

Electronics Supporting Information  
For

## Efficient monolithic quasi-solid-state dye-sensitized solar cells based on poly(ionic liquids) and carbon counter electrodes

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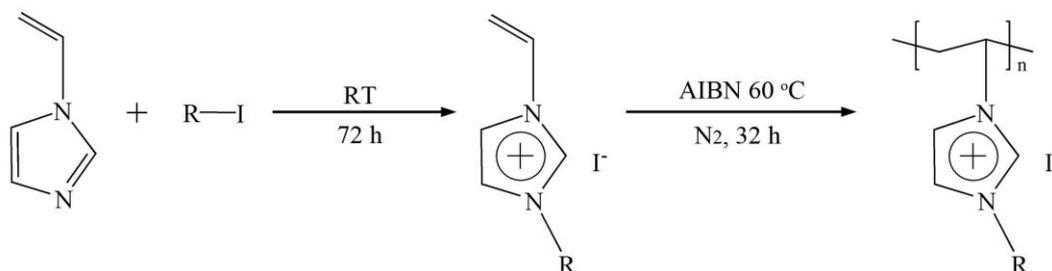
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### 1. Experimental details

#### 1.1. Materials

Iodoethane, 1-iodopropane, 1-iodobutane, 1-iodohexane and 1-vinylimidazole were purchased from Sigma-Aldrich. Azobisisobutyronitrile was purchased from Sinopharm Chemical Reagent Co., Ltd, China. The solvents were purchased from DIKMA Technologies Company and used as purchased. Transparent conductive glass (F-doped SnO<sub>2</sub>, FTO, TEC-15, Pilkington, USA) was used as the substrate for the fabrication of working electrode. Colloidal anatase TiO<sub>2</sub> paste (PASOL HPW-18NR) was obtained from JGC Catalysts and Chemicals Ltd., Japan. The ZrO<sub>2</sub> paste and carbon paste were prepared as we reported previously.<sup>1</sup>

#### 1.2. Synthesis of poly(1-alkyl-3-vinylimidazolium iodide) (PAVII)



Scheme S1 The preparation process of AVII and PAVII

The preparation process of PAVII was shown in Scheme S1. Alkyl iodide (0.102 mol) and 1-vinylimidazole (8 g, 0.085 mol) were dissolved in 20 ml acetonitrile and the mixture was stirred at room temperature for 72 h. Then the reaction mixture was reprecipitated in diethyl ether (200 ml, three times) and dried in a vacuum oven at 60 °C for 24 h to produce ionic liquid (IL) monomer (AVII, coded a, b, c and d, as shown in Fig. S1). <sup>1</sup>H NMR data of 1-propane-3-vinylimidazolium iodide (PVII, monomer c) (CD<sub>3</sub>CN, 600 MHz): δ=9.39(s, 1H), 7.83(s, 1H), 7.61(s, 1H), 7.23-7.27(m, 1H), 5.90-5.93(m, 1H), 5.40-5.42(m, 1H), 4.22(t, 2H), 1.90-1.94(m, 2H), 0.95(t, 3H).

Ionic liquid monomer (5 g), azobisisobutyronitrile (AIBN, 50 mg) and acetonitrile (10 ml) were charged into a reaction tube. The tube was tightly sealed and purged with nitrogen gas. Then, the tube was immersed in an oil bath at 60 °C for 32 h for polymerization. The product of poly(ionic liquid) (PIL) was reprecipitated with diethyl ether and finally dried in a vacuum oven at 60 °C for 24 h. The structure of PAVII (coded A, B, C and D) was also shown in Fig. S1. Gel Permeation Chromatography (GPC) data:  $M_n=1.250 \times 10^4$  g/mol;  $M_w=1.282 \times 10^4$  g/mol; D=1.026.

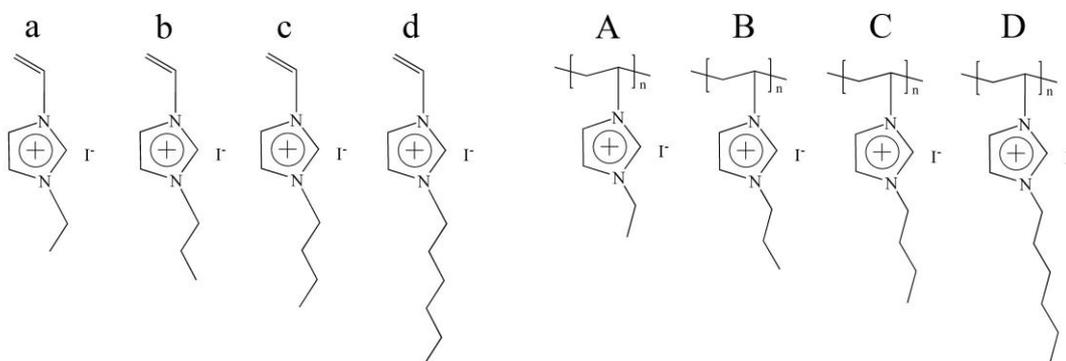


Fig. S1 Chemical structures of AVII (a, b, c and d) and PAVII (A, B, C and D)

For the liquid-state electrolyte (LE), PAVII was dissolved in acetonitrile with a concentration of 0.4 M. For the quasi-solid-state electrolyte (QE), poly(1-propane-3-vinylimidazolium iodide) (PPVII) was dissolved in acetonitrile with a weight ratio of 1:1. Fig. S2 shows the digital images of QE (left) and LE (right).

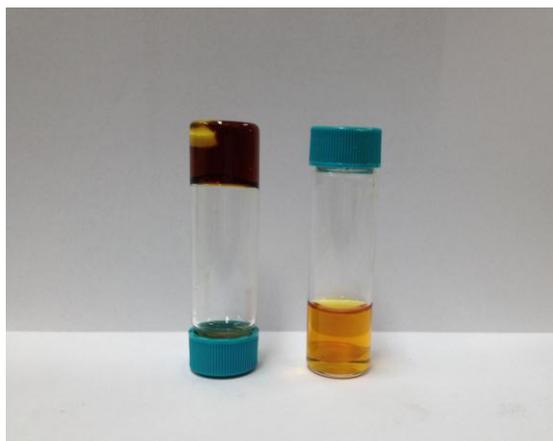


Fig. S2 Digital images of QE (left) and LE (right)

### ***1.3. Fabrication of the monolithic DSSCs***

Based on monolithic structure, electrodes of 20 cells (4×5) were constructed on a single glass substrate.<sup>2</sup> After the pre-treatment of the glass substrate including the laser structuring of the FTO layer and the washing of the glass, a dense TiO<sub>2</sub> layer was deposited on the glass substrate by spray pyrolysis deposition with di-isopropoxytitanium bis(acetyl acetonate) solution. Then a 12 μm nanoporous TiO<sub>2</sub> layer, a 3 μm ZrO<sub>2</sub> layer, and a 30 μm carbon layer were screen-printed on the substrate layer by layer. The TiO<sub>2</sub> layer and ZrO<sub>2</sub> layer were sintered at 500 °C for 30 min, and the carbon layer was sintered at 400 °C for 30 min. After cooling to 80 °C, the substrate was immersed in the acetonitrile and tert-butyl alcohol mixed solution (volume ratio, 1:1) containing 0.5 mM N719 at room temperature for about 24 h.

After dye application, the glass substrate was cut into 20 individuals for further processing. For the LE based device, a sheet of normal glass was placed on the top of the carbon counter electrode, and a hot-melt film was used to seal them together by pressing them under heat. The LE was injected into the interspace between the glass substrate and normal glass sheet through the hole predrilled on the glass sheet. Finally, the hole was sealed with a hot-melt film covered with a thin glass slide under heat. For the QE based devices, a thin layer of the gel electrolyte was spread on the top of the carbon counter electrode using a razor blade, and then a glass sheet was placed onto the gel film. To obtain a complete nanopore filling for the QE, a vacuum condition was applied.<sup>3</sup> Finally, an adhesive was employed to fix and seal the cell.

#### **1.4. Characterization**

The ionic conductivity ( $\sigma$ ) of the electrolyte was measured using the Pt/electrolyte/Pt sandwich type electrode structure. A potentiostat (EG&G, M2273, USA) was applied to measure the impedance (Nyquist plot) of the electrolyte. A perturbation voltage of 10 mV was applied over the frequency range 40 Hz to 1 MHz. The ionic conductivity was calculated by the following equation:

$$\sigma = \frac{L}{AR_b}$$

Here  $L$  is the distance between the Pt electrodes and  $A$  is the area of the electrode. The resistance ( $R_b$ ) is taken at the intercept of the Nyquist plot with the real axis.

Photocurrent density–voltage characteristics were measured with a Keithley 2400 source meter under illumination with an Oriel solar simulator composed of a 1000 W xenon arc lamp and AM 1.5 G filters. Light intensity was calibrated with a normative

silicon cell. The area of cell was  $0.8 \text{ cm} \times 0.8 \text{ cm}$  and the active area for the photocurrent density–voltage characteristics was fixed to  $0.13 \text{ cm}^2$  with a mask. The EIS measurements were carried out by using a potentiostat (EG&G, M2273) with applying bias of the open circuit voltage ( $V_{oc}$ ) under dark condition. The frequency range analyzed was 0.1 Hz to  $10^6$  Hz with ac amplitude of 10 mV. Fourier-transform infrared (FT-IR) spectra were recorded on a Vertex 70 FTIR spectrometer in the range of 4000 to  $400 \text{ cm}^{-1}$ . Thermogravimetric (TG) analysis was performed at a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$  under nitrogen flow. Gel permeation chromatography (GPC) was performed in DMF (containing 0.1% LiBr) at a flow rate of 0.83 ml/min at  $50 \text{ }^\circ\text{C}$ .

## 2. Comparison of the conductivity of IL and PIL solution

**Table S1** Conductivity of IL and PIL solution (0.4 M)

IL	$\sigma/\text{mS cm}^{-1}$	PIL	$\sigma/\text{mS cm}^{-1}$
a	0.82	A	1.145
b	0.99	B	1.611
c	1.06	C	1.864
d	1.06	D	1.932

## 3. EIS data of LE and QE based devices

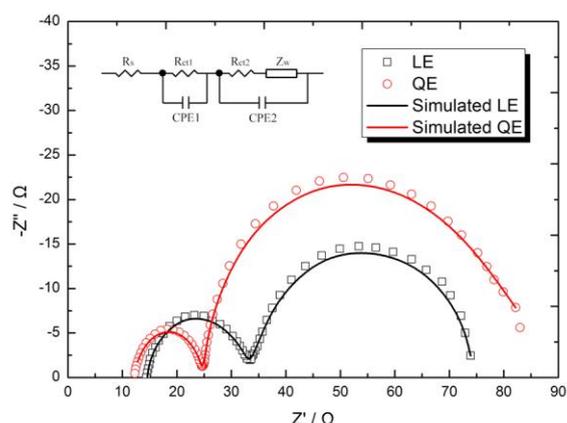


Fig. S3 Electrochemical impedance spectra (EIS) of the devices using LE and QE in the dark with applying a bias of the open circuit voltage. The Nyquist plots are from EIS measurements and the solid lines are the fitted curves.

#### 4. References for supporting information

1. G. Liu, H. Wang, X. Li, Y. Rong, Z. Ku, M. Xu, L. Liu, M. Hu, Y. Yang, P. Xiang, T. Shu, H. Han, *Electrochimica Acta*, 2012, **69**, 334; H.W. Han, U. Bach, Y.B. Cheng, R.A. Caruso, C. MacRae, *Applied Physics Letters*, 2009, **94**, 103102.
2. Y.G. Rong, H.W. Han, *J. Nanophotonics*, 2013, **7**, 073090-1.
3. H.W. Han, U. Bach, Y.B. Cheng, R.A. Caruso, *Applied Physics Letters*, 2007, **90**, 213510.