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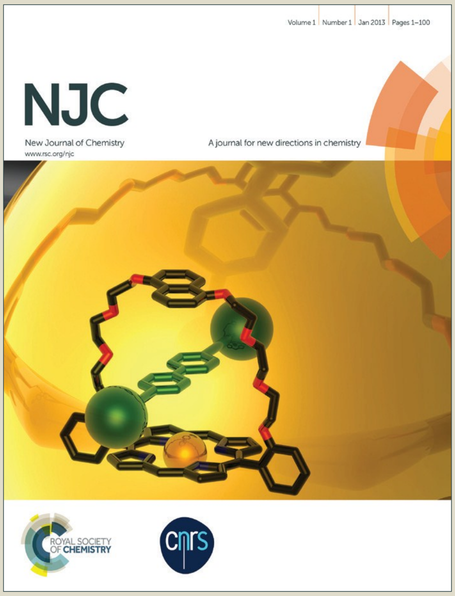

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Enhanced Electrochromic Switching Speed and Electrochemical Stability of Conducting Polymer Film on the Ionic Liquid Functionalized ITO Electrode

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The 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) functionalized ITO substrate was successfully prepared via solution immersion method, then incorporated with poly(4,4',4"-tris[4-(2-bithienyl)phenyl]amine) (PTBTPA) to form the PTBTPA-[BMIM]BF_4 film by electrochemical polymerization, which presents reversible multicolor changes from orange, olive green to dark gray. Interestingly, comparing with the bleached time (t_b) and the colored time (t_c) of the pure PTBTPA film (1.76 s and 4.51 s) at 1100 nm, the PTBTPA-[BMIM]BF_4 film exhibits shorter t_b and t_c (0.87 s and 2.90 s) at the same wavelength. Obviously, the switching speed of the PTBTPA-[BMIM]BF_4 film has been improved significantly, and it is further supported by the electrochemical impedance spectra which demonstrates the PTBTPA-[BMIM]BF_4 film possesses much lower charge transfer resistance. The reduction of charge transfer resistance could be attributed to (1) the private channel provided by the ionic liquid [BMIM]BF_4 as a linker between the polymer and the electrode; (2) the ability of the simultaneous doping and dedoping of ClO_4^- in the electrolyte and BF_4^- ions of the ionic liquid. Moreover, the cyclic stability studies reveal that the PTBTPA-[BMIM]BF_4 film exhibits better durability and retains 70.4% of its original electroactivity after 500 cycles in ionic liquid solution. The results demonstrate the electrochemical and the electrochromic performances could be significantly enhanced through incorporating PTBTPA with the ionic liquid ([BMIM]BF_4).

1. Introduction

Electrochromic (EC) materials can alter their optical properties persistently and reversibly during the electrochemical oxidation and reduction, which have received extensive attention in recent years due to their diverse colors, low power consumption and stable memory effect under open circuit conditions[1-4] for various applications, such as reflectance mirrors, smart windows, optical filters, thin flat panel display, memory devices and military camouflage.[5-7] Initial studies of EC materials mainly focus on inorganic metal oxide such as tungsten oxide (WO_3) and iridium dioxide (IrO_2).[8] With the increased versatility of organic compounds, the conducting polymers (CPs) have been recognized to be one candidate for the next generation of EC materials owing to their excellent processibility, multicolor display property, high coloration efficiency and high optical contrast.[9-10] In addition, the fast switching rate and good electrochemical stability are the two most essential factors for EC materials. However, the relatively slow response speed and poor long-term stability have severely limited the applications of the CPs-based EC materials.[11-12] Therefore, how to improve the response speed and long-term stability of CPs via various methods has become one of the hot spots in EC materials, which could prompt the practical application of CPs-based EC materials. Currently, the ways to solve this problem include two main categories. One is to change the physical structure EC materials by constructing EC nanostructures or nanocomposites. For example, Ge *et. al*[13] prepared PANI films with 3D ordered nanostructures through template-assisted electrodeposition method which exhibited high ion diffusion reversibility and high ion storage, and the switching speed of the films were obviously improved. Xia *et. al*[14] reported a nanoporous NiO/poly(3,4-ethylenedioxythiophene) (PEDOT) composite film with fast switching speed and multicolor electrochromism. Moreover, Our team has also done some efforts to prepare a series of organic-inorganic nanocomposite film to achieve fast switching time and good long-term stability.[15-16] Although the existence of nanostructures can enhance the electrochemical performance of the EC materials (switching time or long-term stability), it also has some disadvantages, such as complicated synthetic process, comparatively high costs and morphology defect, which are not suitable to the large-scale production of the EC materials.

Another approach is to modify the molecular structure of EC materials, such as donor-acceptor conjugated structure, copolymerization or introducing functional groups.[17-19] Among these, the modification of EC materials with ionic liquid is a new emerging method. Ionic liquid is a room temperature molten salts. With the properties of nonvolatile, nonflammable, low toxicity, high ionic conductivity and high thermal stability,[20] ionic liquid have been used in many recent scientific investigations.[21] To date, some works have been done to improve the EC performance of conducting polymers using ionic liquids. Ma *et. al*[22] prepared the devices which deposited poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3-methylthiophene) by employing ionic liquid [BMIM]PF_6 as electrolyte showed the enhanced stability. Pang *et. al*[23] successfully synthesized high quality poly(3-alkylthiophene)s (PMeT, PHexT and POcT) films in ionic liquid ([BMIM]PF_6)(the growth medium and the supporting electrolyte), an optical contrast of 26% and a switching time of 0.9 s were obtained for the copolymer film. Clearly, the use of ionic liquid is an efficient way to achieve considerable electrochromic performance for practical applications.

However, ionic liquid is mainly used as an electrolyte in these studies. There is a little work on the modification of the electrode or conducting polymer by ionic liquid.[24] Zhao *et. al*[25] developed a core-shell composite materials combined an imidazolium-salt-based ionic liquid functionalized carbon nanotube with conducting polymer, the results demonstrate that the ionic liquid as a linker between polymer and CNTs could reduce charge injection barrier and realizes high photovoltaic performance. In this work, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) ionic liquid was introduced to modify the ITO electrode, then the polymer film was prepared via electropolymerizing 4,4',4''-tris[4-(2-bithienyl)pheny]amine (TBTPA) onto the [BMIM]BF_4 functionalized ITO substrate to form a PTBTPA-[BMIM]BF_4 film. On the one hand, [BMIM]BF_4 ionic liquid as a linker between the polymer and the electrode can provide private channel and facilitate the movement of electrons to the electrode and reduce charge transfer barrier. On the other hand, the dissociative BF_4^- of ionic liquid as counterions can simultaneously doped into the polymer film with ClO_4^- in the electrolyte. Therefore, the introduction of the ionic liquid can improve the charge transfer and counterion diffusion properties, which is expecting to improve the electrochromic performance of materials.

2. Experimental

2.1. Chemicals

[BMIM]BF_4 (97%) (Energy Chemical), tetrabutylammonium perchlorate (TBAP, 95%) (Aldrich), acetonitrile (ACN, 99%) (Aldrich), dichloromethane (DCM, 99%) (Aldrich) were purchased and used as received. The monomer of TBTPA was synthesiz according to the previous work of our group.[26] Indium tin oxide (ITO) glass substrates (CSG HOLDING Co., Ltd, Rs ≤ 10Ω□−1, area: 1cm × 4cm) were cleaned by ultrasonic washing in a series of solvents including distilled water, ethanol, methylbenzene and acetone solutions for 15 min respectively.

2.2. Synthesis of the PTBTPA-[BMIM]BF_4 film

The preparation of the PTBTPA-[BMIM]BF_4 film involved two steps. The first step was the modification of the ITO substrate using [BMIM]BF_4 ionic liquid. Briefly, the ITO substrate was soaking in neat [BMIM]BF_4 ionic liquid followed by heating and ultra-sonicating at 60 ^{o}C in air for 2 h to load ionic liquid onto the ITO substrate, then cleaning with ACN, finally blown drying with a stream of nitrogen. The following step was the preparation the PTBTPA-[BMIM]BF_4 film via electropolymerizing TBTPA onto the [BMIM]BF_4-ITO substrate obtained above. All the films used for characterization and measurement in this study were obtained via the constant potential (1.2 V) polymerization of 0.75 mM TBTPA containing 0.1 M TBAP as a supporting electrolyte in DCM/ACN (7:3, by volume) with the ITO or the [BMIM]BF_4-ITO substrates (the active area: 1 cm×3 cm) as working electrode, a platinum (Pt) sheet (4 cm^2) as the counter electrode and a double-junction Ag/AgCl electrode (silver wire coated with AgCl in saturated KCl solution) as the reference electrode. The charge capacity of polymerization was controlled at 4×10^{-2} C, which controlled the thickness of the as-prepared films (about 300 nm), and all the electrochemical experiments are carried out under the room temperature.

2.3. Characterization

Surface morphologies and microstructures of the pure PTBTPA film and the PTBTPA-[BMIM]BF_4 film were recorded using a S-4800 scanning electron microscope (SEM) (Hitachi, Japan). The elemental analysis of film and surface element compositions was performed by energy dispersive X-ray spectroscopy (EDX) (Hitachi, Japan) and X-ray photoelectron spectroscopy (XPS) (Kratos Axis Ultra DLD, Japan). XPS obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKa radiation. The base pressure was about 3×10^{-9} mbar, and the binding energies were referenced to the C1*s* line at 284.6 eV from adventitious carbon. The structural characteristics were investigated using a Nicolet 6700 Fourier-transform infrared spectrometer (FTIR) (Thermo Fisher Nicolet, USA). UV-vis absorption spectroscopy, switching time and optical contrast were carried out on a Shimadzu UV-1800 spectrophotometer (Shimadzu, Japan) integrated with the CHI660E electrochemical analyzer. Cyclic voltammetry, electrochemical dependence and electrochemical stability were performed in three-compartment system, with the film on ITO substrate as the working electrode, a double junction Ag/AgCl (silver wire coated with AgCl in saturated KCl solution) as the reference electrode and a Pt sheet as the counter electrode on a CHI660E electrochemical analyzer (Chenhua, China).

3. Results and discussion

3.1. Morphology and structure analysis

Fig. 1 shows SEM images and EDX patterns of the pure PTBTPA film and the as-prepared PTBTPA-[BMIM]BF_4 film. As shown in the SEM images (Fig. 1a), it can be seen the uneven nanoparticle surface structure of the pure PTBTPA film. Comparing to the pure PTBTPA film, the surface morphology of the PTBTPA-[BMIM]BF_4 film (Fig. 1c) is more uniform after the inserting of [BMIM]BF_4 ionic liquid between PTBTPA and ITO substrate, and the thickness of the films are about 300 nm (inset of Fig. 1a c). The smaller and more uniform structure may lead to larger contact area and more channels which could facilitate counterion diffusion and improve switching speed. From Fig. 1b, the EDX pattern of the pure PTBTPA film contains peaks of C, N, S elements of PTBTPA, as well as In, Sn, Si and other elements derived from the ITO substrate. However, the EDX pattern of the PTBTPA-[BMIM]BF_4 film not only contains all the peaks of C, N, S elements of PTBTPA compound, but also contains F element of [BMIM]BF_4 compound, which demonstrates an effective combination of the [BMIM]BF_4 and the PTBTPA film (Fig. 1d).

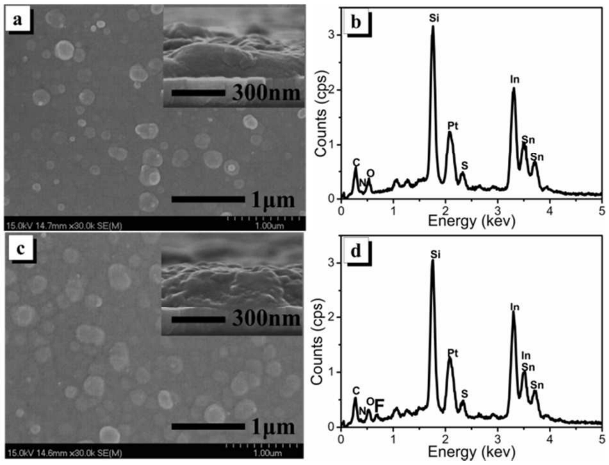

Fig. 1 SEM images and EDX pattern of (a, b) the pure PTBTPA film and (c, d) the PTBTPA-[BMIM]BF_4 film (charge: 0.04 C)

Fig. 2 presents the FTIR spectra of the [BMIM]BF_4-ITO, the pure PTBTPA film and the PTBTPA-[BMIM]BF_4 film. In the spectrum of the pure PTBTPA film, the peak located at 1597 cm^{-1} should be assigned to the C-C stretching vibrations in the phenyl ring.[27] The bands at 1496 and 1461 cm^{-1} are originated from the stretching of thiophene rings.[28] The bands at 1322 and 1291cm^{-1} are attributed to the C-N vibrations.[29] The peak at 793 cm^{-1} is ascribed to the C-S bonds in the thiophene rings.[27] For the [BMIM]BF_4-ITO, the strong and wide adsorption peaks at 3159 cm^{-1} and 2876 cm^{-1} are due to the aliphatic asymmetric and symmetric (C-H) stretching vibrations of the imidazolium ring, and the C=C stretching vibration and imidazole ring stretching vibration is located at 1572 cm^{-1}. The bands at 1171cm^{-1} are attributed to the C-N stretching vibration of the imidazolium ring.[30-31] The peak at 1068 cm^{-1} is corresponding to asymmetric stretching vibrations of B-F.[30] The spectrum of the PTBTPA-[BMIM]BF_4 film contains all the characteristic bands of above two compounds with a little difference (maybe ascribed to the interaction between the two compounds). For instance, the bands at 3160 cm^{-1} and 2875 cm^{-1} are assigned to the aliphatic asymmetric and symmetric (C-H) stretching vibrations of the imidazolium ring. The band at 1170cm^{-1} is due to the C-N stretching vibration of the imidazolium ring. The bands at 1323 and 1290cm^{-1} correspond to the C-N vibrations. The peak at 794 cm^{-1} is due to the C-S bonds in the thiophene rings. Therefore, the spectra of the PTBTPA-[BMIM]BF_4 film demonstrates an effective introduction of the [BMIM]BF_4 into the PTBTPA film.

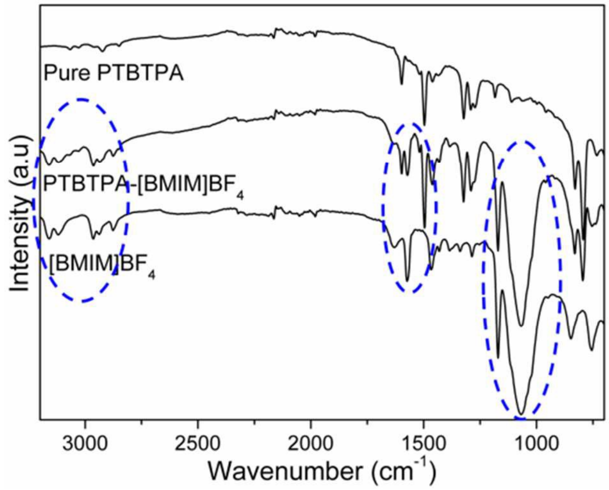

Fig. 2 FT-IR spectra of the neat [BMIM]BF4, the pure PTBTPA film and PTBTPA-[BMIM]BF_4 film

To further analyze the composition of the polymer and the ionic liquid, the XPS test are performed for the [BMIM]BF_4-ITO, the pure PTBTPA and the PTBTPA-[BMIM]BF_4 film (the films are fully dedoping (at neutral) before the XPS test. Fig. 3 presents the XPS survey spectra of the [BMIM]BF_4-ITO, the pure PTBTPA and the PTBTPA-[BMIM]BF_4 film. In the spectrum of the pure PTBTPA film, it reveals the presence of S2*p*, S2*s*, C1*s* components which are observed at 164.7 eV, 228.5 eV and 284.7 eV respectively, confirming the deposition of PTBTPA on the ITO substrate. For the [BMIM]BF_4-ITO, the bands at 194.7 eV and 685.8 eV correspond to B1*s* and F1*s*. However, the XPS spectrum of the PTBTPA-[BMIM]BF_4 film not only contains all the peaks of PTBTPA compound, but also contains B1*s* and F1*s* components from the [BMIM]BF_4 ionic liquid,[32] which demonstrates that the ionic liquid [BMIM]BF_4 remains in the PTBTPA film after the fully dedoping process. The results further confirm the effort combination of [BMIM]BF_4 and the conducting polymer in the [BMIM]BF_4-PTBTPA film.

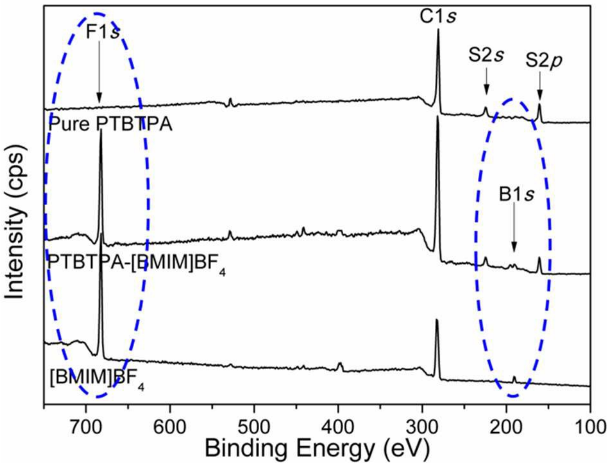

Fig. 3 XPS survey spectra of the pure PTBTPA and the PTBTPA-[BMIM]BF_4 film

3.2.Electrochemical and electrochromic performance

Fig. 4 exhibits cyclic voltammogram (CV) polymerization of 0.75 mM TBTPA in DCM/ACN (7:3, by volume) containing 0.1 M TBAP as a supporting electrolyte on the ITO (Fig. 4a) and the [BMIM]BF_4-ITO substrates (Fig. 4b) from 0 V to 1.4 V at a scan rate of 100 mv/s for 10 cycles. With the increase of scanning cycles, the irreversible oxidation of the monomer appears clearly on the first cycle followed by a typical polymer film growth loops for both two systems, which is indicative of the deposition of electroactive polymeric films on the electrodes. Furthermore, CV curves of the two systems have the similar shapes. As show in Fig. 4a, the onset oxidative potential, oxidative and reductive peak potentials of TBTPA are located at 0.85 V, 0.97 V and 0.81 V respectively. For the PTBTPA-[BMIM]BF_4 film the onset oxidative potential, oxidative and reductive peak potentials of TBTPA are 0.86 V, 1.01 V and 0.84 V, respectively (see Fig. 4b). Obviously, as TBTPA electropolymerized onto the [BMIM]BF_4-ITO or the ITO substrate, the monomer possess similar redox peaks, indicating that the ionic liquid [BMIM]BF_4 have no bad effect on the electropolymerization of the polymer, and it is also easy to electropolymerize TBTPA on the [BMIM]BF_4-ITO substrate.

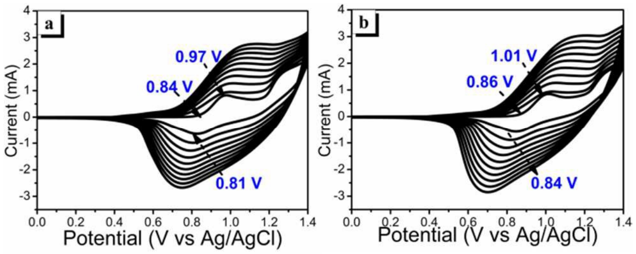

Fig. 4 Cyclic voltammogram polymerization of 0.75 Mm TBTPA in DCM/ACN (7:3, by volume) containing 0.1 M TBAP as a supporting electrolyte on the ITO and the [BMIM]BF_4-ITO substrates from 0 V to 1.4 V at a scan rate of 100 mv/s for 10 cycles

Fig. 5 displays CV curves of the [BMIM]BF_4-ITO, the pure PTBTPA and the PTBTPA-[BMIM]BF_4 film in DCM/ACN (7:3, by volume) containing 0.1 M TBAP as a supporting electrolyte from 0 V to 1.4 V at a scan rate of 100 mv/s. As seen from the Fig. 5, there is no obvious redox for the [BMIM]BF_4-ITO indicating the ionic liquid [BMIM]BF_4 do not exhibit electrochromic behaviour. The pure PTBTPA film displays a main oxidation and reduction peak at 1.23 V and 0.71 V respectively with a gap of 0.52 V. While the PTBTPA-[BMIM]BF_4 film, one main oxidation wave at about 1.26 V and the main reduction peak at around 0.71 V, exhibits the similar redox peaks as that of the pure PTBTPA film with a minor difference. Comparing to the pure PTBTPA film, the similar gap between the oxidation and reduction potential of the PTBTPA-[BMIM]BF_4 film demonstrates that incorporating the ionic liquid [BMIM]BF_4 with PTBTPA could also exhibit good electrochemical activity whilst preserving its original electrochromic performance.

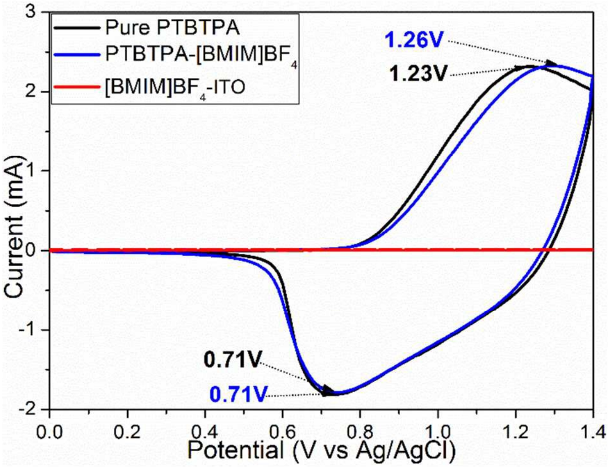

Fig. 5 Cyclic voltammogram curve of the [BMIM]BF_4-ITO, the pure PTBTPA and the PTBTPA-[BMIM]BF_4 film in DCM/ACN (7:3, by volume) containing 0.1 M TBAP as a supporting electrolyte from 0 V to 1.4 V at a scan rate of 100 mv/s

The UV-vis absorbance spectra of the pure PTBTPA and the PTBTPA-[BMIM]BF_4 film are recorded as a function of wavelength under different applied potentials between 0 V and 1.4 V in Fig. 6. In Fig. 6a, a well-defined maximum absorption band centered at 421 nm at the neutral state (0 V) of the pure PTBTPA film should be ascribed to the π-π^* transition of the polymer backbone[33] and it gradually decreases with the increase of the potential. However, the bands at around 709 nm and 1100 nm increase with the increase of potential at the same time, which is attributed to the evolution of polaron and bipolaron bands.[34] As seen from Fig. 6b, the maximum absorption peak of the PTBTPA-[BMIM]BF_4 film locates at 427 nm at the neutral state (0 V), and it also decreases with the increase of the potential. Furthermore, the charge carrier bands at 715 nm and 1100 nm also increase with the increase of the potential. Comparing to the pure PTBTPA film, the maximum absorption peak of PTBTPA-[BMIM]BF_4 film at the neutral state (0 V) emerges red-shift by 6 nm due to the introduction of [BMIM]BF_4 ionic liquid.

Meanwhile, it can be observed the pure PTBTPA film exhibits a multicolor electrochromism with orange at the reduced state (0 V), olive green at the middle state (0.9 V) and dark gray at the oxidized state (1.3 V) respectively. Although the absorption peak of PTBTPA-[BMIM]BF_4 film appears a little red-shift, the color-display does not change substantially and it also exhibits three colors (orange, olive green and dark gray) (Fig. 6b). Therefore, with the introduction of [BMIM]BF_4 ionic liquid, the PTBTPA-[BMIM]BF_4 film still preserves its original multicolor electrochromism performance.

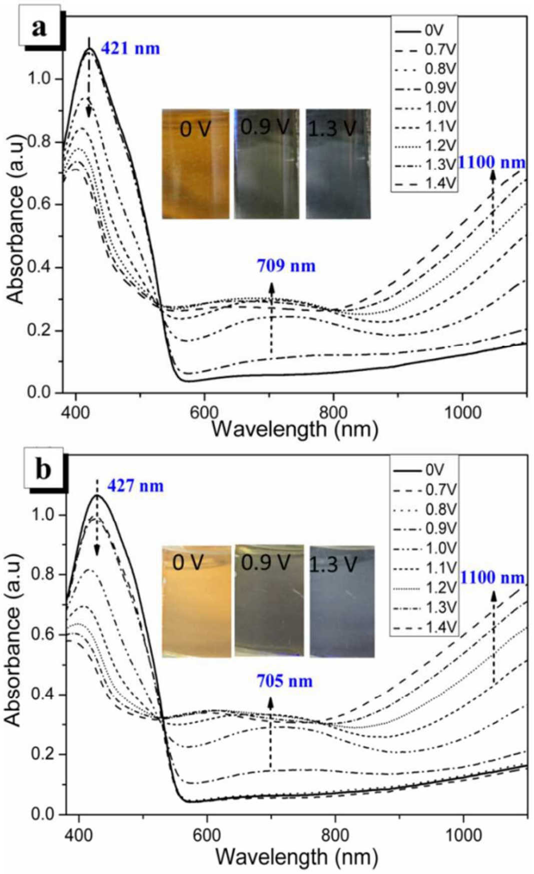

Fig. 6 UV-vis absorbance spectra of (a) the pure PTBTPA film and (b) the PTBTPA-[BMIM]BF_4 film in applied potentials from 0 V to 1.4 V in DCM/ACN (7:3, by volume) containing 0.1 M TBAP at a scan rate of 100 mV/s. and (a) color changes of the pure PTBTPA film, and (b) the PTBTPA-[BMIM]BF_4 film in applied potentials of 0 V, 0.9 V and 1.3 V

The electrochromic switching behaviours of the pure PTBTPA and the PTBTPA-[BMIM]BF_4 film are recorded in order to characterize their optical contrasts. Fig. 7 depicts the optical contrast and the switching response time of the films which are monitored at 1100 nm in DCM/ACN solutions (7:3, by volume) containing 0.1 M TBAP as a supporting electrolyte from 0 V to 1.4 V with a residence time of 5 s. As show in Fig. 7, the pure PTBTPA (a) and the PTBTPA-[BMIM]BF_4 film (c) present similar optical contrast value at 1100 nm (51.2% and 50.5% respectively), demonstrating that the introduction of ionic liquid [BMIM]BF_4 have no significant influence on the optical contrast of the polymer. While the bleached time (t_b) and the colored time (t_c) of the PTBTPA-[BMIM]BF_4 film are 0.87 s and 2.90s at 1100 nm (Fig. 7d) respectively, significantly lower than that of the pure PTBTPA film (1.76 s and 4.51 s) at- the same wavelength (Fig. 7b) (the switching time is defined as the time required 95% transmittance change in the coloring process or bleaching process[34]). Obviously, the switching time of the PTBTPA-[BMIM]BF_4 film is shortened by near half comparing to that of the pure PTBTPA film. According to the schematic plot of electron transfer and counterion diffusion (Fig. 8), the possible reasons for this phenomenon are surmised as follows: (i) For the pure PTBTPA film, ClO_4^- as counterion is doped into the polymer film when applied certain potential. While ClO_4^- and BF_4^- can simultaneously doped into the polymer film from two opposite directions for the PTBTPA-[BMIM]BF_4 film, which speed up the doping process. (ii) The introduction of [BMIM]BF_4 ionic liquid in the PTBTPA-[BMIM]BF_4 film as a linker between the polymer and the electrode that reduces charge transfer barrier, which can facilitate the movement of electrons to the electrode.

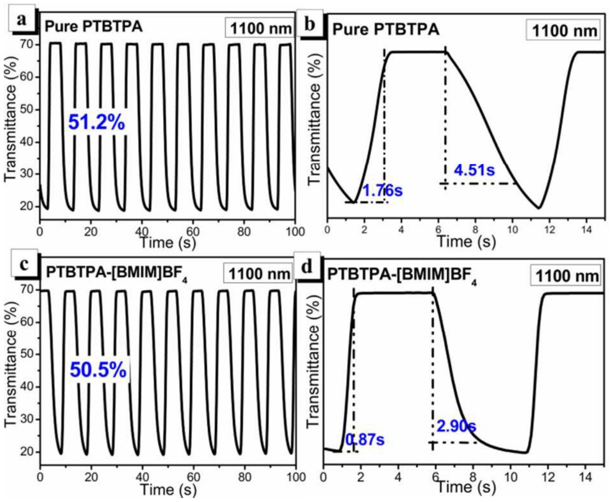

Fig. 7 Optical contrast and switching response time of (a, b) the pure PTBTPA film and (c, d) the PTBTPA-[BMIM]BF_4 film monitored at 1100 nm in DCM/ACN solutions (7:3, by volume) containing 0.1 M TBAP as a supporting electrolyte from 0 V to 1.4 V with a residence time of 5 s

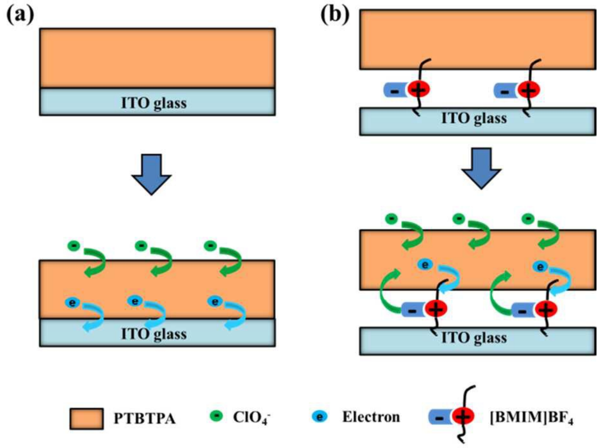

Fig. 8 Schematic plot of electron transfer and counterion diffusion in (a) the pure PTBTPA film and (b) the PTBTPA-[BMIM]BF_4

The electrochemical stability of EC materials toward long-term switching between the colored and bleached states is also an important parameter for the application of EC devices.[35] Fig. 9a, b exhibits the electrochemical stability curves of the pure

PTBTPA and the PTBTPA-[BMIM]BF$_4$ film in DCM/ACN (7:3, by volume) containing 0.1 M TBAP or 0.1 M [BMIM]BF$_4$ from 0 V to 1.4 V at a scan rate of 300 mv/s for 1000 cycles. The CV curve of the pure PTBTPA film reveals it retains 53.9% and 37.7% of its original electroactivity after 300, 500 cycles (Fig. 9a). However, the PTBTPA-[BMIM]BF$_4$ film preserves 78.3%, and 70.4% of its original electroactivity after 300 and 500 cycles respectively, even retains 55.0% of its original electroactivity after 1000 cycles (Fig. 9b). Obviously, the stability of the PTBTPA-[BMIM]BF$_4$ film is much better in DCM/ACN (7:3, by volume) containing 0.1 M [BMIM]BF$_4$ ionic liquid than that of the pure PTBTPA film in DCM/ACN (7:3, by volume) containing 0.1 M TBAP. The reason is mainly ascribed to the smaller size of BF$_4^-$ ion than the ClO$_4^-$ ion, which leads to the lower degree of expansion/shrinkage of the polymer film, thus the polymer exhibits much better electrochemical stability in the electrolyte containing the BF$_4^-$ ionic liquid than that containing ClO$_4^-$ ion. This results implies that the [BMIM]BF$_4$ ionic liquid is helpful for the improvement of electrochemical stability as a medium for application.

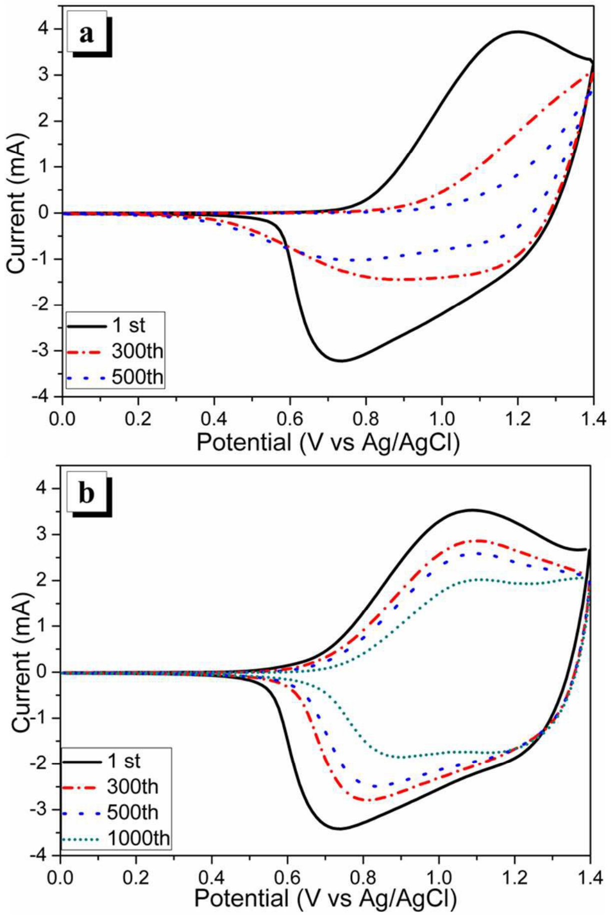

Fig. 9 The electrochemical stability of (a) the pure PTBTPA film and (b) the PTBTPA-[BMIM]BF$_4$ film in DCM/CAN solutions (7:3, by volume) containing 0.1 M TBAP or 0.1 M [BMIM]BF4 form 0 V to 1.4 V at a scan rate of 300 mV/s for 1000 cycles

3.3. Electrochemical impedance measurement

To further verify the above speculation, the electrochemical impedance measurement of the pure PTBTPA and the PTBTPA-[BMIM]BF$_4$ film are measured in DCM/ACN (7:3, by volume) containing 0.1 M TBAP as supporting electrolyte. Generally, the electrochemical impedance spectra consists of three parts, that is, an intercept at the Z' axis, a semicircle in high frequency regions and a straight line in low frequency regions, which are corresponding to the resistance of the electrolyte (Re), the charge transfer resistance (Rct) and the diffusion of electroactive species respectively.[36] As shown in Fig. 10, the Re of the pure PTBTPA and the PTBTPA-[BMIM]BF$_4$ film are about 52 Ω, indicating almost the same resistance of the electrolyte. Moreover, the slope of the straight line at low frequency of the two types films are nearly the same, which means almost the same diffusion of electroactive species. However, the semicircle diameter of the PTBTPA-[BMIM]BF$_4$ film is 13.18 Ω, which is much lower than that of the pure PTBTPA film (66.5 Ω), indicating that the PTBTPA-[BMIM]BF$_4$ film has much lower charge transfer resistance, which may be attributed to (1) the private channel provided by the ionic liquid [BMIM]BF$_4$ as a linker between the polymer and the electrode; (2) the ability of the simultaneous doping and dedoping of ClO$_4^-$ in the electrolyte and BF$_4^-$ ions of the ionic liquid. As a whole, it can be concluded that the PTBTPA-[BMIM]BF$_4$ film, with the incorporation of the [BMIM]BF$_4$ ionic liquid, presents faster charge transfer speed, and therefore leads to faster switching speed.

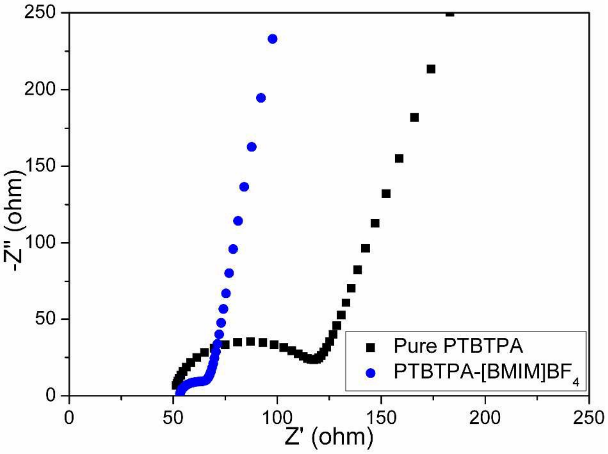

Fig.10 The electrochemical impedance measurement of the pure PTBTPA and the PTBTPA-[BMIM]BF$_4$ film in DCM/ACN (7:3, by volume) containing 0.1 M TBAP as supporting electrolyte

4. Conclusions

In summary, the PTBTPA-[BMIM]BF$_4$ film was prepared via electrochemical polymerization TBTPA onto the [BMIM]BF$_4$ functionalized ITO substrate. The film presents good electrochromic and electrochemical performance incorporating with [BMIM]BF$_4$ ionic liquid. Especially, the switching time has been shortened in half comparing to that of the pure PTBTPA film, and it can be supported by the electrochemical impedance spectra which demonstrates the PTBTPA-[BMIM]BF$_4$ film possesses much lower charge transfer resistance due to the introduction of [BMIM]BF_4 ionic liquid. Moreover, the cyclic stability measurement displays the PTBTPA-[BMIM]BF_4 film has a significant increase of its durability after multi-turn cycles in ionic liquid solution, while the pure PTBTPA film loses almost of its electroactivity after 500 cycles. This work confirms that incorporating [BMIM]BF_4 ionic liquid with the conducting polymer film could improve the electrochromic performance of materials. The further study on the effect of ionic liquid as a medium for synthesis and application on the EC performance is underway.

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Notes and references

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