A greener electrochromic liquid crystal based on ionic liquid electrolytes

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ABSTRACT

An electrochromic liquid crystal (ECLC) material composed of only liquid crystal (LC) and ionic liquid (IL) was developed. The LC containing the substituted diphenylacetylene serves as electrochromic (EC) material to realize transmittance and colour change under the direct current (DC) field, while the IL with the designable cation and anion served as electrolyte. Herein, a series of IL electrolytes was screened to investigate how IL tunes the electro-optic performance of the ECLC cell. By testing the electrochemistry window of ILs in EC cells, IL with the [NTf$_2$] anion shows adequate electrochemical stability when the EC material undergoes oxidation and reduction. The electro-optic performance of ECLC containing 1-ethoxy-4-[2-(4-pentylphenyl) ethynyl]-benzene (PEB) and IL was then evaluated by UV-vis spectrometry under the control of an electrochemical work station. Compared with other PEB-IL, PEB-[Bmim][NTf$_2$] with [Bmim][NTf$_2$] electrolyte shows a satisfactory transmittance at low operating voltage. Furthermore, Pd NPs in situ formed in [Bmim][NTf$_2$] reduced the EC potential and improved the light scattering of the ECLC cell. In this work, we also designed a bifunctional device based on polymer dispersed liquid crystal (PDLC) that hosts electrochromic guest molecules, and analysed the electro-optical and electrochromic properties of LC electrolyte mixtures, in order to gain control of the incident daylight and glare in building and automotive applications.

INTRODUCTION

Electrochromic (EC) materials are the most popular type used in switchable devices. These can reversibly change the transmittance or colour by gaining or losing electrons under oxidation and reduction. Under the direct current (DC) field, the EC cell changes its transmittance or colour and persists in that state until the DC field is removed or reversed. Besides traditional EC materials,[1-7] Lampert[8] sited electrochromism within the wider scope of other forms of driven colour change, such as suspended particle devices,[9,10] polymer-dispersed liquid crystal (PDLC)[11-15] and cholesteric liquid crystal.[16-20] Organic EC materials such as bipyrildiliums, quinones, phthalocyanines, terephthalates and cyanobiphenyls have been widely used in information display and storage, the automotive industry and architecture.[4-7]
EC materials, such as cyanobiphenyls, are also the typical liquid crystal (LC) component, demonstrating the performance of EC and LC at the same time. Nakamura’s group were the first to find an electrochromic liquid crystal (ECLC), composed of LC molecular cyano-alkyl-biphenyls (nCB) and cyano-alkoxy-biphenyls (nCOB) and doped with tetra-alky-ammonium iodide [(C_{n}H_{2n+1})N]^+I^- electrolytes.[21] This research group also proposed a mechanism for coloration and bleaching in the ECLC cell.[22] The application of a DC field causes the migration of positive electrolyte ions to the cathode, forming a coloured complex between them and the LC. Bleaching occurs when the DC field is removed, attributed to the diffusion of halide molecules produced by oxidation at the anode and their reaction with the coloured complex.[23] Electrochromism was observed in both the LC and isotropic state, and in addition the EC performance of nematic, smectic or cholesteric ECLC was influenced by increasing resistivity and changing texture.[21] Nicoletta et al. developed an electrochromic polymer-dispersed liquid crystal (EC-PDLC) with ethyl viologen as the EC material, being able to change both transmittance and colour upon the application of alternating current (AC) and DC field in a single cell.[24,25] They then improved EC-PDLC by introducing commercial LC containing cyanobiphenyls to realise both color and transmittance changes.[26] The preparation process of EC-PDLC was greatly simplified by using commercially available materials.

However, the ECLC cell still has some shortcomings, such as long switching time, insufficient ability and poor electro-optical performance. To resolve these problems, it is necessary to focus research on electrolytes. The traditional aqueous electrolytes used in EC cells often limit EC performance, due to their narrow potential window.[27] Non-aqueous, aprotic electrolytes have been used to improve EC performance but the stability was still limited by trace water and contaminants. [28] Although polymer electrolytes have recently been widely applied in EC cells, a long switching time was still necessary due to the lower conductivity and stability of polymer electrolytes.[29-31] Ionic liquids (IL), due to their negligible volatility, wide potential window and good conductivity, have been widely used in electrochemistry for several years.[32-37] To reduce the switching time and increase cyclability and long-term stability in EC cells, IL electrolytes, especially those containing imidazolium cations, have been used.[38,39] However, the IL electrolytes used in EC cells are usually combined with polymers to overcome leakage while the EC performance is influenced by the additional polymer. Recently, Archer’s group developed IL-nanoparticle (NP) hybrid electrolytes, promoting stable Li electrodeposition.[40-42]

Herein, we report our investigation on ECLC materials based on LC (substituted diphenylacetylene) and IL. According to Scheme 1, the substituted diphenylacetylene species readily undergoes a one-electron oxidation to form a radical cation species. Diphenylacetylenes are soluble and essentially colourless in the neutral, whereas the radical cation generated under oxidation formed a highly coloured, solid precipitate on the electrode. The potential window of a series of ILs was tested in EC cells, and ILs with the [NTf_2]^- anion were proven with a wide window of potential. The EC performance of ECLC with IL electrolytes was carried out by UV-vis spectrometry under the control of an electrochemical work station to investigate the moderating effect of ILs on the electro-optical properties of ECLC cells. In addition, the NP-IL suspension with in situ-formed Pd NPs [43,44] was first used as electrolyte in ECLC, clearly reducing the potential during the colouration process. By screening IL electrolytes and optimisation, satisfactory transmittance difference and cyclability were obtained.

### Experimental

#### Materials

1-ethoxy-4-[2-(4-pentylphenyl)ethynyl]-benzene (PEB, ≥99.5%, Hebei Maison chemical Co., Ltd.), polyethylene glycol (400) diacrylate (PEGDA 400, ≥99%, Sartomer, Exton, PA), isobornyl methacrylate (IBMA, ≥99.5%), 3,5,5-trimethethylhexyl acrylate (TMHA, ≥99.5% Aldrich, St. Louise, MO), Irgacure 651 (Ciba Geigy, Jingjiang
Hongtai Chem. Co. Ltd., China), acetonitrile (anhydrous, ≥99.8%, Xilong Chemical Engineering Co., Ltd.), SLC1717 (T_{N-1} = 365.2 K, n_{e} = 1.519, n_{ε} = 1.720, Δε(1KHz, 20°C) = 12.2, ε(1KHz, 20°C) = 5.1, Shijiazhuang Chengzhi Yonghua Display Materials Co., Ltd. China) and palladium(II) acetate (Pd(OAc)₂, ≥98%, Sigma-Aldrich) were used as received without further purification. The ILs, 1-butyl-3-methylimidazolium bis (trifluoromethanesulfonimide) ([Bmim][NTf₂], >98%), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆], >98%), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄], >98%), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim][OTf], >98%), 1-butyl-3-methylimidazolium trifluoroacetate ([Bmim][TFA], >98%), 1-(2-hydroxyethyl)-3-methylimidazolium bis (trifluoromethanesulfonimide) ([C₂OHim][NTf₂], >98%), 1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonimide) ([Emim][NTf₂], >98%), N-butyl and methylpiperidinium bis (trifluoromethanesulfonimide) ([P_{1,4}][NTf₂], >98%) were all purchased from Shanghai Cheng Jie Chemical Co., Ltd., except for tetrahexylammonium bis (trifluoromethanesulfonimide) ([N₆₆₆₆][NTf₂], >98%) synthesised in the lab as reported in the literature.[45,46] The purity of these ILs was confirmed by NMR spectroscopy and elemental analysis. NMR spectra were obtained at 20°C on a Bruker DMX 400 instrument, and elemental analysis of ionic liquid was carried out under an inert atmosphere with a Thermo Scientific FLASH 2000 Series CHNS/O Analyzer. The ITO electrode was provided by Shenzhen Huanan Xiangcheng Technology Co., Ltd.

Measurements

The optical transmission measurements and UV-vis spectra were carried out on a Perkin Elmer Lambda950 UV/VIS/NIR Spectrometer. All electrochemical experiments were performed in a CHI660E electrochemical work station from Shanhai Chenghua Instruments Co., Ltd. The electro-optic experiments were measured at room temperature by a liquid crystal device (LCD) parameter tester (LCT-5016C, Changchun Liancheng Instrument Co. Ltd., China). High-resolution transmission electron microscopy (HRTEM) was carried out on a Philips Tecnai F20 electron microscope operated at 300 kV. The Pd NPs were dispersed in ethanol following their separation from the ILs by centrifugation. One drop of the solution was placed onto a copper grid coated by a carbon film and dried under vacuum at 343 K for 24 h. The average particle size of the Pd NPs was determined from ca. 300 NPs.

Preparation of samples

The ECLC material was sandwiched between the transparent ITO electrodes with a cell gap of 40 μm, the cell gap being controlled by a 40 μm-thick polyethylene terephthalate (PET) spacer. The ECLC material was prepared by mixing LC and IL according to certain weight proportion as follows: PEB-IL with 1% PEB and 99% IL; SLC1717-IL with SLC1717 of 5–20% or 80–95% and IL of 80–95% or 5–20%; PEB-NP-IL with PEB of 1% and Pd NP (palladium nanoparticle)-IL suspension of 99%; and SLC1717-NP-IL with SLC1717 of 85%; and Pd NP-IL suspension of 15%. The Pd NP-IL suspension was prepared following the literature [44] and diluted tenfold by the same IL before mixing. The EC-PDLC material was prepared by mixing according to weight: SLC1717 45%, [Bmim][NTf₂] 5%, the remaining 50% being a mixture of PEGDA 400, IBMA, TMHA and Irgacure 651 following the literature.[47]

Curing methods

The EC-PDLC mixture was then exposed to ultraviolet (UV) irradiation for about 10.0 minutes from a 35.0 W high-pressure Hg lamp, yielding an intensity at the cell surface of about 6.0 mW cm⁻² at 365.0 nm.

Results and discussion

The potential window available, defined as the potential region with no significant background current, is critical to the electrolytes used in electrochemistry measurements. Compared with the traditional electrolyte, IL can achieve a wider potential window. The potential window of ILs under cyclic voltammetry at the working electrode has been reported previously,[35] but to date there is barely a potential window of IL in ECLC devices due to the limited systematic research on IL electrolytes in ECLC devices. As shown in Figure S1 (Supplementary Information), under conditions of cyclic voltammetry at a scan rate of 50 mV/s, the potential moved from zero in a positive direction when the potential window of IL was tested in a cell composed of two ITO glass electrodes. To investigate how IL structure impacts on the potential window, IL used in the experiment was divided into two groups according to the same cation or the same anion.

The potential window shows significant differences among the ILs with various anionic structures (see Figure S1a). In the IL set with the [Bmim]^+ cation, in spite of [Bmim][NTf₂] and [Bmim][BF₄] both having...
the optimal potential window, [Bmim][NTf₂] is expected to be a more suitable electrolyte due to its better hydrophobicity, lower viscosity and better stability than [Bmim][BF₄]. The potential window of IL tested in the cell seems similar to the data from the traditional working electrode.[35] It is worth noting that water and other impurities, which may narrow the IL potential window significantly, should be avoided experimentally as far as possible.

In contrast to the obvious difference in the potential window of the IL set with different anions (see Figure S1a), all the IL set with various cations (see Figure S1b) showed little difference, with a wide potential window of above 6.0 V. Based on the fact that [C₂OHmim]⁺ with the hydroxyl group is more easily oxidised than other cations, it is reasonable to explain the narrow potential window found in [C₂OHmim][NTf₂]. Due to the performance of a satisfactory potential window, the IL set containing [NTf₂]⁻ was selected as the electrolyte in the following experiments to investigate the ECLC material comprising IL and LC. We also carried out other chronoamperometric measurements under the same conditions; the cyclic voltammograms were the same as in Figure S1 but, regardless, the potential started to become more positive or more negative.

We sandwiched PEB-IL material composed of 1wt% PEB and 99wt% IL as the EC material between ITO electrodes. The EC devices can attain a red state with the application of a DC field. To confirm the colour change of the EC devices, the optical properties were measured. Figure 1 shows the transmission spectra of the cells following the application of DC 2.5 V. Due to the initial state of PEB and IL – white and transparent – in the voltage-off state the mixture of both

sandwiched in the EC cells is the same as the pure IL cell in the transparent state; in the voltage-on state, all five PEB-IL samples are around 512 nm, leading to the red display in the EC cells, as shown in the photographs in Figure 1. Thus, the transmittance difference at 512 nm is recorded to evaluate the EC performance of PEB-IL. In all five samples, PEB-[Bmim][NTf₂] shows the minimum transmittance of 63.3%, while PEB-[Emim][NTf₂] shows the maximum transmittance of 90%. It was not expected that there would be nearly 30% transmittance difference between PEB-[Bmim][NTf₂] and PEB-[Emim][NTf₂], considering their similar structure apart from the butyl or ethyl side chain in the imidazole cation. It is more likely that the alkyl length of imidazole will tune PEB solubility in IL, and the longer butyl chain in [Bmim][NTf₂] will help to dissolve the much weaker polarity PEB molecular, resulting in the larger transmittance difference in PEB-[Bmim][NTf₂]. The transmittance of 81.2% in PEB-[C₂OHmim][NTf₂] is smaller than that in PEB-[Emim][NTf₂], possibly due to the additional hydroxyl group in [C₂OHmim][NTf₂]. PEB-[N₆₆₆₆][NTf₂] and PEB-[PP₁,₄][NTf₂] show transmittance of 67.1 and 75.3%, respectively, as a result of the hydrophobic and long alkyl chain in these two ILs helping to enhance PEB solubility. Compared with [Bmim][NTf₂], the lack of an imidazole group in [N₆₆₆₆][NTf₂] and [PP₁,₄][NTf₂] may reduce the conjugated interaction between IL and PEB, resulting in higher transmittance in PEB-[N₆₆₆₆][NTf₂] and PEB-[PP₁,₄][NTf₂] than in PEB-[Bmim][NTf₂].

The transmittance spectrum of a series of PEB-IL samples was recorded simultaneously in the EC cell at 512 nm under conditions of cyclic voltammetry at a scan rate of 0.05 V/s (see Figure 3). For PEB-[Bmim][NTf₂], as the potential moves from zero in a positive direction, anodic current appears at 1.7 V and reaches a peak at 2.5 V. This anodic current can be attributed to the electrochemical oxidation of PEB, and the transmittance of the cell begins to decrease from 1.7 V owing to the red radical substance formed under the positive current. Along with the increasing positive potential, the transmittance decreases to 52.4% at 2.7 V, showing the maximum transmittance difference (ΔT)max of 47.6% on account of accumulation of red radical substances formed during electrochemical oxidation. When the potential sequentially rises to 3 V in the positive direction, cell transmittance increases along with a reducing amount of red substance, as a result of the coloured substance changing to colourless during the further oxidation process. As the potential moves back from 3.0 to 0 V in a negative direction, cell transmittance gradually increases back to above 90%.

Figure 1. Transmittance spectrum of PEB-IL at DC 2.5 V; the inset shows photographs of the EC cell taken on a light box for the same applied voltage.
due to PEB having more than one oxidation state, if
the potential exceed 2.7 V as shown in
Figure 2, the red
substance, the first oxidation state, reverts to the sec-
ond oxidation state that is colourless during the reduc-
tion process. As shown in
Figure 2b-e, other PEB-IL
cells display similar transmittance change tendency,
with the maximum transmittance change appearing
with the maximum red substance cumulated; therefore,
PEB content in the devices determines the trend of the
transmittance spectrum and cyclic voltammograms, the
scan rate having little effect.

To investigate the effect of IL on the EC perfor-
mance of ECLC composed of PEB-IL, it is necessary
to compare the potential at \((\Delta T)_{\text{max}}\). In
Figure 2b, the
\((\Delta T)_{\text{max}}\) of PEB-[C\text{2}OHmim][NTf\text{2}] at 2.6 V is 13.0%,
less than the 47.6% of PEB-[Bmim][NTf\text{2}] (at 2.7 V). In
Figure 2c, \(\Delta T\) in PEB-[Emim][NTf\text{2}] reaches a maximum at 2.6 V with 20.3%, still lower than in PEB-
[Bmim][NTf\text{2}]. These results show that lower
\((\Delta T)_{\text{max}}\) appears at the lower potential of 2.6 V in PEB-
[C\text{2}OHmim][NTf\text{2}] and PEB-[Emim][NTf\text{2}], compared
with that in PEB-[Bmim][NTf\text{2}]. As shown in
Figure 2d, the \((\Delta T)_{\text{max}}\) in PEB-[PP\text{1,4}][NTf\text{2}] is 50.0%
(at 3.0 V), slightly greater than the 47.6% in PEB-
[Bmim][NTf\text{2}]. Similarly, satisfactory \((\Delta T)_{\text{max}}\) is
obtained at 2.9 V with 44.4% in PEB-[N\text{6666}][NTf\text{2}].
In comparison to 2.7 V in PEB-[Bmim][NTf\text{2}], a higher
potential is needed in PEB-[N\text{6666}][NTf\text{2}] (3.0 V) and
PEB-[PP\text{1,4}][NTf\text{2}] (2.9 V) to obtain the satisfactory
\((\Delta T)_{\text{max}}\).

The ideal ECLC material is expected to realise
obvious transmittance change under low voltage,
because the stability of ECLC will be destroyed under
high voltage. Considering both satisfactory transmit-
tance and low operating voltage, it seems that [Bmim]
[NTf\text{2}] is the most suitable electrolyte for use in
PEB-IL.

IL electrolytes doped with SiO\text{2} NPs have been used
to promote Li electrodeposition.[40–42] Although electrolytes are critical in electrochemistry experiments and
devices, little research has been done to improve elec-
trolyte performance by introducing metal NPs. In the
current experiment, metallic Pd NPs were introduced
into the IL electrolyte and were expected to improve its
performance in EC cells. To avoid additional impuri-
ties from the preparation or transfer process of Pd NPs
in the IL electrolyte, the Pd NPs were prepared in [Bmim][NTf$_2$] by thermal decomposition of palladium acetate, with no additional stabiliser or solvent.

TEM characterisation (see Figure 3a) reveals that Pd NPs were formed in [Bmim][NTf$_2$] with narrow size distribution and small average size (6.8 ± 1.1 nm), consistent with the previous literature.[44] A lattice spacing of 2.2 Å shown in the Pd NPs suggests a face-centred structure by exposing (111) lattice planes. Moreover, the uniform spherical Pd NPs in situ formed in [Bmim][NTf$_2$] are stable and well dispersed in IL. The Pd NP-[Bmim][NTf$_2$] suspension, after tenfold dilution by [Bmim][NTf$_2$], was used as the electrolyte to dissolve PEB.

The transmittance spectrum of PEB-NP-IL was tested in an EC cell at 512 nm, under cyclic voltammetry simultaneously at a scan rate of 0.05 V/s (see Figure 3b). As the potential moves from zero in a positive direction, anodic current appears at 1.2 V and reaches a peak at 2.1 V, which is 0.4 V lower than that in PEB-[Bmim][NTf$_2$] (see Figure 3a). In addition, the potential at (ΔT)$_{\text{max}}$ is 2.4 V in PEB-NP-[Bmim][NTf$_2$], lower than in PEB-[Bmim][NTf$_2$] (2.7 V). However, the (ΔT)$_{\text{max}}$ of PEB-NP-[Bmim][NTf$_2$] is 45.0%, similar to that of PEB-[Bmim][NTf$_2$] (47.6 %). Compared with PEB-[Bmim][NTf$_2$], the additional Pd NPs in PEB-NP-[Bmim][NTf$_2$] contribute to achieving higher (ΔT)$_{\text{max}}$ of the EC cell at the lower potential. The improved EC performance in PEB-NP-[Bmim][NTf$_2$] is speculated to be related to Pd NPs, by means of their participation in the oxidation of PEB as catalysts or improving the electrochemical performance of IL electrolytes, such as conductivity, mass transfer efficiency or viscosity. In spite of electrolytes composed only of IL or Pd NP-IL suspension, it is still difficult to identify the precise influences and more detailed experiments would be needed for further understanding.

The evaluation on EC performance of PEB-IL comprising a typical LC molecular-PEB and IL electrolyte suggests that the IL electrolytes indeed affect the EC performance of PEB-IL. However, compared with the model LC molecular, we are more concerned about the ECLC composed of commercial LC and IL, owing to their potential applications in the EC display field. Based on the above research on PEB, a commercial LC, SLC1717, containing PEB and other similar molecular, was chosen for use in ECLC. Figure 4a shows SLC1717 mixed with [Bmim][NTf$_2$] in a ratio of 5–20 wt%, and the transmittance difference spectrum of the ECLC material was recorded at 2.5 V. DC of 2.5 V is too low to induce orientation of the liquid crystal molecules in the EC device. Notably, due to the liquid state of both the commercial LC and IL, it is much easier to mix them by simply stirring. As the weight ratio of SLC1717 increases from 5 to 15 wt%, the (ΔT)$_{\text{max}}$ of ECLC increases 15.1 to 30.5%. When SLC1717 content continually increases to 20 wt%, the (ΔT)$_{\text{max}}$ of ECLC reduces to 24.7%. The transmittance difference of ECLC begins to reduce with LC content above 15 wt%, probably because of poor LC solubility arising from the phase separation of LC and IL.

Figure 4b shows the transmittance difference of ECLC with LC as parent, by mixing SLC1717 of 80–95 wt% with [Bmim][NTf$_2$]. Decreased LC content gives an increase in (ΔT)$_{\text{max}}$, with 85 wt% of LC content having the highest (ΔT)$_{\text{max}}$. Similar to Figure 4a, the (ΔT)$_{\text{max}}$ of ECLC begins to decrease to 12.6% when the LC content is further reduced to 80 wt%, owing to poor IL solubility in LC. These results reveal that a good compatibility of LC and IL is beneficial to improving the EC performance of
ECLC. In addition, the $(\Delta T)_{\text{max}}$ peak position shifts from 512 nm (in Figure 4a with IL as parent phase) to 517 nm (in Figure 5b with LC as parent phase). It is speculated that IL electrolytes affect EC performance, not only by adjusting LC compatibility but also by influencing the electrochemical reaction related to the EC process.

The speed of the oxidation and reduction reactions will determine the switching capability of the ECLC. To investigate the switching characteristics of the current ECLC, the transmittance of SLC1717-[Bmim][NTf$_2$] (15 wt% IL) and SLC1717-NP-[Bmim][NTf$_2$] (15 wt% Pd NP-IL suspension) was tested by repeated redox-stepping experiments at 512 nm, as shown in Figure 5. During the test, the ECLC cell switched from transparent to red state by the sequential application of the following biases: 2 V (5 s), 0 V (20 s). Following the DC electric sequence, SLC1717-[Bmim][NTf$_2$] (the broken line) varies transmittance from 100% in the bleached state to 93.3% in the coloured state, with $\Delta T$ of 6.7%. The response times to achieve the coloured and bleached states are $\tau_c = 5$ and $\tau_b = 20$ s, respectively.

In SLC1717-NP-[Bmim][NTf$_2$], the transmittance changes from 100% in the bleached state to 81.8% in the coloured state, with a higher $\Delta T$ than that in SLC1717-[Bmim][NTf$_2$]. This means that SLC1717-NP-[Bmim][NTf$_2$] has better optical modulation. For the Pd NP-IL electrolyte, more coloured substances are accumulated during the same coloration sequence, because of Pd NPs in IL assisting reduction of the potential for coloration reaction. However, a longer response time than 20 s is needed to retrieve the bleached state of about 100%. Further study on the optimisation of the functionalised IL electrolyte is necessary to achieve a satisfactory EC performance in the display application.

In order to highlight the electrochromic properties and, simultaneously, the liquid crystal properties of the ECLC material, a new bifunctional device of EC-PDLC film was designed. Using the preparation procedure outlined in the Preparation section, we made EC-PDLC films that show four distinct states with varying applied voltage (see Figure 6). Figure 6a shows the opaque state of the cell, which is due to light scattering by liquid crystal droplets, and the transparent one is attributed to liquid crystal director reorientations. When only DC was applied to the cell, the cell became coloured and opaque; the coloured state is a consequence of electrochromic reactions, which take place at the cathode between IL and ECLC, as shown in Figure 6b. When AC was applied, the alignment of the LC molecular was parallel to the applied electric field and the ordinary refractive index of the LC matched the refractive index of the polymer; therefore, the cell became transparent and non-coloured, as shown in Figure 6c. When both AC and DC electric fields

![Figure 4](image-url) (colour online) Transmittance difference spectrum of SLC1717-[Bmim][NTf$_2$] with a certain weight ratio of SLC1717 to [Bmim][NTf$_2$] at 2.5 V.

![Figure 5](image-url) (colour online) Transmittance spectra during a colouration and bleaching sequence for SLC1717-[Bmim][NTf$_2$] (broken line) and SLC1717-NP-[Bmim][NTf$_2$] (solid line).
were present, the cell became transparent and coloured, as shown in Figure 6d.

EC-PDLCs show a field-dependent transmittance similar to that of conventional PDLCs. The field-dependent transmittance of EC-PDLC is shown in Figure 7. There is no particular effect due to the presence of electrolyte with respect to conventional PDLCs.

**Conclusion**

A green ECLC material based on LC and IL electrolyte, capable of changing colour from colourless to red within a few seconds, has been developed. A wide electrochemistry window of more than 3 V was obtained in EC cells by using a series of ILs with the [NTf₂]- anion. The transmittance difference spectrum of the PEB-IL with PEB as a typical LC molecular was carried out in various ILs with [NTf₂]−, and PEB-[Bmim][NTf₂] attained a transmittance difference of 36.7% at 512 nm, the highest among five samples. The transmittance spectrum of PEB-IL was then recorded in the EC cell at 512 nm under cyclic voltammetry simultaneously, with PEB-[Bmim][NTf₂] showing a transmittance difference maximum of 47.6% at 2.7 V. Considering attainment of both satisfactory transmittance and low operating voltage, it seems that [Bmim][NTf₂] is the most suitable electrolyte used in PEB-IL. Compared with PEB-[Bmim][NTf₂], the additionally introduced Pd NPs in PEB-NP-[Bmim][NTf₂] can further increase the transmittance difference at the lower potential. A commercial LC containing PEB and other similar molecular was used in ECLC and EC-PDLC, and a satisfactory transmittance difference and cyclicity were obtained with an optimised LC content. The combination of electrically controlled transmittance of PDLC films with the colour control of electrochromic devices can be achieved by adding electroactive molecules in a PDLC film, which would trigger potential application in large-area displays, smart windows, and electro-optical shutters.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**Funding**

This work was supported by the Major Project of International Cooperation of the Ministry of Science and Technology [Grant No. 2013DFB50340], the National Science Foundation of China (NSFC) [Grant Nos. 51203003, 51173155, 51303008, 51302006], the Issues of Priority Development Areas of the Research Fund for the Doctoral Program of Higher Education of China [Grant No. 20120001130005], the Key (Key grant) Project of the Chinese Ministry of Education [Grant No. 313002], the Major Project of Beijing Science and Technology Program [Grant No. Z141100003814011] and the Project of Beijing Science and Technology Program [Grant NO Z151100003315023].

**References**

[1] Monk PMS, Mortimer RJ, Rosseinsky DR, editors. Electrochromisum fundamentals and applications. Weinheim: VCH; 1995.

[2] Thakur VK, Ding GQ, Ma J, et al. Hybrid materials and polymer electrolytes for electrochromic device applications. Adv Mater. 2012;24:4071–4096. doi:10.1002/adma.201200213.
[3] Mortimer RJ, Dyer AL, Reynolds JR. Electrochromic organic and polymeric materials for display applications. Displays. 2006;27:2–18. doi:10.1016/j.displa.2005.03.003.

[4] Argun AA, Aubert PH, Thompson BC, et al. Multicolored electrochromism polymers: structures and devices. Chem Mater. 2004;16:4401–4412.

[5] Meng H, Tucker D, Chaffins S, et al. An unusual electrochromic device based on a new low-bandgap conjugated polymer. Adv Mater. 2003;15:146–149. doi:10.1002/adma.200390030.

[6] Rosseinsky DR, Mortimer RJ. Electrochromic systems and the prospects for devices. Adv Mater. 2001;13:783–793. doi:10.1002/1521-4095(200106)13:11<783::AID-ADMA783>3.0.CO;2-D.

[7] Sapp SA, Sotzing GA Reynolds JR. High contrast ratio and fast-switching dual polymer electrochromic devices. Chem Mater. 1998;10:2101–2108.

[8] Lampert CM. Chromogenic smart materials. Mater Today. 2004;7:28–35. doi:10.1016/S1369-7021(04)00123-3.

[9] Araki S, Nakamura K, Kobayashi K, et al. Electrochemical optical-modulation device with reversible transformation between transparent, mirror, and black. Adv Mater. 2012;24:122–126.

[10] Tsuboi A, Nakamura K, Kobayashi N, A localized surface plasmon resonance-based multicolor electrochromic device with electrochemically size-controlled silver nanoparticles. Adv Mater. 2013;25:3197–3201. doi:10.1002/adma.201205214.

[11] Kuringen van Huub PC, Eikelboom GM, Shishmanova IK, et al. Responsive nanoporous smectic liquid crystal polymer networks as efficient and selective adsorbents. Adv Funct Mater. 2014;24:5045–5051. doi:10.1002/adfm.201400428.

[12] Guo JB, Cao H, Wei J, et al. Polymer stabilized liquid crystal films reflecting both right- and left-circularly polarized light. Appl Phys Lett. 2008;93:201901. doi:10.1063/1.3003869.

[13] Chen XW, Wang L, Chen YJ, et al. Broadband reflection of polymer-stabilized chiral nematic liquid crystals induced by a chiral azobenzene compound. Chem Commun. 2013;50:691–694. doi:10.1039/C3CC47438K.

[14] Wang L, He WL, Wang Q, et al. Polymer-stabilized nanoparticle-enriched blue phase liquid crystal films. J Mater Chem C. 2013;1:6526–6531. doi:10.1039/c3tc31253d.

[15] Broer DJ, Lub J, Mol GN. Wide-band reflective polarizers from cholesteric polymer networks with a pitch gradient. Nature. 1995;378:467–469. doi:10.1038/378467a0.

[16] He WL, Pan GH, Yang Z, et al. Wide blue phase range in a hydrogen-bonded self-assembled complex of chiral fluoro-substituted benzoic acid and pyridine derivative. Adv Mater. 2009;21:2050–2053. doi:10.1002/adma.v21:20.

[17] Hu W, Zhao HY, Song L, et al. Electrically controllable selective reflection of chiral nematic liquid crystal/chiral ionic liquid composites. Adv Mater. 2010;22:468–472. doi:10.1002/adma.v22:4.

[18] Wang L, He WL, Xiao X, et al. Low voltage and hysteresis-free blue phase liquid crystal dispersed by ferroelectric nanoparticles. J Mater Chem. 2012;22:19629–19633. doi:10.1039/c2jm34013e.

[19] Wang L, He WL, Xiao X, et al. Wide blue phase range and electro-optical performances of liquid crystalline composites doped with thiophene-based mesogens. J Mater Chem. 2012;22:2383–2386. doi:10.1039/C2JM15461G.

[20] Liu F, Wang JJ, Ge ZH, et al. Electro-responsive 1-D nanomaterial driven broad-band reflection in chiral nematic liquid crystals. J Mater Chem C. 2013;1:216–219. doi:10.1039/C2TC00166G.

[21] Nakamura K, Kaneko S, Ito Y, et al. Electrochemically induced coloration of liquid crystal materials. J Appl Phys. 1982;53:1792. doi:10.1063/1.330678.

[22] Nakamura K, Nakada K, Ito Y, et al. Electrochromic characteristics of liquid-crystal materials. J Appl Phys. 1985;57:135. doi:10.1063/1.335376.

[23] Nakamura K, Oda Y. Sekikawa T, et al. Electrochromic characteristics of organic materials with a simple molecular structure. Jpn J Appl Phys 1-Regular Pap Short Notes Rev Pap. 1987;26:931–935. doi:10.1143/JJAP.26.931.

[24] Nicoletta FP, Chidichimo G, Cupelli D, et al. Electrochromic polymer-dispersed liquid-crystal film: a new bifunctional device. Adv Funct Mater. 2005;15:995–999. doi:10.1002/adfm.200400403.

[25] Nicoletta FP, Cupelli D, Filpo GD, et al. Electrochromism in switchable nematic emulsions. Appl Phys Lett. 2004;84:4260. doi:10.1063/1.1758294.

[26] Cupelli D, Filpo GD, Chidichimo G, et al. Photoswitching in polymer-dispersed liquid crystals J. Appl Phys. 2006;100:024506. doi:10.1063/1.2218272.

[27] Pantaloni S, Passerini S, Scrosati B. Solid-state thermo-electrochromic display. J Electrochem Soc. 1987;134:753–755. doi:10.1149/1.2100548.

[28] Granqvist CG. Handbook of inorganic electrochromic materials. Amsterdam (Netherlands): Elsevier; 1995.

[29] Lu W, Fadeev AG. Qi B, et al. Stable conducting polymer electrochemical devices incorporating ionic liquids. Mattes Synth Met. 2003;135-136:139–140. doi:10.1016/S0379-6779(02)00558-1.

[30] Lu W, Fadeev AG. Qi B, et al. Fabricating conducting polymer electrochromic devices using ionic liquids. J Electrochem Soc. 2004;151:H33–H39. doi:10.1149/1.1640635.

[31] Marcilla R, Alcaide F, Sardon H, et al. Tailor-made polymer electrolytes based upon ionic liquids and their application in all-plastic electrochromic devices. Electrochem Commun. 2006;8:482–488. doi:10.1016/j.elecom.2006.01.013.

[32] Armand M, Endres F, MacFarlane DR, et al. Ionic-liquid materials for the electrochemical challenges of the future. Nat Mater. 2009;8:621–629. doi:10.1038/nmat2448.

[33] Buzzeo MC, Evans RG Compton RG. Non-haloaluminate room-temperature ionic liquids in electrochemistry - A review. Chem Phys Chem. 2004;5:1106–1120. doi:10.1002/cphc.200301017.

[34] Lu W, Fadeev AG, Qi B, et al. Use of ionic liquids for pi-conjugated polymer electrochromic devices.
[35] Ohno H. Electrochemical aspects of ionic liquids. Hoboken, NJ: Wiley; 2011.

[36] Zhang J, Bond AM. Practical considerations associated with voltammetric studies in room temperature ionic liquids. Analyst. 2005;130:1132–1147. doi:10.1039/b504721h.

[37] Xin BW, Hao JC. Imidazolium-based ionic liquids grafted on solid surfaces. Chem Soc Rev. 2014;43:7171–7187. doi:10.1039/C4CS00172A.

[38] Surca Vuk A, Jovanovski V, Pollet-Villard A, et al. Imidazolium-based ionic liquid derivatives for application in electrochromic devices. Sol Energy Mater Sol Cells. 2008;92:126–135. doi:10.1016/j.solmat.2007.01.023.

[39] Brazier A, Appetecchi G, Passerini S, et al. Ionic liquids in electrochromic devices. Electrochim Acta. 2007;52:4792–4797. doi:10.1016/j.electacta.2007.01.025.

[40] Lu Y, Das SK, Moganty SS, et al. Ionic liquid-nanoparticle hybrid electrolytes and their application in secondary lithium-metal batteries. Adv Mater. 2012;4:4430–4435. doi:10.1002/adma.201201953.

[41] Lu YY, Korf K, Kambe Y, et al. Ionic-liquid-nanoparticle hybrid electrolytes: applications in lithium metal batteries. Angew Chem Int Ed. 2014;53:488–492. doi:10.1002/anie.v53.2.

[42] Lu Y, Moganty SS, Schaefer JL, et al. Ionic liquid-nanoparticle hybrid electrolytes. J Mater Chem. 2012;22:4066–4072. doi:10.1039/c2jm15345a.

[43] Yuan X, Sun G, Asakura H, et al. Development of palladium surface-enriched heteronuclear Au-Pd nanoparticle dehalogenation catalysts in an ionic liquid. Chem Eur J. 2013;19:1227–1234. doi:10.1002/chem.201203605.

[44] Yuan X, Yan N, Katsyuba SA, et al. A remarkable anion effect on palladium nanoparticle formation and stabilization in hydroxyl-functionalized ionic liquids. Phys Chem Chem Phys. 2012;14:6026–6033. doi:10.1039/c2cp23931k.

[45] Sun J. MacFarlane D Forsyth M. Synthesis and properties of ambient temperature molten salts based on the quaternary ammonium ion. Ionics. 1997;3:356–362. doi:10.1007/BF02375710.

[46] Wang S, Jiang S, Nie J. Lanthanide bis[(trifluoromethyl)sulfonyl]imides as reusable catalysts for mononitration of substituted benzenes in ionic liquids. Adv Synth Catal. 2009;351:1939–1945. doi:10.1002/adsc.v351:11/12.

[47] Kashima M, Cao H, Liu H, et al. Effects of the chain length of crosslinking agents on the electro-optical properties of polymer-dispersed liquid crystal films. Liq Cryst. 2010;37:339–343. doi:10.1080/02678290903568495.