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Supplementary Information

Electrospun Membranes of Imidazole-Grafted PVDF-HFP Polymeric Ionic Liquids for Highly Efficient Quasi-Solid-State Dye-Sensitized Solar Cells

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12 Preparation of home-made TiO₂ paste

13 A home-made paste for scattering TiO_2 layer was made by several steps as follow. (1) The TiO_2 14 nanocrystal solution was synthesized via mixing 0.5 M titanium (IV) isopropoxide (TTIP) in 15 0.1 M nitric acid aqueous solution and then heating to 88 °C for 8 h. (2) After cooling down, the solution was put into an autoclave (PARR 4540, USA) and heated up to 240 °C for 12 h. 16 17 (3) Subsequently, the autoclaved TiO_2 colloid was concentrated to contain 8 wt% of TiO_2 nanoparticles. (4) With respect to the weight of TiO₂ nanoparticles, the 25 wt% of poly(ethylene 18 19 glycol) (PEG, MW~20,000) and 100 wt% of ST-41 (average diameter ~ 200 nm, Ishihara Sangyo, Ltd., Japan) were added to obtain the scattering paste. 20

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22 Analytical technique

The molecular structures of the synthesized polymeric ionic liquids were confirmed by ¹H and
 ¹³C nuclear magnetic resonance (NMR, Varian Unity plus, 400MHz) spectroscopy; both spectra

were obtained using the polymer sample dissolved in the solvent of dimethyl sulfoxide (DMSO-1 d₆). Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum 100) and the 2 thermogravimetric analysis (TGA, PerkinElmer, Pyris 1) were performed using directly the 3 polymer samples. Gel permeation chromatograph (GPC) has been carried out to evaluate the 4 increase in polymer unit of PFII PILs with a Viscotek GPC system (Malvern, UK, column 300 5 \times 810 mm, flow rate of 1 ml/min, temperature of the column set to 60 °C, DMF with 0.02 M 6 LiBr as solvent, polypropylene (PP) as standard). Field-emission scanning electron microscopy 7 (FE-SEM, Nova NanoSEM 230, FEI, Oregon, USA) was used to observe the surface 8 morphology of the electrospun polymer membrane. X-ray diffraction (XRD, X'PERT) analysis 9 10 and Raman spectroscopy (Thermo, Nicolet Almega XR; Microscope: Olympus, BX51; Laser: 11 780 nm, 100 mW) were conducted using the PFII and PVDF-HFP membranes to investigate the influence of imidazolium on the crystallinity. 12

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Linear sweep voltammetry (LSV), cyclic voltammetry (CV) and electrochemical impedance 14 spectra (EIS) technique were performed via a potentiostat/galvanostat (PGSTAT 30, Autolab, 15 Eco-Chemie, the Netherlands) equipped with an FRA2 module between 10 mHz to 65 kHz. A 16 dummy cell with a structure of FTO/Pt/soaked PFII membrane/Pt/FTO was used, where the 17 18 soaked **PFII** membrane was prepared as mentioned above by soaking the membrane into the liquid electrolyte (0.6 M DMPII, 0.035 M I₂, 0.1 M GuSCN, and 0.5 M tBP in MPN/ACN, at 19 the volume ratio of 1:1). In the case of the EIS analysis for measuring the ionic conductivity 20(σ), a standard sodium chloride (NaCl, Orion 011006, Thermo Scientific, $\sigma = 12.9$ mS cm⁻¹) 21 solution was used to obtain the constant of cell gap/active area (d/A) for the dummy cell. The 22 impedance spectra were obtained between 10 mHz to 65 kHz, under the open-circuit condition, 23 with an AC amplitude of ± 10 mV. The cyclic voltammetry curve was obtained at a scan rate of 24 100 mV s⁻¹, in a three-electrode electrochemical system, with Ag/Ag⁺ electrode as the reference 25 26 electrode, platinum-coated FTO prepared via a simple sputtering deposition technique as the working electrode, and a Pt foil as the counter electrode. The **PFII** membranes were absorbed
 with liquid electrolyte composed of 0.01 M LiI, 0.001 M I₂ and 0.1 M LiClO₄ in ACN and used
 as the QSS electrolyte for CV measurement.

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The photovoltaic data of the DSSC (J-V curves as well as the long-term stability) were collected 5 by the same potentiostat/galvanostat under 1 Sun illumination (AM 1.5G, 100 mW cm⁻²) using 6 a class A quality solar simulator (XES-301S, AM1.5G, San-Ei Electric Co. Ltd., Osaka, Japan). 7 The incident light intensity was calibrated with a standard Si cell (PECSI01, Peccell 8 Technologies, Inc., Kanagawa, Japan). The interfacial properties of a DSSC were measured by 9 10 the above-mentioned EIS technique and transient absorption spectroscopy (TAS, LP 908, 11 Edinburgh Instruments). Pulsed laser excitation was applied using Spectra Physics Quanta-Ray INDI-Series Pulsed Nd: YAG lasers (λ =355 nm, 10 Hz repetition rate); the analyzer light was 12 13 produced by a 150 W Xenon probe source and was detected by a TMS302A type detector using an excitation beam at 540 nm. The data for the TAS measurement were collected at 760 nm in 14 the time scale of $t > 10 \mu s$. 15



2 Figure S1 ¹³C Nuclear magnetic resonance spectra for (a) the PFII-based polymeric ionic
3 liquid (b) PVDF-HFP.



2 3 Figure S2¹H Nuclear magnetic resonance spectra for (a) the PFII-based polymeric ionic liquid (b) PVDF-HFP.



3 Figure S3 Gel permeation chromatography (GPC) curves of pristine PVDF-HFP as well as
4 PFII PILs.

3 Figure S4 a) The XRD analysis and b) the Raman spectroscopy for the PVDF-HFP and
4 polymeric membranes of PFII-F, PFII-E, and PFII-S.

3 Figure S5 Thermogravimetric analytic spectra for the polymers of pristine PVDF-HFP,
4 intermediate 1, intermediate 2, and final PFII.

- 3 Figure S6 Field-emission scanning electron microscopy images for the cross-section of
- 4 polymer membrane of (a) **PFII-F**, (b) **PFII-E**, (c) **PFII-S** and (d) PVDF-HFP.

Figure S7 a) Linear sweep voltammetry curves, obtained at a scan rate of 100 mV s⁻¹ and b)
electrochemical impedance spectra for the dummy cells with a structure of
FTO/Pt/electrolyte/Pt/FTO, where the liquid and the soaked PFII membrane are individually
used as the electrolyte.

Figure S8 The cyclic voltammetry curve, obtained at a scan rate of 100 mV s⁻¹, in a three
electrode electrochemical system, where the liquid and the soaked PFII membrane are used as
the electrolyte respectively.

3 Figure S9 The photocurrent density-voltage curve of the DSSC with the electrolyte of the
4 pristine PVDF-HFP membrane soaked with liquid electrolyte.

1 Table S1 The compositions of the precursors for the synthesis of these PFII polymeric ionic

2 liquids.

PIL ^a	Precursors				Molar ratio of
	PVDF-HFP ^b	CAAm ^c	BIm ^d	KIe	BIm/PVDF-HFP ^f
PFII-F	20 g	4.4 g (47.0 mmol)	2.9 g (23.5 mmol)	7.8 g (47.0 mmol)	1:4
PFII-E	20 g	2.2 g (23.5 mmol)	1.5 g (11.8 mmol)	3.9 g (23.5 mmol)	1:8
PFII-S	20 g	1.1 g (11.8 mmol)	0.8 g (5.9 mmol)	2.0 g (11.8 mmol)	1:16

3 a) Polymeric ionic liquid; b) Poly(vinylidene fluoride-co-hexafluoropropylene), 20 g of PVDF-

4 HFP equals to 94.0 mmol of monomer; ^{c)} 2-chloroacetamide; ^{d)} 1-butylimidazole; ^{e)} potassium

5 iodide; ^{f)} polymers containing different molar ratios of BIm/PVDF-HFP are denoted as **PFII-F**

6 (1/4, one forth), **PFII-E** (1/8, one eighth), and **PFII-S** (1/16, one sixteenth).

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8 Table S2 Molecular weights of pristine PVDF-HFP and PFII polymeric ionic liquids.

	$M_{\rm w}$ (g/mol)	$M_{\rm n}$ (g/mol)
PVDF-HFP	5161	5108
PFII-F	6977	6921
PFII-E	5887	5704
PFII-S	5333	5139

⁹

10 Table S3 Electrochemical parameters for the liquid and PFII–based polymeric ionic liquids.

Electrolyte	$J_{\rm pc}$ (mA cm ⁻²)	$E_{1/2}$ (V) vs. Ag/Ag ⁺
Liquid	2.48	-0.07
PFII-F	2.48	-0.07
PFII-E	2.34	-0.07
PFII-S	1.43	-0.07

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