SYNTHESIS OF A NOVEL FAMILY OF PORPHYRIN WITH TRIPHENYLAMINE DONOR GROUPS TO BE APPLIED IN DYE SENSITIZED SOLAR CELLS

Ana Aljarilla,* John N. Clifford, Laia Pellejà, Antonio Moncho,* Susana Arrechea,* Pilar de la Cruz,* Fernando Langa* and Emilio Palomares*bc

aInstitute of Nanoscience, Nanotechnology and Molecular Materials (INAMOL), Campus de la Fábrica de Armas (UCLM), Toledo, Spain. E-mail: Fernando.Langa@uclm.es; Fax: 34 9252 68840; Tel: 34 9252 68843;
bInstitute of Chemical Research of Catalonia (ICIQ), Avda. Països Catalans 16, Tarragona E-43007, Spain. E-mail: jncifford@iciq.es; Fax: +34 9779 20224; Tel: +34 9779 20200.
cICREA, Avda. Lluís Companys 28, Barcelona E-08030, Spain.

ABSTRACT

The solar cells of third generation, which can be classified in hybrids and organics, are the target of uncountable studies and developments along the last few years. These cells present low fabrication cost, flexibility, lightness, and stability. In this work two new Zinc–porphyrin 1a and 1b, bearing triphenylamine donor groups were synthesized and their efficiencies measured in nanocrystalline TiO₂ dye sensitized solar cells employing iodide/tri-iodide and tris(1,10-phenanthroline) cobalt electrolytes. Optimized sensitization time for the TiO₂ photoanode was found to depend on the electrolyte employed: devices based on iodide/tri-iodide showed better efficiencies with shorter sensitization times (1.5 hours) whereas those based on tris(1,10-phenanthroline) cobalt showed better efficiencies with longer sensitization times (6 hours). From UV-Vis absorption spectra it is estimated that there is roughly twice as much dye loaded onto the TiO₂ film sensitized for 6 hours compared to the 1.5 hour film.

KEYWORDS: porphyrin, photovoltaics, dyes, sensitizer

INTRODUCTION

Research into Dye Sensitized Solar Cells (DSCs) continues to be an extremely active area.1–4 After considerable time in which DSCs based on Ru(II) polypyridyl sensitizers were clearly the most efficient, DSCs based on fully organic sensitizers have recently made huge strides forward in development.5,6 In particular, there are many recent examples of DSC devices employing iodide/tri-iodide (I⁻/I₃⁻) with >10% device efficiency based on D-π-A porphyrins designed by Diau and co-workers.7–9 Indeed, with recently developed novel cobalt based complexes10–13 porphyrins have shown their promise with the current highest efficiency recorded for a DSC device of 12.05% being based on a cell containing a porphyrin sensitizer and a tris(bipyridyl) cobalt electrolyte.12 Regardless of the red/ox couple, porphyrins offer several distinct advantages over Ru(II)polypyridyl sensitizers due to their high molar extinction coefficients, sharp absorption bands and high photostability.15,17
However, their properties in DSCs still need to be fully investigated and molecular structure-device function rules need to be outlined to fully understand device performance for devices based on these dyes.

We investigate the performance of two porphyrin sensitizers, 1a and 1b (Scheme 1), in DSC devices employing I^+I^- and tris(1, 10-phenanthroline) cobalt electrolytes.

RESULTS AND DISCUSSION

Synthesis of 1a and 1b

Scheme 2 illustrates the synthetic route to dyes 1a and 1b. We prepared the free base porphyrins 2a,b in 14% and 11% yield respectively, according to the Lindsey method.\(^1\) This procedure improves significantly the yield with respect to previous procedures described for similar porphyrins (4-6%).\(^2\) 2a,b were reacted with zinc acetate in chloroform giving the metallated porphyrins 3a,b in 91% and 95% yield after purification by column chromatography (silica gel, Hex/CHCl\(_3\), 1:1). Finally, the trimethylsilyll group was quantitatively removed by TBAF and in situ reacted with p-iodobenzoic acid under Pd-catalyzed Sonogashira coupling conditions affording the target dyes 1a,b in 70 and 63% yield respectively. The intermediate and final compounds were fully characterized by means of UV-Vis, FT-IR, \(^1\)H and \(^13\)C NMR spectroscopies; the structures of all compounds were confirmed by MALDI-TOF mass spectrometry.
The thermal stabilities of compounds 1a and 1b were evaluated by thermogravimetric analysis (TGA) under nitrogen, with a heating rate of 10 °C/min. The decomposition temperatures (Td) were estimated from the TGA plot as the temperature of the intercept of the leading edge of the weight loss curve. Under these conditions, compounds 1a and 1b display excellent thermal stability up to 220 °C which are in principle satisfactory for application in photovoltaic devices.

Absorption, emission, electrochemistry and computational calculations

The absorption spectra of dyes 1a,b in dichloromethane (CH₂Cl₂) solution are shown in Fig. 1. Both dyes exhibit the typical features of zinc porphyrins, with an intense Soret band between 400-500 nm and less intense Q bands in the range 550 to 700 nm (see Table 1). As expected, the absorption bands are not very sensitive to the nature of the substituents, pointing to weak electronic interactions between the porphyrin and the attached moiety in the ground state. Due to the presence of the hexyloxy groups in dye 1b, a bathochromic shift is observed in the Q band, while in the Soret band an enhancement in bandwidth is observed. For the fluorescence spectra in CH₂Cl₂ the trend for the variation of the emission wavelength is similar to that of the absorption bands. The emission bands at 652 nm (1a, λexc= 450 nm) and 669 nm (1b, λexc= 449 nm) (Fig. 1) were totally quenched after adsorption onto TiO₂ indicating efficient photoinduced electron transfer from the dyes to the TiO₂ nanoparticles.

The redox properties of 1a,b were investigated by cyclic voltammetry and square wave voltammetry in tetrahydrofuran (THF). In the cathodic side, compounds 1a,b show the first reversible oxidation peaks at 0.33 and 0.28 V respectively; the presence of the electron-donating alkoxy groups significantly reduces the oxidation potential of 1b compared to 1a. On the reduction side, both compounds show first reduction potentials at -0.52 V and -0.57 V as irreversible waves, showing that the electron-donating alkoxy groups in 1b increase its reduction potential with respect to 1a, as one would expect. The \( E_{\text{HOMO}} \) values of 1a to 1b vary only by 0.05 eV and were determined as -5.43 eV (1a) and -5.38 eV (1b), indicating regeneration is energetically feasible by I/I₃⁻ (\( E_{\text{redox}} = -4.75 \text{ eV} \)) and Co(II)(phen)_3/Co(III)(phen)_3 (\( E_{\text{redox}} = -5.06 \text{ eV} \)) red/ox couples. The \( E_{\text{LUMO}} \) values also indicate that efficient electron injection into the TiO₂ conduction band (\( E_{\text{TiO2}} = -4.00 \text{ eV} \)) is also energetically possible.

![Fig. 1](image-url) Normalized absorption spectra of dyes 1a (-) and 1b (--) in dichloromethane solution (10⁻⁵ M).
### Table 1 Absorption, emission and electrochemical data of dyes 1a and 1b.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ $^a$/nm ($\log\varepsilon$)</th>
<th>$\lambda_{\text{em}}$$^a$/nm</th>
<th>$E_{\text{red}}$$^b$ (V)</th>
<th>$E_{\text{ox}}$$^b$(V)</th>
<th>$E_{\text{HOMO}}$$^c$(eV)</th>
<th>$E_{\text{LUMO}}$$^d$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>630 (4.18), 572 (4.02), 450 (5.08), 306 (4.71)</td>
<td>652</td>
<td>-0.52</td>
<td>0.33</td>
<td>-5.43</td>
<td>-3.50</td>
</tr>
<tr>
<td>1b</td>
<td>637 (4.39), 579 (4.07), 449 (5.12), 305 (4.77)</td>
<td>669</td>
<td>-0.58</td>
<td>0.28</td>
<td>-5.38</td>
<td>-3.49</td>
</tr>
</tbody>
</table>

$^a$10$^{-5}$ M, CH$_2$Cl$_2$. $^b$[10$^{-3}$ M] in THF versus Fc/Fc+, glassy carbon, Pt counter electrode, 20 ºC, 0.1 M Bu$_4$NClO$_4$, scan rate = 100 mV s$^{-1}$. $^c$Calculated using equation $E_{\text{LUMO}}$ (vs. vacuum) = -5.1 - $E_{\text{ox}}$ (vs. Fc/Fc+) in eV. $^d$ $E_{\text{LUMO}}$ was calculated using $E_{\text{LUMO}} = E_{\text{HOMO}} + E_0$, where $E_0$ is the intersection of the absorption and emission spectra.

In order to gain insight into the geometries and electronic properties of dyes 1a and 1b, computational studies were performed using density functional theory (DFT) at the B3LYP/6-31G level. Regarding geometry, for both dyes the dihedral angles between the phenyl ring and the porphyrin macrocycle ($\phi$) are similar ($\phi \sim -65^\circ$) and are in agreement with those calculated for similar systems (Fig. 2). The HOMOs were found to be delocalized through both the porphyrin macrocycle and TPA for both 1a and 1b, whereas the LUMOs are extended along the porphyrin system, the linker and the acid group, indicating electronic coupling with the TiO$_2$ nanocrystals. The HOMO-LUMO gap is similar for both dyes although the LUMO level of dye 1b is higher (-2.45 eV) than that of 1a (-2.61 eV) due to the electronic coupling of the alkoxy groups of the TPA moieties. HOMO and LUMO (Fig. 3) are overlapped, favouring the HOMO to LUMO electronic transitions.

![Fig. 2](image1.jpg) Optimized structure for dye 1b (hexyl groups have been changed by methyl for calculations).

![Fig. 3](image2.jpg) Frontier orbitals of dye 1b: HOMO (left) and LUMO (right).
Device properties

Fig. 4 and Table 2 show the IV curves and device characteristics, namely $J_{SC}$, $V_{OC}$, fill factor (FF) and overall efficiency ($\eta$), for sensitizers 1a and 1b in DSC devices based on $I/\Gamma_3$ and Co(II)(phen)$_3$/Co(III)(phen)$_3$ electrolytes.

**Table 2** Photovoltaic performance of cells recorded under AM 1.5G 1 sun illumination.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Time</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1.5 hours$^a$</td>
<td>10.09</td>
<td>0.63</td>
<td>67</td>
<td>4.19 (5.14)</td>
</tr>
<tr>
<td>1a</td>
<td>6 h$^b$</td>
<td>8.51</td>
<td>0.62</td>
<td>62</td>
<td>3.27 (3.93)</td>
</tr>
<tr>
<td>1b</td>
<td>1.5 hours$^a$</td>
<td>7.83</td>
<td>0.62</td>
<td>70</td>
<td>3.40 (4.15)</td>
</tr>
<tr>
<td>1b</td>
<td>6 h$^b$</td>
<td>6.18</td>
<td>0.61</td>
<td>69</td>
<td>2.54 (3.60)</td>
</tr>
<tr>
<td>1a</td>
<td>1.5 hours$^b$</td>
<td>3.67</td>
<td>0.75</td>
<td>75</td>
<td>2.06 (2.53)</td>
</tr>
<tr>
<td>1a</td>
<td>6 h.$^b$</td>
<td>3.17</td>
<td>0.76</td>
<td>74</td>
<td>2.48 (3.11)</td>
</tr>
<tr>
<td>1b</td>
<td>1.5 hours$^b$</td>
<td>3.82</td>
<td>0.77</td>
<td>66</td>
<td>1.61 (2.01)</td>
</tr>
<tr>
<td>1b</td>
<td>6 h$^b$</td>
<td>4.44</td>
<td>0.75</td>
<td>72</td>
<td>2.05 (2.45)</td>
</tr>
<tr>
<td>YD2-o-C8$^c$</td>
<td></td>
<td>15.25</td>
<td>0.76</td>
<td>72</td>
<td>8.42 (11.20)</td>
</tr>
</tbody>
</table>

$^a$ Electrolyte: 0.6 M 1-butyl-3-methylimidazolium iodide (BMIIL), 0.1 M lithium iodide, 0.05 M iodine and 0.5 M 4-tert-butyliyridine in a 1:1 mixture of acetonitrile-valeronitrile. $^b$ Electrolyte: 0.2 M tris(1,10-phenanthroline)cobalt(II)(TFSI)$_2$, 0.02 M tris(1,10-phenanthroline) cobalt(III)(TFSI)$_3$, 0.1 M lithium perchlorate and 0.5 M 4-tert-butylypyridine in a 85:15 mixture of acetonitrile-valeronitrile. $^c$ Electrolyte: 0.5 M 1-butyl-3-methylimidazolium iodide (BMIIL), 0.05 M lithium iodide, 0.05 M iodine, and 0.5 M 4-tert-butylypyridine in a 85:15 mixture of acetonitrile-valeronitrile. *Data in parenthesis recorded without mask.

Employing $I/\Gamma_3$ electrolyte, the best device efficiencies (Fig. 4(a)) were obtained after 1.5 hours sensitization time with maximum efficiencies of 5.14% and 4.15% for 1a and 1b respectively (without mask). These values compare well with a recent study by Liu et al. involving similar dyes.19
Upon the longer sensitization time of 6 hours the device efficiency drops to 3.93% and 3.60% for 1a and 1b respectively (without mask). The principle reason for this is a loss in $J_{sc}$. When cobalt electrolyte is used, however, the dependence of device efficiency on sensitization time is reversed (Fig. 4(c)). The best efficiencies are recorded for 6 hours sensitization (3.11% and 2.45% for 1a and 1b respectively). Again, the main difference appears to be accounted for by a difference in $J_{sc}$. The increase in device $V_{oc}$ (approx. 140 mV) afforded by employing Co(II)(phen)$_3$/Co(III)(phen)$_3$ with respect to I$_3^-$ is in line with that observed in other studies. Finally, under similar conditions the YD2-o-C8 device gave an efficiency of 11.20% (without mask) indicating testing conditions are indeed comparable with studies demonstrating the best literature values for porphyrin based DSCs. Fig. 4(b) and (d) show the IPCE spectra for all of the devices measured in this study. These spectra show the contributions to device current from the Soret and Q bands centred at around 450 and 650nm respectively. Integration of these spectra agrees with the $J_{sc}$ values for the same devices in Fig. 4(a) and (c).

In order to have an indication of dye loading in these devices, the absorption spectra of thin films of transparent TiO$_2$ films (6 μm) were measured after 1.5 hours and 6 hour sensitization in 0.2 mM solutions of 1a and 1b in chlorobenzene (Fig. 5). These data indicate that there is roughly twice as much dye loading on the films for 6 hours compared to the equivalent film of 1.5 hours.

CONCLUSIONS

Two zinc-porphyrin sensitizers were synthesized and their efficiencies measured in dye sensitized solar cells employing I$_3^-$ and Co(II)(phen)$_3$/Co(III)(phen)$_3$ electrolytes. Optimized sensitization times were found to depend on the electrolyte used with devices based on I$_3^-$ showing better efficiencies with shorter sensitization times (1.5 hours) while those based on Co(II)(phen)$_3$/Co(III)(phen)$_3$ showing better efficiencies with longer sensitization times (6 hours). UV-Vis absorption spectra indicate that there is roughly twice as much dye loaded onto the TiO$_2$ film sensitized for 6 hours. This work demonstrates how device preparation must be tailored carefully.
depending on the electrolyte red/ox couple used.

ACKNOWLEDGEMENTS
Financial support from the Ministry of Science and Innovation of Spain, (CTQ2010-17498, PLE2009-0038 and Consolider- Ingenio Projects HOPE CSD2007-00007) is gratefully acknowledged. EP would also like to thank the EU for the ERCstg PolyDot, and the Catalan government for the 2009 SGR-207 projects.

NOTES AND REFERENCES


