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Ion diffusion and electrochromic performance of poly(4,4′,4″-tris[4-(2-bithienyl)phenyl]amine) based on ionic liquid as electrolyte

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ABSTRACT

Ionic liquids 1-butyl-3-methyl-imidazolium tetrafluoroborate ([BMIM]BF_4), 1-butyl-3-methylimidazoliumhexafluorophosphate ([BMIM]PF_6) and conventional medium tetrabutylammonium perchlorate (TBAP) were utilized as electrolyte for the preparation of poly(4,4′,4″-tris[4-(2-bithienyl)phenyl]amine) (PTBTPA) films and assembling of EC devices. FTIR spectra and EDX pattern demonstrate an effective doping of the anion into the PTBTPA film at the oxidation state. SEM images investigate the thickness of the polymer films and the morphologies of crimped structure at the oxidation state. The ion diffusion distance (the thickness of polymer film) plays a more critical role for the EC switching speed. According to the electrochemical impedance spectra, the improved ionic conductivity with ionic liquid [BMIM]BF_4 as the electrolyte promote ions more easily dope into the polymer film which leads to the higher optical contrast. In addition, the size of doping anion during the redox process has essential influence on the electrochemical stability.

1. Introduction

Electrochromism is broadly defined as reversible optical change in a material with reversible color change upon oxidation or reduction induced by an external voltage. Among electrochromic (EC) materials, conjugated polymers have gained popularity owing to their diverse colors, high optical contrast, fast switching speed and good processibility [1–3] for various potential applications, such as smart windows, anti-glare mirrors, displays and memory devices [4–6]. Polythiophene, polycarbazole, polypyrrole, polytriphenylamine and their derivatives have been widely studied in the past few years [7]. In our previous work, a series of EC polymers, such as poly(1,4-bis(3-hexylthiophen-2-yl) benzene) (PBHThBe) [8], poly(9-(4-nitrophenyl)-3,6-di(thiophen-2-yl)-9H-carbazole) (PNDTC) [9], poly(N^1,N^4-bis(4-(1H-pyrrol-1-yl) phenyl)-N^1,N^4-diphenylbenzene-1,4-diamine) (PDPTPA) [10] and poly (4,4′,4″-tris[4-(2-bithienyl) phenyl]amine) (PTBTPA) [11] were synthesized and investigated, which exhibited rich colors upon various applied potentials, good optical contrast and fast response time.

Although conjugated polymer based EC materials has received a lot of research, there still exists an obscure understanding on the EC mechanism. The general explanation as follows: at the oxidized (colored) state, conjugated polymers (p-doping) lose electron with positive charge in the polymer backbone and anions coming from the supporting salt then enter the oxidized polymer film to counter charge [12]. On the contrary, for the reductive (bleached) state of conjugated polymers, counter anions exit from the polymer backbone and the polymer film removes the electronic conjugation to revert the electrically insulating form. Therefore, electrochromism in conjugated polymers occurs through changes in the polymer's π-electronic character accompanied by reversible insertion/extraction of ions upon electrochemical oxidation and reduction, which has significant influence on the electrochromic performance, including optical contrast, switching speed and cyclic stability. So how do the electronic transfer and ionic diffusion affect EC performance of conducting polymers?

Lee *et al.* [13] prepared PEDOT nanotube arrays using porous alumina template. The thin walls (10-20 nm) of nanotubes rendered the shorter ion diffusion distance which led to ultrafast switching speed (<10 ms). Li *et al.* [14] reported PANI films with 3D ordered nanostructures through template-assisted method and indicated the enhanced optical switching properties due to the interconnected porous structure which benefits for the fast penetration of ions. Xiong *et al.* [15] prepared covalently bonded PANI-SWCNT hybrids, and the improved electron transport and

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further doping function led to much better optical contrast and switching kinetics. They [16] also synthesized C_{60}-PANI: PSS hybrid materials, the enhanced optical contrast and switching kinetics could be ascribed to the improved ionic and electrical conductivities and a loose packing morphology. Tu *et al.* [17] reported TiO_2-polyaniline core/shell nanorod array composites, and the high optical modulation and good cycling performance were mainly attributed to the core/shell structure, formation of the donor-acceptor system and the porous space among the nanorods, which made the ion diffusion easier and provided larger surface area for charge-transfer reactions.

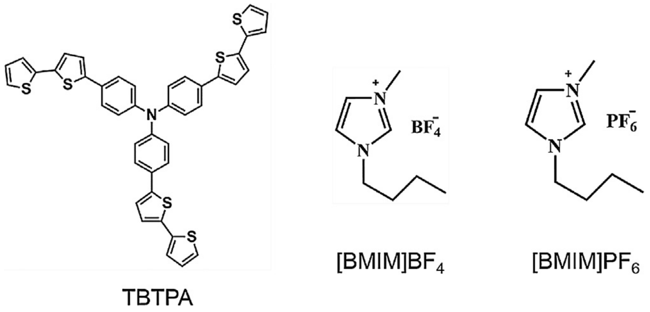
On the whole, it can be concluded that the switching speed, optical contrast and cyclic stability are mainly in connection with electrical and ionic conductivity of the polymer film, ion diffusion distance in polymer film, the polymer film morphology and the interface active area, etc. However, which factor is more crucial for EC performance? Until now, there is a lack of a comprehensive and systematic in-depth study. As well-known, ionic liquids have been gaining an exponential interest owing to their excellent thermal, chemical and electrochemical stability as well as high ionic conductivity and broad electrochemical window [18]. It has been found that the use of ionic liquids as electrolytes for electropolymerization leads to improved electrochemical activities, optoelectronic properties and altered surface morphologies in comparison with conventional media [19]. In addition, ionic liquids as electrolytes for assembling EC devices have been also employed to obtain good electrochemical and electrochromic performance.

Consequently, in this work the ionic liquids or conventional electrolyte were utilized to tune the ionic conductivity of polymer film, the size of doping ion, the diffusion distance of doping ion, the polymer film morphologies, and further investigate their influence on the EC properties. Herein, ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4), 1-butyl-3-methylimidazoliumhexafluorophosphate ([BMIM]PF_6) and conventional electrolyte tetrabutylammonium perchlorate (TBAP) were employed as the electropolymerization medium of the polymer PTBTPA films and assembling of EC devices. SEM images was used to investigate the morphologies and thickness of the polymer films. FTIR spectra and EDX pattern was carried out to demonstrate the doping anion into the polymer films at the oxidation state. Electrochemical impedance measurement was utilized to provide ion diffusion properties. The main goal for this work is to provide more information about the relationship between ionic diffusion and EC performance.

2. Experimental

2.1. Chemicals

1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4, 98%, Aladdin, Scheme 1), 1-butyl-3-methylimidazoliumhexafluorophosphate ([BMIM]PF_6, 98%, Aladdin, Scheme 1), tetrabutylammonium perchlorate (TBAP, 98%, Energy Chemical), commercial HPLC grade acetonitrile (ACN, 99%, Aladdin), dichloromethane (DCM, 99%, Aladdin) were purchased and used as received. The monomer of 4,4′,4′′-tris[4-(2-bithienyl) phenyl]amine (TBTPA, Scheme 1) was synthesized according to the reference [20]. Indium tin oxide (ITO) glass substrates (Kaivo Optoelectronic Technology Co., Ltd., Rs ≤ 10 $\Omega\square^{-1}$, area: 0.9 cm × 4 cm) were cleaned by ultrasonic in a series of solvents including distilled water, ethanol, methylbenzene and acetone solutions for 15 min respectively.



Scheme 1. The structure of monomer TBTPA and ionic liquids [BMIM]BF_4, [BMIM]PF_6.

2.2. Characterization

Surface morphologies and microstructures of polymer films were investigated by S-4800 scanning electron microscope (SEM) (Hitachi, Japan). The elemental analysis and element compositions of polymer films was performed by energy dispersive X-ray spectroscopy (EDX) (Hitachi, Japan) and a Nicolet 6700 Fourier-transform infrared spectrometer (FTIR) (Thermo Fisher Nicolet, USA) with KBr pellets. Before measurements, all the polymer films on ITO substrates were washed by the clean ACN/DCM solutions and dried in the oven. The electrochemical properties, including cyclic voltammogram, electrochemical stability and electrochemical impedance measurement were performed in a three-compartment system containing 0.1 mol/L supporting electrolyte (TBAP, [BMIM]BF_4 or [BMIM]PF_6) in DCM/ACN solutions (7: 3, by volume) on a CHI660E electrochemical analyzer (Chenhua, China). Spectroelectrochemical test, switching time and optical contrast were carried out on a Shimadzu UV-1800 spectrophotometer (Shimadzu, Japan) integrated with the CHI660E electrochemical analyzer. The images of polymer films were taken by Canon 60D.

2.3. Fabrication of PTBTPA films and EC devices

All the polymer films used for characterization and measurement were obtained via constant potential polymerization of 0.75 mmol/L TBTPA containing 0.1 mol/L supporting electrolyte in DCM/ACN solutions (7: 3, by volume) at 1.2 V with the ITO substrates (the active area: 0.9 cm × 3 cm) as working electrode, a platinum (Pt) sheet (2 cm × 2 cm) as counter electrode and a Ag/AgCl electrode (silver wire coated with AgCl in saturated KCl solution) as reference electrode. The charge capacity of polymerization was controlled at 4×10^{-2} C, and all the electrochemical experiments are carried out under the room temperature (25 °C). The polymer films are named as T-PTBTPA, B-PTBTPA and P-PTBTPA prepared in containing TBAP, [BMIM]BF_4 or [BMIM]PF_6 as supporting electrolyte, respectively.

All the EC devices (the liquid prototype devices) were assembled: T-PTBTPA, B-PTBTPA or P-PTBTPA films as working electrode, 0.1 mol/L TBAP, [BMIM]BF_4 or [BMIM]PF_6 in DCM/ACN solutions as supporting electrolyte, a platinum (Pt) wire as counter electrode and a Ag/AgCl electrode as the reference electrode, which are labeled as T-PTBTPA-T, T-PTBTPA-B, B-PTBTPA-T, B-PTBTPA-B and P-PTBTPA-P, respectively. And the T-PTBTPA, B-PTBTPA and P-PTBTPA films doped fully in the oxidation state at 1.4 V in 0.1 mol/L supporting electrolyte (TBAP, [BMIM]BF_4 or [BMIM]PF_6) were labeled T-PTBTPA-T_o, T-PTBTPA-B_o, B-PTBTPA-T_o, B-PTBTPA-B_o and P-PTBTPA-P_o, respectively.

3. Results and discussion

3.1. Electropolymerization and electrochemical property

Fig. 1 displays the successive cycle voltammetry polymerization of 0.75 mmol/L TBTPA containing 0.1 mol/L supporting electrolyte