Supplementary Information.

This file contains additional experimental and analytical information. The organic ionic plastic crystals were synthesised according to the literature procedures.[1-4]

Chemicals:

N-methylpyrrolidine, iodomethane, bromoethane and 1-bromopropane were supplied from Sigma-Aldrich. N-methylpyrrolidine was distilled over KOH before use. Iodomethane was freshly distilled prior to use. Bromoethane and 1-bromopropane were purchased with purity higher than 98 % and were employed with no further purification. The tetrafluoroborate, hexafluorophosphate, dicyanamide and thiocyanate salts were prepared in a two-step process. Metathesis with silver tetrafluoroborate, potassium hexafluorophosphate, silver dicyanamide or silver thiocyanate follows the formation of the corresponding halides salt. In all experiments, distilled deionized water was used.

Procedure:

N,N-dimethylpyrrolidinium dicyanamide, [C_1mpyr][$N(CN)_2$] **(1)**

Silver dicyanamide (20.0 g, 0.11 mol) was added to a solution of *N,N*-dimethylpyrrolidinium iodide, **(5)** (24.9 g, 0.11 mol) in 100 ml of distilled water and stirred for 24 hours at room temperature. The solid silver iodide was removed by filtration (filter paper then 20 μm syringe microfilter) prior to complete evaporation of the solvent. The solid product was recrystallised several times from acetonitrile/diethyl ether. The neat product was further dried under vacuum at room temperature for several days. The product was obtained in the form of white crystals (16 g, 0.096 mol, 85 %). ^{1}H NMR δ (d_6-DMSO, 300 MHz) ppm 2.0 - 2.2 (m, 2H), 3.1 (s, 3H), 3.4 - 3.5 (m, 2H). MS (ESI): ES$^+$ *m/z* 100.1 ($C_6H_{14}N^+$), ES$^-$ *m/z*, 66 ($N(CN)_2^-$).

Tetraethylammonium dicyanamide, [Et_4N][$N(CN)_2$] **(2)**

Silver dicyanamide (20 g, 0.11 mol) was added to a solution of tetraethylammonium bromide (23 g, 0.10 mol) in water (100 ml) and stirred overnight at room temperature. The solid silver bromide was removed by filtration (filter paper then 20 μm syringe microfilter) and the solvent evaporated using a rotary evaporator. The solid product was recrystallised several times from isopropanol/dichloromethane. The neat product was dried in vacuo at 60 ºC for one week. The product was obtained in the form of off white crystals (19.8 g, 0.10 mol, 92 %). ^{1}H NMR δ (d_6-DMSO, 300 MHz) ppm 1.4 - 1.5 (m, 3H), 3.3 - 3.5 (q, 2H). MS (ESI): ES$^+$ *m/z* 130 ($C_6H_{14}N^+$), ES$^-$ *m/z*, 86.7 (BF_4^-).

N-ethyl-N-methylpyrrolidinium tetrafluoroborate, [C$_2$mpyr][BF$_4$] **(3)**

Silver tetrafluoroborate (10.0 g, 0.05 mol) was added to a solution of *N*-ethyl-*N*-methylpyrrolidinium bromide (9.6 g, 0.05 mol) in water (50 mL) and the mixture stirred at room temperature overnight. The solid silver bromide precipitate was removed by filtration (filter paper then 20 μm syringe microfilter) and the filtrate evaporated to dryness on a rotary evaporator. The solid product was recrystallised several times from acetonitrile/dichloromethane. The solid product was dried in vacuo for a week at room temperature. The product was obtained in the form of white crystals (9 g, 0.045 mol, 90 %). ^{1}H NMR δ (d_6-DMSO, 300 MHz) ppm 2.0 - 2.2 (m, 2H), 3.0 (s, 3H), 3.2 - 3.3 (m, 2H), 3.4-3.5 (m, 2H). MS (ESI): ES$^+$ *m/z* 114.1 ($C_7H_{17}N^+$), ES$^-$ *m/z*, 86.7 (BF_4^-).

N-ethyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide, [C$_2$mpyr][NTf$_2$] ***(4)***

Lithium bis(trifluoromethanesulfonyl)amide (25.0 g, 0.09 mol) was added to a solution of *N*-ethyl-*N*-methylpyrrolidinium bromide (17.5 g, 0.09 mol) in water (100 ml) and stirred at room temperature overnight. The solid product was isolated by filtration and rinsed several times with distilled water before being dried under vacuum at room temperature for several days. The product was obtained in the form of white crystals (33.2 g, 0.08 mol, 94 %). ^{1}H NMR δ (d_6-DMSO, 300 MHz) ppm 1.2 - 1.3 (m, 3H), 2.0 - 2.1 (m, 2H), 2.9 (s, 3H), 3.2 - 3.5 (m, 2H). MS (ESI): ES$^+$ *m/z* 113.9 ($C_7H_{16}N^+$), ES$^-$ *m/z*, 280 (NTf_2^-).

N,N-dimethylpyrolidinium iodide, [C$_1$mpyr][I] **(5)**

Iodomethane (20 ml, 0.32 mol) was added dropwise to *N*-methylpyrrolidine (33 ml, 0.32 mol) in ethylacetate (120 ml) and the solution stirred overnight at room temperature under nitrogen atmosphere. The white precipitate formed was isolated by filtration under a nitrogen atmosphere and recrystallised from acetonitrile/ethylacetate. The product was obtained in the form of white crystals (69 g, 0.30 mol, 95 %). ^{1}H NMR δ (d_6-DMSO, 300 MHz) ppm 2.0 -

2.2 (m, 2H), 3.1 (s, 3H), 3.4 - 3.5 (m, 2H). MS (ESI): ES^+ *m/z* 100.1 ($C_6H_{14}N^+$), ES^- *m/z*, 126.9 (I^-).

N,N-dimethylpyrolidinium thiocyanate, [C_1mpyr][SCN] **(6)**

Silver thiocyanate (20 g, 0.12 mol) was added to a solution of *N,N*-dimethylpyrrolidinium iodide (27 g, 0.12 mol) in water (100 ml). The precipitated silver iodide was removed by filtration (filter paper then 20 µm microfilter) before evaporating the solvent on a rotary evaporator. The solid product was recrystallised several times from isopropanol/diethylether before drying in vacuo for several days at room temperature The product was obtained in the form of off-white crystals (16.4 g, 0.10 mol, 86 %). ^{1}H NMR δ (d_6-DMSO, 300 MHz) ppm 2.0 - 2.2 (m, 2H), 3.1 (s, 3H), 3.4 - 3.5 (m, 2H). MS (ESI): ES+ m/z 100.1 ($C_6H_{14}N^+$), ES- m/z, 58 (SCN^-).

N,N-dimethylpyrrolidinium hexafluorophosphate, [C_1mpyr][PF_6] **(7)**

Potassium hexafluorophosphate (10 g, 0.054 mol) was added to *N,N*-dimethylpyrrolidinium iodide (12 g, 0.054 mol) in water (50 ml) and the mixture stirred at room temperature overnight. The solid product was isolated by filtration, rinsed thoroughly with distilled water and dried under vacuum at room temperature for several days. The product was obtained in the form of white crystals (11.8 g, 0.048 mol, 89 %). ^{1}H NMR δ (d_6-DMSO, 300 MHz) ppm 2.0 - 2.2 (m, 2H), 3.1 (s, 3H), 3.4 - 3.5 (m, 2H). MS (ESI): ES^+ *m/z* 100.1 ($C_6H_{14}N^+$), ES^- *m/z*, 144.9 (PF_6^-).

Electrolyte Fabrication:

All plastic crystals electrolytes were prepared in a nitrogen glove box. [C_2mim][I] was synthesised according to literature method.[5] Lithium iodide (LiI), iodine (I_2) and N-methylbenzimidazole (NMB) were purchased from Sigma-Aldrich and used as received. [C_2mim][I] and LiI were mechanically stirred together for several hours at 100 ºC before addition of the organic ionic plastic crystals. The resulting mixtures were stirred for a further 5 mins before NMB and I_2 were added to the hot melt and the electrolyte stirred for another 10 mins. The composition of the electrolytes is shown below;

Matrix	**Concentration of additives**			
	$[C_2mim][I]$	**LiI**	**I_2**	**N-methylbenzimidazole**
$[C_2mpyr][BF_4]$	2.50 M	0.10 M	0.23 M	0.25 M
$[C_1mpyr][N(CN)_2]$	2.50 M	0.10 M	0.23 M	0.25 M
$[C_1mpyr][I]$	-	0.10 M	0.23 M	0.25 M
$[C_1mpyr][SCN]$	2.50 M	0.10 M	0.23 M	0.25 M
$[Et_4N][N(CN)_2]$	2.50 M	0.10 M	0.23 M	-
$[C_2mpyr][NTf_2]$	2.50 M	0.10 M	0.23 M	0.25 M
$[C_1mpyr][PF_6]$	2.50 M	0.10 M	0.23 M	0.25 M

The thermal properties of the organic ionic plastic crystals and the electrolytes were analysed by differential scanning calorimetry. A representative example is shown below for the highest performing material. Addition of the electrolyte components results in an extra transition at around 50 ^{o}C and depression of the melting point, but the electrolyte is still in the solid state over a suitable operating temperature range.

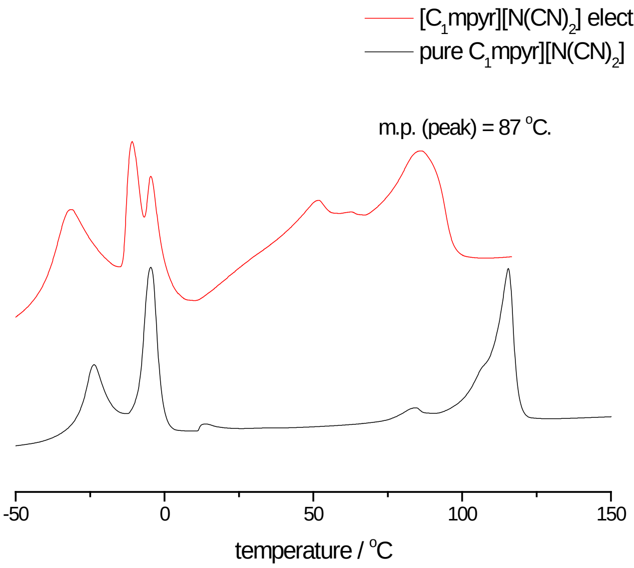

Figure 1. DSC trace for the $[C_1mpyr][N(CN)_2]$ plastic crystal, pure and with the added electrolyte components.

Electrochemical methods:

The **diffusion coefficient** of the iodide and triiodide was determined using thin layer voltammetry. The OIPC electrolyte was held between two symmetrical electrodes (platinised FTO glass) separated by a 25 μm thick Surlyn spacer. This instrumental setup allows steady state conditions to be obtained (Figure 2).

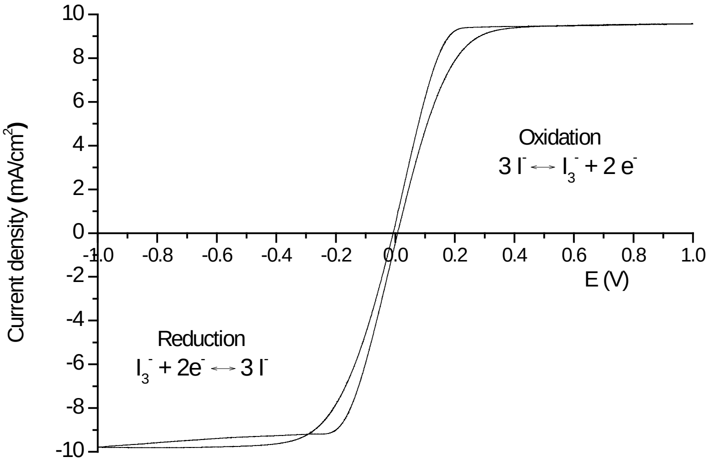

Figure 2. Electrochemical determination of the limiting current and hence the diffusion of I^- and I_3^- through the [C_1mpyr][I]-based electrolyte.

The steady state current is given by the following equation:

$$I_{ss} = \frac{2nFADc}{l}$$

where n is the number of electrons transferred, F is the Faraday constant, A is the cross-section of the enclosed electrolyte, D is the diffusion coefficient, c is the concentration of the redox species and l is the distance between the two electrodes. Electrochemical measurement of the symmetrical cell was performed on a multi-channel PAR VMP2Z potentiostat using EC-lab software in a Faraday cage. The diffusion coefficients of the redox species were determined by cyclic voltammetry at a scan rate of 5mV/s in the potential range of -1 to 1 V at 80°C. This technique relies on the ability to achieve a steady state with a clearly determinable limiting current. Below 80 ^{o}C, the diffusion coefficient and hence I_{ss} are decreased; as a result of this the signal to noise ratio is significantly decreased and determination of the steady state current is not sufficiently accurate for all the different OIPC electrolytes. Use of a microelectrode to measure the diffusion coefficients, at room temperature or at 80 ^{o}C, gave significantly lower currents and thus even poorer signal to noise.

Using the same cell design (FTO-Pt/electrolyte/FTO-Pt) the Pt/electrolyte interface was analysed by **electrochemical impedance spectroscopy**. The EIS was performed in the frequency range of 0.01 Hz to 200 kHz at a peak-to-peak amplitude of 20 mV at room temperature.

The data was fitted using the following equivalent circuit:

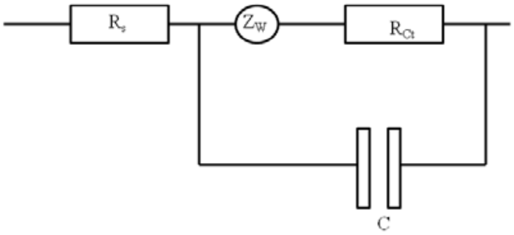

Figure 3. The equivalent circuit used to fit EIS data.

Where R_s is the series resistance, Z_w is the Warburg impedance, R_{ct} is the charge transfer resistance and C is the double layer capacitance.

Device characterisation;

The photovoltaic parameters for the DSSC utilising the [C_1mpyr][$N(CN)_2$]-based electrolyte under different sun intensities, varied using meshes in front of a Xenon lamp (data from best cell reported) are shown below;

Sun intensity	5.8% Sun	10.3% Sun	14.9% Sun	38.5% Sun	68.0% Sun	100.0% Sun
Voltage / mV	688	707	720	749	766	775
Current / mA cm^{-2}	0.5	0.9	1.3	3.3	6.0	8.6
Fill Factor	0.79	0.79	0.79	0.79	0.78	0.77
Efficiency / %	4.6	4.9	5.1	5.0	5.3	5.2

The photocurrent action spectrum of the DSSC utilising the best plastic crystal, [C_1mpyr][$N(CN)_2$], is shown in Figure 4.

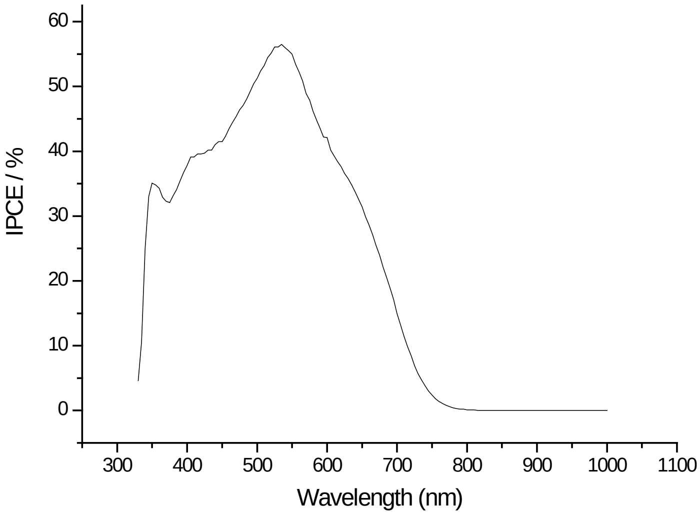

Figure 4. The IPCE spectra for the DSSC with [C_1mpyr][$N(CN)_2$]. The maximum IPCE is 56.5% @ 535 nm. The I_{sc} calculated from the IPCE spectrum is 8.53 mA cm^{-2}.

References:

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2 Golding, J. et al., N-Methyl-N-alkylpyrrolidinium Hexafluorophosphate Salts: Novel Molten Salts and Plastic Crystal Phases. *Chem. Mater.* **13** (2), 558-564 (2001).

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4 Pringle, J. M. et al., Physical trends and structural features in organic salts of the thiocyanate anion. *Journal of Materials Chemistry* **12** (12), 3475-3480 (2002).

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