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

Disciplines
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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)† 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 (TiO2). 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, regenerates 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 materials7,8 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 pyridinium and ammonium15 cations have been investigated. Phosphonium-based ILs16–17 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 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(trifluoromethanesulfon)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 C1mim/IL/LiI/I2/NMB (12:12:16:1:6.7:4 by mol, NMB = N-methylbenzimidazole) with varying ILs as the third component. The following ILs were used in this study: C1mimBCN, P1224NTf2, P222(101)NTf2, P222(201)NTf2, N1123NTf2, N2226NTf2, C7mimNTf2, C7mimNCN, C3mimBF4 and C3mimSCN, each chosen because of its stability and fluidity. For comparison, the physical properties including density, viscosity and ionic conductivity of the

Fig. 1 Structures of porphyrin dyes GD2, GD3 and P159.
Table 1  Physical properties of pure ionic liquids at 25 °C

<table>
<thead>
<tr>
<th>Pure ionic liquids</th>
<th>Density (g cm⁻³) ± 0.01</th>
<th>Viscosity (mPas) ± 0.1</th>
<th>Conductivity/m Scm⁻¹ ± 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂mimB(CN)₄</td>
<td>1.04</td>
<td>21</td>
<td>16.1</td>
</tr>
<tr>
<td>C₂mimBF₄</td>
<td>1.28</td>
<td>38</td>
<td>17.5</td>
</tr>
<tr>
<td>C₂mimNTf₂</td>
<td>1.51</td>
<td>33</td>
<td>10.3</td>
</tr>
<tr>
<td>C₂mimN(CN)₂</td>
<td>1.09</td>
<td>19</td>
<td>20.2</td>
</tr>
<tr>
<td>C₂mimSCN</td>
<td>1.11</td>
<td>21</td>
<td>22.2</td>
</tr>
<tr>
<td>N₁₁₂₃NTf₂</td>
<td>1.41</td>
<td>101</td>
<td>2.30</td>
</tr>
<tr>
<td>P₂₂₂(NTf₂)</td>
<td>1.40</td>
<td>71</td>
<td>2.60</td>
</tr>
<tr>
<td>P₂₂₂(101)NTf₂</td>
<td>1.39</td>
<td>44</td>
<td>4.40</td>
</tr>
<tr>
<td>P₂₂₂(101)NTf₂</td>
<td>1.42</td>
<td>35</td>
<td>3.58</td>
</tr>
</tbody>
</table>

a Measured at 30 °C.

imidazolium and phosphonium ILs, as measured in this work, are summarized in Table 1. C₂mimN(CN)₂ had the highest conductivity and N₁₁₂₃NTf₂ the lowest. The introduction of the ether side chain significantly decreased the viscosity of the phosphonium ionic liquids and thus P₂₂₂(101)NTf₂ was of comparable viscosity to the well known C₂mimNTf₂. However the “cyano” (i.e. the SCN, N(CN)₂, C(CN)₃, and B(CN)₃) ILs of the C₂mim cation retained the lowest viscosity.

DSSCs were prepared using porphyrin-dyed 18 μm thick TiO₂ photoanodes (0.16 cm²) assembled into standard sealed sandwiched cells with a platinised counter electrode, and vacuum backfilled electrolyte as described in the Supporting Information. The typical IV characteristics of the DSSCs using GD2, GD3 and P159, in this case using the C₁mimI/C₂mimI/C₂mimB(CN)₄/LiI/I₂/NMB electrolyte. The best performance was obtained with P159. At 1 Sun illumination, Vₜₜ, Iₑₑ, 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 Iₑₑ 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⁻ with the porphyrin thus increasing recombination of I₂ with the TiO₂ as previously demonstrated by Mozer et al. 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 TiO₂, as proposed for amphiphilic ruthenium sensitisers.

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.

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.
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 triiodide. However, higher concentrations of iodine also increases the dark current, resulting in lower $V_{oc}$ and lower efficiency.

The results for a number of other ionic liquids containing quaternary ammonium and phosphonium cations in DSSCs sensitised with P159 are given in Table 2. These phosphonium ionic liquids indicate the possible practical use of the phosphonium and ammonium ionic liquids in DSSCs.

<table>
<thead>
<tr>
<th>IL</th>
<th>$V_{oc}$/mV</th>
<th>$I_{sc}$/mA cm$^{-2}$</th>
<th>ff</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2mimB(CN)$_2$</td>
<td>624 (±5)</td>
<td>11.9 (±0.2)</td>
<td>0.66 (±0.02)</td>
<td>4.9 (±0.1)</td>
</tr>
<tr>
<td>C2mimN$_2$TF$_2$</td>
<td>647 (±2)</td>
<td>8.3 (±0.06)</td>
<td>0.78 (±0.01)</td>
<td>4.2 (±0.1)</td>
</tr>
<tr>
<td>C2mimBF$_4$</td>
<td>613 (±3)</td>
<td>5.8 (±0.1)</td>
<td>0.74 (±0.00)</td>
<td>4.0 (±0.3)</td>
</tr>
<tr>
<td>C2mimN(CN)$_2$</td>
<td>652 (±5)</td>
<td>6.9 (±0.1)</td>
<td>0.73 (±0.04)</td>
<td>4.8 (±0.2)</td>
</tr>
<tr>
<td>P222(101)NTF$_2$</td>
<td>631 (±4)</td>
<td>9.3 (±0.7)</td>
<td>0.70 (±0.03)</td>
<td>4.7 (±0.2)</td>
</tr>
<tr>
<td>P222(101)NTF$_2$</td>
<td>649 (±5)</td>
<td>7.4 (±0.8)</td>
<td>0.74 (±0.02)</td>
<td>3.6 (±0.1)</td>
</tr>
<tr>
<td>P222(101)NTF$_2$</td>
<td>664 (±6)</td>
<td>7.0 (±0.3)</td>
<td>0.76 (±0.01)</td>
<td>3.5 (±0.1)</td>
</tr>
<tr>
<td>N$_{222}$NTF$_2$</td>
<td>636 (±7)</td>
<td>7.9 (±0.2)</td>
<td>0.75 (±0.03)</td>
<td>3.8 (±0.0)</td>
</tr>
<tr>
<td>N$_{1123}$NTF$_2$</td>
<td>644 (±4)</td>
<td>7.8 (±0.1)</td>
<td>0.78 (±0.00)</td>
<td>3.9 (±0.1)</td>
</tr>
<tr>
<td>ACN</td>
<td>698 (±7)</td>
<td>12.3 (±0.1)</td>
<td>0.69 (±0.05)</td>
<td>6.0 (±0.1)</td>
</tr>
</tbody>
</table>

### References