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Solar Cells

A High-Efficiency Panchromatic Squaraine Sensitizer for Dye-Sensitized Solar Cells**

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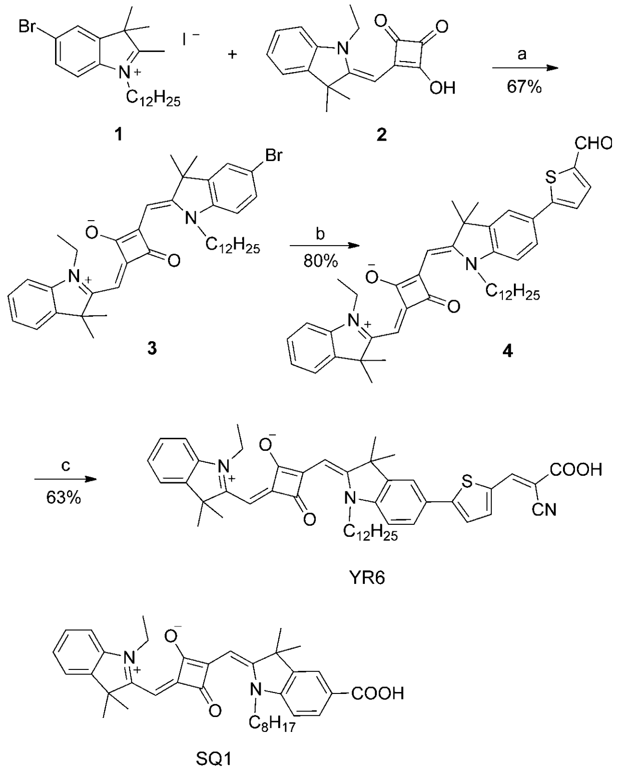
Since they were first reported in 1991,[1] dye-sensitized solar cells (DSCs) have advanced to the point where they can be considered as a contributor to the solar energy conversion market. State-of-the-art DSCs are currently characterized by solar-to-electric power conversion efficiencies (PCEs) of 9–12%.[2] To increase PCEs, it would be useful to develop sensitizers that exhibit increased light-harvesting ability in the near-infrared (NIR) region.

Squaraine dyes are promising for long-wavelength visible and NIR sensitization because of their strong absorption in this region.[3] A PCE of 4.5% under AM 1.5 solar conditions has been obtained using the indoline-terminated dye SQ1 (Scheme 1);[4] a bathochromic shift of the main absorption band and an increase of the PCE to 5.4% has been obtained for a similar dye in the which conjugation is slightly extended.[5] More recently, a PCE of 6.29% has been obtained using a more markedly unsymmetrical mixed pyrrole/indoline squaraine that also exhibits a red-shift of its main absorption peak relative to that of SQ1.[6] This previous work has demonstrated the efficacy of an unsymmetrical design for electron injection and of increased π conjugation to bathochromically shift the main low-energy absorption band;[5,6] however, the possibility that higher-energy absorption bands in squaraines can also contribute to the photocurrent in DSCs has only recently been investigated.[7] Herein we report the synthesis and optical, electronic, and photovoltaic properties of the unsymmetrical bis(indoline) squaraine sensitizer YR6 (Scheme 1), which incorporates more extended conjugation beyond the squaraine core than SQ1, as well as the more strongly π-accepting carboxycyanovinyl group as a surface-anchoring group instead of a directly attached carboxylic acid.[8] These features lead to a red-shift of the absorption maximum and to the presence of additional higher-energy bands that contribute to panchromatic absorption of YR6.



Scheme 1. Synthesis of YR6 and structure of SQ1. Reagents and conditions: a) toluene/*n*-butanol (2:1), reflux, 20 h; b) 5-formylthiophen-2-ylboronic acid, [PdCl$_2$(dppf)]·CH$_2$Cl$_2$, K$_2$CO$_3$, toluene, MeOH, microwave, 70°C, 15 min; c) cyanoacetic acid, piperidine, CH$_3$CN, reflux, 4 h. dppf = 1,1′-bis(diphenylphosphanyl)ferrocene.

Scheme 1 shows the synthesis of the squaraine sensitizer YR6 (see the Supporting Information for full details). The asymmetrically bromo-functionalized bis(indoline) squaraine **3** was synthesized by following reported reaction conditions for related species.[9] After microwave-assisted Suzuki coupling with 5-formylthiophen-2-ylboronic acid the aldehyde precursor **4** was isolated in high yield; this precursor was further condensed with cyanoacetic acid to afford YR6. The long alkyl chain attached to the nitrogen atom closer to the anchor end was chosen to improve solubility. As shown in

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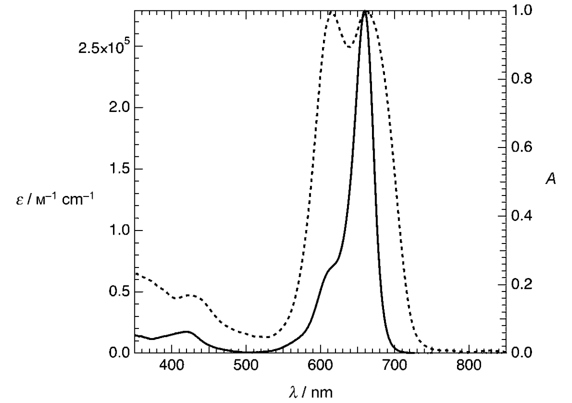

Figure 1. Absorption spectra of YR6 in ethanol (solid line) and on a 2.8 μm TiO_2 film (dotted line) derivatized by immersion in a solution of 0.1 mM YR6 and 10 mM chenodeoxycholic acid in ethanol for 24 h.

Figure 1, the UV/Vis/NIR absorption spectrum of YR6 in EtOH shows an absorption maximum at 659 nm with a high molar absorptivity of $279\,000\,\text{M}^{-1}\,\text{cm}^{-1}$. The red-shift of 23 nm from the SQ1 absorption maximum at 636 nm is consistent with the expected effect of extending the conjugation. The additional absorption of YR6 at shorter wavelengths is significant compared to that of SQ1, which shows negligible absorption in the 350–450 nm range, while the molar absorptivity of YR6 in EtOH varies from 6000 to $17\,000\,\text{M}^{-1}\,\text{cm}^{-1}$ in this region. When the dye is adsorbed onto a 2.8 μm nanocrystalline TiO_2 film, this absorption on the high-energy side of the absorption maximum is still observed, as well as a considerable broadening and a splitting of the low-energy band, presumably largely because of dye–dye interactions. The use of chenodeoxycholic acid (CDCA) as an additive in SQ1 dye solutions has been shown to significantly affect the absorption spectra of dye-coated titania films obtained from these solutions.[10] Spectra of YR6 on titania are also affected; the optical density of the YR6 absorption is reduced in the presence of CDCA (see the Supporting Information), thus suggesting reduction of the YR6 loading on titania because of competitive adsorption between CDCA and YR6. In addition, addition of CDCA and/or reduction of the dye concentration in the dipping solution leads to a slight narrowing of the split low-energy band, presumably because of reduction of the degree of dye aggregation, which can adversely affect performance.[10] As in the case of SQ1, the solar cell performance of YR6 is significantly enhanced by the use of CDCA.

Cyclic voltammetry of YR6 in a 0.1M solution of tetra-*n*-butylammonium hexafluorophosphate in CH_2Cl_2 indicated half-wave potentials corresponding to molecular oxidation and reduction of +0.10 and −1.64 V (versus $[FeCp_2]^+/[FeCp_2]$) respectively; these values correspond to potentials of approximately +0.80 and −0.94 V versus the normal hydrogen electrode (NHE).[11] The potential for the I_3^-/I^- redox couple is approximately +0.44 V versus NHE,[12] thus the YR6 oxidation potential is appropriate for regeneration of YR6 from its radical cation by an I_3^-/I^- electrolyte. In order to inject electrons efficiently into the TiO_2 conduction band, the excited-state oxidation potential of the dye should be at least as reducing as −0.66 V versus NHE.[11c,13] The excited-state energy $E^{(0,0)}$ for YR6 was estimated to be 1.86 eV from the intersection of normalized absorption and fluorescence spectra. The value of $E^{(0,0)}$ indicates an excited-state oxidation potential of −1.06 V versus NHE; this potential is sufficient for electron injection into the conduction band of TiO_2.

The photovoltaic characteristics of YR6-sensitized solar cells with a liquid electrolyte and a solid-state hole-transport material are shown in Figures 2 and 3, respectively (detailed procedures and conditions for solar-cell fabrication and measurements are described in the Supporting Information). Under standard global AM 1.5 simulated solar conditions, the YR6-sensitized cell with a standard I_3^-/I^--based liquid electrolyte gave a short-circuit photocurrent density (J_{sc}) of 14.8 $\text{mA}\,\text{cm}^{-2}$, an open-circuit voltage (V_{oc}) of 642 mV, and a fill factor (*FF*) of 0.71, thus corresponding to an overall PCE η of 6.74%, as derived from the equation $\eta = J_{sc}V_{oc}FF$. This efficiency stands out among the previously reported squaraine-sensitized cells, as does the very broad range of wavelengths over which high incident-photon-to-current efficiencies (IPCEs) are obtained. It is worth noting that the closest related compound, namely the mixed pyrrole/indoline squaraine dye reported in Ref. [6], only gave a PCE of 6.29% when a much thicker layer of TiO_2 was used; when using thicknesses comparable to that used here (6 μm), the PCE was significantly lower (4.48%). The high-energy absorption contributes to the photovoltaic performance of the sensitizer and a high IPCE is observed at these wavelengths, as observed for a previous sensitizer.[7a] Other factors such as aggregation may play a role in the panchromatic response, since the spectrum of the dye adsorbed onto TiO_2 is significantly different from the spectrum in solution. Although each of these factors

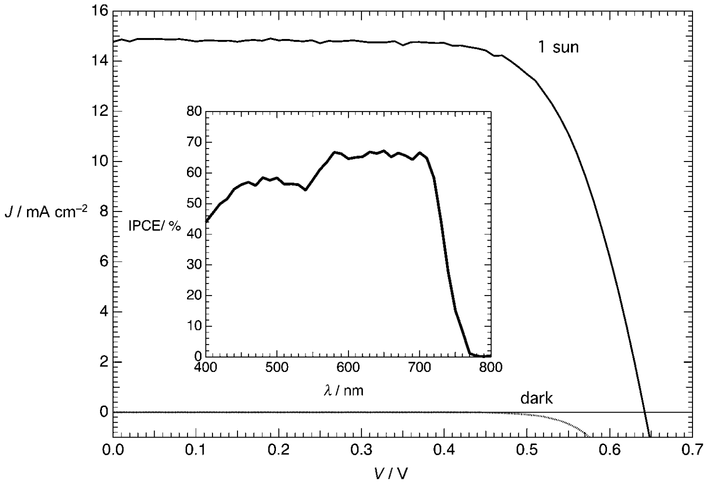

Figure 2. Current–voltage characteristics and IPCE (inset) of a liquid DSC with an active area of 0.2 cm^2 (mask area) in which a nanocrystalline TiO_2 film, supported on a conducting glass sheet, is derivatized with a monolayer of YR6 in the presence of chenodeoxycholic acid and using the JH34 redox electrolyte (see the Supporting Information).

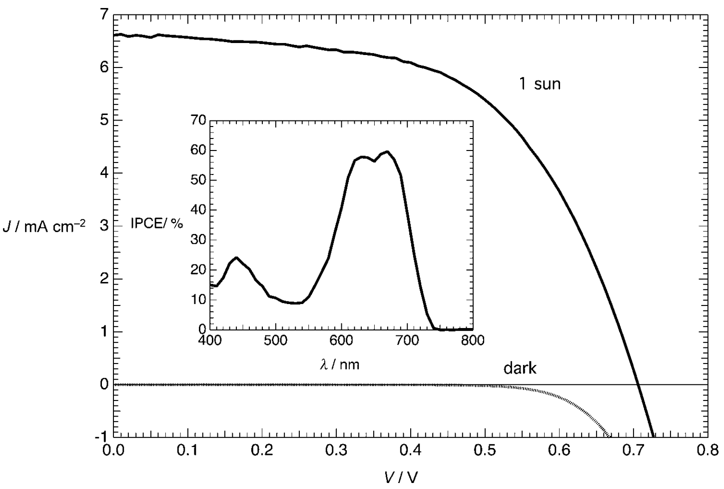

Figure 3. Current–voltage characteristics and IPCE spectrum (inset) of a solid-state DSC with an active area of 0.29 cm^2 in which a nanocrystalline TiO_2 film, supported on a conducting glass sheet, is derivatized with a monolayer of YR6 in the presence of chenodeoxycholic acid and uses a hole-transporting material (see the Supporting Information).

contributes to the increased overall efficiency, a major factor is the red-shifted absorption of YR6. DSCs that contain YR6 display a measurable IPCE response that extends to approximately 770 nm, with an IPCE of over 20 % observed for wavelengths as long as 740 nm, while for cells that contain the SQ1 sensitizer, an IPCE of below 20 % is seen for wavelengths longer than 700 nm. The differences between the responses of SQ1 and Y6 in this region are consistent with their absorption spectra on TiO_2; in the YR6 spectra the low-energy absorption maximum is at 663 nm and the absorbance at 700 nm is 40 % of that at the maximum, while the absorption maximum of SQ1 adsorbed on TiO_2 is at 651 nm, with very little absorption at wavelengths longer than 700 nm.[4]

Using a solid-state organic hole-transport material in place of the liquid electrolyte, and a TiO_2 film thickness of 2 μm, a lower short-circuit current density is seen, with some difference in the IPCE plot (Figure 3). Although the J_{sc} value (6.61 mA cm^{-2}) and fill factor (0.58) in the SSDSC were lower than in the liquid cell, the V_{oc} value (706 mV) was higher, as is characteristic for solid-state cells,[5] and the SSDSC performed well with an overall efficiency of 2.69 % at full sun. This value is higher than the efficiency of the current top-performing squaraine-sensitized SSDSC (2.15 % for the dye reported in Ref. [5]). The factors previously discussed for the liquid DSC also influence the SSDSC performance, and, therefore, further development of squaraine dyes with near-IR absorption for SSDSCs is warranted.

In conclusion, the squaraine sensitizer YR6 displays an outstanding PCE of 6.74 % in liquid DSCs and 2.69 % in SSDSCs under standard global AM 1.5 solar conditions. The high efficiencies are related to both the red-shifted absorption of YR6 compared to previous squaraine sensitizers, as well as to its high absorptivity ($> 10000\,\text{M}^{-1}\,\text{cm}^{-1}$ in solution) over much of the visible spectrum. This YR6 sensitizer opens up many possibilities for squaraine sensitizer development, where squaraines may be designed with functionalities that lead to both a red-shifted absorption maximum as well as panchromatic absorption for increased solar power conversion efficiency. Promising further avenues to explore could involve incorporating other donor and acceptor moieties on the indoline termini to increase the hole–electron separation in the excited state and to provide additional absorption in the higher-energy region of the spectrum.

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