Porphyrin dye-sensitised solar cells utilising a solid-state electrolyte

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Materials and methods

Succinonitrile (99 %) lithium iodide (99.9 %) and iodine (99.99 %) were purchased from Sigma Aldrich and used as received. [C_4mpyr][I] was synthesised according to literature procedures and recrystallised several times from acetonitrile/ethylactetate.[1] SiO_2 (7nm) was purchased from Degussa. All chemicals were stored in a nitrogen glove box and the electrolytes were also prepared inside the glove box.

Thermal analysis

Differential Scanning Calorimetry (DSC) characterization was performed on a heat flux type DSC. A T.A Instruments Q100 differential scanning calorimeter was used. Scans were carried out at a heating/cooling rate of 10°C /min in the range of -140 °C to 150 °C or -100 °C to 80 °C. Thermal scans below room temperature were calibrated with the cyclohexane solid-solid transition and melting point at -87.0 °C and 6.5 °C respectively. Thermal scans above room temperature were calibrated with the indium, tin and zinc with the melting points of 156.6 °C, 231.9 °C and 419.5°C respectively. All DSC analysis was performed using an aluminum pan with a sample weight of approximately 5 mg. Moisture sensitive and hygroscopic compounds were loaded in a nitrogen glove box. Entropies are normalised for succinonitrile content.

AC conductivity measurement

The ionic conductivity of all samples was evaluated using a.c. 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 as 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. A locally designed dip cell was used and the cell constant was determined using 0.01M KCl.

Electrochemical Impedance Spectroscopy

Electrochemical measurements were carried out using a multi-channel PAR VMP2Z potentiostat using EC-lab software. The diffusion coefficients of the redox species were determined using cyclic voltammetry at a scan rate of 2mV/s in the potential range of 0.4V to -0.5V, in an argon glovebox and using a three-electrode set up. The microelectrode was polished with alumina after each measurement.

Electrochemical Impedance Spectroscopy (EIS) was used to analyze the Pt/electrolyte interface. The EIS was performed in the frequency range of 0.01Hz to 500KHz at a peak-to-peak amplitude of 20mV. The symmetrical cell used for the EIS measurements consisted of two pieces of platinised FTO glass with 25μm surlyn as a spacer to contain the electrolyte. The electrochemical impedance spectra of the symmetric cell is shown in Figure S3 and Figure S4 illustrates the equivalent circuit for this type of cell.

Raman Spectroscopy

Raman spectra were recorded with a Renishaw inVia Raman microcope utilizing a 514 nm incident laser (Innova 70C ArKr laser) with a 270 mW power at the laser head and a 6% neutral density filter placed between the laser and the instrument.

Preparation of the 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 one transparent layer of 18 nm titania nanoparticles (~6 μm each) and a scattering layer of 400 nm TiO_2 (~6 μm) followed by sintering at 500 ^{o}C.

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 (P159) 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

Platinised FTO glass (made via chemical deposition of 10 mM of hexachloroplatinic acid in isopropanol and heating 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 at 80°C by vacuum backfilling, and then the holes were sealed with a 25 µm Surlyn sheet and a microscope coverslip. The device was allowed to cool before testing.

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 300 ms for the solid electrolyte based cells. The settling time is the delay between the application of a bias and the current measurement. A longer settling time is required for solid state electrolyte in order to avoid artefacts due to mass transport limitation of the redox couples in the electrolyte.The cells were masked by placing in a black metal holder and testing jig that ensured illumination of only the working electrode area and illumination only through the top of the cell, not the sides. The power of the simulated light was calibrated with a reference Silicon photodiode and the test cells were positioned mechanically to ensure that they were placed in exactly the same position as the calibration cell.

Table S1. Summary of the data obtained from the thermal analysis traces.

Compound	**II - I**		**I - melt**	
	Peak Ts-s (°C) ± 2	**ΔS (J mol^{-1} K^{-1}) ± 0.01**	**Peak Tm (°C) ± 2**	**ΔS (J mol^{-1} K^{-1}) ± 0.01**
Succinonitrile	-32	23	58	9.5
Succinonitrile + 2wt % SiO_2	-31	26	58	11.0
Succinonitrile + 5wt % SiO_2	-32	23	61	10.0
Succinonitrile + 10wt % SiO_2	-32	21	53	9.7
Succinonitrile + $[C_4mpyr][I]$ + I_2 **A1**	-35	21	49	5.1
Succinonitrile + $[C_4mpyr][I]$ + I_2 + LiI + NMB **A2**	-35	21	41	5.0
Succinonitrile + $[C_4mpyr][I]$ + I_2 + LiI + NMB + 5wt % SiO_2 **A3**	-35	19	40	4.0

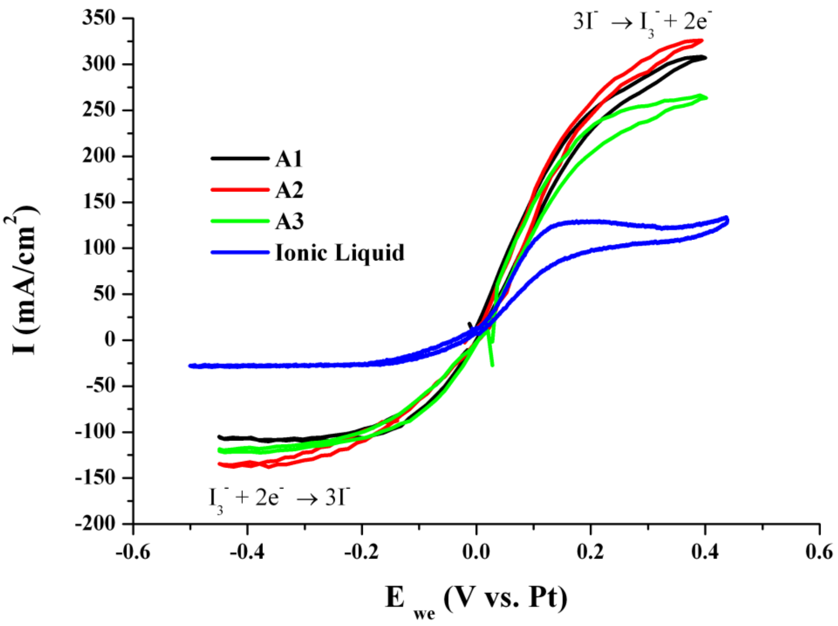

Fig. S1. Cyclic voltammetry of the molecular plastic crystal based electrolytes and an ionic liquid electrolyte, using a Pt microelectrode working electrode (radius 5µm), Pt wire reference and counter electrodes with a Pt microelectrode at 30 ºC and a scan rate of 20 mVs^{-1}. The ionic liquid electrolyte is composed of 0.5M *N*-methyl-*N*-butylpyrrolidinium iodide ([C_4mpyr][I]), and 0.1M I_2 in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, [C_2mim][NTf_2].

The apparent diffusion coefficient (D_{app}, Table 1) was calculated from the cathodic and anodic limiting currents according to: $I_{lim}= 4nCrFD_{app}$, where n is the number of electrons transferred per species, C is the concentration of the electroactive species, r is the radius of the microelectrode and F is Faraday's constant.

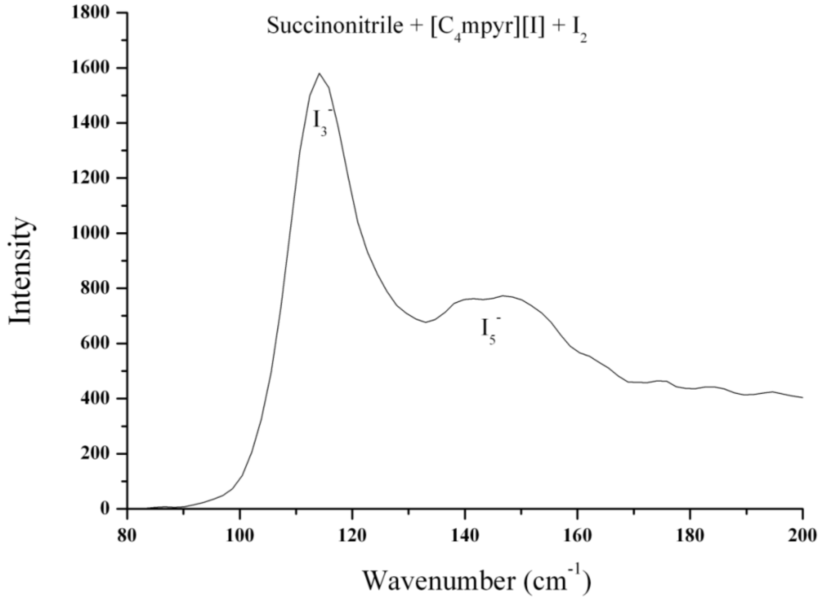

Fig. S2. The Raman spectrum of electrolyte A1. The spectrum of the electrolyte containing 0.05M I_2 showed no I_5^- peak, but the I_5^- peak was also observed in the electrolyte containing 0.2M I_2. The band around 114 cm^{-1} was assigned to the symmetric stretch of I_3^- and the band around 148 cm^{-1} was assigned to I_5^-, as previously reported. [2]

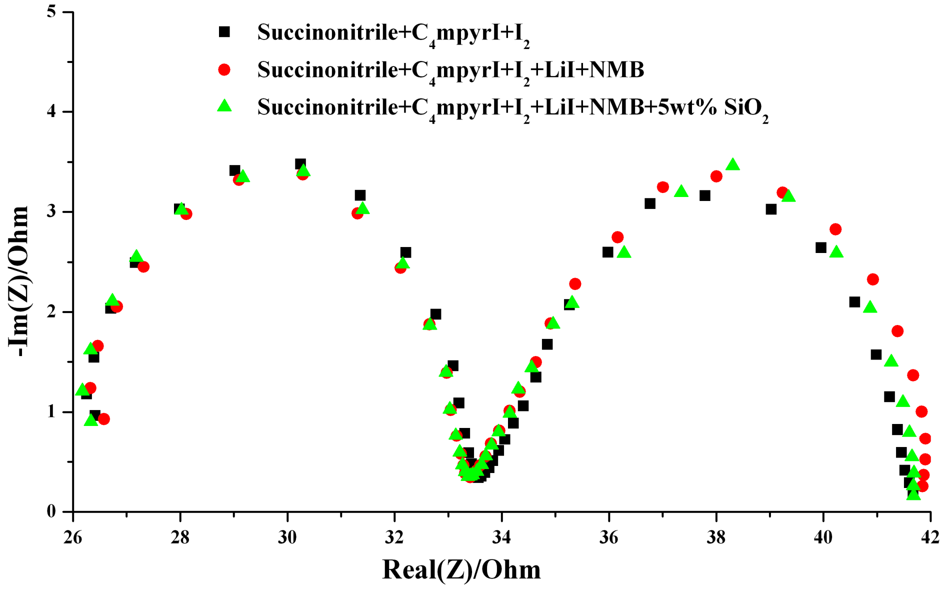

Fig. S3. Electrochemical impedance spectra of the symmetric cells consisting of two pieces of platinised FTO glass, taken at zero bias, ac amplitude 10 mV.

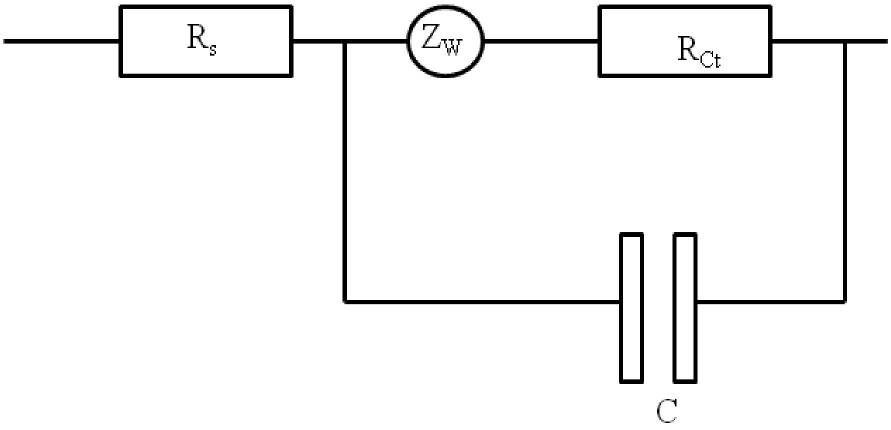

Fig. S4. The equivalent circuit for EIS spectra in Figure S3, where R_s is series resistance, R_{ct} is the charge transfer resistance, C is the double layer capacitance and Z_W is the Warburg impedance.

Table S2. Data parameters obtained from Figure S3

Electrolytes	**R_s**	**R_{CT}**	**C(μF)**
A1	26.2	6.9	2.5
A2	26.8	6.7	2.5
A3	26.3	6.5	2.5

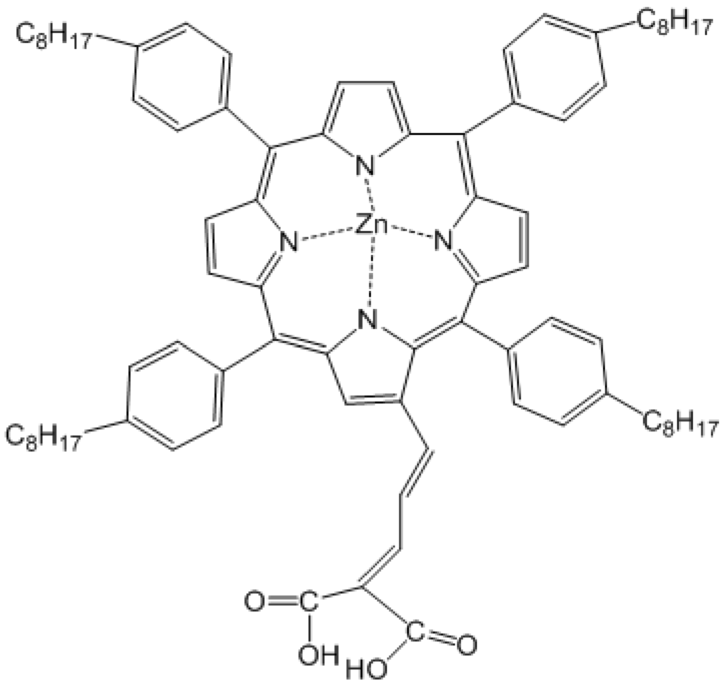

Fig. S5. The structure of the porphyrin sensitiser P159.

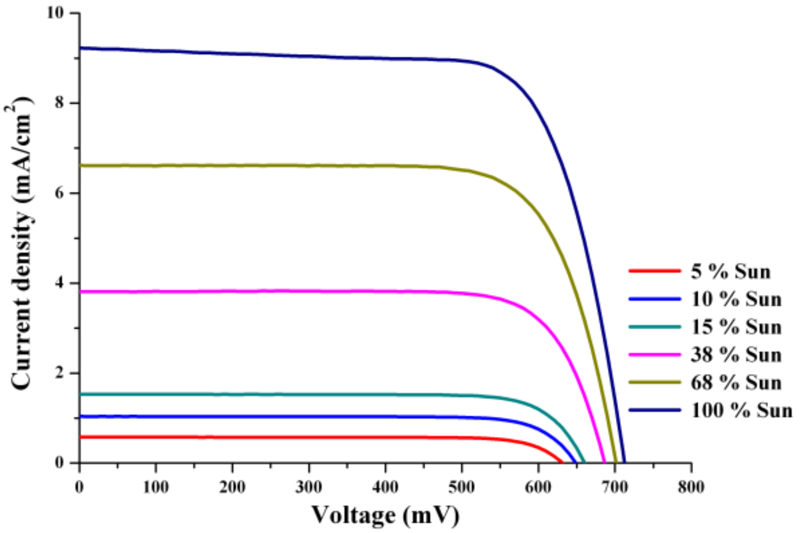

Fig. S6. IV characteristics of the DSSC utilising the P159 dye and the A3 electrolyte at different light intensities.

Table S3. IV parameters, at different light intensities, for the P159-DSSC with electrolyte A3**.**

Sun intensity	**V_{oc} (mV)**	**I_{sc} (mA cm^{-2})**	***ff***	**η (%)**

(%)				
5	632 (± 3)	0.6 (± 0.2)	0.78 (± 0.01)	5.0 (± 0.2)
10	649 (± 2)	1.1 (± 0.1)	0.78 (± 0.01)	5.1 (± 0.3)
15	**660 (± 2)**	**1.5 (± 0.2)**	**0.77 (± 0.01)**	**5.3 (± 0.2)**
38	687 (± 3)	3.8 (± 0.3)	0.77 (± 0.01)	5.2 (± 0.1)
68	702 (± 2)	6.6 (± 0.2)	0.74 (± 0.03)	5.1 (± 0.1)
100	712 (± 2)	9.2 (± 0.1)	0.73 (± 0.02)	4.8 (± 0.2)

References.

1. P. Bonhote, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168-1178.
2. W. Kubo, K. Murakoshi, T. Kitamura, S. Yoshida, M. Haruki, K. Hanabusa, H. Shirai, Y. Wada and S. Yanagida, *J. Phys. Chem. B*, 2001, **105**, 12809-12815.