Supplementary Information

Energy Level Alignment in CdS Quantum Dot Sensitized Solar Cells Using Molecular Dipoles.

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Experimental:

Mesoporous TiO_2 films were prepared by electrophoretic deposition (EPD) of Degussa P25 particles with an average particle diameter of 25 nm onto Fluorine doped Tin Oxide (FTO) covered glass substrates (Pilkington TEC 15) with 15 Ω/square sheet resistance. Films were deposited in two consecutive cycles of 30 seconds at a constant current density of 0.4 mA/cm^2 and dried at 120 ºC for ~ 5 min in between the cycles. Following the EPD process the electrodes were dried in air at 150 °C for 30 min, pressed with 800 kg/cm^2 using a hydraulic press, and sintered at 550°C for one hour. Flat compact TiO_2 electrodes were prepared by spray pyrolysis of a precursor containing Ti-isopropoxide (0.2 M) and acetyl acetone (0.4 M) in ethanol onto FTO coated glass substrates (TEC 15) using an ultrasonic spray head (Licos, Austria) while the substrates were heated by a hot plate to 500°C and the electrodes were sintered at 550°C for 1h. For CdS deposition the TiO_2 electrodes were dipped into 0.1 M $Cd(ClO_4)_2$ and then immersed into 0.1 Na_2S aqueous solution at room temperature. This procedure was repeated five times for flat electrodes and ten times for mesoporous films. For molecular modification the CdS sensitized films were immersed in 10 mM of benzenethiol derivatives over night.

A two electrode configuration was used to measure the performance of the cell using an aqueous polysulfide electrolyte consisting on 1 M sodium sulfide (Na_2S), and 0.1 M sulfur (S). A Pt-coated conducting FTO glass served as a counter electrode. We note that Pt is not the most suitable counter electrode material for polysulfide electrolyte. With a Pt counter electrode an S-shape of the photocurrent–voltage (I-V) characteristics and subsequently a low fill factor is often observed. I-V measurements were performed with an Eco-Chemie Potentiostat. A 300W Xenon arc lamp (Oriel) calibrated to 100 mW/cm^2 served as a light source.

Optical transmission and absorption spectra of the electrodes were measured with a spectrophotometer (carry 500 scan UV-VIS_NIR spectrophotometer, Varian USA).

Dipole moments of the free molecule were computed with Density Functional Theory (DFT).

Contact angles were measured with contact angle goniometer under ambient conditions (Rame-Hart Model 100).

Transmission Spectra:

The transmission spectra of the CdS sensitized flat TiO_2 electrodes modified with BT derivatives are shown in Figure S1. The black solid line shows the transmission spectrum of an unmodified flat TiO_2 layer, deposited onto a FTO covered glass slide. One can see that the optical properties do not show any trend with the BT derivatives, thus providing strong evidence that the observed effects on the PV onset and photocurrent can be attributed to a shift of the CdS QD energy levels with respect to the TiO_2.
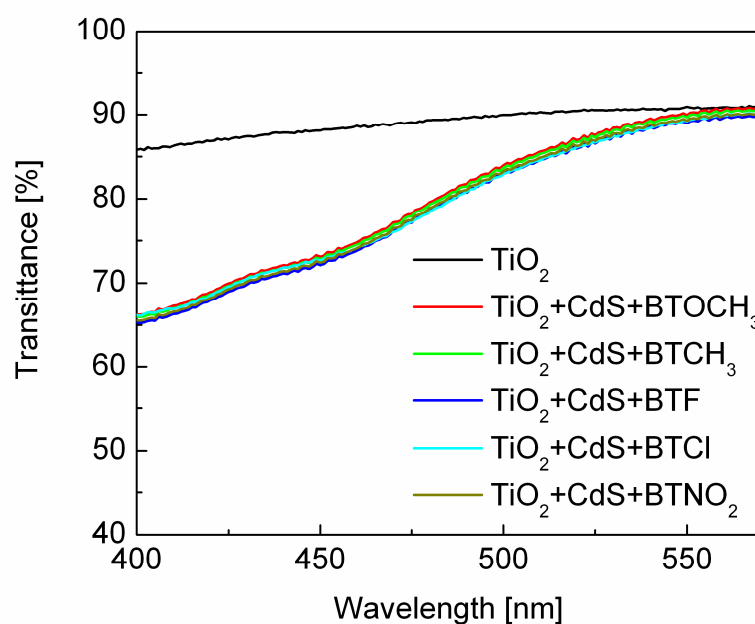

Figure S1: Transmittance of a compact TiO_2 layer, deposited onto FTO coated glass substrate (black line) in comparison with molecular modified CdS sensitized compact TiO_2 layers. A molecular dipole dependent change of the absorption is not observed.

The Electrostatic Potential Distribution within Individual QDs:

In the following the electrostatic potential distribution across the TiO$_2$/CdS/molecule/electrolyte interfaces, as depicted in Fig. 3d-f will be discussed in more detail. CdS QDs have diameters of a couple of nanometers and are not sufficiently doped to screen electric fields from the surrounding. Thus the potential distribution inside the QD is determined by the potential on the QD surface, e.g. at the TiO$_2$/CdS and CdS/molecule interface. Equipotential lines within individual QDs are shown in Fig. 3d for a situation where the potential is constant throughout each interface and where the potential at the TiO$_2$/CdS interface is different from the one at the CdS/molecule interface. Energy band diagrams (Fig. 3e and 3f) show a potential step at the TiO$_2$/CdS interface (ΔE_i) due to an interface dipole caused by charge redistribution at this heterojunction. The origin for charge redistribution can be a strongly polarized bond at the interface. We note that the strength and polarity of ΔE_i is a function of the electron affinity, work function and density of interface states of the materials forming the junction and can also depend on the deposition conditions, i.e. the surface pH during chemical bath deposition.

Molecules with a dipole moment pointing away from the QD surface (positive dipole moment) shift the electrostatic potential at the QD/molecule/electrolyte interface downwards, (schematically shown in Fig. 3e for one individual QD) while the TiO$_2$ does not shift with respect to the electrolyte. Note that the TiO$_2$ surface is not completely covered with CdS QDs and that the thiols do not bind to the oxide surface such that a fraction of the TiO$_2$ surface is in direct contact with the electrolyte and is not affected upon molecular modification. The dipole related potential drop at the CdS/molecule/electrolyte interface (ΔE_D) leads to an electric field throughout the QD, such that the energy levels of the electron and hole wavefunctions are lowered and electron injection from the excited QD into the TiO$_2$ conduction band is energetically hindered. This situation is reversed when molecules with a negative dipole moment (pointing towards the QD) are absorbed. The energy levels are shifted upwards with respect to the TiO$_2$ bands, such that electron injection into the TiO$_2$ becomes possible, as schematically shown in Fig. 3f.