Electronic Supplementary Information (ESI)

for the Paper:

Contribution from a hole-conducting dye to the photocurrent in solid state dye-sensitized solar cells

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I. Electrochemical Measurements

Cyclic voltammetry measurements were carried out to determine the oxidation potential of the two dyes investigated herein.

SQ was measured adsorbed to a TiO_2 film on conducting FTO glass. **TVT** was measured as a spin-coated solid film on conducting FTO glass. The sensitized electrodes served as working electrode in the electrochemical measurement. A graphite electrode was used as a counter electrode and an Ag/AgCl in contact with LiCl in ethanol as reference electrode. The Fc/Fc^+ redox couple with a formal oxidation potential of 0.63 *vs* NHE[1] was used as a reference in these measurements. The ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide (99%, io-li-tec, IL-0023-HP-0050) served as solvent in these measurements. The scan speed was 0.1 V/s.

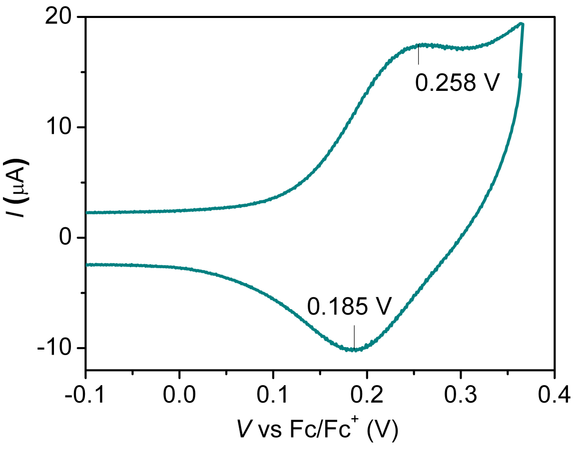

Fig. S1: Cyclic voltammogram of **SQ**

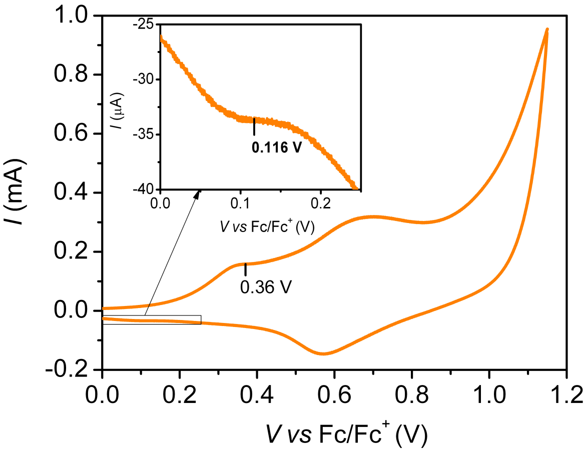

Fig. S2 Cyclic voltammogram of TVT in acetonitrile solution.

The cyclic voltammograms for **SQ** and **TVT** are shown in Fig. S1 and Fig. S2, respectively. The oxidation potentials E^0 were determined from the mean value of the cathodic E_{pc} and anodic E_{pa} peak potentials. For **TVT** the pc was poorly pronounced and is shown enlarged in the inset of Fig. S2. The oxidation potentials of **SQ** and **TVT** were determined to be 222 mV and 238 mV *vs.* Fc/Fc$^+$, respectively. In relation to NHE the formal oxidation potentials amount to 850 mV (**SQ**) and 870 mV (**TVT**).

II. De-aggregation of SQ by TVT, spiro-MeOTAD or cDCA

The addition of spiro-MeOTAD onto squaraine-sensitized samples (in this case the SQ02 sensitizer was used) also gave rise to a decreased dimer signal shown in Fig. S3. In addition, this graph shows the absorption of spiro-MeOTAD below 400 nm giving rise to the current generated in this region in the **SQ**/spiro-MeOTAD samples.

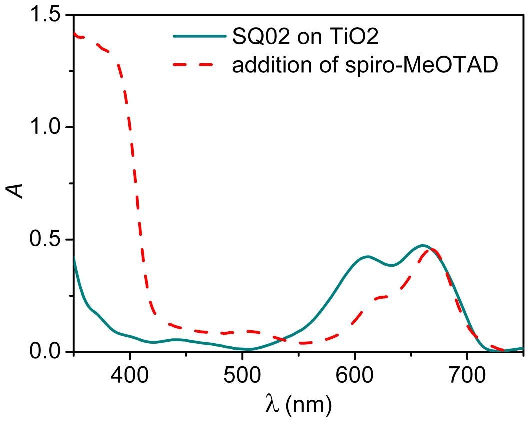

Fig. S3: De-aggregation of SQ02 (turquois, solid) upon addition of spiro-MeOTAD (red, dashed)

III. LHE of *PL*-samples and effect of cDCA on *PL*-measurements

Fig. S4 shows the absorption spectrum of the samples used for the photoluminescence measurements.

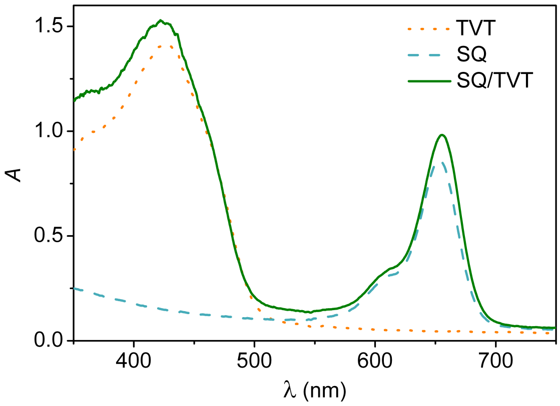

Fig. S4: Absorption *A* of photoluminescence samples on ZrO_2; both dyes (green, solid), reference with **1** (orange, dotted) and compound **2** chemisorbed in presence of cheno-deoxycholic acid (blue, dashed).

The reference samples with **SQ** and **TVT** had a similar absorbance. The measured *PL* spectra were adjusted for the difference in the number of absorbed photons between the **SQ**/**TVT** sample and the reference samples. Using the co-adsorber cDCA there was no further de-aggregation upon addition of the hole transporting dye **TVT**.

Fig. S5 shows the effect of the amount of aggregation on the *PL* of **SQ**. When using the co-adsorber cDCA the *PL* was an amount of magnitude more intense compared to samples witout co-adsorber. The partial deaggregation of **SQ** upon addition of the hole-transporting dye or spiro-MeOTAD lead to a slight increase in the *PL*.

In Fig. S6 the emission spectrum of samples without additional cDCA is shown. As shown in Fig. S5 the *PL* of **SQ** depends on its aggregation. This made it difficult to estimate the energy transfer from **TVT** to **SQ** for these samples without cDCA as we could not use the sample with **SQ** only as a reference.

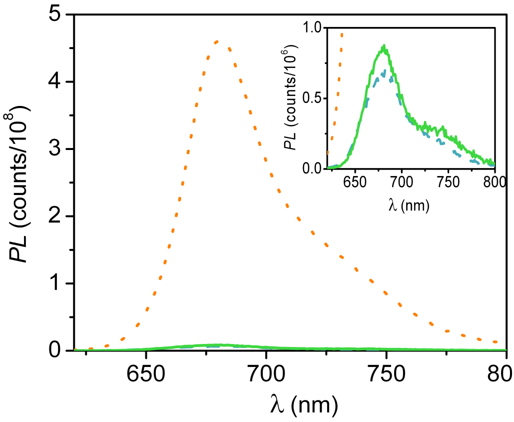

Fig. S5: Dependency of *PL* on degree of aggregation of SQ. SQ samples sensitized with 10 mM cDCA gave rise to an order of magnitude higher *PL* (dotted orange) Introduction of TVT on SQ samples also lead to a slightly increased PL (inset, solid green) compared to SQ by without any additives (inset, blue)

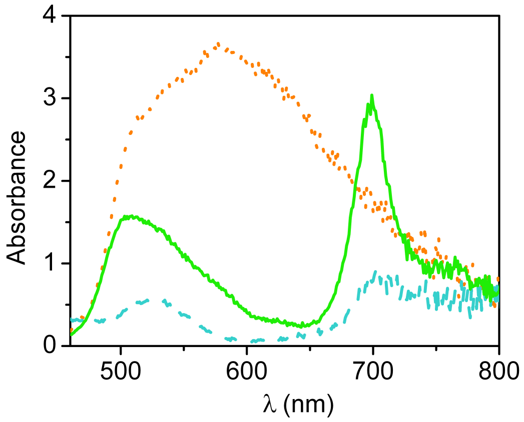

Fig. S6 The photoluminescence (*PL*) of **SQ** on meso-porous ZrO_2 is compared for films dyed from 0.2 mM **SQ** solution (blue, dashed), additional **TVT** (green solid) and films dyed in 0.2 mM SQ and 10 mM cheno-deoxycholic acid. Aggregation leads to *PL* quenching.

References

1. V. V. Pavlishchuk and A. W. Addison, *Inorganica Chimica Acta*, 2000, **298**, 97.