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Abstract
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Keywords
electrolyte, liquid, dye, ionic, sensitised, porphyrin, solar, cells

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Ionic liquid electrolyte porphyrin dye sensitised solar cells†

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Ionic liquid electrolytes based on a number of imidazolium, quaternary ammonium and phosphonium cations have been developed for porphyrin dye sensitised solar cells yielding efficiencies of up to 5.2% at 0.68 Sun.

As concerns about fossil fuel depletion and climate change increase, alternative ways to supply the world's energy needs with more environmentally friendly technologies such as wind energy, hydro energy and solar energy are being extensively investigated. Dye sensitised solar cells are one such technology. Since 1991, dye sensitized solar cells (DSSCs)[1] have attracted great interest because of their high light-to-electricity conversion efficiency, easy fabrication and potentially low production cost. The highest efficiency reached to date is around 12% utilising a ruthenium-based dye and an organic electrolyte.[2–4] In a DSSC, upon illumination, the dye is excited by a photon, and injects an electron into the conduction band of the underlying semiconductor (TiO_2). The oxidised dye is subsequently regenerated by electron donation from the electrolyte, which typically contains an iodide/triiodide redox couple. The iodide is then, in turn, regenerated by reduction of the triiodide at the counter electrode. The redox couple is usually dissolved in an organic solvent; this component can limit the lifetime performance of the DSSC because of the volatility of the organic solvent. To address this problem, efforts are being made to replace the organic solvents with non-volatile materials such as those based on p-type semiconductors,[5,6] hole conducting materials[7,8] and polymeric solid electrolytes.[9–12] These materials, however, show poor transport properties as compared with liquid-based electrolytes. Ionic liquids (ILs) have been shown to be useful alternatives due to their high ionic conductivity and negligible volatility. Since the discovery of ionic liquids, many families including those based on imidazolium,[13,14] pyrrolidinium and ammonium[15] cations have been investigated. Phosphonium-based ILs[16,17] have been researched less due to their typically higher viscosity. Nevertheless, they have wide electrochemical windows and, depending on the anion, they can be thermally and chemically more stable than the corresponding ammonium ILs.

Eutectic mixtures of room temperature ILs have also been shown to be very effective in DSSCs.[18]

Porphyrin dyes for DSSC cells have also been the subject of intense research in recent years because of the intrinsic advantages that these materials present[19–24] over the ruthenium-based dyes; they are cheaper, do not involve scarce elements and have potentially unlimited availability.

To date, however, porphyrin sensitised DSSCs using an ionic liquid based electrolyte have not been demonstrated; this is an important step towards a long-lived cell. In this paper, we report such IL-based porphyrin DSSCs including the synthesis of a novel phosphonium IL, (diethylisobutylmethyl phosphonium bis(trifluoromethanesulfonyl)amide), which appears to be one of the optimum materials for porphyrin DSSCs. Different ionic liquid mixtures are also investigated.[18] Fig. 1 shows the zinc porphyrin dyes used in this study.

Full details of materials, chemical abbreviations, methods and equipment used is provided in the Supporting Information.†

Several combinations of the ionic liquids were investigated. According to the literature, binary mixtures, as well as more complex multi-component eutectic mixtures, work well with ruthenium-based DSSCs.[25–28] Thus, these ionic liquids were studied for the first time with porphyrin DSSCs. The general composition of the ionic liquid electrolytes was C_1mimI/C_2mimI/**IL**/LiI/I_2/NMB (12 : 12 : 16 : 1 : 1.67 : 4 by mol, NMB = *N*-methylbenzimidazole) with varying ILs as the third component. The following ILs were used in this study: C_2mimB(CN)$_4$, $P_{1224}NTf_2$, $P_{222(101)}NTf_2$, $P_{222(201)}NTf_2$, $N_{1123}NTf_2$, $N_{2226}NTf_2$, C_2mimNTf_2, C_2mimN(CN)$_2$, C_2mimBF_4 and C_2mimSCN, each chosen because of its stability and fluidity. For comparison, the physical properties including density, viscosity and ionic conductivity of the

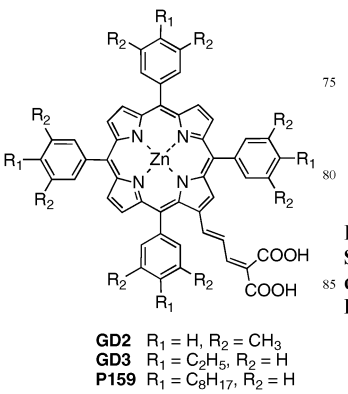

Figure 1: Structures of porphyrin dyes GD2, GD3 and P159.

Fig. 1 Structures of porphyrin dyes GD2, GD3 and P159.

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† Electronic supplementary information (ESI) available: Full details of materials, chemical abbreviations, methods, equipment used, composition of electrolytes, construction of DSSCs, synthesis of $P_{1224}NTf_2$ and *I–V* data for the three porphyrin dyes using standard electrolyte. See DOI: 10.1039/b926087k

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Table 1 Physical properties of pure ionic liquids at 25 °C

Pure ionic liquids	Density (g cm^{-3}) ± 0.01	Viscosity (mPas) ± 0.1	Conductivity/m Scm^{-1} ± 1
$C_2mimB(CN)_4$	1.04	21	16.1
C_2mimBF_4	1.28	38	17.5
$C_2mimNTf_2$	1.51	33	10.3
$C_2mimN(CN)_2$	1.09	19	20.2
$C_2mimSCN$	1.11	21	22.2
$N_{1123}NTf_2$	1.41	101	2.30
$P_{1224}NTf_2$[a]	1.40	71	2.60
$P_{222(201)}NTf_2$[30]	1.39	44	4.40
$P_{222(101)}NTf_2$[30]	1.42	35	3.58

[a] Measured at 30 °C.

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imidazolium and phosphonium ILs, as measured in this work, are summarized in Table 1. $C_2mimN(CN)_2$ had the highest conductivity and $N_{1123}NTf_2$ the lowest. The introduction of the ether side chain significantly decreased the viscosity of the phosphonium ionic liquids and thus $P_{222(201)}NTf_2$ was of comparable viscosity to the well known $C_2mimNTf_2$.[30] However the "cyano" (*i.e.* the SCN, $N(CN)_2$, $C(CN)_3$[29] and $B(CN)_4$) ILs of the C_2mim cation retained the lowest viscosity.

DSSCs were prepared using porphyrin-dyed 18 μm thick TiO_2 photoanodes (0.16 cm^2) assembled into standard sealed sandwiched cells with a platinised counter electrode, and vacuum backfilled electrolyte as described in the Supporting Information.† Fig. 2 shows the typical IV characteristics of the DSSCs using GD2, GD3 and P159, in this case using the $C_1mimI/C_2mimI/C_2mimB(CN)_4/LiI/I_2/NMB$ electrolyte. The best performance was obtained with P159. At 1 Sun illumination, V_{oc}, I_{sc}, and the ff are 637 mV, 10.5 mA cm^{-2} and 0.71, respectively, yielding η = 4.7%. After light soaking for an hour, the performance of the device slightly increased, yielding an efficiency of 4.9% with an increase in I_{sc} to 11.9 mA cm^{-2}. Similar open circuit voltage was observed for all of the dyes, as expected as they have similar electronic configuration, but a much higher short circuit current density was observed for P159. The poor performance of GD2 and GD3 could be due to the interaction of I_3^- with the porphyrin thus increasing recombination of I_3^- with the TiO_2 as previously demonstrated by Mozer *et al.*[19] In contrast to GD2 and GD3, P159 has long hydrophobic alkyl chains on the peripheral benzene rings, providing a barrier layer for back electron transfer from the TiO_2, as proposed for amphiphilic ruthenium sensitisers.[31]

Fig. 3 shows the current density–voltage characteristics as a function of light intensity for the P159 dye. The highest efficiency of 5.2% was achieved at 68% Sun.

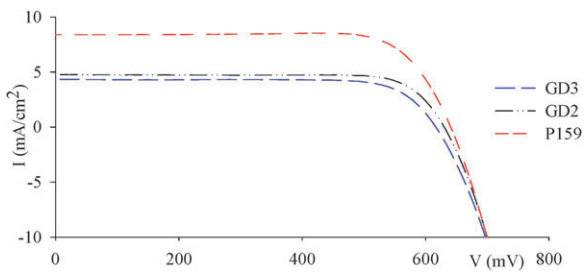

Fig. 2 *IV* curves of DSSCs with different porphyrin dyes GD2, GD3 and P159 using an ionic liquid electrolyte ($C_2mimI/C_1mimI/C_2mimB(CN)_4/LiI/I_2/NMB$) under simulated sunlight AM1.5.

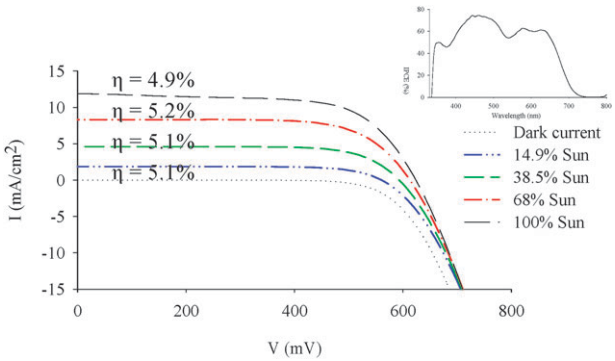

Fig. 3 *IV* characteristics of DSSC with P159 sensitizer and the ionic liquid electrolyte ($(C_2mimI/C_1mimI/C_2mimB(CN)_4/LiI/I_2/NMB)$ in the dark and under simulated AM1.5 light with different light intensities. The working area is 0.16 cm^2. The inset shows the IPCE curve for a device constructed with P159 and the same ionic liquid electrolyte.

The incident photon-to-current conversion efficiency (IPCE) spectrum of a cell containing the same ionic liquid electrolyte with the P159 dye is shown in the inset to Fig. 3. The IPCE is 64% in the broad range from 650 nm to 575 nm and reaches a maximum of 74% at 450 nm. The integral of the curve yields a short circuit current of 11.6 mA cm^{-2} which is consistent with the best efficiency cells.

Table 2 shows the influence of different ionic liquids in the mixture with the best performing dye (P159) as compared to the data for the $C_2mimB(CN)_4$ cell described above. Even though $C_2mimSCN$ and $C_2mimN(CN)_2$ show similar viscosity and ionic conductivity as $C_2mimB(CN)_4$, they show relatively poor performance in the DSSCs. Fredin *et al.*[32] reported that $C_2mimSCN$ gave the best efficiency in monolithic Ru-based DSSCs due to the formation of pseudo halides such as I_2SCN^-, which may lower the concentration of triiodide. This is not observed in our case. One possible explanation was that the thiocyanate might interact with the porphyrin dye. As shown in Table 2, the performance of DSSCs was not highly correlated with the physical properties of the ionic liquids. $C_2mimSCN$ and $C_2mimN(CN)_2$ are highly hygroscopic and distinctly basic as compared to $C_2mimB(CN)_4$, hence there might be some interaction with the dye in these cases.

The best of the IL cells (the $C_2mim\ B(CN)_4$ result) compares quite favourably with the standard acetonitrile electrolyte (Table 2-bottom), the IL only lowering the efficiency by about 1% as a result of the higher viscosity of these systems.

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Table 2 Photovoltaic characteristics of DSSCs with porphyrin P159 using different ILs in electrolyte C_1mimI/C_2mimI/IL/LiI/I_2/NMB after light soaking for 30 mins

IL	V_{oc}/mV	I_{sc}/mA cm^{-2}	ff	η (%)
C_2mimB(CN)$_4$	**624** (±5)	**11.9** (±0.2)	**0.66** (±0.02)	**4.9** (±0.1)
C_2mimNTf$_2$	647 (±2)	8.3 (±0.6)	0.78 (±0.01)	4.2 (±0.1)
C_2mimSCN	649 (±4)	5.3 (±0.4)	0.78 (±0.01)	2.7 (±0.2)
C_2mimBF$_4$	613 (±3)	5.8 (±0.1)	0.74 (±0.00)	2.6 (±0.0)
C_2mimN(CN)$_2$	652 (±10)	6.9 (±0.3)	0.73 (±0.04)	3.2 (±0.2)
$P_{222(101)}$NTf$_2$	631 (±4)	8.9 (±0.3)	0.70 (±0.03)	3.9 (±0.2)
$P_{222(201)}$NTf$_2$	649 (±5)	7.4 (±0.5)	0.74 (±0.02)	3.6 (±0.1)
P_{1224}NTf$_2$	664 (±6)	7.0 (±0.3)	0.76 (±0.01)	3.5 (±0.1)
N_{2226}NTf$_2$	636 (±7)	7.9 (±0.2)	0.75 (±0.03)	3.8 (±0.0)
N_{1123}NTf$_2$	644 (±4)	7.8 (±0.1)	0.78 (±0.00)	3.9 (±0.1)
	Standard acetonitrile electrolyte			
ACN	698 (±7)	12.3 (±0.1)	0.69 (±0.05)	6.0 (±0.1)

A decrease is mainly observed in I_{sc} due to the slow diffusion of the triiodide. Higher concentrations of the iodide source and iodine are needed to avoid the mass transport limitation of the I_{sc}. However, higher concentrations of iodine also increases the dark current, resulting in lower V_{oc} and lower efficiency.

In the lower half of Table 2 are the results for a number of other ionic liquids containing quaternary ammonium and phosphonium cations in DSSCs sensitised with P159. Phosphonium ionic liquids are usually based on relatively large cations and therefore they tend to have high viscosities. Here we report the use of a new, small cation phosphonium ionic liquid and two commercially available low viscosity phosphonium ionic liquids. These phosphonium ionic liquids are studied as they were generally thought to be more stable than the corresponding imidazolium-based ionic liquids. An efficiency of 3.9% was achieved at 1 Sun for $P_{222(101)}$NTf$_2$; the other variants being slightly lower in efficiency. C_2mimNTf$_2$ remained the highest efficiency member of this NTf$_2$ anion family when used with the P159 dye.

On-going investigations using transient light absorption to look at recombination rates and electron lifetime measurements are being undertaken to understand the behaviour of these ionic liquids with the porphyrin dyes.

In summary, porphyrin dye sensitised solar cells containing electrolytes based on mixtures of ionic liquids were fabricated. The influence of different anions and cations was investigated. The highest efficiency was recorded for cells containing the C_2mimB(CN)$_4$ ionic liquid with a power conversion efficiency of 5.2% achieved at 68% Sun intensity. The relatively high efficiency and promising results for the phosphonium and ammonium ionic liquids indicate the possible practical use of these electrolytes with the porphyrin dyes.

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