Supporting Information: Discrimination between FRET and Non-FRET Quenching in a Photo-chromic CdSe Quantum Dot / Dithienylethene Dye System

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Experimental Methods

Synthesis of CdSe QD. We modified an existing procedure for the synthesis of highly fluorescent CdSe QD.[1] For a typical reaction a mixture of 0.0257 g CdO powder, 0.904 g oleaic acid and 1 g octadecene were heated in a three neck flask to obtain a colorless solution (Cd-precursor). The Se-precursor was achieved by diluting 0.0316 g Se in 0.58 g trioctylphosophine in a supersonic bath. Subsequently, the precursor solutions were mixed at room temperature. In a 50 ml three neck reaction flask 5.5 g ODE and 4 g oleyamine were heated to 215 °C under argon flow. The precursor solution was swiftly injected into the reaction flask. After 2 min the heating mantle was removed. After cooling to approx. 100 °C, ethanol was added until precipitation of the QD occurred. After centrifugation and decantation the particles were dispersed in $CHCl_3$. The synthesis yielded spherical shaped CdSe nanocrystals (c.f. Figure S1) of about 3.6 nm in diameter.
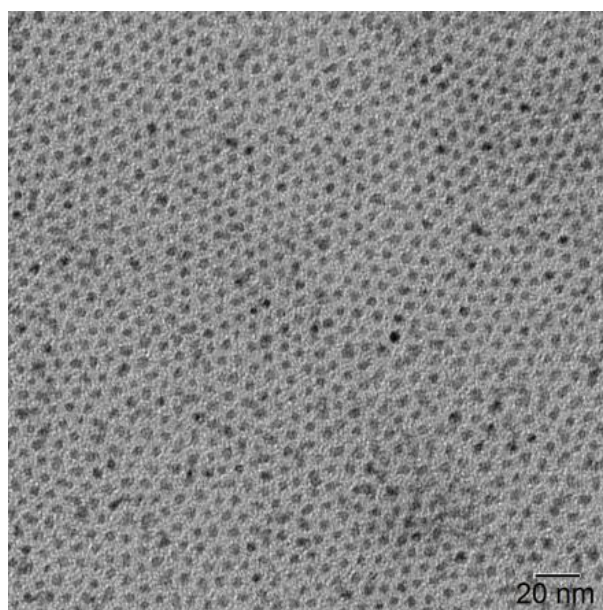

Figure S1. TEM image of the CdSe nanocrystals applied in the photochromic system.

Synthesis of the DTE-linker conjugate and preparation of the QD/DTE coupled system. The synthesis of the DTE-linker conjugate has already been published.[2] The QD/DTE coupled system is done by mixing specific amounts of the single components. For that purpose DTE suspensions in $CHCl_3$ (DTE is poorly dissolvable in $CHCl_3$; see Figure S2) were prepared to exclude any effects due to an altered solvent. The mixture was allowed to react for approx. 15 min. A syringe filter was used to remove unreacted DTE and aggregated QD (the

multifunctional anchoring can promote aggregation of the QD) yielding a clear solution without any indication of inhomogeneity.
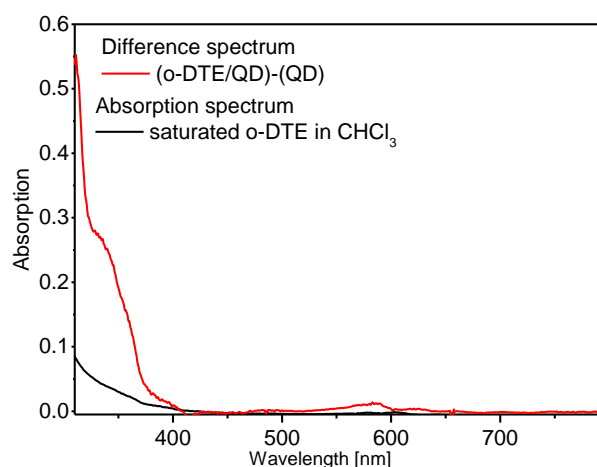

Figure S2. Absorption spectra of o-DTE/QD after subtraction of the QD contribution and pure saturated o-DTE in $CHCl_3$ recorded in quartz cuvettes in with 1 mm optical path length. For the measurement of saturated DTE undissolved DTE was removed with a syringe filter. The resulting DTE solution had a low concentration of 0.92 µM.

Determination of the absolute DTE concentration. The absolute DTE concentration was determined in the open form because only in this state 100% of the isomer can be achieved. For comparison we also determined a concentration for the pss state. The procedure was as follows: At first the extinction coefficients at 330 nm and 620 nm have been determined for pure open DTE and pure pss DTE in $MeOH/CHCl_3$ (10:90) without QD. The values are given in Table S1. Subsequently, the open DTE absorption in the coupled system at 330 nm and the pss DTE absorption in the coupled system at 620 nm were measured after subtraction of the QD contribution. On the basis of these absorption values (Table S1), the determined extinction coefficients and Lambert-Beer's law DTE concentration values of 52 µm and 43 µm are calculated.

The lower concentration calculated for the pss state of the coupled system indicates that the switching to this state yielded a weaker absorption at 620 nm compared to pure DTE in solution. Consequently, we assume that switching to the closed form is reduced on the QD surface compared to pure DTE in solution. The reduced switching we can express by: 100-((100*43)/52) = 17 %.

Table S1: Extinction coefficients of o-DTE and pss-DTE in MeOH/CHCl$_3$ solution, optical densities of o-DTE and pss-DTE after subtraction of QD contribution and DTE concentration calculated

ε_{330} (o-DTE in MeOH/CHCl$_3$) [M^{-1}cm^{-1}]	$5.1*10^4$
ε_{620} (pss-DTE in MeOH/CHCl$_3$) [M^{-1}cm^{-1}]	$1.7*10^4$
OD$_{330}$ ((o-DTE/QD)-(QD)) (1 cm optical path length)	2.7
OD$_{620}$ ((pss-DTE/QD)-(QD)) (1 cm optical path length)	0.74
c (DTE) calc. from (o-DTE/QD)-(QD) [μM]	52
c (DTE) calc. from (pss-DTE/QD)-(QD) [μM]	43

Energetic situation. To estimate possible electron transfer mechanisms, the reduction and oxidation potentials of o-DTE and closed DTE are compared with the exciton oxidation and reduction potential of the QD (schematic representation in Figure S3). Oxidation and reduction potentials of the open and closed isomer of the carboxy-substitiuted DTE (DTE-COOH) are taken from Ref. 3. The exciton oxidation and reduction potentials of were calculated from the valence band and conduction band potentials (1.244 and -0.456 V vs. NHE) of bulk CdSe, the electron and hole effective masses (0.13 and 0.45 m$_0$ [m$_0$ = mass of free electron]) and the transition energy of the first exciton (2.172 eV).[4]
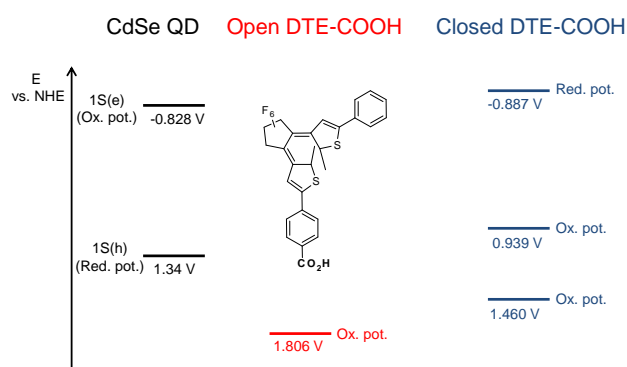

Figure S3. Schematic representation of (exciton) oxidation and reduction potentials of DTE-COOH (chemical structure of open isomer is depicted in the middle) and QD.

Spectroscopic experiments. Absorption spectra have been measured in fused silica cuvettes of 1 cm (switching experiments) or 1 mm (TCSPC experiments) optical path length on a Jasco V-5300 and an Analytik Jena S 600. Fluorescence spectra have been measured in fused silica cuvettes of 1 cm optical path length on a Jasco FP-8500 spectrometer. The TCSPC setup is

described elsewhere.[5] Excitation pulses at a central wavelength of 388 nm had energies of 18 – 60 nJ.

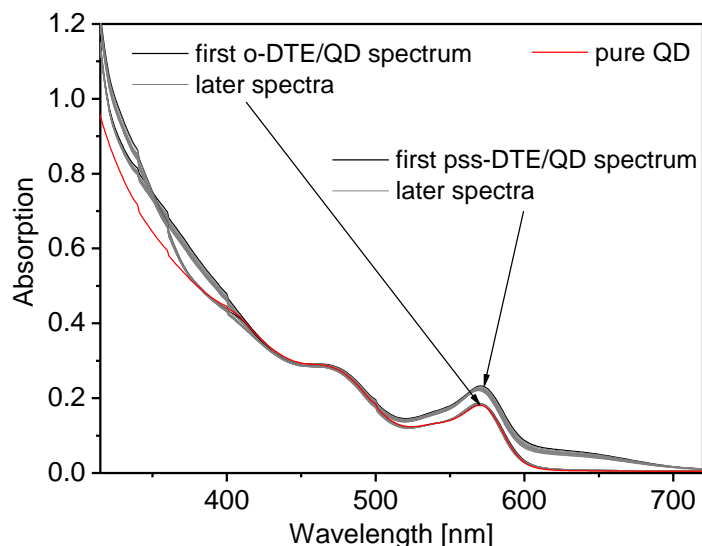*Absorption spectra during the switching cycles.*

Figure S4. Absorption spectra of DTE/QD during switching cycles. Light sources: Hamamatsu LC8 lamp in combination with a OG590 filter (Schott) and a UV diode (Roithiner Lasertechnik); On-switching: irradiation at $\lambda = 320$ nm (230 μW/cm^2, illumination time = 600 sec); off-switching: irradiation at $\lambda > 590$ nm (34 mW/cm^2, illumination time = 600 sec; Start concentrations: QD = 1.4 μM, DTE = 3.5 μM.

Fluorescence spectra during the switching cycles.
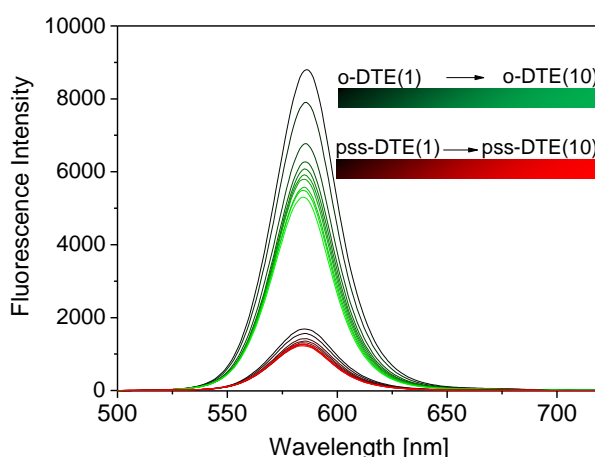

Figure S5. Fluorescence spectra of DTE/QD during switching cycles (o-DTE and pss-DTE represents the complex with DTE in the open and pss, respectively; switching number is given in brackets) Illumination conditions were identical to the absorption experiments depicted in Figure S4.
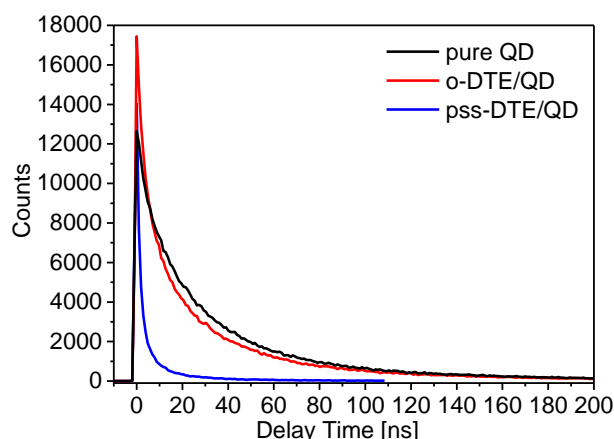
Non-normalized fluorescence decay curves.

Figure S6. Non-normalized fluorescence decay curves recorded at 590 nm after photoexcitation of pure QD, o-DTE/QD and pss-DTE/QD at 388 nm. Excitation pulse energies: pure QD: 18 nJ, o-DTE/QD: 27 nJ and pss-DTE/QD: 60 nJ.

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