A novel blue dye for near-IR 'dye-sensitised' solar cell applications†

Anthony Burke, Lukas Schmidt-Mende, Seigo Ito and Michael Grätzel*

Received (in Cambridge, UK) 30th June 2006, Accepted 25th September 2006
First published as an Advance Article on the web 30th October 2006
DOI: 10.1039/b609266g

A squaraine dye incorporating two carboxylic acid attaching groups has been synthesised and used successfully in both liquid and solid-state solar cells, with solar energy to electricity conversion efficiencies (η) under AM 1.5 G irradiation (100 mW cm^{-2}) of 3.7 and 1.5% and short-circuit current densities (J_{sc}s) of 8.6 and 4.2 mA cm^{-2}, with open-circuit voltages (V_{oc}) of 591 and 681 mV and fill factors (FF) of 73 and 53%, respectively.

As has been well publicised, concerns for the environment and the finite nature of fossil fuels, have led to the growth of interest and development in the field of renewable energy. The sun provides a huge 3.78 × 10^{24} J to the planet in the form of photons a year.[1] Harnessing this energy therefore, could easily compensate for our world energy needs. Near-IR dyes are particularly interesting because of their possible applications in transparent solar cells *e.g.* for windows and tandem cells. Current 'dye-sensitised' solar cells[2–4] are very effective in the region between 400–800 nm after which though they tail off to low or zero internal current to photon conversion efficiency (IPCE) values. If the AM 1.5 G (Air Mass 1.5 Global) spectrum[5] is converted to photon flux, over the range 300–4000 nm, it can be seen that a large proportion of usable photons extending up to 1200 nm are not used. Traditional silicon devices do use these photons but at a cost; the loss of effective V_{oc}. A tandem cell incorporating a standard 'dye-sensitised' solar cell (DSSC) connected in series with a second cell sensitised by an organic dye, capable of absorbing photons up to 1000 nm, should enable the same harvesting potential as above, though without loss in V_{oc}. The organic dye would in fact be the first cell in the array, as organic dyes generally have much higher extinction coefficients. This allows thinner TiO_2 layers to be used, whilst retaining the high optical density (OD) required for effective photon to current conversion efficiency. The thinner the TiO_2 layer, the higher the transmission of photons in the shorter wavelength region of the visible spectrum. Providing the cells have the same J_{sc}, connecting two cells in series will have the advantage of increasing the cell potential (V_{oc}) through the absorption of otherwise redundant photons and thereby increase the overall cell efficiency. Integration of the photon flux between 300–700 nm and 700–1000 nm from the AM 1.5 G spectrum shows only an 8% difference in available photons, suggesting a current match is entirely possible.

Squaraines were first reported by Treibs and Jakob in 1965[7] and since then interest has steadily grown.[6–11] Initial tests showed that commercial squaraines were capable of electron injection into TiO_2. Although these molecules lacked any attaching groups, IPCE values of 4–10% were obtained. Squaraines are also an ideal choice, due to their extremely high extinction coefficients ($E_{max} \approx 2 \times 10^{-5}\ M^{-1}cm^{-1}$) and their inherent stability, over their cyanine analogues, across the methine chain section. In these dyes, the methine chain is stabilized toward photoisomerisation and oxidation by the 'rigid' squaric acid moiety.

It has recently been drawn to our attention that two other groups have also been working on squaraine based solar cells.[12,13] The first group worked on anilino-squaraines closely following the work of Ralf Petermann.[6] Although these dyes perform well, they are some what blue shifted and would be less useful for use as the infrared component in a tandem DSSC. The second group have also worked on squaraines though as the benzindole analogue of the dyes was not produced, the dyes reported here are also somewhat blue shifted with respect to 'our squaraine dye' B1 (Fig. 1). The extinction coefficient would also suffer due to the loss of conjugation with the benzene rings, thus requiring slightly thicker layers for cell fabrication and high ODs.

B1 was the first in a series of dyes to be produced that extend the absorption of DSSCs into the near-IR range. Fig. 2 shows the absorption spectrum of B1 in ethanol. As it can be seen the absorption is both broadened and shifted toward the red upon absorption on the film. In the case of the liquid cells it was found that the cells functioned best in the presence of chenodeoxycholic acid (CDCA) and that higher potentials were obtained with *t*-butylpyridine. The high concentration (10 M excess) of CDCA should have hindered the formation of aggregates and as such it is assumed that the red shift of the main peak to 679 nm results from the coupling of the π^* orbital with the TiO_2 3d orbitals. The second peak which is seen at ~630 nm is due to a transition to a

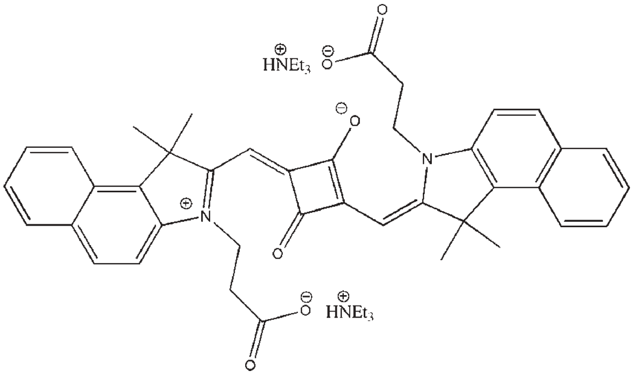

Fig. 1 Molecular structure of the squaraine dye B1.

Laboratoire de Photonique et Interfaces, Institute des Sciences et Ingénierie Chimiques, École Polytechnique Federal Lausanne, CH-1015, Lausanne, Switzerland. E-mail: michael.grätzel@epfl.ch; Fax: +41-216934111; Tel: +41-216933112

† Electronic supplementary information (ESI) available: Experimental. See DOI: 10.1039/b609266g

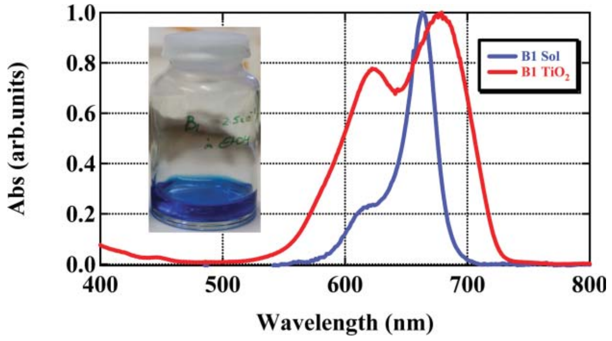

Fig. 2 UV-vis curves (normalised) of B1 (blue) in ethanol (6.28 × 10^{-5} M) and adsorbed on an 8 μm TiO_2 electrode (red).

higher energy vibronic level, which results from an effective wavefunction overlap in the first excited state.

The current-density–voltage (*J*–*V*) curves of the liquid and solid-state cells are shown below (Fig. 3). Despite the narrow absorption in the near-IR, the liquid cells still give a short-circuit current density of 8.6 mA cm^{-2}, an open-circuit voltage of 591 mV and a fill factor of 73%, giving an impressive overall efficiency of 3.7%. To the best of our knowledge, this is the highest reported efficiency for a squaraine based organic 'dye-sensitised' solar cell. Integration of the IPCE curves of the liquid devices resulted in a good current match, suggesting that the response of the cells was linear with illumination intensity (*I*). The linear dependence was also confirmed from the J_{sc}s obtained for the *J*–*V* curves at 0.1 and 1 Sun. Fig. 4 shows typical IPCE curves for these devices. It can be seen that the peak of the IPCE of the liquid device is ~4 times greater than that of the solid-state device with the amorphous organic hole-transporter 2,2′,7,7′-tetrakis-(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-*spiro*-bifluorene (*spiro*-OMeTAD). The significant difference in the IPCE values seen here for the liquid and solid-state devices can be simply explained by the rate of the back-electron transfer (BET) process to the *spiro*-OMeTAD in solid-state cells. Considering the charge diffusion length L_D where $L_D = \sqrt{(D\tau)}$,[14] with *D* being the charge diffusion coefficient and τ the charge lifetime. The electron lifetime is much shorter in the solid-state[15] than in the liquid devices.[16] Therefore, even if the charge transport properties are identical L_D will be much shorter in the solid-state devices. The L_D is not nescessarily constant with illumination intensity, since *D* may vary independantly with *I*. As *I* increases L_D is likely to also increase. In the liquid cells the L_D is much greater than the film thickness and therefore, we observe a linear intensity dependance of J_{sc}. However, for the solid-state device L_D is comparable with film thickness.[17] Therefore small variations in L_D with *I* will result in variations in J_{sc} and explain the superlinearity of the J_{sc}. Furthermore, in the absence of UV light a Schottky barrier can be present at the SnO_2/TiO_2 interface that can further reduce the J_{sc} when measuring under monochromatic light.[18] A trade off between film thickness and light harvesting must be made in the solid-state devices and typically a film of only ~2 μm is used, compared to the 8–15 μm films used in the liquid solar cells. However, the high molar extinction coefficient, 1.8 × 10^{-5} $M^{-1}cm^{-1}$, of the organic dye B1 facilitated the use of a thin film without significant loss in the OD, resulting in the high efficiency of this solid-state device.

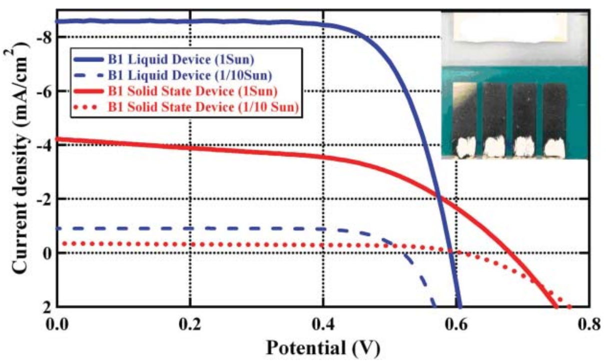

Fig. 3 *J*–*V* curves at (1 and 1/10 Sun) for the liquid (blue lines) and solid-state (red lines) DSSC devices, respectively.

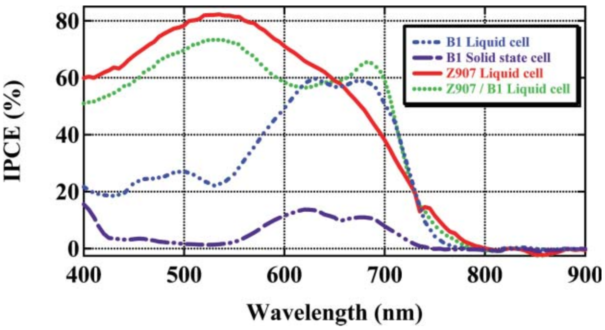

Fig. 4 IPCEs of three liquid cells sensitised with Z907 (red), B1 (blue) and a Z907/B1 (green) mix, respectively. The IPCE of the solid-state device is also shown (purple line).

Another challenge in the solid-state devices is the effective penetration of the hole-transporter material into the pores of the nanoporous TiO_2 film. Due to the large size of the *spiro*-OMeTAD molecules, small cavities within the nanoporous film may remain unfilled. Photons absorbed in this region will not add to the current as the excited dye will simply relax back to the ground state *via* recombination. It should be noted however, that the highest performance of solid-state 'dye-sensitised' solar cells currently yields an efficiency of just over 4%.[2,3] Nevertheless, solid-state cells sensitised with B1 have a short-circuit current density of 4.2 mA cm^{-2}, an open-circuit voltage of 681 mV and a fill factor of 53%, leading to a respectable overall efficiency of 1.5%.

Improvements can still be made, however, to optimise the concentration of CDCA used as the co-adsorbant to prevent aggregation of the dye. The CDCA competes with the dye for surface adsorption on the TiO_2 thus limiting dye uptake and hence optimisations will inevitably result in increased performance.

One advantage of solid-state devices is the higher V_{oc} obtained, *i.e.* 681 *vs.* 591 mV in liquid electrolyte cells. This is due not only to the redox level of the hole conductor, which is slightly more positive than the respective I^-/I_3^- couple used in the latter but also to the thinner TiO_2 films which help to increase charge collection efficiency. This increase in potential is generally very useful when dealing with purely organic dye sensitisers as the dyes themselves tend to have a lower LUMO with respect to their ruthenium based organometallic counterparts. In the case of B1 however, cyclic voltametry revealed that *versus* SCE, E^{ox} and E^{red} were +0.43 V and −1.11 V, respectively, with $E^{ox} - E^{red}$ (1.54 V). The LUMO level was calculated spectroscopically giving a value of −1.43 V *vs.* SCE. This suggests that B1 should have no problems injecting into TiO_2. The difference of −320 mV between the energy of the LUMO and E^{red} is in good agreement with Loutfy and Sharp.[19]

To demonstrate the idea of complimentary absorption and possible applications for red to near-IR dyes such as B1, so called 'cocktail-cells' were produced. (Fig. 4) The IPCE curves show two individual cells sensitised with a heteroleptic amphiphilic ruthenium dye Z907[20] and B1, respectively, and the 'cocktail-cell' containing both dyes as sensitisers. The mixed dye system was not optimised and thus yielded a slightly lower overall performance. It is interesting to note however, that the peak at 679 nm comes from the blue dye and that its IPCE value is slightly higher than that of a simple B1 cell. The IPCE has also increased by 6% from 60 to 66%. The reduction in the IPCE value for Z907 is related directly to its decreased concentration on the surface as the cells were dipped for only 2 hours as opposed to the standard 24 hours. As can be seen, the blue and red dyes demonstrate the desired complementary absorption. This also suggests that the cells could be enhanced through modification of the dipping time to increase red dye uptake. Of course the available number of surface sites for the blue dye will be reduced if more red dye is present, however this should not pose a problem given the high extinction coefficient of B1. It is interesting to note that even though considerably less B1 is present in the cocktail cell there is still an increase in the IPCE value. Therefore, it should be possible to further optimise the concentration of the red dye, without reducing the IPCE of the blue dye. Integration of a calculated photocurrent for an optimised cell suggests a possible increase of ∼4% in cell efficiency.

3-(2-Carboxyethyl)-1,1,2-trimethyl-1*H*-benzo[*e*]indolium iodide was prepared from the nucleophilic substitution reaction of 2,3,3-trimethylbenzo[*e*] indole and 3-iodopropanoic acid. The mixture was heated to 110 °C in 1,2-dichlorobenzene for 8 h. The product was isolated as a yellow powder with yield 86%. As the NMR and CHN both showed the product to be pure no further purification was necessary. ^1H NMR (400 MHz, D_2O) δ (ppm) 1.62 (6H, s, CH_3), 3.07 (2H, t, J = 6.67 Hz, CH_2), 4.76 (2H, t, J = 6.71 Hz, CH_2), 7.57 (1H, t, J = 7.35 Hz, ArH), 7.65 (1H, t, J = 7.20 Hz, ArH), 7.77 (1H, d, J = 8.97 Hz, ArH), 7.96 (1H, d, J = 8.03 Hz, ArH), 8.02 (1H, d, J = 8.98 Hz, ArH), 8.12 (1H, d, J = 8.39 Hz, ArH). Note: 2-methyl group not seen due to rapid exchange with solvent. CHN C (52.8) 52.0, H (4.93) 4.89, N (3.42) 3.12. HRMS (Q-TOF): *m*/*z* calcd. for [M] $C_{18}H_{20}NO_2$ 282.1494; obtained 282.1493. Mp 217–218 °C (decomp.).

(4*E*)-4-{[3-(2-Carboxyethyl)-1,1-dimethyl-1*H*-benzo[*e*]indolium-2-yl]methylene}-2-{(*E*)-[3-(2-carboxyethyl)-1,1-dimethyl-1,3-dihydro-2*H*-benzo[*e*]indol-2-ylidene]methyl}-3-oxocyclobut-1-en-1-olate triethylammonium salt was synthesised from 3-(2-carboxyethyl)-1,1,2-trimethyl-1*H*-benzo[*e*]indolium iodide and squaric acid in the presence of base. The mixture was heated to reflux in a mixture of *n*-butanol : toluene. The product was isolated as the triethylammonium salt through the reaction of the product with triethylamine in methanol with a yield 20–25%. ^1H NMR (200 MHz, MeOD) 1.30 (18H, t, J = 6Hz, CH_3), 2.07 (12H, s, CH_3), 2.77 (4H, t, J = 6 Hz, CH_2), 3.35 (12H, q, J = 6 Hz, CH_2), 4.57 (4H, t, J = 6 Hz, CH_2), 6.11 (2H, s, CH), 7.46 (2H, t, J = 8 Hz, ArH), 7.64 (2H, t J = 8 Hz, ArH), 7.72 (2H, d, J = 10 Hz, ArH), 7.98 (4H, d, J = 10 Hz, ArH), 8.28 (2H, d, J = 8 Hz, ArH). HRMS (Q-TOF): *m*/*z* calcd. for $[M^{+1}]$ $C_{40}H_{36}N_2O_6$ 641.2651; obtained 641.2642. UV-vis (MeOH) λ_{max} 663 nm. Mp 230 °C (decomp.).

In conclusion, a blue organic squaraine dye incorporating two carboxylic acid attaching groups has been synthesised and for the first time successfully used in both liquid and solid-state solar cells. The devices gave efficiencies of 3.7% and 1.5% at 1 Sun for the liquid and solid-state cells respectively. To the best of our knowledge, these are the highest efficiencies obtained so far for a squaraine sensitised DSSC.

The authors would like to thank Dr Shaik Zakeeruddin for the dye Z907 used in the mixed liquid DSSC devices. We would also like to thank Dr Udo Bach, Dr Oliver Kohle and Dr Henry Snaith for helpful advice and discussions.

References

1 T. Markvart, *Solar Electricity*, Wiley, Chichester, 2nd edn, 2000.
2 L. Schmidt-Mende, S. M. Zakeeruddin and M. Grätzel, *Appl. Phys. Lett.*, 2005, **86**, 013504.
3 L. Schmidt-Mende, U. Bach, R. Humphry-Baker, T. Horiuchi, H. Miura, S. Ito, S. Uchida and M. Grätzel, *Adv. Mater.*, 2005, **17**, 813.
4 D. Poplavskyy and J. Nelson, *J. Appl. Phys.*, 2003, **93**, 341.
5 R. Hulstrom, R. Bird and C. Riordan, *Sol. Cells*, 1985, **15**, 365.
6 R. Petermann, *Squaraine mit Verlaengerter Konjugation*, PhD thesis, Mainz University, Germany, 2001.
7 A. Treibs and K. Jakob, *Angew. Chem.*, 1965, **77**, 680.
8 H. E. Sprenger and W. Ziegenbein, *Angew. Chem.*, 1966, **78**, 78937.
9 A. Treibs and K. Jakob, *Liebigs Ann. Chem.*, 1968, **123**, 712.
10 R. W. Biegelow and H. Freund, *Chem. Phys.*, 1986, **107**, 159.
11 P. M. Kazmaier, G. K. Hamer and R. A. Burt, *Can. J. Chem.*, 1990, **68**, 530.
12 C. Li, W. Wang, X. Wang, B. Zhang and Y. Cao, *Chem. Lett.*, 2005, **35**, 554.
13 S. Alex, U. Santhosh and S. Das, *J. Photochem. Photobiol.*, 2005, **172**, 63.
14 L. Peter, N. Duffy, R. Wang and K. Wijayantha, *J. Electroanal. Chem.*, 2002, **524**, 127.
15 H. Snaith, S. Zakeeruddin, L. Schmidt-Mende, C. Klein and M. Grätzel, *Angew. Chem., Int. Ed.*, 2005, **44**, 6413.
16 Z. Zhang, S. Zakeeruddin, B. O'Regan, R. Humphry-Baker and M. Grätzel, *J. Phys. Chem. B*, 2005, **109**, 21818.
17 J. Krüger, R. Plass, M. Grätzel, P. J. Cameron and L. Peter, *J. Phys. Chem. B*, 2003, **107**, 7536.
18 H. Snaith and M. Grätzel, *Adv. Mater.*, 2006, **18**, 1910.
19 R. Loutfy and J. Sharp, *Photogr. Sci. Eng.*, 1976, **20**, 165.
20 M. Zakeeruddin, M. K. Nazeeruddin, R. Humphry-Baker, P. Quagliotto, C. Barolo, G. Viscardi and M. Grätzel, *Langmuir*, 2002, **18**, 952.