

An iodine-free electrolyte based on Ionic liquid polymer for all-solid-state dye-sensitized solar cells

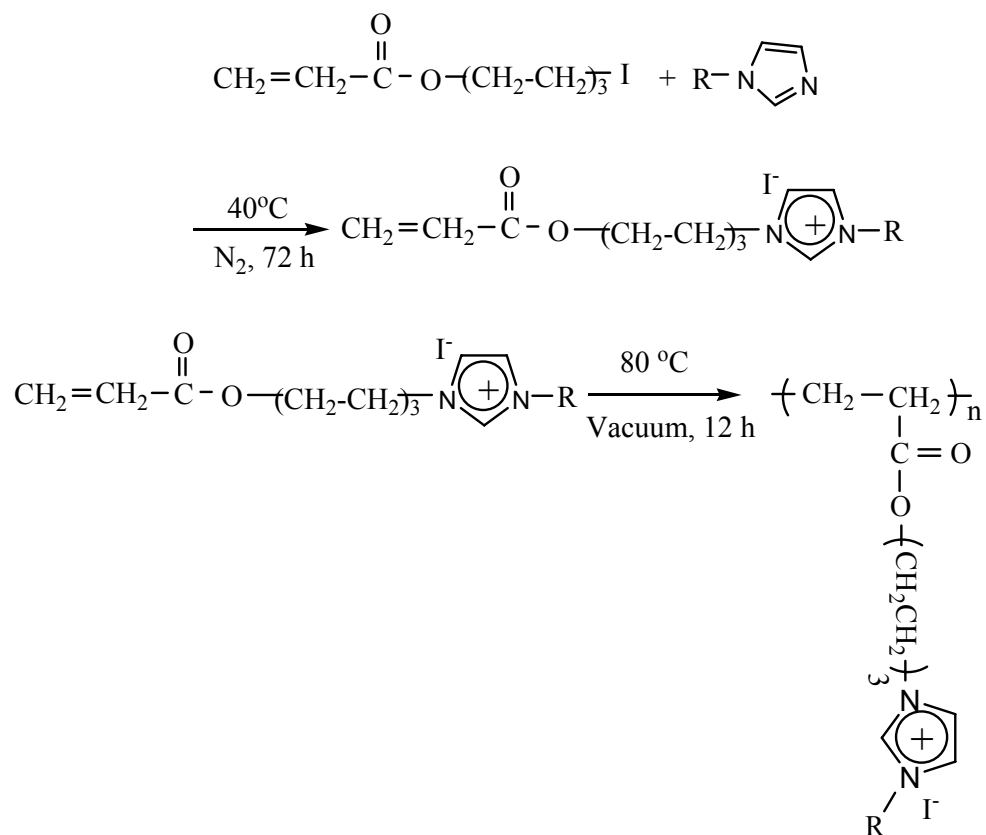
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1 The preparation process of PAAII

The preparation process of PAAII was shown in Scheme S1. 1-iodohexyl-6-acrylate was reacted with one and half molar amount of N-alkylimidazole at 40 °C under dry N₂ atmosphere for 72 h. The products were washed three times with diethyl ether. Then ionic liquid monomers, 1-alkyl-3-(acryloyloxy)hexylimidazolium iodide, were obtained. PAAII were synthesized by a thermal bulk polymerization of ionic liquid monomer at 80 °C for 12 h under vacuum condition.



Scheme S1 The preparation process of PAAII

2 The temperature dependence of the ionic conductivity of PAAII

The temperature dependence of the ionic conductivity for PAAII is shown in Fig. S1. All samples show Arrhenius behavior in the observed temperature range. The ionic conductivity of polymer A, B, C and D at room temperature are $1.55 \times 10^{-4} \text{ Scm}^{-1}$, $3.63 \times 10^{-4} \text{ Scm}^{-1}$, $0.72 \times 10^{-4} \text{ Scm}^{-1}$ and $0.39 \times 10^{-4} \text{ Scm}^{-1}$, respectively.

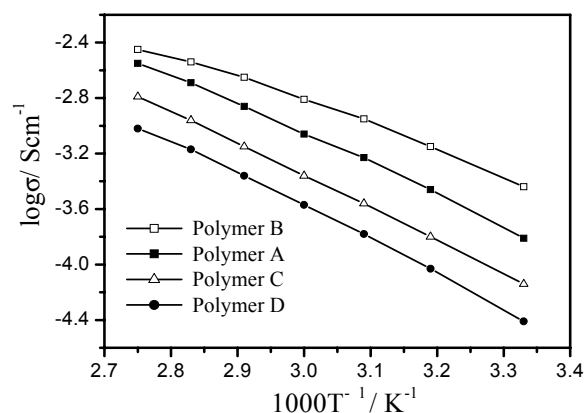


Fig. S1 Ionic conductivity-temperature plot of PAAII

2 The dark current of dye-sensitized solar cells (DSCs) with PEAII electrolyte containing various amount of iodine

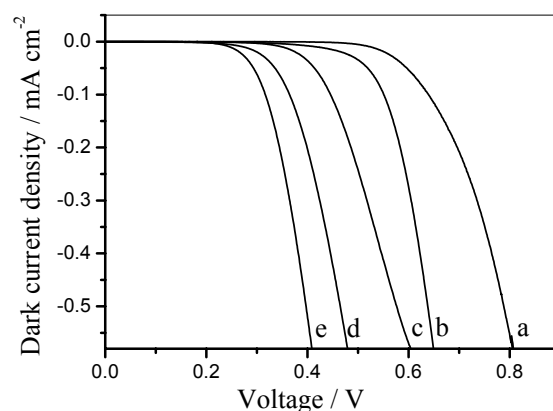


Fig. S2 Dark current-voltage curves of all-solid-state DSCs with PEAII electrolyte containing various amounts of iodine (a: 0; b: 3 wt%; c: 5 wt%; d: 10 wt%; e: 15 wt%)

Fig. S2 shown the current-voltage characteristics of all-solid-state DSCs with PEAII electrolyte in the dark. It can be seen that the dark current of the cell increase with increasing in the content of iodine in electrolyte. The photovoltaic performance of DSCs is kinetically limited by the dark reaction occurring in the photoelectrochemical system, where the electrons from the conductive band of TiO_2 recombine with the oxidized species (here, it is triiodide) of the redox couple according to $\text{I}_3^- + 2\text{e}^- (\text{TiO}_2 \text{ CB}) \rightarrow 3\text{I}^-$. An increase of the content of iodine in electrolyte leads to an increase in the concentration of I_3^- and then accelerates the capture of conductive band electrons. Thus, the dark current in DSCs increase with the increasing in the content of iodine.

3 The photoluminescence excitation and emission spectrum for PEAII

Fig. S3 show the photoluminescence excitation and emission spectrum for PEAII. The Stokes shift is 288 nm. The large stokes shift implies the existence of π - π stacking interaction in PEAII (*B. S. Nehls et al. Org. Biomol. Chem.*, 2005, 3:3213).

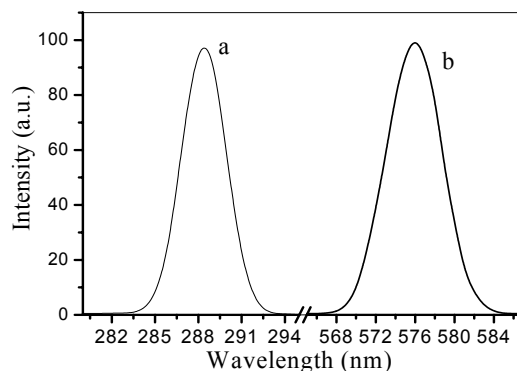


Fig. S3 The photoluminescence excitation (a) and emission (b) spectrum for PEAI

4 Chemical structure of the PEAI chain

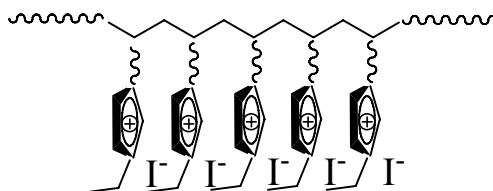


Fig. S4 Chemical structure of the PEAI chain

5 Electrochemical impedance spectroscopy measurement of all-solid-state DSCs with PEAI electrolyte

Electrochemical impedance spectroscopy measurement was performed with a Solartron 1287 electrochemical interface system equipped with a Solartron 1255B frequency response analyzer within the frequency range from 0.01-10⁶ Hz in the dark. The magnitude of the alternative signal was 10 mV.

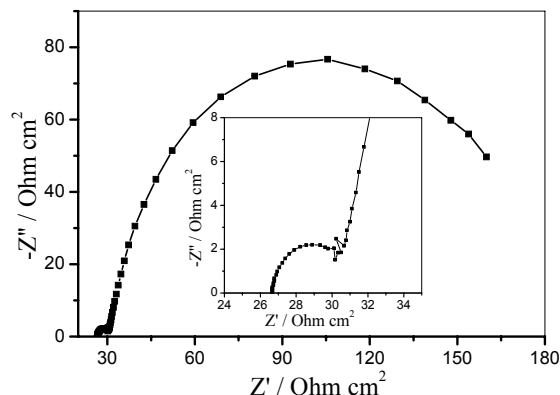


Fig. S5 Nyquist plot of all-solid-state DSCs with PEAI electrolyte in the dark. The inset is expanded range of the ordinate and abscissa in high-frequency part.

Electrochemical impedance spectroscopy is a useful tool to analyze the ionic and electronic processes occurring in DSCs. The Nyquist plot for a DSC usually exhibits three semicircles in the frequency range of 0.01-10⁶ Hz, which are attributed to Nernst

diffusion within the electrolyte, the electron transfer at the TiO₂ photoanode/electrolyte interface and the redox reaction at the counter electrode in the order of increasing frequency. Fig. S5 shows two semicircles in the Nyquist plot of all-solid-state DSC with PEAI electrolyte. The small semicircle in high frequency is attributed to the charge-transfer process at the PEAI/counter electrode interface, and the big one is attributed to the electron transfer at the TiO₂/PEAI electrolyte interface. The Nernst diffusion impedance for charge transport in PEAI electrolyte is not directly observed due to a slower recombination reaction at the TiO₂ photoanode/PEAI electrolyte interface. The charge-transfer resistance (R_{ct}) at PEAI/counter electrode interface determined from the diameter of the semicircle in high frequency (see the inset in Fig. S5) is 4.5 $\Omega\text{ cm}^2$. This tiny R_{ct} means that the charge transfer at the PEAI/counter electrode interface is facile.