with a residence of 5 s.

tion time of PEDOT are 0.50 and 0.41 s at 620 nm while P(EDOT:TPAC₆IL-BF₄) shows the oxidation time of 0.37 s and the reduction time of 0.30 s at 580 nm with the improvement of 26% and 27%, respectively. The oxidation time and reduction time of PEDOT are 0.50 and 0.68 s at 1100 nm while P(EDOT:TPAC₆IL-BF₄) shows the oxidation time and reduction time of 0.38 and 0.45 s with the improvement of 24% and 34%, respectively. It is clear that P(EDOT:TPAC₆IL-BF₄) shows shorter switching time than PEDOT. It is speculated that the looser flocculent structure and the pendent ionic liquids of the copolymer P(EDOT:TPAC₆IL-BF₄) are beneficial to ion insertion/extraction, which may result in the shorter switching time.

In addition, the coloration efficiency (CE) is also an important parameter for the electrochromic materials, which can be calculated by Eq. (1)

$$CE = \Delta OD / Q_d \quad (1)$$

where Q_d represents the injected charge density as a function of the active electrode area that can be stated for 95% of the full optical switch, which was investigated *via* chronoamperometric experiments (in Fig. S4 in ESI). ΔOD can be obtained from Eq. (2)

$$\Delta OD = \log(T_{\text{bleached}} / T_{\text{colored}}) \quad (2)$$

where T_{bleached} and T_{colored} represent the transmittance values of polymer films in the oxidized state and the neutral state, respectively.^[33,34] The CE values of the PEDOT film are

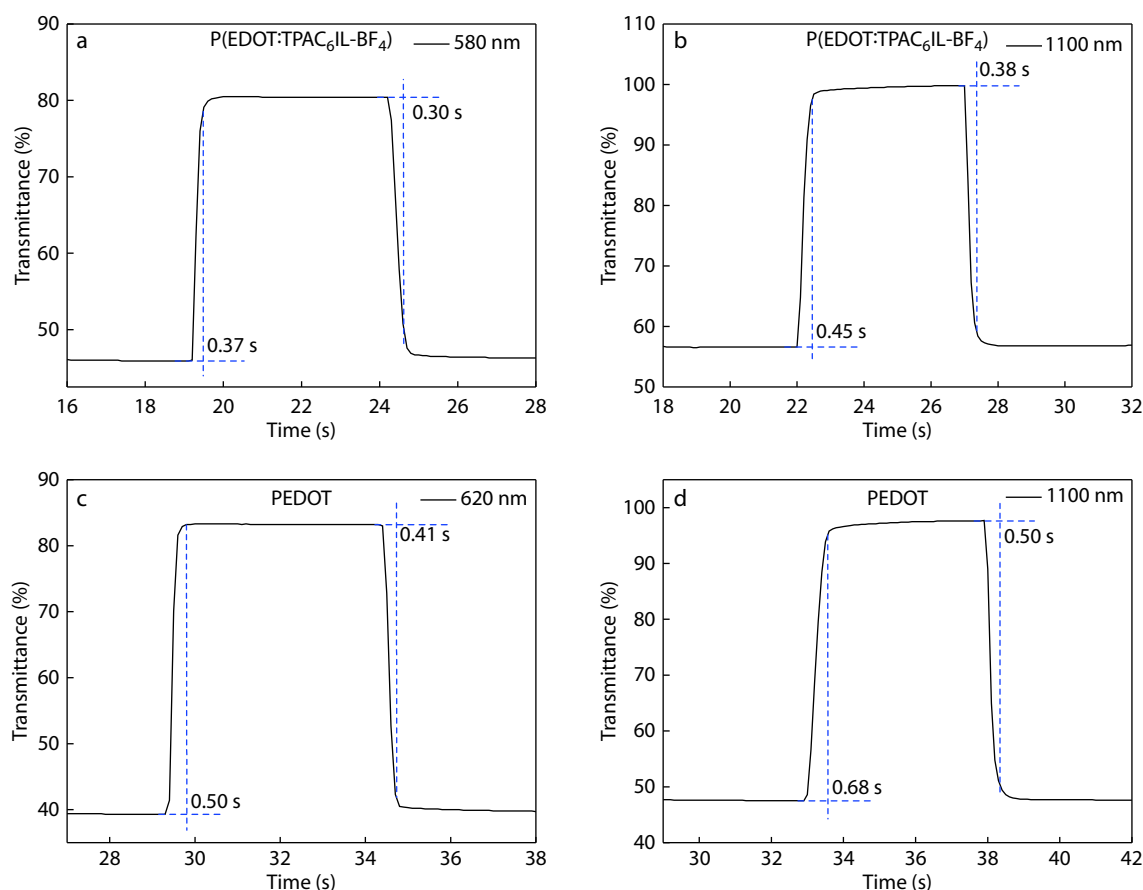


Fig. 6 Switching time of P(EDOT:TPAC₆IL-BF₄) film at (a) 580 and (b) 1100 nm, and PEDOT film at (c) 620 and (d) 1100 nm in 0.1 mol·L⁻¹ TBAP/ACN solution between 0 and 1.2 V with a residence of 5 s.

108.6 cm²·C⁻¹ at 620 nm and 141.1 cm²·C⁻¹ at 1100 nm, while the CE values of P(EDOT:TPAC₆IL-BF₄) film are 109.7 cm²·C⁻¹ at 580 nm and 149.0 cm²·C⁻¹ at 1100 nm. All the above-mentioned electrochromic properties of PEDOT and P(EDOT:TPAC₆IL-BF₄) are summarized in Table 1.

Ion Diffusion Character

In order to further explore the reasons for different switching time of P(EDOT:TPAC₆IL-BF₄) and PEDOT films, the ion diffusion characters were further analyzed by electrochemical impedance experiments in Fig. 7. The electrochemical impedance spectroscopy (EIS) consists of electrolyte resistance (R_e), charge transfer resistance (R_{ct}) and the Warburg diffusion resistance (Z_w). The ionic conductivity of polymer film can be obtained according to Eq. (3)

$$\sigma = \frac{l}{R_{ct}A} \quad (3)$$

where l represents the thickness of the polymer film, A represents the effective area of the electrode surface (0.9 cm × 2.3 cm) and R_{ct} represents the diameter value of the semicircle. The Warburg coefficient (σ_w) can be calculated according to Eq. (4)

$$Z' = R_e + R_{ct} + \sigma_w \omega^{-0.5} \quad (4)$$

where ω represents the angular frequency and thus σ_w is the slope of the $\omega^{-0.5} \sim Z'$ curve. Based on these data, the ion diffusion coefficient D can be obtained by Eq. (5)

$$D = 0.5 \times \left(\frac{RT}{AF^2 \sigma_w c} \right)^2 \quad (5)$$

where T represents the temperature (283 K), R represents the gas constant (8.314 J·mol⁻¹·K⁻¹), F represents the Faraday constant (96500 C·mol⁻¹), and c represents the molar concentration of doped ions (0.1 mol·L⁻¹).

The Warburg coefficients σ_w of P(EDOT:TPAC₆IL-BF₄) and PEDOT films are 54.3 and 93.4 Ω·cm²·s^{-0.5}, respectively. Therefore, P(EDOT:TPAC₆IL-BF₄) film exhibits higher ion diffusion coefficient of 2.62×10⁻¹⁰ cm²·s⁻¹ compared with 8.84×10⁻¹¹ cm²·s⁻¹ of PEDOT. In addition, P(EDOT:TPAC₆IL-BF₄) shows a similar ion conductivity (7.55×10⁻⁸ S·cm⁻¹) to that of PEDOT (7.10×10⁻⁸ S·cm⁻¹). For P(EDOT:TPAC₆IL-BF₄), the increased ion diffusion coefficient should be mainly attributed to the presence of the imidazolium-based ionic liquid in the copolymer structure, which is beneficial to ion transport be-

Table 1 Electrochromic properties of P(EDOT:TPAC₆IL-BF₄) and PEDOT films.

Polymer	Optical contrast		Switching time (s)		Coloration efficiency (cm ² ·C ⁻¹)	
P(EDOT:TPAC ₆ IL-BF ₄)	35% at 580 nm	44% at 1100 nm	0.37, 0.30 at 580 nm	0.38, 0.45 at 1100 nm	109.7 at 580 nm	149.0 at 1100 nm
PEDOT	44% at 620 nm	50% at 1100 nm	0.50, 0.41 at 620 nm	0.50, 0.68 at 1100 nm	108.6 at 620 nm	141.1 at 1100 nm

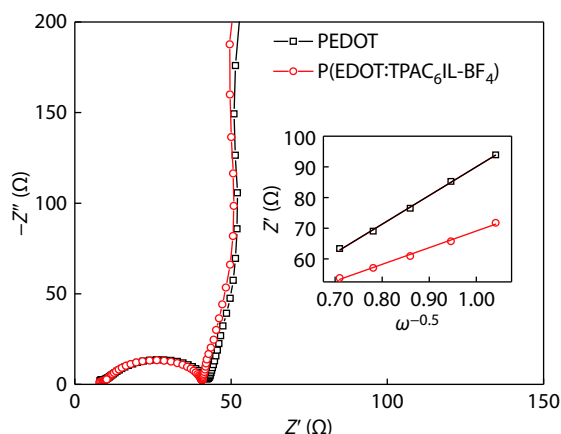


Fig. 7 Electrochemical impedance spectra of P(EDOT: TPAC₆IL-BF₄) and PEDOT films at the frequency range from 0.01 Hz to 1 MHz. Inset is the relationship curves between Z'' and $\omega^{-0.5}$ at the low frequencies.

havior and thereby reduces the switching time of the copolymer P(EDOT:TPAC₆IL-BF₄). Therefore, the results prove that the introduction of pendent ionic liquids into the copolymers is an effective method for shortening the switching time of electrochromic polymers.

Electrochromism in Free Supporting Electrolyte

Spectroelectrochemical spectra of the copolymer P(EDOT: TPAC₆IL-BF₄) without adding any supporting electrolyte were recorded in Fig. 8. It can be observed that with the increase of the applied potential (1.0, 1.2, 1.4 and 1.6 V for 100 s), the maximum absorption peak located at 580 nm decreases and a new one emerges at 1100 nm, accompanied with the color change from dark blue to light blue. The copolymer film can also return to the neutral dark blue with 0 V for 300 s. Although the electrochromic switching time is quite longer due to the low ionic conductivity without additional electrolyte than one in 0.1 mol·L⁻¹ TBAP/ACN solution, it still intrigues that the copolymer with imidazolium-based ionic liquid can perform the electrochromic behavior in free supporting electrolyte. Due to the inherent ionic liquid anions at the side chain of the

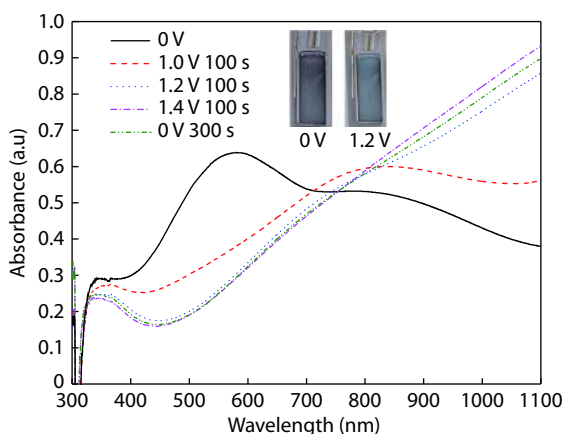


Fig. 8 Spectroelectrochemical spectra of P(EDOT:TPAC₆IL-BF₄) film in ACN solution without adding any supporting electrolyte under different potentials.

copolymer, anions around pendent imidazole cations may transfer around the positively charged polymer backbone to balance the charge as applied positive potential. This particular molecule structure renders the electrochromism of the conjugated copolymer in free supporting electrolyte solution. In addition, it further provides the evidence that the pendent imidazolium-based ionic liquid is beneficial to the improvement of electrochromic switching efficiency.

CONCLUSIONS

A triphenylamine derivative (TPAC₆IL-BF₄) was designed and synthesized, and then the copolymer P(EDOT:TPAC₆IL-BF₄) was prepared via electrochemical copolymerization of monomers TPAC₆IL-BF₄ and EDOT. The cyclic voltammetry and UV-Vis absorption spectra indicate the successful formation of the copolymer film. SEM images and EIS tests reveal that P(EDOT:TPAC₆IL-BF₄) exhibits looser morphology and better ion diffusion character than PEDOT owing to the introduction of imidazole-based ionic liquid, which is beneficial to the electrolyte ion insertion/extraction in the electrochromic process. Therefore, the copolymer P(EDOT:TPAC₆IL-BF₄) shows shorter switching time of 0.37 s, 0.30 s at 580 nm and 0.38 s, 0.45 s at 1100 nm compared with PEDOT. Moreover, P(EDOT:TPAC₆IL-BF₄) exhibits electrochromism even in free supporting electrolyte. The work may provide a potential direction for the design and synthesis of high-performance electrochromic materials with pendent ionic liquids.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-021-2525-z>.

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