SUPPORTING INFORMATION

Enhancing the efficiency of a dye sensitized solar cell due to the energy transfer between CdSe quantum dots and a designed Squaraine dye

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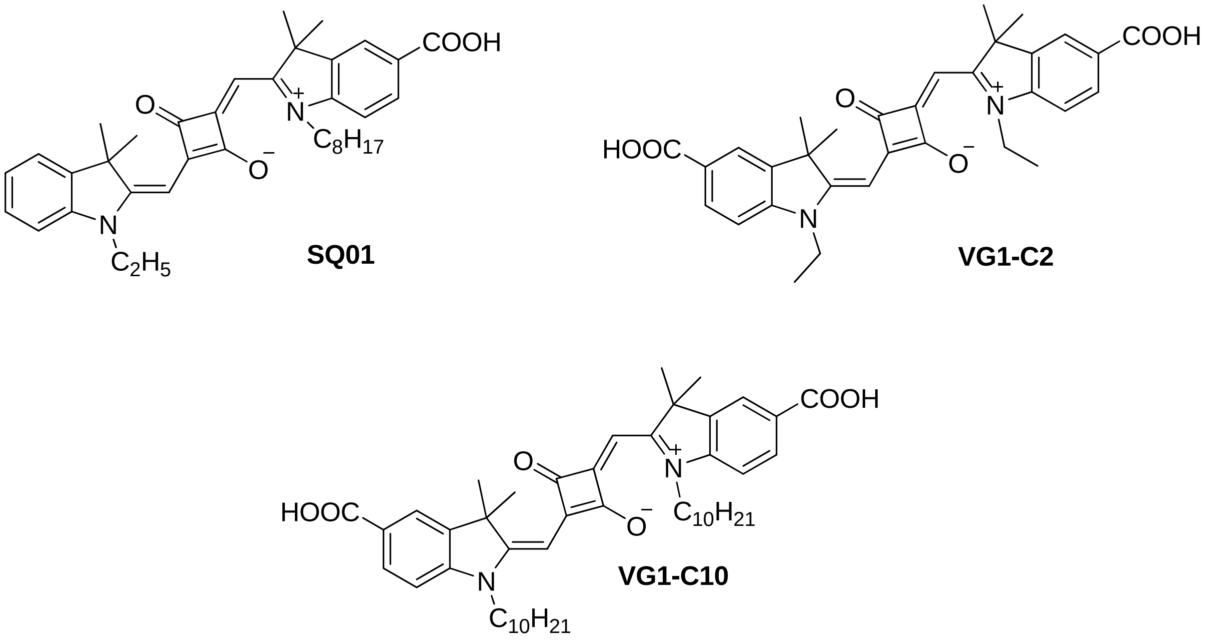
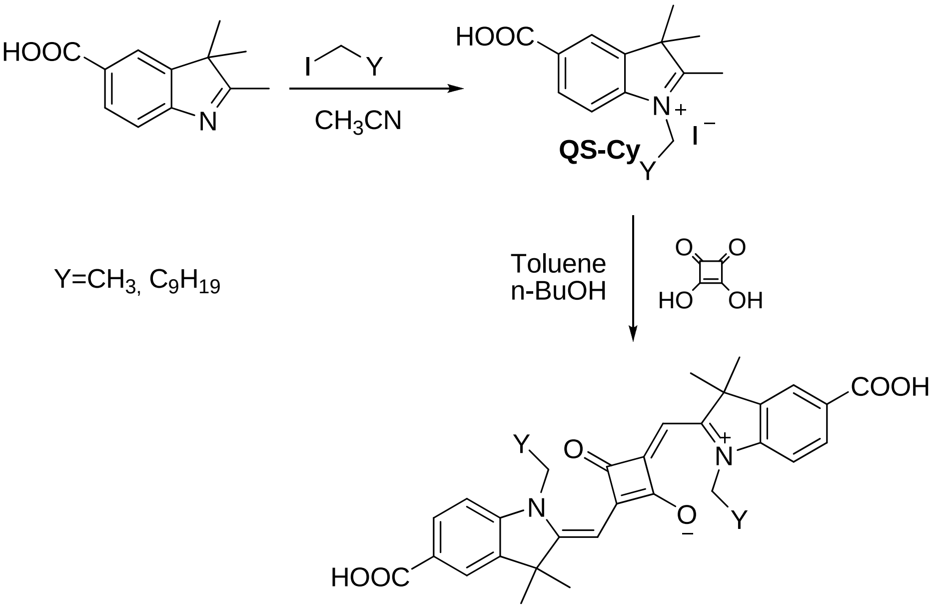


SQ01 **VG1-C2** **VG1-C10**

Figure 1-SI Structures of the studied squaraines.



QS-Cy

Y=CH_3, C_9H_{19}

VG1-Cy

Scheme 1 SI: Synthetic pathway

1. Synthesis

1.1 CdSe QDs synthesis

All reactions were performed under an inert Ar atmosphere on a Schlenk line. Cadmium oxide (CdO, 99%), 1-hexadecylamine (HDA, 99%), tri-n-octylphosphine (TOP, 90%), and tri-n-octylphosphineoxide (TOPO, 99%) were purchased from Aldrich. Selenium powder (Se, 99.99%) was purchased from Chempur. Prior to their use HDA was degassed at 100 °C for 30 min while TOPO and TOP were degassed at 190 °C for 1 h.

In a three-neck flask, 0.2 mmol of CdO and 0.5 g of stearic acid were heated to 180 °C until the mixture became clear and then cooled down to room temperature. 3 ml of HDA and 6 ml of TOPO were added to the mixture and degassed again at 100 °C for 15 minutes. The mixture was then heated to 310 °C under vigorous stirring and 1 ml of 1 M TOPSe was swiftly injected. The temperature was lowered to 280 °C for the nanocrystal growth for ~3 minutes. The heating was removed after the desired sized particles (emission at 600 nm) were formed and then the solution was suddenly cooled to room temperature by putting a water bath. To isolate the QDs, a toluene/methanol (MeOH) (1:1 vol:vol) mixture was added, followed by centrifugation at 3000 rpm for 5 minutes. The resulting precipitate could readily be dispersed in a number of organic solvents, including hexanes, toluene or chloroform.

1.2 Synthesis of squaraine dyes

1.2.1 Materials and structural characterization

All the chemicals were purchased from Sigma Aldrich, and were used as received. The glassware used for the quaternarization synthesis was heated overnight in an oven at 150°C and assembled in the oven, then cooled under Ar flux before starting the reactions. TLC was performed on silica gel 60 F254 plates using dichloromethane (DCM) and MeOH (90:10) as eluents.

ESI-MS spectra (positive ions) were recorded using a LCQ Deca XP plus spectrometer (Thermo), with electrospray interface and ion trap as mass analyzer. The flow injection effluent was delivered into the ion source using nitrogen as sheath and auxiliary gas.

^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Bruker Avance 200 NMR in acetone, dimethylsulfoxide-d_6 (DMSO-d_6) using their signals as a reference. NMR signals are described by use of s for singlet, d for doublet, t for triplet, m for multiplet.

SQ01, QS-C2, VG1-C2 were synthesized and characterized previously[1].

1.2.2 QS-C10

1.5 g (7.38 mmol) of 2,3,3-trimethyl-3*H*-indole-5-carboxylic acid and 5.9 g of 1-iododecane were dissolved in 50 ml CH_3CN and refluxed under argon for 24 h. The solvent was evaporated and the crude product was washed with diethyl ether several times and filtered off. The product obtained was a pink powder. 1.8 g (51.7 %); ^{1}H NMR (200 MHz, DMSO-d_6): ppm = 8.37 (s, 1H), 8.30 (d, J = 8.0 Hz 1H), 7.99 (d, J = 8.0 Hz, 1H), 4.54 (t, 2H), 1.97 (m, 2H), 1.56-1.40 (m, 14H), 1.65 (s, 3H), 1.29 (s, 6H), 0.88 (t, 3H).

1.2.3 VG1-C10

1 g (2.12 mmol) of 5-carboxy-2,3,3-trimethyl-1-decyl-3*H*-indolium iodide and 120 mg of 3,4-dihydroxycyclobut-3-ene-1,2-dione were dissolved in a mixture of 10 ml toluene and 10 ml *n*-butanol. The mixture was refluxed with a Dean-Stark apparatus for 6 h. After 10 min the solution turned green and after 1 h to blue-green color. The solvent was removed by distillation until the product precipitated. The crude product was recrystallized with n-butanol and filtered off. The

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[1] a) J. Park, C. Barolo, F. Sauvage, N. Barbero, C. Benzi, P. Quagliotto, S. Coluccia, D. Di Censo, M. Grätzel, M. K. Nazeeruddin, G. Viscardi, *Chem. Commun.* **2012**, accepted; b) S. Kuster, F. Sauvage, M. K. Nazeeruddin, M. Grätzel, F. A. Nüesch and T. Geiger, *Dyes and Pigments*, 2010, **87**, 30-38

product was obtained as a blue-grey powder. 437 mg (53.9%) ^{1}H NMR (200 MHz, DMSO-d$_6$) ppm = 8.03 (s, 2H), 7.97 (d, 2H), 7.44 (d, 2H), 5.90 (s, 2H), 4.13 (q, 4H), 1.70 (s, 12H), 1.40–1.20 (m, 32H), 0.86 (t, 6H). ^{13}C NMR (50MHz, Acetone-d$_6$) ppm = 182.06, 180.59, 169.90, 167.09, 146.13, 141.71, 130.28, 126.26, 123.20, 109.88, 87.78, 48.68, 31.79, 26.68, 26.37, 22.22, 13.53. MS (ESI-) *m/z*: 763.50 [764.48 calcd. for [($C_{48}H_{64}N_2O_6$)]

2. Experimental procedures

2.1 UV spectra - Determination of the λ_{max} and molar absorption coefficients

A certain amount of the dye (typically 7-10 mg) was dissolved in 10 ml of DMSO. 0.25 ml aliquot of this solution was diluted to 25 ml with a proper solvent (stock solution). Three samples were performed by diluting 1.0, 2.5 and 5 ml of this solution to 25 ml. The solutions obtained were analyzed by UV-Vis spectroscopy (Cary 300 Bio) using quartz cuvettes (1 cm pathway length). Absorbance at the λ_{max} for the each solution was plotted vs. dye concentration with subsequent linear fitting. The slope of the plot is the molar absorption coefficient (ε). For the purpose of reproducibility this determination was repeated twice by preparing two more dye stock solutions in DMSO which were subjected to the same dilution procedure. The logε obtained from the two separate data sets were compared: if their difference was less or equal to 0.02 with respect to their average values, the data were considered acceptable and the average of the two values was taken. Otherwise, one more dye stock solution was prepared; the whole procedure was repeated until the difference of 0.02 was attained.

2.2 Fluorescence Emission spectra

Fluorescence measurements were performed using a Fluorolog 2 (Jobyn Ivon). The excitation wavelength was set at 600 nm. A few mg of the dye was loaded in a test tube and a few ml of a proper solvent were added. The test tubes were sonicated for approx. 1 min, and left for about 30 minutes to accomplish complete solubilization. The sample was used to prepare more diluted solutions, and their absorbance at λ_{max} was determined in order to ensure that the absorbance is maintained lower of 0.1 units of absorbance. For every solution fluorescence emission spectrum was detected and λ_{em} was obtained.

Two standards, Rhodamine 101 dissolved in EtOH/0.01 M HCl and Cresyl Violet in MeOH, were measured under the same conditions as for squaraine samples.

Operative conditions (Rhodamine 101 quantum yield = 0.96 and Cresyl Violet = 0.54)[2]:

- Rhodamine 101: λ_{ex} = 535, emission range: 545-800 nm, excitation and emission slits: 3 nm.
- Cresyl Violet: λ_{ex} = 520, emission range: 530-800 nm, excitation and emission slits: 3 nm.

The quantum yield[3] is determined by:

$$\phi_x = \phi_{ST} \frac{A_x}{A_{ST}} \frac{I_{ST}}{I_X} \left(\frac{\eta_x^2}{\eta_{ST}^2} \right) \qquad \text{(eq. 1)}$$

where Φ_x is the measured quantum yield for the sample, Φ_{ST} in the quantum yield of the standard dye (Rhodamine 101 or Cresyl violet), A_x and A_{ST} are the integrated areas under the fluorescence emission curve of the sample and the standard reference respectively, I_{ST} and I_x are the absorbance of the standard dye and the sample respectively, η_x and η_{ST} are the refractive indexes for the solvents in which the sample and the standard reference are dissolved respectively. The reported quantum yield is the average of the values obtained vs Rhodamine 101 and Cresyl Violet respectively.

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[2] *Anal. Chem.*, **2009**, 81, 6285-6294

[3] Lakowicz JR. Principles of fluorescence spectroscopy. New York: Springer- Verlag; 2006.

Fluorescence lifetimes were obtained on a Fluorolog 2 spectrofluorimeter equipped with a NanoLED source (emitting at 635nm) using a photon counting detector (TBX04). The fluorescence decay was recorded at 650 or 670 nm.
The same solutions as for the quantum yield determination were used. The data were fitted to a single exponential function giving the lifetime.

2.3 IR Spectroscopy measurements

FT-IR spectra of the dye powder were recorded in KBr pellets on a Shimadzu FT-IR Spectrometer (FTIR 8400). The resolution was set at 1 nm and the data were baseline subtracted and treated with triangle apodization function. Dyes adsorbed on TiO_2 electrodes were analyzed using ATR (diamond, MKII Golden Gate) from Specac.

2.4 Optical Characterization of QDs

UV-Vis absorption spectra were recorded using a Cary 50 spectrophotometer (Varian Inc.). Fluorescence measurements were performed with a FluoroMax-4 spectrofluorimeter (HORIBA Jobin Yvon Inc.). Time resolved PL traces were recorded on a Fluorolog-3 spectrofluorimeter (HORIBA Jobin Yvon Inc.) using a 200 ps pulsed laser diodes emitting at 470 nm and 635 nm (for pure VG1-C10 film). All measurements were performed at room temperature. The PL QY of the CdSe QDs was evaluated according to the procedure described in ref.[1] using Rhodamine 6G and Rhodamine 101 solutions in ethanol as reference standards (PL QY = 95 and 96%, respectively).

2.5 CdSe QDs/VG1-C10 composite films preparation

Composite films were prepared by drop-casting QDs+VG1-C10 mixtures of different compositions in THF onto quartz glass plates with subsequent drying.

3. Optical Characterization

3.1 Optical Characterization of squaraine dyes

3.1.1 UV-VIS

UV-VIS spectra were collected for the squaraine dyes using six different solvents: THF, DCM, DMSO, acetonitrile (ACN), ethanol (EtOH) and MeOH, in the concentration range of $1 \cdot 10^{-6}$ - $5 \cdot 10^{-5}$ M. The spectra showed substantial negative solvatochromism: the λ_{max} decreases when the solvent polarity increases. The solvatochromic behaviour is demonstrated in Figure 2-SI and solvatochromic data along with logε, FWHM (Full Width at Half Maximum) and the oscillator strength are reported in Table 1-SI,

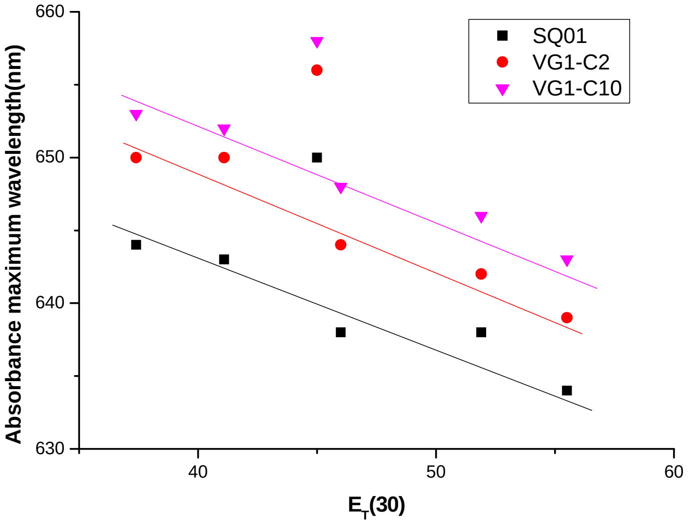

Figure 2-SI: negative solvatochromic behaviour for UV-Vis λ_{max} vs $E_T(30)$, line is from regression, excluding DMSO outlier data .

Table 1-SI: Absorption maxima (λ_{max}) for the SQ01 and VG1-C10 squaraines in different solvents

Solvent	SQ01				VG1-C2				VG1-C10			
	λ_{max}	Logε	FWHM	O. Str.	λ_{max}	Logε	FWHM	O. Str.	λ_{max}	Logε	FWHM	O. Str.
THF	644	5.39	592	0.63	650	5.48	556	0.73	653	5.53	577	0.84
DCM	643	5.38	611	0.63	650	5.60	564	0.97	652	5.57	583	0.94
DMSO	650	5.21	590	0.41	656	5.45	596	0.73	658	5.41	644	0.72
ACN	638	5.30	670	0.58	644	5.44	602	0.72	648	5.48	620	0.81
EtOH	638	5.36	589	0.58	642	5.43	590	0.69	646	5.44	649	0.77
MeOH	634	5.39	632	0.67	639	5.47	583	0.74	643	5.52	621	0.89

A careful analysis of the λ_{max} shift reveals that the addition of the second carboxyl group (asymmetric squaraine SQ01 vs symmetric VG1-C10) leads to a red shift of 6 nm. The oscillator strength, while varying for different solvents, is high for VG1-C10. This accounts for a better ability of symmetric molecules to absorb light than the asymmetric ones confirming the literature data. A study of the aggregation ability of these dyes was performed in EtOH, since it was used for dye absorption onto TiO_2. The correlation with concentration was linear with excellent $r^2= 0.999$. The aggregation was thus excluded in the concentration range examined.

3.1.2 Fluorescence Measurements

Fluorescence emission was studied in the same solvents used for the UV spectra. The dyes were studied by the steady-state and time resolved spectroscopy.

Spectra acquired in the different solvents gave the solvatochromic results shown in Figure 3-SI and summarized in Table 2-SI. The emission maximum, the Stokes shift and the E_{0-0} transition were determined.

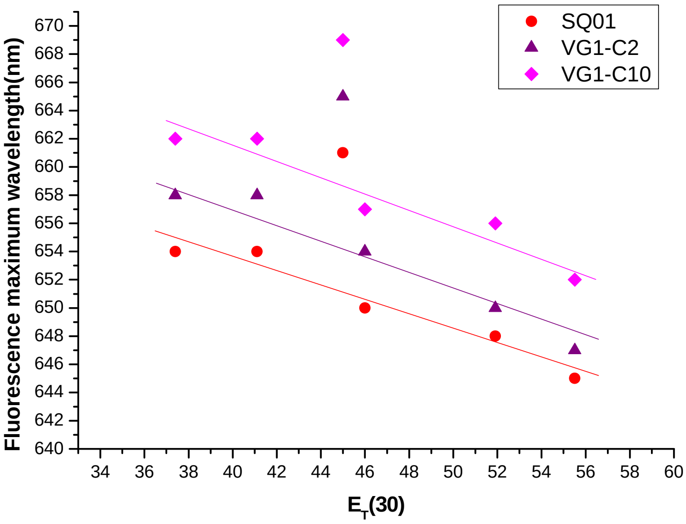

Figure 3-SI: Emission properties of squaraine VG1-C10: line is from regression, excluding DMSO data.

Table 2-SI: Emission maxima (λ_{em}) for the squaraine VG1-C10 in different solvents.

Solv.	SQ01			VG1-C2			VG1-C10		
	λ_{em} [nm]	Stokes Shift	ΔE_{0-0} [eV]	λ_{em} [nm]	Stokes Shift	ΔE_{0-0} [eV]	λ_{em} [nm]	Stokes Shift	ΔE_{0-0} [eV]
THF	648			654	10.0	1.91	662	9	1.89
DCM	650	13.5	1.93	654	11.5	1.91	662	10	1.89
DMSO	656	12.5	1.91	661	11.0	1.89	669	11	1.87
ACN	646	15.0	1.95	650	11.5	1.93	657	9	1.89
EtOH	642	12.0	1.95	648	9.5	1.93	656	8	1.91
MeOH	642	13.5	1.96	645	10.5	1.94	652	9	1.91

The negative solvatochromic behavior, already shown for the UV spectra, was evident also in the emission spectra. DMSO behaves anomalously also in this case. From the intersection of the absorption and emission spectra the zeroth-zeroth transition ΔE_{0-0} was evaluated. ΔE_{0-0} correlates with solvent polarity in agreement with the solvent polarity dependence for λ_{max}. The transition gap increases (while λ_{max} decreases) with solvent polarity. In agreement with the UV-VIS results, the incorporation of a second carboxyl leads to the red shift of λ_{em} of about 6 nm. An analysis of the Stokes shifts shows that for the symmetrical squaraine VG1-C10 the Stokes shift is in the range of 8-16 nm. The introduction of two carboxyl groups slightly reduces the E_{0-0} value and this is in agreement with a larger extension of the conjugation which is also reflected by the λ_{max} red shift.

The quantum yields and the results of time resolved spectroscopy are shown in Table 3-SI.

Table 3-SI: Lifetime, quantum yield, fluorescence constant and non-radiative constant for the squaraines

	SQ01				VG1-C10			
Solvent	τ	ϕ_{fl}	k_{fl}	k_{nr}	τ	ϕ_{fl}	k_{fl}	k_{nr}
	[ns]		$/10^{7}$ s^{-1}	$/10^{7}$ s^{-1}	[ns]		$/10^{7}$ s^{-1}	$/10^{7}$ s^{-1}
THF	0.975	0.506	51.90	50.67	1.742	0.33	18.94	38.46
DCM	0.640	0.359	56.09	100.16	1.600	0.39	24.38	38.13
DMSO	0.813	0.234	28.78	94.22	1.30	0.25	19.23	57.69
ACN	0.274	0.036	13.18	351.79	0.944	0.18	19.07	86.86
EtOH	0.649	0.267	41.14	112.94	1.140	0.33	28.95	58.77
MeOH	0.277	0.150	54.15	306.86	1.750	0.21	12	45.14

Every modification that reduces the rotational ability of indolenine groups can increase quantum yield, lifetimes and thus may provide an enhancement of the performance of resulting solar cells. When this rotation is inhibited, e.g. due to the presence of long alkyl chains, the quantum yield increases.

Fluorescence decay acquired by lifetime measurements in all the solvents was fitted by a mono-exponential function and only in a few cases a bi-exponential function was used. The analysis of the data presented in Table 3-SI shows that, in general, the increase of solvent polarity causes a reduction in the observed lifetime. The introduction of long alkyl chains can increase considerably the lifetime. The lifetime of VG1-C10 was nearly doubled with respect to the reference structure SQ01 already reported.

As a final confirmation, if we take into account some relationships between quantum yield and lifetimes:

$$\varphi_f = \frac{k_f}{k_f + k_{nr}} \quad \text{(eq. 4);} \qquad \tau = \frac{1}{k_f + k_{nr}} \quad \text{(eq. 5);} \qquad k_f = \frac{\phi_f}{\tau_f} \quad \text{(eq. 6)}$$

$$k_{nr}^{tot} = k_f(\phi_f^{-1} - 1) \qquad \text{(eq. 7)}$$

We could obtain the constant that account for all the non-radiative processes that reduce fluorescence. Obviously, the non-radiative process that suppresses fluorescence is more efficient in polar solvents. At the same time, the addition of longer alkyl chains into the indolenines causes a consistent reduction of these processes, in agreement with the previously demonstrated increase of lifetimes and quantum yields.

In order to explain and rationalize our results, we refer to a twisted intramolecular charge transfer state (TICT) mechanism, which was first proposed for cyanine and was found to be valid also for squaraines accounting for their very short lifetimes and low quantum yield.[4] This TICT mechanism also accounts for the substantially higher reduction of squaraine lifetimes obtained in polar solvents comparing to the less polar ones.

The addition of two carboxyl and two alkyl chains into a squaraine (from SQ1 to VG1-C10) reduces the rotational ability of indolenine moieties, thus increasing lifetimes and quantum yields.

Taking into account all the above stated reasons VG1-C10 has been chosen as the most perspective squaraine for the fabrication of the hybrid dye-QDs sensitized solar cells.

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[4] Tatikolov, A.S.; Costa, S.N.B. *J. Photochem. Photobiol.. (2001), 140, 147-156; b)* Gude C.; Rettig, W. *J. Phys. Chem. A* (2000),104, 8050-8057; c) Rettig, W. In *Electron Transfer I; Mattay, J., Ed.; Topics in Current Chemistry*, Vol. 169; Springer-Verlag: Berlin, 1994

4. Fabrication and characterization of the solar cells

TiO_2 double layer film composed of 8 μm transparent and 5 μm scattering layers was prepared by screen-printing and treated with a 40mM titanium tetrachloride solution as previously reported[2]. The films were heated at 500 °C in air for 30 min before use, then dipped in 0.5 mM dye solutions in ethanol containing 10 mM 3α,7α-dihydroxy-5β-cholic acid (chenodeoxycholic acid, CDCA) for overnight at room temperature. Before the QDs deposition the electrodes were rinsed with ethanol. The CdSe QDs were spin coated on top of the dye-covered titania layer at 2500 rpm for 10 s from a solution with a concentration of approx. 50mg/ml. After the QDs deposition, the solar cells fabrication was completed according to the procedure previously reported[2].The cobalt electrolyte consisted of 0.22M $[Co(II)\text{-} (bpy)_3](B(CN)_4)_2$, 0.05 M $[Co(III)(bpy)_3](B(CN)_4)_3$, 0.1 M $LiClO_4$, and 0.2 M tert-butylpyridine in acetonitrile[3].

Photovoltaic measurements have been performed as described in reference [4]. An AM 1.5 solar simulator equipped with a 450W xenon lamp (Model No. 81172, Oriel) with output calibrated to 100 MW cm^2 using a reference Si photodiode containing an IR-cutoff filter (KG-3, Schott) in order to reduce the mismatch between the simulated light and AM 1.5 (in the region of 350–750 nm) to less than 2% with measurements verified at two PV calibration laboratories [ISE (Germany), NREL (USA)]. I–V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of the photocurrent were 10 mV and 40 ms, respectively. The photovoltaic measurements were taken using a metal mask with an aperture area of 0.159 cm^2. A similar data acquisition system was used to determine the monochromatic incident photon-to-electric current conversion efficiency. Under full computer control, light from a 300 W xenon lamp (ILC Technology, USA) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., U.K.) onto the photovoltaic cell under test. The monochromator was incremented through the visible spectrum to generate the IPCE (λ) as defined by IPCE (λ) 1⁄4 12400(Jsc/λφ), where λ is the wavelength, Jsc is the short-circuit photocurrent density (mA cm^{-2}), and φ is the incident radiative flux (mW cm^{-2}).

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[4] J. S. Bendall, L. Etgar, S. C. Tan, N. Cai, P. Wang, S. M. Zakeeruddin, M. Grätzel, M. E. Welland, *Energy Environ. Sci.*, **2011**, DOI: 10.1039/c1ee01254a.