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PAPER

# Bis-imidazolium based poly(ionic liquid) electrolytes for quasi-solid-state dye-sensitized solar cells<sup>†</sup>

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Bis-imidazolium based poly(ionic liquid), poly(1-butyl-3-(1-vinylimidazolium-3-hexyl)-imidazolium bis(trifluoromethanesulfonyl)imide) (Poly[BVIm][HIm][TFSI]) and mono-imidazolium based poly(ionic liquid), poly(1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide) (Poly[BVIm] [TFSI]), were synthesized and dissolved in room temperature ionic liquids (ILs) to form quasi-solid-state electrolytes for dye-sensitized solar cells (DSSCs), without using any volatile organic solvent. Compared with mono-imidazolium based poly[BVIm][TFSI], bis-imidazolium based poly[BVIm][HIm] [TFSI] electrolytes showed a higher thermal stability and conductivity due to the charge transport networks formed in the gel electrolytes via the  $\pi$ - $\pi$  stacked imidazolium rings. The DSSCs based on the poly[BVIm][HIm][TFSI] gel electrolyte showed a superior long-term stability and yielded a power conversion efficiency of 5.92% under the simulated air mass 1.5 solar spectrum illumination at 100 mW cm<sup>-2</sup>. This study offered a feasible method to fabricate quasi-solid-state DSSCs in future practical applications.

# Introduction

Dye-sensitized solar cells (DSSCs) have attracted both academic and industrial interest due to their high-efficiency, potential lowcost and easy-handling fabrication.<sup>1</sup> Recently, a photoelectric conversion efficiency over 12% has been achieved by incorporating a cobalt(11/111)-based tris(bipyridy) tetracyanoborate complex as the redox mediator in conjunction with a donor- $\pi$ -bridge-acceptor zinc porphyrin dye in a liquid electrolyte.<sup>2</sup> Cells with high conversion efficiency have been achieved by using organic liquid electrolyte, however, the existence of the liquid electrolyte in DSSCs suffers from several drawbacks such as the leakage and volatilization of organic solvent, the possible desorption of the surface-coated dyes, the corrosion of the counter electrodes and the limited long-term performance which restricts the widespread commercialization of DSSCs.3 Several methods, including p-type semiconductors,<sup>4</sup> organic and inorganic hole conductors<sup>5,6</sup> and gel and polymer electrolytes,<sup>7-17</sup> have been proposed to reduce the evaporation and leakage of the liquid electrolyte by using solid or semi-solid electrolytes to overcome the drawbacks.

Among the solid and semi-solid electrolytes studied, polymer based quasi-solid-state electrolytes have been attracting a great deal of interest because of their good contact with the nanocrystalline TiO<sub>2</sub> electrodes and counter electrodes, maintaining good ionic conductivity, reducing the cell leakage problems and their comparable efficiencies to cells using liquid electrolytes.<sup>10,18</sup> Polymers or co-polymers, such as poly(ethylene oxide) (PEO),<sup>10</sup> poly(styrene-co-acrylonitrile) (poly-(St-AN)),<sup>11</sup> poly(ethylene glycol) (PEG),<sup>18</sup> poly(methylmethacrylate) (PMMA),<sup>19</sup> poly-(acrylonitrile-co-vinyl acetate) (PAN-VA)<sup>20</sup> and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)9,21 have been applied as the gel electrolytes. However, preparation of these polymer-based quasi-solid-state electrolytes usually requires conventional volatile organic solvents, such as acetonitrile and 3methoxypropionitrile,<sup>9-21</sup> which gives rise to potential problems such as flammability and high-temperature instability.

To overcome the evaporation problems of organic solvent liquid electrolytes, room temperature ionic liquid (IL) based electrolytes have been extensively studied and applied in DSSCs due to their negligible vapor pressure, high ionic conductivity and thermal stability, wide electrochemical window, the ability to dissolve organic and inorganic solutes and tunable solvent properties.<sup>22,23</sup> However, the devices with room temperature IL-based electrolytes are still suffering leakage problems in practical use. More recently, growing attention has been paid to poly(ionic liquids) (poly(ILs)) because they show specific functions such as

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the transport of target ions, a specific polar environment and mechanical strength, corresponding to their polymer structure. Poly(ILs) have been successfully applied in quasi-solid-state DSSCs with high power conversion efficiency and excellent long-term stability of the devices.<sup>24–26</sup> In our previous report, mono-imidazolium based poly(ionic liquid), poly(1-butyl-3vinylimidazolium bis(trifluoromethanesulfonyl)imide) (poly [BVIm][TFSI]) was synthesized and applied in quasi-solid-state DSSCs. The superior long-term stability of the fabricated DSSCs indicated that the poly(IL) based gel electrolyte could overcome the drawbacks of the volatile solvents. However, the power conversion efficiency of the devices fabricated with mono-imidazolium type poly(IL)-based electrolyte is still low.

Compared with monocationic ILs, dicationic ILs show higher thermal stability, lower volatility and more flexibility in tuning the physicochemical properties.<sup>27-30</sup> Here, bis-imidazolium-based poly(IL), poly(1-butyl-3-(1-vinylimidazolium-3-hexyl) imidazolium bis(trifluoromethane-sulfonyl)imide) (poly[BVIm][HIm] [TFSI]), was synthesized and dissolved in the room temperature ILs to form a gel electrolyte for high-performance quasi-solidstate DSSCs. The fabricated bis-imidazolium based poly(IL) gel electrolyte displayed a better power conversion efficiency than mono-imidazolium based poly(IL) and is close to the efficiency of ionic liquid electrolytes. In addition, the good long-term stability of poly[BVIm][HIm][TFSI]/ionic liquid electrolytes indicates that the bis-imidazolium based poly(IL) gel electrolyte is a promising candidate for solar cells with good durability.

# **Experimental procedure**

## Materials

Iodoethane, 1-iodopropane, 1-bromobutane, 1,6-dibromohexane, 1-methylimidazole, 1-butylimidazole, 1-vinylimidazole, Nbutylbenzimidazole (NBB) and guanidine thiocyanate (GNCS) were purchased from Alfa Aesar. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was kindly provided by Rhodia and used as received. 1-Ethyl-3-methylimidazolium iodide (EMII), 1-propyl-3-methylimidazolium iodide (PMII) and 1-ethyl-3-methylimidazolium thiocyanate (EMISCN) were synthesized according to the previous report.<sup>31</sup> TiCl<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub> were purchased from Aldrich. cis-Bis(isothiocyanato) bis(2,20bipyridyl-4,40-dicarboxylato) ruthenium(II) ([RuL<sub>2</sub>(NCS)<sub>2</sub>]) was purchased from Solaronix SA (Switzerland) and used without further purification. Fluorine-doped tin oxide overlayer (FTO) glass electrodes (7  $\Omega$  Sq<sup>-1</sup>) and slurries containing 20 nm-sized mesoporous and 200 nm-diameter light-scattering colloidal TiO<sub>2</sub> were purchased from Dalian Hepat Chroma Solar Tech. Co., Ltd (China).

# Synthesis of ILs and poly(ILs)

Poly(ILs), poly(1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide) (poly[BVIm][TFSI]) and poly(1-butyl-3-(1-vinylimidazolium-3-hexyl)-imidazolium bis(trifluoromethanesulfonyl)imide) (poly[BVIm][HIm][TFSI]) were synthesized as shown in Scheme 1.

Mono-imidazolium based ionic liquid, 1-butyl-3-vinylimidazolium bromide ([BVIm][Br]), was firstly synthesized *via* the reaction of 1-bromobutane with 1-vinylimidazole at room



Scheme 1 General synthetic route for the bis- and mono-imidazolium based poly(ILs).

temperature for 72 h. <sup>1</sup>HNMR (400 MHz, CDCCl<sub>3</sub>): 10.98 (s, 1H), 7.77 (s, 1H), 7.50 (dd, 1H), 7.46 (m, 1H), 5.95 (m, 1H), 5.36 (m, 1H), 4.38 (t, 3H), 1.91 (m, 2H), 1.37 (m, 2H), 0.96 (t, 3H) (see ESI, Fig. S1<sup>†</sup>).

Mono-imidazolium based poly(IL), poly[BVIm][Br], was prepared *via* free radical polymerization of 1-butyl-3-vinylimidazolium bromide in ethanol at 60 °C under a nitrogen atmosphere for 24 h. Anion-exchange of poly[BVIm][Br] with LiTFSI in aqueous solution yielded poly(1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide) (poly[BVIm] [TFSI]).<sup>32,33</sup>

3-(6-Bromohexyl)-1-butyl-imidazolium bromide ([BrHBIm] [Br]) was synthesized *via* the reaction of 1-butylimidazole (3.10 g, 0.025 mol) and 1,6-dibromohexane (18.30 g, 0.075 mol) in ethanol, and the solution was reacted at 60 °C under a nitrogen atmosphere for 48 h. The product was purified using a silica gel column with acetone/methanol (v/v = 3:1) as the eluent. <sup>1</sup>HNMR: (400 MHz, CDCCl<sub>3</sub>): 10.66 (s, 1H), 7.35 (s, 1H), 7.31 (s, 1H), 4.37 (m, 4H), 3.40 (t, 2H), 1.93 (m, 6H), 1.50 (m, 2H), 1.40 (m, 4H), 0.97 (t, 3H) (see ESI, Fig. S2†).

The bis-imidazolium ionic liquid, 1-butyl-3-(1-vinylimidazolium-3-hexyl)-imidazolium bromide ([BVIm] [HIm][Br]), was synthesized *via* the reaction of [BrHBIm][Br] (2.95 g, 0.008 mol) with 1-vinylimidazole (1.13 g, 0.012 mol) at room temperature for 96 h. <sup>1</sup>HNMR: (400 MHz, D<sub>2</sub>O): 8.77 (s, 1H), 7.76 (s, 1H), 7.55 (s, 1H), 7.47 (m, 2H), 7.10 (m, 1H), 5.78 (dd, 1H), 5.41 (m, 1H), 4.18 (m, 5H), 3.47 (t, 1H), 1.83 (m, 6H), 1.30 (m, 6H), 0.89 (t, 3H) (see ESI, Fig. S3†).

Bis-imidazolium based poly(IL), poly[BVIm][HIm][Br], was prepared *via* free radical polymerization of [BVIm][HIm][Br] in ethanol at 60 °C under a nitrogen atmosphere for 24 h. Anionexchange of poly[BVIm][HIm][Br] with LiTFSI in aqueous solution yielded poly[BVIm][HIm][TFSI].<sup>32</sup>

#### Preparation of electrolytes

Room temperature IL electrolyte composed of 0.1 M I<sub>2</sub>, 0.5 M NBB, 0.1 M GNCS, EMII/PMII/EMISCN (6:6:7, v/v/v) was dried and stirred at room temperature before the application. Then 25 wt% of poly[BVIm][TFSI] and poly[BVIm][HIm][TFSI] was added into the liquid electrolyte and stirred at 70 °C to form a quasi-solid-state gel electrolyte.

#### Fabrication of quasi-solid-state DSSCs<sup>34,35</sup>

The cleaned FTO glass was covered with perforated adhesive tape to control the thickness and area of the mesoporous TiO<sub>2</sub> film, the area of TiO<sub>2</sub> film was about  $0.283 \text{ cm}^2$ . Two layers of TiO<sub>2</sub> particles were deposited onto cleaned FTO glass and used as photoelectrodes. A 7 µm-thick film of 20 nm-sized TiO2 particles was deposited onto the FTO glass electrode by the doctor-blade technique. The film was dried at 125 °C for 5 min. Then, a second 5 µm-thick layer of 200 nm light-scattering anatase particles were coated on the top of the first TiO<sub>2</sub> layer. The resulting TiO<sub>2</sub> films were annealed at 500 °C for 30 min. After cooling to 80 °C, the obtained TiO<sub>2</sub> electrode was immersed in 0.5 mM [RuL<sub>2</sub>(NCS)<sub>2</sub>] ethanol solution at room temperature for 24 h. Afterwards, the dye-coated TiO<sub>2</sub> electrode was washed with anhydrous ethanol and dried with nitrogen stream. To prepare the Pt counter electrode, two drops of 2 mM H<sub>2</sub>PtCl<sub>6</sub> in ethanol were placed onto the cleaned FTO glass substrate, followed by drying and annealing at 400 °C for 15 min.

DSSCs were fabricated by sandwiching gel electrolytes between a dye-sensitized TiO<sub>2</sub> electrode and a Pt counter electrode, which were separated by a 25  $\mu$ m thick hot melt ring (Surlyn, Dupont) and sealed by heating. The gel electrolytes were heated to 70 °C under stirring until the gels completely melted. The internal space of the cell was filled with electrolytes *via* vacuum backfilling. The electrolyte injection hole on the thermally platinized FTO counter electrode was finally sealed with a Surlyn sheet and a thin glass by heating.

## Characterization and photovoltaic measurements

<sup>1</sup>H NMR spectra were carried out on a Varian 400 MHz spectrometer using chloroform-d (CDCl<sub>3</sub>) or deuterated water (D<sub>2</sub>O) as a solvent (Fig. S1–S3†). Fourier-transform infrared (FT-IR) spectra were recorded on a ProStar LC240 FTIR spectrometer in the range of 4000–400 cm<sup>-1</sup>. Thermal analysis of polymers was evaluated using a Perkin Elmer TGA 4000 thermogravimetric analyzer under a nitrogen atmosphere with a heating rate of 10 °C min<sup>-1</sup>. The conductivity of the electrolytes was characterized in an ordinary cell composed of a Teflon tube and two identical stainless steel electrodes (diameter of 1 cm) on a CHI660c electrochemical workstation at room temperature, using the AC impedance method over the frequency range of 1 Hz to 1 MHz. The conductivity was calculated using the following equation:

$$\sigma = \frac{l}{RS} \tag{1}$$

where  $\sigma$  is the conductivity in S cm<sup>-1</sup>, *R* is the ohmic resistance of the electrolyte, *l* is the distance between the two electrodes and *S* is the area of the electrodes.<sup>36</sup>

Steady-state voltammetry was tested in a conventional photo electrochemical cell equipped with a radius of 5.0  $\mu$ m platinum ultramicroelectrode (CHI107) as the working electrode, and a platinum foil as a counter electrode and reference electrode. The electrochemical impedance spectra (EIS) of the devices were tested using a CHI660c electrochemical workstation using the AC impedance method, the forward bias voltage for the impedance measurement was -0.70 V and the frequency ranged from  $0.01-10^5$  Hz under dark condition and the amplitude was

5 mV. The photocurrent density-voltage (J-V) curves of the assembled DSSCs shielded by an aluminum foil mask with an aperture area of 0.1 cm<sup>2</sup> were measured with a digital source meter (Keithley, model 2612) under simulated air mass (AM) 1.5 solar spectrum illumination at 15, 50, and 100 mW cm<sup>-2</sup>, respectively. Incident photo-to-current conversion efficiency (IPCE) plotted as a function of excitation wavelength was recorded on a Keithlev 1612 source meter under the irradiation of a Xenon lamp with a monochromater (Oriel Cornerstone<sup>TM</sup> 260 1/4). Hermetically sealed cells were used for long-term stability tests. For thermal stress the cells were covered with a UV cut-off filter, put on the magnetic heater at 60 °C and were irradiated at open circuit under one sun visible-light soaking. The photo-electrochemical parameters, such as the fill factor (FF) and light-to-electricity conversion efficiency  $(\eta)$  were calculated according to the previous reports.37

# **Results and discussion**

Scheme 1 shows the facile synthetic strategy for the synthesis of bis- and mono-imidazolium based poly(ILs). The chemical structure of the produced poly(ILs) was confirmed by FT-IR spectra (Fig. 1). The adsorption peaks centred at  $3150 \text{ cm}^{-1}$  and 2940 cm<sup>-1</sup> are attributed to the C–H stretching vibration mode of the imidazole ring and the alkyl chains. An absorption peak at 1138 cm<sup>-1</sup> can be assigned as the stretching and asymmetric stretching vibrations of the C–N of the imidazole rings. The C= N stretching vibration belonging to the imidazole ring is observed at about 1628 cm<sup>-1</sup>. The absorption peaks corresponding to the TFSI anion are observed at 1357, 1198 and 1048 cm<sup>-1</sup>.<sup>25,32,38,39</sup> Compared with poly[BVIm][TFSI], no new peaks were observed in poly[BVIm][HIm][TFSI]. However, the characteristic absorption peaks belonging to the alkyl chains, TFSI anions and imidazole rings were highly intensified (Fig. 1).

The thermostability of the synthesized poly[BVIm][TFSI] and poly[BVIm][HIm][TFSI] were studied by thermogravimetric analysis (TGA). As shown in Fig. 2 the poly[BVIm][HIm][TFSI] showed a thermal stability up to about 350 °C (Fig. 2A), which is higher than that of poly[BVIm][TFSI] (~322 °C, Fig. 2B). The higher thermal stability of poly[BVIm][HIm][TFSI] than poly[BVIm][TFSI] might be due to the higher charge density in the dicationic poly(ILs) than the monocationic poly(ILs). The



Fig. 1 FTIR spectra of poly(ILs) (A) poly[BVIm][TFSI], (B) poly [BVIm][HIm][TFSI].



**Fig. 2** TGA curves of poly(ILs) (A) poly[BVIm][HIm][TFSI] and (B) poly[BVIm][TFSI] under a nitrogen gas flow (100 mL min<sup>-1</sup>). Heating rate: 10 °C min<sup>-1</sup>.

small displacement of the ion's vibrations could suppress the decompositions of the ions.<sup>28</sup> Such a high thermal stability of PILs will be beneficial for durable high temperature DSSCs.

It is well known that the efficiency of the DSSC is critically dependent on the ion conductivity and diffusion coefficient of  $I_3^-$  of the electrolyte applied in the cell.<sup>40,41</sup> Fig. 3 shows the steady-state voltammograms of the ionic liquid and poly(IL) based electrolytes. The apparent diffusion coefficient of triiodide  $(D_{app}(I_3^-))$  was calculated from the anodic and cathodic steady-state  $I_{ss}$  by using the following equation:

$$I_{\rm ss} = 4nrFCD_{\rm app} \tag{2}$$

where *n* is the number of electrons per molecule, *F* is the Faraday constant, *r* is the radius of the ultramicroelectrode and *C* is the bulk concentration of the electroactive species.<sup>42,43</sup>

The calculated ionic conductivity and diffusion coefficient values of  $I_3^-$  are summarized in Table 1. It can be clearly seen that both the ionic conductivity and diffusion coefficient values of the poly[BVIm][HIm][TFSI]-based gel electrolyte are higher than those of the poly[BVIm][TFSI]-based gel electrolyte. The ionic conductivities were 6.76, 2.92 and  $5.83 \times 10^{-3}$  S cm<sup>-1</sup> and the diffusion coefficients of  $I_3^-$  were 4.05, 2.23 and  $3.93 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> for the ionic liquid, poly[BVIm][TFSI] and poly[BVIm][HIm] [TFSI] based electrolytes, respectively.



Fig. 3 Steady-state voltammograms of different electrolytes with a platinum ultramicro-electrode at a scan rate of 10 mV s<sup>-1</sup> at 25 °C.

It should be noted that the values of both the ion conductivity and diffusion coefficient of the poly[BVIm][HIm][TFSI] gel electrolyte are only a little lower than those of the ionic liquid based liquid electrolyte, however, they are much higher than those of poly[BVIm][TFSI]. It has been demonstrated that the  $\pi$ - $\pi$  stacked imidazolium rings of the PILs provide the charge transport from the counter electrode to the photoanode.24,44 However, the higher charge density of the dicationic poly(ILs) would lead to a higher ion conductivity, in which therefore  $I_3^$ and I<sup>-</sup> can move more freely than in monocationic poly(ILs).<sup>25</sup> In the case of dicationic poly(IL) units, two imidazolium cations were covalently attached to the polymer main chain. The weak interaction force between the alkyl chain and the imidazolium cation and the flexibility of the imidazolium cation enables the electron to be easily transferred in the electrolyte.<sup>24</sup> Thus, the ionic conductivity and diffusion coefficient of  $I_3^-$  in the poly [BVIm][HIm][TFSI]-based gel electrolyte still reached reasonable values.

Fig. 4a shows the J-V curves of the DSSCs fabricated with ionic liquid, poly[BVIm][TFSI] and poly[BVIm][HIm][TFSI] based electrolytes under simulated AM 1.5 solar spectrum illumination at 100 mW cm<sup>-2</sup>, respectively. The photovoltaic parameters including open circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ), fill factor (FF) and the photoelectric conversion efficiency ( $\eta$ ) of the DSSCs are summarized in Table 1 as well.

As it can be seen the electrochemical parameters of the devices containing poly(ILs) electrolytes decreased if compared with the ionic liquid electrolyte due to the limited transport property of the gel electrolytes. The increase in  $J_{sc}$  of the poly[BVIm][HIm] [TFSI]-based gel electrolyte is related to the improved diffusion coefficients of  $I_3^-$ , that the dye molecules could be regenerated more easily and the  $\pi$ - $\pi$  stacked imidazolium rings of poly [BVIm][HIm][TFSI] could provide the charge transport from the counter electrode to the photoanode.<sup>45,46</sup> The enhanced  $V_{\rm oc}$  is assigned from the suppression of the dark current at the TiO<sub>2</sub>/ electrolyte interface. The dark current originates from the reduction of  $I_3^-$  by conduction band electrons from TiO<sub>2</sub>.<sup>37</sup> As shown in Fig. 4b the onset of the dark current is shifted by approx. 31 mV from the poly[BVIm][HIm][TFSI] to the poly [BVIm][TFSI] based gel electrolyte. The lower dark current onset value indicates the lower  $I_3^-$  reduction rate ( $k_{et}$ ). The decrease of  $k_{\rm et}(I_3^{-})$  should lead to an increase of  $V_{\rm oc}$  according to the following equation:25

$$V_{\rm oc} = \frac{kT}{e} \ln \left( \frac{I_{\rm inj}}{n_{\rm cb} k_{\rm et} [I_3^-]} \right)$$
(3)

where  $I_{inj}$  is the flux of charge resulting from sensitized injection related to the electron back transfer rate,  $n_{cb}$  is the concentration of electrons at the TiO<sub>2</sub> surface and  $k_{et}$  is the rate constant for  $I_3^$ reduction. It is not surprising that the poly[BVIm][TFSI] based cell yielded the lowest  $V_{oc}$  due to its highest dark current. At the interface of the dye-coated TiO<sub>2</sub> photoanode and electrolyte, a higher diffusion coefficient of  $I_3^-$  to the Pt counter electrode for the I<sup>-</sup> form could also lead to a lower  $I_3^-$  reduction ( $k_{et}$ ) rate, restraining the dark current and obtaining a higher  $V_{oc}$ , as the described explanation. Furthermore, the diffusion of I<sup>-</sup> to the dye-coated TiO<sub>2</sub> photoanode is in favor of the regeneration of

Table 1	The performance of the DSSCs bas	d on different electrolytes under simulated AM	4 1.5 solar spectrum illumination at 100 mW cm <sup>-2</sup>
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Electrolyte <sup>a</sup>	Conductivity/ $10^{-3}$ S cm <sup>-1</sup>	$I_{\rm ss}({\rm I_3}^-)/10^{-7}~{\rm A}$	$D_{\rm app}({\rm I_3}^-)/10^{-6}~{\rm cm}^2~{\rm s}^{-1}$	V <sub>oc</sub> /V	$J_{\rm sc}/{ m mA}$ cm <sup>-2</sup>	FF	η
Ionic liquid electrolyte	6.76	1.56	4.05	0.695	12.93	0.702	6.31
poly[BVIm][TFSI]	2.92	0.86	2.23	0.645	10.72	0.690	4.77
poly[BVIm][HIm][TFSI]	5.83	1.52	3.93	0.676	12.92	0.678	5.92

<sup>*a*</sup> Ionic liquid electrolyte contains 0.1 M I<sub>2</sub>, 0.5 M NBB, and 0.1 M GNCS in a mixture of EMII/PMII/EMISCN (6:6:7, v/v/v). poly[BVIm][TFSI] and poly[BVIm][TFSI]-based gel electrolytes were prepared by dissolving the corresponding polymer (25 wt%) in the ionic liquid electrolyte.



Fig. 4 The J-V curves of the DSSCs assembled with different electrolytes (a) under simulated AM 1.5 solar spectrum irradiation at 100 mW cm<sup>-2</sup>; (b) in the dark. Cells were tested using a mask with an aperture area of 0.1 cm<sup>2</sup>.

dye for sustaining the operation. Therefore, the poly[BVIm] [HIm][TFSI] based cell shows a higher  $V_{\rm oc}$  (0.676 V) and a higher  $\eta$  (5.92%) in the polymer gel devices.

The incident photon-to-current conversion efficiency (IPCE) curves of these DSSCs are shown in Fig. 5. The maximum IPCE value at 530 nm is 78.41%, 55.08%, 67.72% for ionic liquid, poly[BVIm][TFSI] and poly[BVIm][HIm][TFSI] based electrolytes, respectively. The IPCE values of these devices are



Fig. 5 The IPCE curves of DSSCs based on different electrolytes.

consistent with the photoelectric conversion efficiency ( $\eta$ ). The photovoltaic performance parameters of the devices under different light intensity illuminations are also summarized in Table 2. The device containing the poly[BVIm][HIm][TFSI] gel electrolyte displays a maximum  $\eta$  of 6.47% under the simulated air mass 1.5 solar illumination with an intensity of 50 mW cm<sup>-2</sup>.

Electrochemical impedance spectroscopy (EIS) technique was used to reveal the appreciable difference in the charge transfer resistance at the conducting layer/TiO2, Pt/electrolyte, dye coated TiO<sub>2</sub>/electrolyte interface and diffusion of the  $I^{-}/I_{3}^{-}$ redox electrolyte, especially for understanding the recombination dynamics at the dye coated TiO<sub>2</sub>/electrolyte.<sup>47</sup> Fig. 6a shows the Nyquist plot of the ionic liquid electrolyte, poly[BVIm][TFSI] and poly[BVIm][HIm][TFSI] gel electrolyte based cells measured at -0.7 V bias in a dark environment and the values of resistance are listed in Table 3. From high to low frequency, three semicircles are observed in the Nyquist plots.  $R_1$ ,  $R_2$  and  $R_3$  represent the charge-transfer resistance at the counter electrode, the resistance of the TiO<sub>2</sub>/FTO, TiO<sub>2</sub>/electrolyte interface and the Nernst diffusion in electrolyte, respectively. The dark reaction impedance of the intermediate frequency semicircle in the Nyquist plot revealed the electron recombination at the dye coated TiO<sub>2</sub> electrode/electrolyte interface which was caused by the conduction band electrons of the mesoscopic TiO<sub>2</sub> electrode captured by the  $I_3^-$  ions. The bigger the diameter of the middle frequency semicircle is, the slighter the charge recombination at the dye-coated TiO<sub>2</sub> photoanode/electrolyte interface is.<sup>21,36</sup> The charge-transfer resistance  $(R_2)$  values of the poly[BVIm][TFSI] and poly[BVIm][HIm][TFSI] based gel electrolytes were calculated to be 65.3 and 74.8  $\Omega$ , respectively, indicating that the charge-transfer resistance  $(R_2)$  at the dye-coated TiO<sub>2</sub> photoanode/electrolyte interface of the poly[BVIm][HIm][TFSI] gel electrolyte cell increased, reducing the charge recombination at the dye-coated TiO<sub>2</sub> photoanode/electrolyte interface due to the enhanced charge transport properties of an  $I^{-}/I_{3}^{-}$  redox couple in the gel electrolyte.

 Table 2
 The PCE values of DSSCs based on different electrolytes under simulated AM 1.5 solar irradiation

	PCE under different incident light intensities irradiation				
Electrolyte	1.0 sun	0.5 sun	0.15 sun		
lonic liquid electrolyte poly[BVIm][TFSI] poly[BVIm][HIm][TFSI]	6.31% 4.77% 5.92%	6.87% 5.14% 6.47%	6.33% 4.86% 6.03%		



**Fig. 6** The EIS Nyquist plots (a) and Bode phase plots (b) in the dark for DSSCs based on different electrolytes.

 Table 3
 The parameters obtained by fitting the EIS of the DSSCs fabricated with the different electrolytes

Device	$R_1/\Omega$	$R_2/\Omega$	$R_3/\Omega$	$f_{\rm max}/{\rm Hz}$	τ <sub>e</sub> /ms
Ioinc liquid electrolyte	4.2	100.7	14.3	5.486	29.01
poly[BVIm][TFSI]	3.8	65.3	23	9.766	16.30
poly[BVIm][HIm][TFSI]	3.7	74.8	18.5	6.643	23.96

Fig. 6b shows the Bode phase plots of EIS spectra display the characteristic frequency peaks of the charge transfer process for all the cells. The effective lifetime of the electrons ( $\tau_e$ ) before



Fig. 7 Time-course variation of the normalized efficiency for the DSSCs during accelerated aging tests at  $60 \,^{\circ}$ C.

recombination in the  $TiO_2$  photoelectrode can be related to the inverse of the characteristic frequency and is estimated by the following equation:<sup>48</sup>

$$\tau_{\rm e} = \frac{1}{\omega_{\rm max}} = \frac{1}{2\pi f_{\rm max}} \tag{4}$$

where  $f_{\text{max}}$  is the maximum frequency of the low-frequency peak. The maximum frequency of the middle-frequency peak ( $f_{\text{max}}$ ) and the lifetime of electrons are also summarized in Table 3. The electron lifetime for recombination ( $\tau_e$ ) for an ionic liquid electrolyte-based cell gives the highest value of 29.01 ms, while the poly[BVIm][TFSI]-based cell shows the lowest value of 16.30 ms, and the poly[BVIm][HIm][TFSI]-based cell gives a value of 23.96 ms. Compared with the poly[BVIm][TFSI]-based cell, the poly[BVIm][HIm][TFSI]-based cell yields a longer electron recombination lifetime, which favors the electron transport through a longer distance with less diffusive hindrance and finally leading to enhanced photoconversion efficiency.<sup>7</sup>

The long-term stability of the fabricated DSSCs was investigated via an accelerating aging test of sealed devices. The cells were covered with a UV cutoff filter, put on a magnetic heater at 60 °C and were irradiated at open circuit under one sun visiblelight soaking. The total efficiencies were normalized to the values measured on the first day, as shown in Fig. 7. During the first several days, the efficiency of all the cells was enhanced due to the increased regeneration rate of the dye.9 It should be noted that both the poly(IL) electrolytes exhibit superior long-term stability than the ionic liquid electrolyte because the gel network hindered the leakage of the liquid electrolyte effectively. The poly[BVIm] [HIm][TFSI] based cell retains about 96% of the initial efficiency even after a test of about 1200 h, which is slightly higher than the poly[BVIm][TFSI] based cells (~92% of the initial efficiency). This is probably because poly[BVIm][HIm][TFSI] is more thermal stable than poly[BVIm][TFSI]. However, the ionic liquid electrolyte based cells only retain  $\sim$ 73% of their initial efficiency, which might be due to the possible electrolyte leakage. These results indicate that the quasi-solid-state DSSCs based on poly [BVIm][HIm][TFSI] gel electrolyte have an excellent long-term stability.

## Conclusions

In summary, bis-imidazolium based dicationic poly[BVIm][HIm] [TFSI] electrolytes have been prepared and employed for the fabrication of organic solvent free quasi-solid-state DSSCs. The resultant device shows an efficiency of 5.92% under the simulated air mass 1.5 solar spectrum illumination at 100 mW cm<sup>-2</sup>, which is higher than that of the monocationic poly[BVIm][TFSI]-based gel electrolyte. Furthermore, the poly[BVIm][HIm][TFSI] gel electrolyte exhibits a superior long-term stability than ionic liquid-based liquid electrolyte and monocationic poly(IL) gel electrolyte. These results offer us a feasible method to quasisolid-state DSSCs in future practical applications.

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