Ionic Liquid Electrolyte Porphyrin Dye Sensitised Solar cells

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Materials and Methods

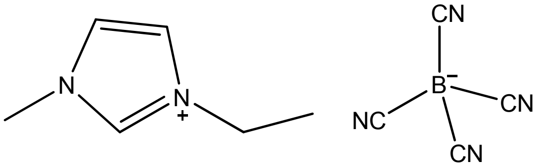
Solvents and reagents were purchased from commercial suppliers and were used without further purification. 1-ethyl-3-methylimidazolium tetracyanoborate **($[C_2mim][B(CN)_4]$**), 1-ethyl-3-methylimidazolium thiocyanate ($[$**$C_2mim][SCN]$)** and 1-butyl-3-methylimidazolium iodide ($[$**$C_4mim][I]$** were purchased from Merck, used as received and handled in a nitrogen filled glove box.

Triethyl(2-methoxyethyl)phosphonium bis(trifluoromethylsulfonyl)amide **($[P_{222(201)}][NTf_2]$** and triethyl(methoxymethyl) phosphonium bis(trifluoromethylsulfonyl) amide **($[P_{222(101)}][NTf_2]$)** were obtained from Nippon Chemicals. These were also handled only in the glove box. Diethyl-isobutylmethylphosphonium tosylate **($[P_{1224}][C_7H_8SO_3]$)** was kindly provided by Cytec Inc.

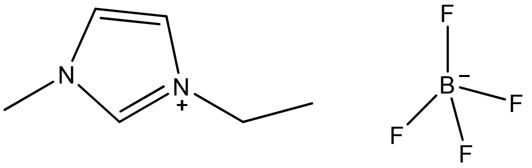
Diethyl-isobutylmethylphosphonium bis(trifluoromethane-sulfonyl) amide **($[P_{1224}][NTf_2]$)**, 1-ethyl-3-methylimidazolium iodide **($[C_2mim][I]$**), 1,3-dimethylimidazolium iodide **($[C_1mim][I]$)**, 1-propyl-3-methylimidazolium iodide ($[$**$C_3mim][I]$)**, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide **$[C_2mim][NTf_2]$),** 1-ethyl-3-methylimidazolium dicyanamide **($[C_2mim][N(CN)_2]$)** and hexyltriethylammonium bis(trifluoro-methanesulfonyl) amide **($[N_{2226}][NTf_2]$)** were synthesised by a literature method.[1] These were dried prior to use and handled in the glove box. Porphyrins GD2, GD3 and P159 were prepared according to a literature method.[2, 3]

Titania paste (18 nm) was provided by JGC Catalysts and Chemicals Ltd. (Kitakyushu-Shi, Japan). FTO glass ($15\Omega\square^{-1}$) was purchased from Nippon Sheet Glass and Surlyn (Dupont) from Solaronix (Aubonne, Switzerland). DSSCs were fabricated according to literature procedures.[4, 5]

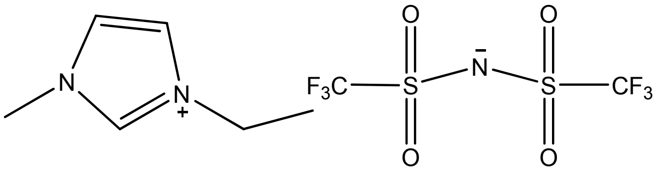
Structure of ionic liquids and abbreviations



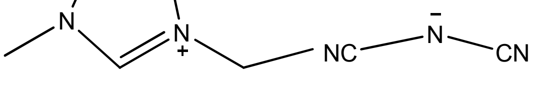
1-ethyl-3-methylimidazolium tetracyanoborate
([C_2mim][$B(CN)_4$])



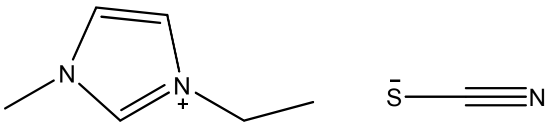
1-ethyl-3-methylimidazolium tetrafluoroborate
([C_2mim][BF_4])



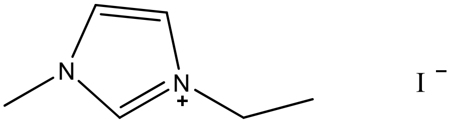
1-ethyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)amide
([C_2mim][NTf_2]



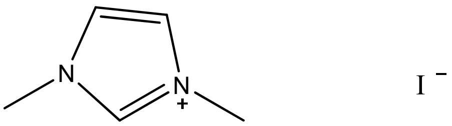
1-ethyl-3-methylimidazolium dycanamide
([C_2mim][$N(CN)_2$])



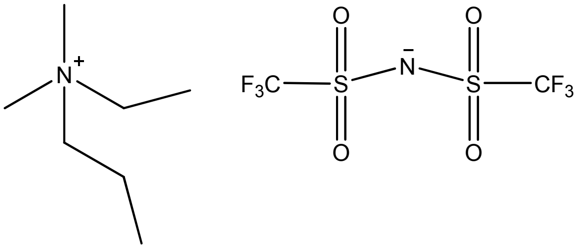
1-ethyl-3-methylimidazolium thiocyanate
([C_2mim][SCN])



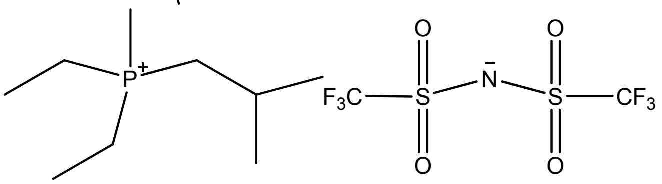
1-ethyl-3-methylimidazolium iodide
([C_2mim][I])



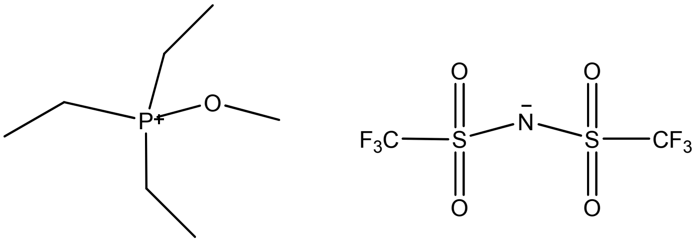
dimethylimidazolium iodide
([C_1mim][I])



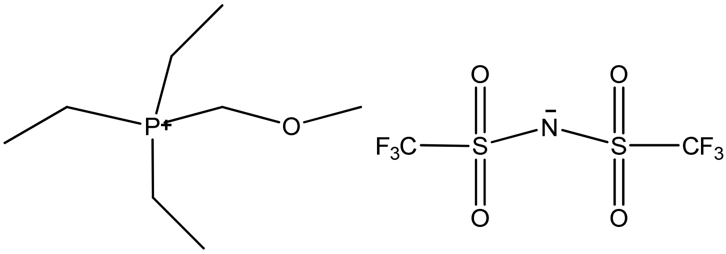
Dimethylethylpropylammonium
bis(trifluoromethylsulfonyl)amide
([N_{1123}][NTf_2])



triisobutyldiethylmethylphosphonium
bis(trifluoromethylsulfonyl) amide
([P_{1224}][NTf_2])



triethyl(methoxymethyl)phosphonium
bis(trifluoromethanesulfonyl) amide
([$P_{222(101)}$][NTf_2])



triethyl(methoxyethyl)phosphonium
bis(trifluoromethanesulfonyl) amide
([$P_{222(201)}$][NTf_2])

Preparation of photoanode

For solar cell assembly and testing, preparation of the photoanodes of the DSSC involved the application of a dense layer of titania to clean FTO glass by spray pyrolysis of titanium diisopropoxide bis(acetylacetonate), 75% in isopropanol, followed by screen printing of two transparent layers of the 18 nm titania nanoparticles (~6 μm each) and a scattering layer of 400 nm TiO_2 (~6 μm) followed by sintering. The photoanodes (working electrode area 0.16 cm^2) were then stored in a plastic container. Prior to device construction, the photoanodes were re-sintered at 500 ˚C for 30 minutes, cooled to 80˚C and then immersed in 0.2 mM dye solutions in the dark and kept at room temperature for 2 hours. The dyed films were then removed in the dark, washed with ethanol and dried. The dyed photoanode and counter electrode were sandwiched with 25 μm Surlyn and sealed using a pneumatic finger and resistive heater for 26 s.

Preparation of counter electrodes

A platinised FTO glass (chemical deposition of 10 mM of hexachloroplatinic acid in isopropanol and sintered at 400˚C for 15 mins.) was used as counter electrode.

Electrolyte filling

The electrolytes were injected into a pre-drilled hole in the counter electrode by vacuum backfilling, and then the holes were sealed with a 25 μm Surlyn sheet and a microscope coverslip.

When the cells were filled with either the SCN or $N(CN)_2$ – based ionic liquids a change in colour was observed; the films turns darker. This change was observed with only these two ionic liquids, hence interaction between these ionic liquids and the dye is proposed. This is also suggested by the UV-Vis analysis of the film, which also shows no trace of the free base.

Photoelectrochemical measurement

Photoelectrochemical measurements were performed using a simulated sunlight (AM1.5, 1000 Wm^{-2}) using an Oriel solar simulator with an AM1.5 filter. A Keithley 2400 source meter was used to record the current–voltage plots, from +800 to −300 mV, with 10 mV steps and a settling time of 40 ms for acetonitrile-based cells and 300 ms for ionic liquid-based cells. The devices were light soaked under simulated light (AM1.5, 1000Wm^{-2}) for 30mins and then tested after 5 mins.

Density, Viscosity and Ionic conductivity measurements

Density measurements of the ionic liquids was carried out using an Anton Paar DMA 5000 density meter. To measure the viscosity, an Anton Paar AMVn was used.

The ionic conductivity of all samples was evaluated using ac impedance spectroscopy. The measurements were performed with a frequency response analyzer (FRA, Solartron 1296), driven by Solartron impedance measurements software version 3.2.0. The temperature was controlled using a Eurotherm Model 2204 temperature controller). The data typically presented a single semicircle from which the conductance of the samples was determined using the real axis intercept in the Nyquist plot of the impedance data.

Salt Preparation and Preliminary Characterisation

NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400Hz using deuterated dimethylsulphoxide as the solvent. All samples were referenced to the residual solvent resonance at 2.50 ppm. ESI were carried out on a Micromass Platform II API QMS Electrospray Mass Spectrometer with a cone voltage of 25 V or 35 V. Methanol was used as the mobile phase unless specified otherwise. Analyses were conducted in both positive (ESI^{+}) and negative (ESI^{-}) modes. DSC experiments were performed on a T.A. Instruments Perkin-Elmer Q100. Samples of mass 5-20 mg were sealed in a vented aluminium pan and placed in the furnace with a 50 ml/min Nitrogen stream; the temperature was raised at 10°C/min.

Synthesis of Diethyl-isobutylmethylphosphonium bis(trifluoromethylsulfonyl)amide ($P_{1224}NTf_2$)

$P_{1224}NTf_2$ was obtained from the reaction of diethylmethylisobutylphosphonium tosylate (20g, 0.06 mol) and lithium bis(trifluoromethylsulfonyl)amide (17.4g, 0.06 mol) in distilled water. The mixture was allowed to stir overnight at room temperature. The precipitate was washed several times with distilled water and then dried in vacuo for several days. (Crude yield 90%).^{1}H NMR (*d*-dmso/ δ ppm): 1.04-1.02 (d, 5.9H), 1.17-1.09 (m, 6H), 1.83-1.72 (d, 3H), 2.07-1.97 (m, 1H), 2.24-2.12 (m, 6H) (dES-MS: ES+ m/z [P1224]+. 161 ES- m/z 280 NTf_2. m.p. by DSC = 30°C.

Electrolyte compositon

The standard acetonitrile-based (ACN) electrolyte was composed of an acetonitrile:valeronitrile mixture (75:25 vol%), iodine (0.03 M), 4-*tert*-butylpyridine (TBP) (0.5 M), 1-butyl-3-methyl-imidazolium iodide (0.6 M), and lithium iodide (0.1 M). The effect of an additive other than TBP was also investigated in the acetonitrile-based electrolyte. N-methylbenzimidazole (NMB) was in the ionic liquid systems used due to its low vapour compared to TBP, which is beneficial for long term stability testing.

Standard electrolytes (ACN)

An acetonitrile-based electrolyte was used as a control for comparison with the ionic liquids based electrolytes. Table S1 shows the photovolatic performance of GD2, GD3 and P159 using standard electrolyte. Interestingly P159 showed the best performance out of the three dyes.

Table S1: Photovoltaic performance of GD2, GD3 and P159 using standard electrolyte.

		V_{oc} (mV)	I_{sc} (mA/cm^2)	ff	η (%)
GD2	TBP	616 (±4)	12.1 (± 0.2)	0.68 (± 0.01)	5.1 (± 0.1)
GD3	TBP	645 (± 6)	12.1 (± 0.2)	0.69 (± 0.02)	5.4 (± 0.2)
P159	TBP	698 (± 7)	12.3 (± 0.1)	0.69 (± 0.05)	6.0 (± 0.1)
P159	NMB	667 (± 5)	11.2 (± 0.4)	0.70 (± 0.02)	5.2 (± 0.4)

References for supporting information

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4. Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide and L. Han, *Jpn. J. Appl. Phys.,*, 2006, **45**, L638-L640.
5. M. Gratzel, *J. Photochem. Photobiol., C*, 2003, **4**, 145-153.