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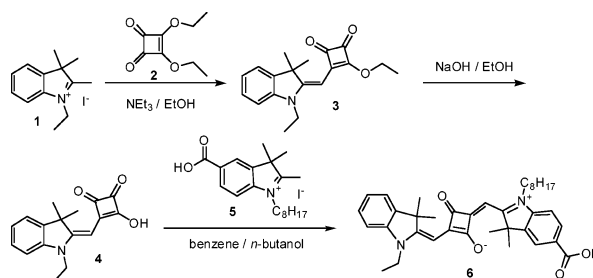
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Efficient Far Red Sensitization of Nanocrystalline TiO<sub>2</sub> Films by an  
Unsymmetrical Squaraine DyeJun-Ho Yum,<sup>†</sup> Pablo Walter,<sup>‡</sup> Simon Huber,<sup>‡</sup> Daniel Rentsch,<sup>‡</sup> Thomas Geiger,<sup>‡</sup> Frank Nüesch,<sup>\*,†</sup>  
Filippo De Angelis,<sup>§</sup> Michael Grätzel,<sup>†</sup> and Mohammad K. Nazeeruddin<sup>\*,†</sup>*Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, School of Basic Sciences,  
Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland, Laboratory for Functional Polymers, Empa,  
Swiss Federal Laboratories for Materials Testing and Research, Überlandstrasse 129, CH-8600 Dübendorf,  
Switzerland, and Istituto CNR di Scienze e Tecnologie Molecolari (ISTM), c/o Dipartimento di Chimica,  
Università di Perugia, I-06123 Perugia, Italy*

Received May 4, 2007; E-mail: mdkhaja.nazeeruddin@epfl.ch

Dye-sensitized solar cells (DSSCs) have attracted significant attention as low-cost alternatives to conventional solid-state photovoltaic devices.<sup>1–3</sup> In these cells, the most successful charge-transfer sensitizers employed are ruthenium polypyridyl complexes, yielding 9–11% solar-to-electric power conversion efficiencies under AM 1.5.<sup>4</sup> The majority of the ruthenium complexes reported to date show absorption in the visible region at around 535 nm. Essential for efficient conversion of solar energy by DSSC is the spectral match of the sensitizer absorption to the solar radiation, and in this regard, the ruthenium complexes are inadequate. Therefore, development of sensitizers with extended absorption and spectral sensitivity into the infrared region is essential. Squaraines are well-known for their intense absorption in the red/near-IR regions, and for that reason, they are an excellent option to explore for solar cell applications.<sup>5</sup>

Various groups have tested squaraines as sensitizers on wide band gap oxide semiconductors and obtained rather low power conversion efficiencies.<sup>6–10</sup> The reported low efficiencies of squaraines are due to aggregation and lack of directionality in the excited state.<sup>11</sup> There are several basic requirements guiding the molecular engineering of an efficient sensitizer. The excited-state redox potential should match the energy of the conduction band edge of the oxide. Light excitation should be associated with vectorial electron flow from the light-harvesting moiety of the sensitizer toward the semiconductor surface, providing for efficient electron transfer from the excited dye to the TiO<sub>2</sub> conduction band. Finally, a strong conjugation across the chromophore and anchoring groups is required for a good electronic coupling between the lowest unoccupied orbital (LUMO) of the dye and the TiO<sub>2</sub> conduction band. In order to satisfy these essential requirements, we have designed and developed a novel asymmetrical squaraine sensitizer that has a carboxylic acid group directly attached to the chromophore. In this paper, we report on the synthesis, electronic, and photovoltaic properties of the squaraine sensitizer. Scheme 1 shows the synthetic strategy used to obtain squaraine sensitizer (see Supporting Information for synthetic details). The UV/vis absorption spectrum (see Figure S1 in Supporting Information) of the squaraine sensitizer in ethanol shows an absorption maximum at 636 nm with high molar extinction coefficient ( $\epsilon = 158\,500\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ) corresponding to  $\pi$ – $\pi^*$  charge-transfer (CT) transitions. When the squaraine sensitizer is excited within the CT absorption band at room temperature in an air-equilibrated ethanol solution, it exhibits a strong luminescence maximum at 659 nm. The absorption spectrum of the squaraine sensitizer adsorbed on a 4  $\mu\text{m}$  TiO<sub>2</sub> film shows features similar to

**Scheme 1.** Synthetic Strategy used for the Squaraine Dye

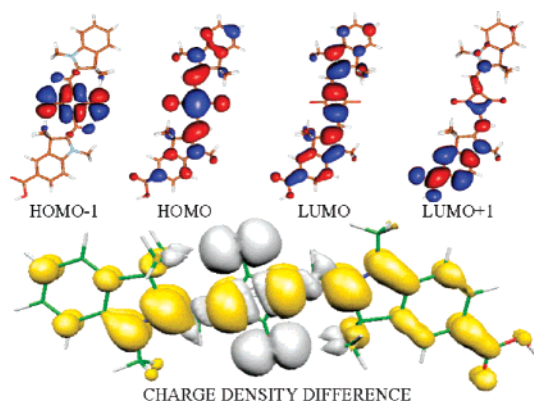
those seen in the corresponding solution spectrum but exhibits a slight red shift of 15 nm due to the interaction of the anchoring group with the surface (see Figure S2 in Supporting Information).

Cyclic voltammetry measurements were performed in acetonitrile solution with 0.1 M tetrabutylammonium tetrafluoroborate using ferrocene as internal standard at 0.69 V vs NHE. The squaraine oxidation and reduction potentials were obtained at  $E_{1/2} = 0.98$  and  $-0.78$  V vs NHE, respectively. The optical transition energy  $E^{(0-0)}$  of the squaraine sensitizer is at 1.92 eV, yielding an excited-state reduction potential of  $-0.94$  V vs NHE, which is negative enough to allow electron transfer into the TiO<sub>2</sub> conduction band.<sup>12</sup>

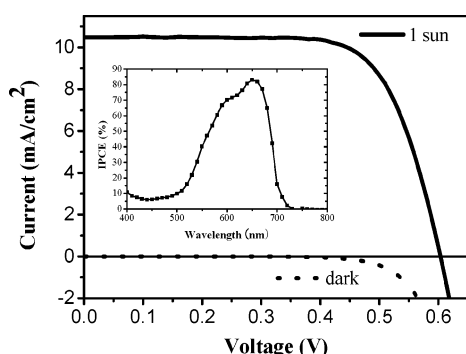
To gain insight into the nature of the excited states of the squaraine dye, we performed DFT/TDDFT calculations on a model in which the octyl substituents have been replaced by methyls and optimized its geometrical structure followed by calculation of the lowest vertical excitations. In doing so, we considered a  $C_s$  symmetry and used the BPW91 functional and a 6-311g\* basis set, as implemented in the G03 program package. Inspection of the electronic structure of the squaraine dye revealed that the HOMO is delocalized throughout the dye, while the HOMO-1, 0.23 eV below the HOMO, is entirely localized within the squaraine core, both orbitals belonging to the dye  $\pi$  framework (Figure 1). The LUMO, 1.32 eV above the HOMO, is a  $\pi^*$  orbital delocalized throughout the dye, with sizable contributions arising from the carboxylic group, while the LUMO+1, calculated 1.13 eV above the LUMO, is entirely localized in the dye portion bearing the carboxylic substituent. Excited-state TDDFT calculations predict an isolated intense transition at 596 nm ( $f = 1.301$ ), that is, only 0.13 eV blue-shifted compared to the experimental absorption maximum. This transition is mainly composed by HOMO–LUMO and HOMO–LUMO+1 excitations, the former being the dominant contribution, thus giving rise to a charge flow from the squaraine core to the outer molecular region. The resulting excited state is potentially strongly coupled to the semiconductor surface, due to charge delocalization involving the anchoring carboxylic group. This

<sup>†</sup> Swiss Federal Institute of Technology.<sup>‡</sup> Swiss Federal Laboratories for Materials Testing and Research.<sup>§</sup> Università di Perugia.

## COMMUNICATIONS



**Figure 1.** Top: isodensity plot of selected molecular orbitals of the squaraine dye. Bottom: charge density difference between the excited (596 nm) and ground state; the yellow (white) color indicates an increase (decrease) of charge density in a given molecular region.



**Figure 2.** Photocurrent action spectrum (inset) and current–voltage characteristics of the squaraine dye obtained with a nanocrystalline TiO<sub>2</sub> film supported onto a conducting glass sheet and derivatized with a monolayer of squaraine dyes in the presence of chenodeoxycholic acid. A sandwich-type cell configuration was used to measure the spectrum.

factor, together with the high dye molar extinction coefficient, is probably responsible of the high photocurrent and overall photovoltaic efficiency measured experimentally; see below.

The screen-printed double layer TiO<sub>2</sub> film consisting of a 10  $\mu$ m transparent layer and a 4  $\mu$ m scattering layer was prepared and treated with 0.05 M titanium tetrachloride solution using a previously reported procedure.<sup>4,13</sup> The films were heated to 500 °C in air and sintered for 20 min before use. Dye solutions were prepared in the concentration range of  $1 \times 10^{-4}$  M solution in ethanol containing 1, 10, and 60 mM 3a,7a-dihydroxy-5b-cholic acid (cheno) as an additive. The electrodes were dipped into the dye solution for 4 h at 22 °C, and the dye-coated electrodes were rinsed quickly with ethanol and used as such for photovoltaic measurements. The fabrication procedure for solar cells, the testing conditions, and the equipment used were reported in a previous work.<sup>4</sup>

Figure 2 shows the photocurrent action spectrum obtained with a sandwich cell. The incident monochromatic photon-to-current conversion efficiency (IPCE) plotted as a function of excitation wavelength shows 85% efficiency. Under standard global AM 1.5 solar condition, the squaraine-sensitized cell gave a short circuit photocurrent density  $j_{sc}$  of  $10.50 \pm 0.20$  mA/cm<sup>2</sup>, an open circuit voltage of  $603 \pm 30$  mV, and a fill factor (ff) of  $0.71 \pm 0.03$ , corresponding to an overall conversion efficiency  $\eta$  of 4.5%, as derived from the equation  $\eta = j_{sc} \times V_{oc} \times ff$  (Figure 2). The high efficiency of the squaraine sensitizer is attributed to the particular molecular design. First, the carboxylic acid group is part of the

conjugated  $\pi$ -system of the dye and provides strong electronic coupling to the conduction band of TiO<sub>2</sub>. Second, the asymmetry created by the octyl chain prevents surface aggregation and limits self-quenching of the excited state. To the best of our knowledge, these results represent a major breakthrough in the design and development of squaraine-based sensitizers.

In order to see the impact of high molar extinction coefficient of the squaraine sensitizer on photovoltaic properties, we have fabricated solar cells using transparent TiO<sub>2</sub> membranes of various thicknesses. The photocurrent increased with the thickness of the TiO<sub>2</sub> nanocrystalline layer. On the other hand, the photovoltage decreased with increasing thickness. Despite the very narrow absorption band of the squaraine sensitizer, devices using a 2.5  $\mu$ m thin TiO<sub>2</sub> layer yielded remarkably high photocurrent and IPCE of 8.20 mA/cm<sup>2</sup> and 80%, respectively, which we have attributed to the high molar extinction coefficient of the dye. Further optimization was achieved by using 10 mM concentration of cheno as coadsorbing additive (see Table S1 in Supporting Information).

In conclusion, we have demonstrated that selective functionalization of squaraine sensitizer yielded very high incident monochromatic photon-to-current conversion and 4.50% power conversion efficiency under one sun. Our data demonstrate that creating directionality and inhibiting self-quenching of the excited state of the sensitizer are the key for unprecedented efficiency of squaraines. This should spark a broad spectrum of interest in the field of organic sensitizers useful for photovoltaic windows that transmit part of the visible light.

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**Supporting Information Available:** Experimental and synthetic details of the sensitizer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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