Molecular Design of Squaraine Dyes for Efficient Far-red and Near-IR Sensitization of Solar Cells

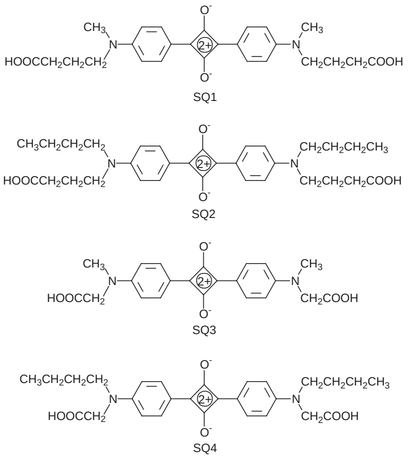
Chao Li, Weibo Wang, Xuesong Wang,* Baowen Zhang,* and Yi Cao
Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, P. R. China

(Received January 11, 2005; CL-050039)

The introduction of short carboxyl anchoring groups into anilino-squaraines resulted in a much improved photosensitization on nanocrystalline TiO_2 electrode over far-red/near-IR region, yielding a maximum monochromatic incident photon-to-current conversion efficiency of 73% at 670 nm.

Owing to the high photoelectric conversion efficiency (η) at low cost dye-sensitized nanocrystalline semiconductor solar cells (DSSCs) based on Ru(II) polypyridyl complexes and TiO_2 have been attracting wide scientific and technological interest over the past decade.[1] Dithiacyanato-bis(dicarboxy-bipyridyl)-Ru(II) (N3) has been keeping the record efficiency in DSSCs,[1b] however, the low molar extinction coefficient and the lack of absorption in the far-red/near-IR region limited further improvement in η. Though many efforts were focused on extending the absorption to the longer wavelengths, few Ru(II) complexes[1c] exhibit strong absorption in the red, and their preparation and purification were not straightforward, e.g. the so-called "black dye"[1c] of a Ru(II) complex having 4,4′,4″-tricarboxyl-2:2′,6′:2″-terpyridine as the main ligand. Organic dyes, not only having the potential advantages such as higher molar extinction coefficients but also easier procedures and lower cost in preparation and purification over their counterparts Ru(II) polypyridyl complexes, received more and more attention for application in DSSCs, and recently organic dyes, e.g. coumarin-dye NKX-2311 and NKX-2677, polyene-dye NKX-2569, and indoline-dye with high η in DSSCs comparable with Ru(II) polypyridyl complexes were developed.[2]

Squaraine dyes are well known for their intense absorption in far-red/near-IR, and as a result were widely investigated as far-red/near-IR sensitizers for large bandgap semiconductor in light of solar energy conversion,[3] and photocurrent quantum yield per absorbed photon of near unity was observed for a squaraine sensitized tin disulfide single crystals under sufficiently positive bias.[4] However, upon photosensitizing nanocrystalline TiO_2, low monochromatic incident photon-to-current conversion efficiencies (IPCEs) and low η were obtained. The weak coupling between the used squaraines and TiO_2 conduction band due to the lacking of carboxyl anchoring groups and the fast interfacial recombination of injected electrons with oxidized squaraines[3a,3b] may account for their unsatisfactory performance in DSSCs and should be overcome in such applications. We herein reported the application of four new carboxyl-containing squaraines (SQ1–SQ4, Scheme 1) in DSSCs, where carboxyl anchoring groups may simultaneously promote electron injection and restrict electron recombination, and as a result, IPCE and η up to 73 and 3.4%, respectively were observed, representing the highest IPCE and η values so far in squaraine-based organic-dye-sensitized semiconductor solar cells over far-red/near-IR region.



Scheme 1. Molecular structures of SQ1–SQ4.

SQ1–SQ4 were synthesized by refluxing one equivalent of squaric acid with two equivalents of corresponding carboxyl-containing aniline in 2-propanol in the presence of orthoformate for 2 h, and purified by recrystallization from DMSO/CH_2Cl_2.

Dye-sensitized nanocrystalline TiO_2 photoanodes (9-µm thick) were prepared following the reported methods.[1b] TiO_2 paste (Ti–Nanoxide T, Solaronix SA) were spread onto fluorine-doped tin oxide conducting glass (20 Ω/□) and sintered at 450 °C for 30 min. Then TiO_2 electrodes were soaked in a DMSO solution of squaraines (1 mM) at room temperature for 2 h. After rinsed with absolute ethanol, the electrodes were dried under a stream of dry air. The sandwich-type cells consisted of a dye-sensitized nanocrystalline TiO_2 photoanode, a Pt-loaded conducting glass as cathode, and an electrolyte solution which was 0.5 M LiI, 0.05 M I_2, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI) in methoxyacetonitrile (MAC).

SQ1–SQ4 all exhibit a sharp and intense absorption band in DMSO solution with maximum of 651.5, 655.5, 643.0, and 647.5 nm, respectively (see Figure A in supporting information). The absorption maximum blue shift of SQ3 and SQ4 with

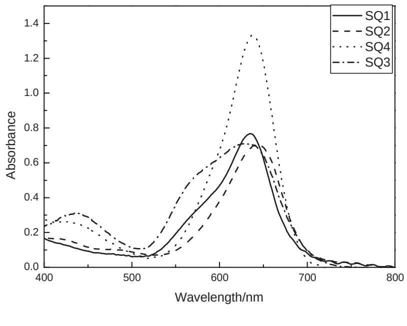


Figure 1. Absorbance of SQ1–SQ4 on TiO_2 electrodes.

respect to that of SQ1 and SQ2 can be attributed to the stronger electron-withdrawing ability of short carboxyl group (–CH_2-COOH) than long carboxyl group (–$(CH_2)_3$COOH), which is consistent with the positive shift of the oxidation potentials of SQ3 (0.80 V vs SCE) and SQ4 (0.80 V) than those of SQ1 (0.71 V) and SQ2 (0.71 V) measured with cyclic voltammetry. The molar extinction coefficients at $\lambda_{\max}$ are 3.77, 3.21, 1.99, $2.99 \times 10^5\,M^{-1}cm^{-1}$ for SQ1–SQ4 respectively, one order of magnitude larger than Ru(II) polypyridyl complexes. Upon adsorption on TiO_2 electrodes the absorption spectra of SQ1–SQ4 were broadened significantly (Figure 1). While SQ1 and SQ2 existed mainly in monomer on the TiO_2 surface, H-type aggregation occurred apparently for SQ3 and SQ4 which was signaled by the appearance of a new absorption band in the region of 400–500 nm,[5] suggesting short carboxyl anchoring groups favor interactions between dyes and/or between dye and TiO_2.

Figure 2 shows action spectra of IPCEs for SQ-based DSSCs. The close similarity between the action spectra and the absorption spectra on TiO_2 indicates the photocurrent originated from the excited squarains including both their monomers and aggregates. The short carboxyl anchoring groups in SQ3 and SQ4 seem play a twofold role. On the one hand, they may enhance the interaction of dyes with TiO_2 by shortening their distance, and therefore promote electron injection.[6] On the other hand, they raise the oxidation potential of dyes and enlarge the energy gap between oxidized SQ and I^-/I_3^- couples, as a result may speed up the reduction of oxidized SQ by I^- and restrict the recombination of injected electrons with oxidized dyes.[7] These reasons lead to efficient sensitization in far-red/near-IR region with the IPCE maximum of 73% for SQ4, which is the highest IPCE value for squaraine-based organic-dye-sensitized solar cells reported so far, and even higher than that of N3 in this region (the IPCE of N3 was 60% at 670 nm[1d]). Moreover, short carboxyl anchoring groups favor the formation of H-aggregate, enhance the light harvesting over the blue and green light region, and consequently improve the short-circuit photocurrent[5] and η (see below).

The conspicuous photoelectric conversion properties of SQ3, SQ4 were further confirmed in measurements of photocurrent-voltage characteristics of squaraine-based DSSCs (see Table 1 in supporting information). Though no detailed cell optimization was carried out, short-circuit photocurrents of 10.3 mA/cm^2, open-circuit photovoltages of 0.35 and 0.38 V, and fill factors of 0.54 and 0.52 were achieved for SQ3 and SQ4-sensitized cell, respectively, corresponding to η values of 3.2 and 3.4%, which are the highest conversion efficiencies obtained so far among squaraine-based organic-dye-sensitized solar cells, implying rational structure design can endow squaraines promising photosensitizing behaviors in DSSCs. It was reported that anilino-squaraine can give persistent radical cation upon one-electron oxidation,[8] a desirable property for DSSC application with regard to stability.

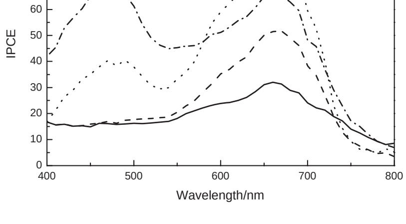


Figure 2. IPCE for SO1–SQ4 sensitized TiO_2 electrodes.

J_{sc} increased linearly with the increase of the light intensity till 60 mW/cm^2, but the increasing extent of J_{sc} diminished with the further increase of the light intensity, probably limited by the ion transportation in the electrolyte. The V_{oc} values obtained were relatively low (0.35–0.38 V), therefore, the cell optimization will be focused on the improvement of the V_{oc}. The V_{oc} values were higher for DSSCs sensitized by SQ2 and SQ4 containing longer hydrophobic alkyl chains, in which the dark currents were diminished at the same bias potentials with respect to the cells sensitized by SQ1 and SQ3 (see Figure B in supporting information). Such observation can be attributed to the blocking effect of the long alkyl chains upon the I_3^-,[9] which urges us to synthesize squaraines bearing both short carboxyl groups and longer alkyl chains (e.g. substituting $C_{12}H_{25}$ or $C_{16}H_{33}$ for C_4H_9 in SQ4) for achieving higher V_{oc}.

Squaraines had been successfully used to cooperatively sensitize TiO_2 electrode with Ru(II) polypyridyl complex.[3c] While Ru(II) polypyridine complexes absorb blue and green light efficiently, squaraine dyes can harvest red and near-IR light, and therefore their cooperation may lead to a panchromatic sensitizing system for DSSCs. Thus, the improved photosensitizing properties encourage us to continue co-sensitizaton approach with SQ4-like squaraines.

We thank the Ministry of Science and Technology of China for support (G2000028204).

References

1 a) B. O'Regan and M. Grätzel, *Nature*, **353**, 737 (1991). b) M. Grätze, *J. Photochem. Photobiol., A*, **164**, 3 (2004). c) M. K. Nazeeruddin, P. Péchy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, and M. Grätzel, *J. Am. Chem. Soc.*, **123**, 1613 (2001). d) M. Grätzel, *J. Photochem. Photobiol., C*, **4**, 145 (2003).
2 a) K. Hara, K. Sayama, Y. Ohga, A. Shinpo, S. Suga, and H. Arakawa, *Chem. Commun.*, **2001**, 569. b) K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, and H. Arakawa, *New J. Chem.*, **27**, 783 (2003). c) K. Hara, M. Kurashige, S. Ito, A. Shinpo, S. Suga, K. Sayama, and H. Arakawa, *Chem. Commun.*, **2003**, 252. d) T. Horiuchi, H. Miura, K. Sumioka, and S. Uchida, *J. Am. Chem. Soc.*, **126**, 12218 (2004).
3 a) P. V. Kamat, S. Das, K. G. Thomas, and M. V. George, *Chem. Phys. Lett.*, **178**, 75 (1991). b) P. V. Kamat, S. Hotchandanl, M. Lind, K. G. Thomas, S. Das, and K. G. Thomas, *J. Chem. Soc., Faraday Trans.*, **89**, 2397 (1993). c) D. Zhang, W. Wang, Y. Liu, X. Xiao, W. Zhao, B. Zhang, and Y. Cao, *J. Photochem. Photobiol., A*, **135**, 235 (2000).
4 N. Takeda and B. A. Parkinson, *J. Am. Chem. Soc.*, **125**, 5559 (2003).
5 K. Saito, *J. Phys. Chem. B*, **105**, 4235 (2001).
6 K. Sayama, K. Hara, Y. Ohga, A. Shinpou, S. Suga, and H. Arakawa, *New J. Chem.*, **25**, 200 (2001).
7 S. Das, K. G. Thomas, and M. V. George, "Photophysical and Photochemical Properties of Squaraines in Homogeneous and Heterogeneous Media," p 467.
8 L. Eberson, *J. Phys. Chem.*, **98**, 752 (1994).
9 P. Wang, S. M. Zakeeruddin, J. Moser, and M. Gratzel, *J. Phys. Chem. B*, **107**, 13280 (2003).

Published on the web (Advance View) March 12, 2005; DOI 10.1246/cl.2005.554