

Electronic Supplementary Information

Benzimidazolyl Functionalized Ionic Liquids as an Additive for High Performance Dye-Sensitized Solar Cells

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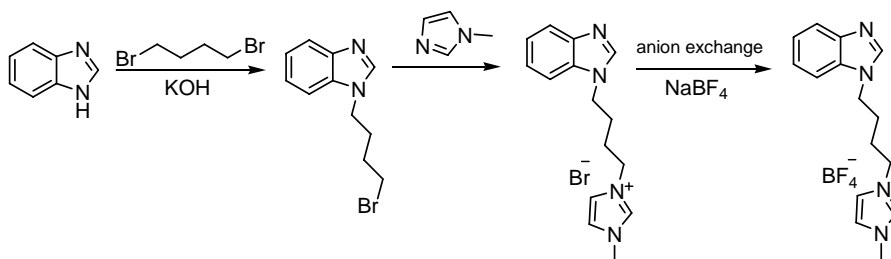
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10 1. Chemicals

Benzimidazole, 1-methylimidazole, 1,4-dibromobutane, sodium tetrafluoroborate (NaBF_4), lithium iodide, *tert*-butyl alcohol were purchased from Alfa Aesar and used as received. N-butylbenzimidazole (NBB), 4-*tert*-butylpyridine (TBP), and iodine (I_2) were purchased from Fluka. TiCl_4 and H_2PtCl_6 were purchased from Aldrich. *cis*- $\text{RuLL}'(\text{SCN})_2$ ($\text{L}=4,4'$ -dicarboxylic acid-2,2'-bipyridine, $\text{L}'=4,4'$ -dinonyl-2,2'-bipyridine) (Z907) was purchased from Solaronix SA (Switzerland) and used without any further purification. Fluorine-doped tin oxide overlayer (FTO) glass electrodes ($10 \Omega/\text{Sq}$), slurries containing 20-nm-sized mesoporous and 200-nm-diameter light-scattering TiO_2 colloidal were purchased from Dalian Hepat Chroma Solar Tech. Co., Ltd (China). 1,3-Dimethylimidazolium iodide (DMII), 1-ethyl-3-methylimidazolium iodide (EMII), 20 1-ethyl-3-methylimidazolium tetracyanoborate (EMITCB), guanidinium thiocyanate (GSCN) and 1, 2-dimethyl-3-propylimidazolium (DMPII) were purchased from Merck.

2. Synthesis of benzimidazolyl functionalized ionic liquids



Scheme S1. Synthetic procedures for the preparation of benzimidazolyl functionalized ionic liquids.

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2.1 Synthesis of N-(4-bromobutyl) benzimidazole.

To a stirred solution of benzimidazole (4.73g, 40 mmol) and 1, 4-dibromobutane (43.18g, 200 mmol) in 80 mL of DMF was added ground power KOH (4.48g, 80 mmol). The mixture was continued for 5 h at 0 °C. Water (120 mL) was added and the product was extracted into ether (4 × 50 mL). The ether extracts were washed with H₂O, dried (MgSO₄), and evaporated. The compound was chromatographed on silica gel with CHCl₃/CH₃OH (12:1 v/v) to give 6.5g N-(4-bromobutyl) benzimidazole (yield: 64%, yellow viscous oil). ¹HNMR (400 MHz, CDCl₃): 7.91 (s, 1H), 7.82 (dd, 1H), 7.41 (dd, 1H), 7.28-7.32 (m, 2H), 4.23 (t, 2H), 3.40 (dd, 2H), 2.08 (m, 2H), 1.88 (m, 2H).

2.2 Synthesis of 3-(4-(benzimidazolyl)butyl)-1-methylimidazolium bromide ([BMImB]Br)

10 [BMImB]Br was synthesized and prepared as follow.^[S1] The mixture of excess 1-methylimidazole (8.12 g, 100 mmol) and N-(4-bromobutyl) benzimidazole (5.06 g, 20 mmol) in 20 ml CH₃OH was stirred at 50 °C for two days and then cooled down. After the evaporation of the solvent, the crude product was washed with heated ethyl acetate several times and then washed with diethyl ether at room temperature to provide 5.16 g yellow viscous oil (yield: 77%, yellow viscous oil). ¹HNMR (400 MHz,
15 DMSO-d₆): 9.09 (s, 1H), 8.25 (dd, 1H), 7.74 (s, 1H), 7.69 (s, 1H), 7.63 (m, 2H), 7.23 (m, 2H), 4.30 (t, 2H), 4.20 (t, 2H), 3.83 (s, 3H), 1.78 (m, 2H). Formula mass: 335.24. Microanalysis Calcd.: C, 53.74%; H, 5.72%; N, 16.72%. Found: C, 53.71%; H, 5.77%; N, 16.66%.

2.3 Synthesis of 3-(4-(benzimidazolyl)butyl)-1-methylimidazolium tetrafluoroborate ([BMImB]BF₄)

20 Anion-exchange of [BMImB]Br with superfluous NaBF₄ aqueous solution was utilized to produce 3-(4-(benzimidazolyl)butyl)-1-methylimidazolium tetrafluoroborate ([BMImB]BF₄).^[S1] In a typical experimental procedure, 3.35 g (10 mmol) [BMImB]Br was added to 1.43 g (13 mmol) sodium tetrafluoroborate solution. The mixture was stirred at room temperature for 24 hr. The resulting yellow solid of 3-(4-(benzimidazolyl)butyl)-1-methylimidazolium tetrafluoroborate ([BMImB]BF₄) was
25 filtered and washed with cold water several times and then dried at 80 °C for 24 h in a vacuum oven

(Yield: 60%). ^1H NMR (400 MHz, DMSO- d_6): 9.05 (s, 1H), 8.23 (dd, 1H), 7.72 (s, 2H), 7.68 (s, 1H), 7.62 (t, 1H), 7.24 (m, 2H), 4.29 (m, 2H), 4.19 (m, 2H), 3.82 (s, 3H), 1.78 (m, 4H). Formula mass: 34.14. Microanalysis Calcd.: C, 52.65%; H, 5.61%; N, 16.38%. Found: C, 52.58%; H, 5.68%; N, 16.30%. The bromide content via anion chromatography was \sim 10 ppm.

5 3. Device fabrication

The fabrication of DSSCs was assembled reported previously.^[S2,S3] The cleaned FTO glass was covered at two parallel edges with an adhesive tape to control the thickness of mesoporous TiO_2 film. Two layers of TiO_2 particles were deposited onto cleaned FTO glass and used as photoelectrodes. A 10- μm -thick film of 20-nm-sized TiO_2 particles was deposited onto the FTO glass electrode by the doctor-blade technique. The film was dried at 125 $^\circ\text{C}$ 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_2 layer. The resulting TiO_2 films were annealed at 500 $^\circ\text{C}$ for 15 min. After cooling to 80 $^\circ\text{C}$, the obtained TiO_2 electrode was immersed in 0.3 mM solution of Z907 in acetonitrile and *tert*-butyl alcohol at room temperature for 24 h. Afterward, the dye-sensitized TiO_2 electrode was washed with anhydrous ethanol and dried with nitrogen stream. To prepare the Pt counter electrode, two drops of 5 mM H_2PtCl_6 in ethanol was placed onto the cleaned FTO glass substrate, followed by drying and annealing at 400 $^\circ\text{C}$ for 15 min.

DSSCs were fabricated by sandwiching either the liquid or polymer electrolyte between a dye-sensitized TiO_2 electrode and a Pt counter electrode. The resulting cells were placed in vacuum to remove air to guarantee optimum filling and fine electrical contact. The produced devices were sealed with epoxy resin for measurements.

4. Characterization and Photovoltaic Measurements

^1H NMR spectra were recorded on a Varian 400 MHz spectrometer. The conductivity of electrolytes was characterized in an ordinary cell composed of Teflon tube and two identical stainless steel electrodes (diameter of 1 cm) on a CHI660c electrochemical workstation at room temperature. The viscosity measurement was carried out on viscometer (Haake[®] Rheo Stress 6000, Germany). The

Labram HR800 microRaman spectrometer equipped with a 633 nm argon laser (25 mW) was used in recording the Raman spectra. EIS measurements on a Tafel plots were recorded on a CHI660c electrochemical workstation at room temperature in two-electrode mode of DSSCs. The EIS of devices were tested using a CHI660c electrochemical workstation. Under dark conditions, the bias 5 voltage for the impedance measurement was -0.70 V and the frequency ranged from 0.01-10⁵ Hz. The photocurrent density-voltage (J-V) curves of the assembled DSSCs shielded by an aluminum foil mask with an aperture area of ~0.1 cm² 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⁻², respectively. Incident photo-to-current conversion efficiency (IPCE) plotted as a function of excitation 10 wavelength was recorded on a Keithley 2612 source meter under the irradiation of a Xenon lamp with a monochromator (Oriel CornerstoneTM 260 1/4). The photoelectrochemical parameters, such as the fill factor (FF) and light-to-electricity conversion efficiency (η) were calculated according to the previous reports.

15 5. TGA of Employed Additives

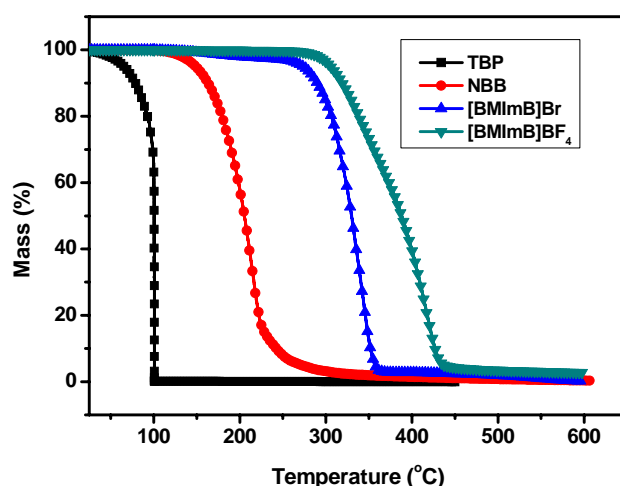


Fig. S1 TGA curves of employed additives.

6. Dark Current-voltage Characteristics of DSSCs Fabricated with Liquid and IL Electrolytes

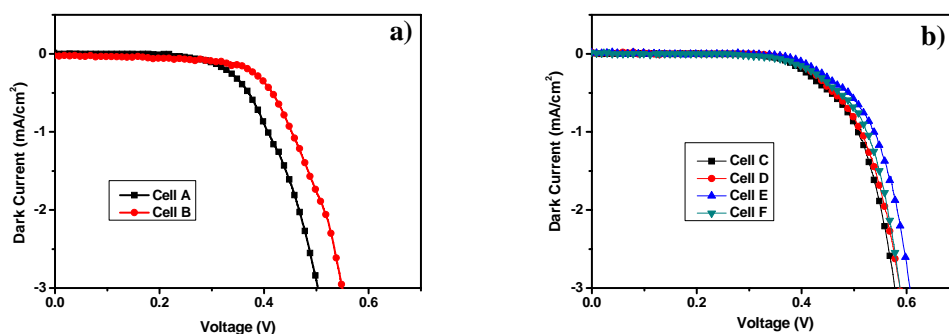


Fig. S2 Dark current-voltage characteristics of DSSCs: a) Cells A and B, b) Cells C, D, E and F.

5 The onset of the dark current is shifted by approx. 20-50 mV after introducing the ionic liquid additives. The lower dark current onset values indicate the lower I_3^- reduction, leading to an increase of V_{oc} . [S2]

10 7. EIS for DSSCs Containing Volatile Liquid and Ionic Liquid Electrolytes

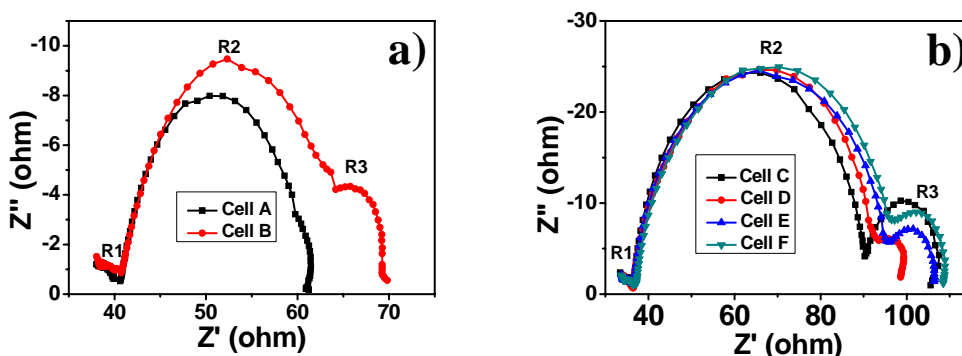


Fig. S3 Nyquist plots of electrochemical impedance spectra measured for DSSCs containing: a) 15 volatile liquid electrolyte Cells A and B, b) ionic liquid electrolyte Cells C, D, E and F at -0.70 V in the dark.

8. IPCE for DSSCs Containing Volatile Liquid and Ionic Liquid Electrolytes

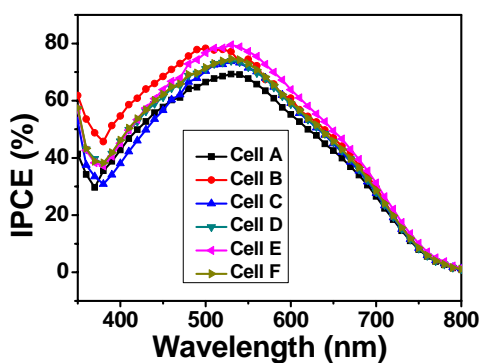


Fig. S4 The IPCE vs. wavelength profiles for devices based on liquid electrolyte Cells A and B, and 5 ionic liquid electrolyte Cells C, D, E and F.

9. EIS parameters of DSSCs fabricated with volatile liquid and ionic liquid electrolytes

Table S1 The parameters obtained by fitting the EIS of the DSSCs fabricated with the volatile liquid and ionic liquid electrolytes.

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Cell/additive	R_1/Ω	R_2/Ω	R_3/Ω
A/TBP	2.37	19.11	1.42
B/[BMIm]Br	2.38	23.32	5.18
C/NBB	2.63	53.73	17.15
D/TBP	1.71	57.06	5.87
E/[BMIm]Br	2.32	59.02	10.94
F/[BMIm]BF ₄	2.30	59.53	12.91

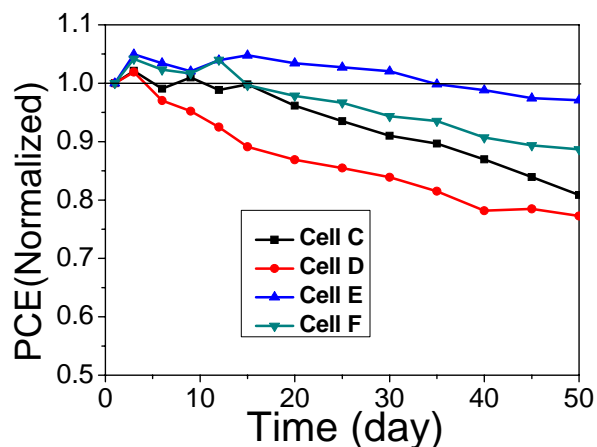


Fig. S5 Time-course variation of the normalized efficiency of ionic liquid-based DSSCs fabricated with NBB, TBP, [BMImB]Br and [BMImB]BF₄, respectively.

5 Reference:

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- S2. M. K. Nazeeruddin, A. Kay, I. Radicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382–6390.
- 10 S3. S. Ito, T. N. Murakami, P. Comte, R. Charvet, R. Humphry-Baker and M. Grätzel, *Thin Solid Film*, 2008, **516**, 4613–4619.