

Supporting Information

Correlated Single Quantum Dot Blinking and Interfacial Electron Transfer Dynamics

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Preparation of QD-F27 complex. QDs used for this study were obtained from Ocean NanoTech, LLC, USA. They consist of a CdSe core, a multi-shell of CdS_{3ML}ZnCdS_{2ML}ZnS_{2ML} and octadecylamine capping ligands. Fluorescein 27 (F27) was purchased from Exciton, USA. QD-F27 complexes were prepared by adding F27 to QD heptane solutions, and the mixtures were sonicated for 30 min and kept in the dark for a few hours. The samples were filtered to remove undissolved dyes. The F27-to-QD ratio was controlled by adding different amounts of F27 and/or adjusting the time of mixing. Figure S1 shows the UV-VIS absorption spectra of the QD-F27 complex at different dye-to-QD ratios.

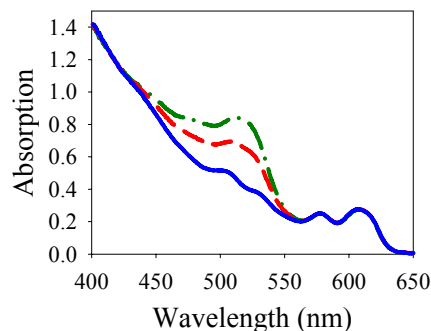


Figure S1. UV-VIS. absorption spectrum of free QDs (blue) and QD-F27 complexes at different dye-to-QD ratios (green: high ratio sample B, pink: low ratio, sample A).

To prepare samples for single QD studies, we start out with QD in heptane solution with concentrations of $\sim 10^{-11}$ M. Sample **1** is free QDs without F27. Samples **2** and **3** are QD-F27 complexes which were obtained by mixing QD with F27 for ~ 6 and ~ 12 hours, respectively, prior to filtering out undissolved F27. The F27-to-QD ratio of Sample **3** is believed to be higher than that of Sample **2** because of the longer mixing time. This is confirmed by the shorter QD fluorescence lifetime of sample **3**. Unfortunately at this low concentration, we were not able to obtain reliable UV-vis absorption spectra. Attempt to prepare single QD sample by diluting the samples used for transient absorption studies was not successful. It was found that the fluorescence decay became slower when the QD concentration became lower than $\sim 10^{-10}$ M (data not shown), indicating a decrease of F27-to-QD ratio (due to dissociation of F27 from QD). For single QD studies, samples **1** to **3** were cast on glass cover slips and dried in air. Raster scanned single particle

fluorescence images show well-separated single QDs. An example is shown in Figure S2 for sample 3.

Nanosecond transient absorption and ensemble-averaged fluorescence measurements. Nanosecond transient absorption was performed with the EOS spectrometer (Ultrafast Systems LLC). The pump pulses (~150 fs) at 400 nm (40 nJ/pulse) were from a home-built femtosecond amplified laser system. The pump beam is about ~300 μm in diameter, which corresponds to a peak excitation power density of 380 MW/cm^2 at the sample. The probe pulse (a 0.5 ns white light source operating at 1 KHz) was synchronized with the femtosecond amplifier and the delay time was controlled by a digital delay generator. The probe light was detected in a fiber optic-coupled multichannel spectrometer with a CMOS sensor. The absorbance change was calculated from the intensities of sequential probe pulses with and without the pump. Ensemble-averaged fluorescence lifetime of QD and QD/dye complexes were measured both in heptane solution in a cuvette of 2 mm path length and in air on glass cover slips. The emissions of samples in heptane solution and in air on glass were detected by a Micro-channel-plate-photomultiplier tube (Hamamatsu R3809U-51) and an avalanche photodiode (APD, Perkin Elmer SPCM-AQR-14), respectively. The outputs of detectors were amplified and analyzed by a TCSPC board (Becker&Hickel SPC 600).

Single QD spectroscopy. Single QD fluorescence detection was carried out with a home-built scanning confocal microscope. Femtosecond laser pulses (~100 fs) with a repetition rate of 80 MHz were generated from a mode-locked Ti:Sapphire laser (Tsunami oscillator pumped by 10 W Millennia Pro, Spectra-Physics). The output

centered at 800 nm was passed through a pulse picker (Conoptics, USA) to reduce the repetition rate by a factor of 9, and then frequency doubled in a BBO crystal to generate 400 nm excitation pulses. The excitation beam (~ 150 nW) was focused through an objective ($100\times$ N.A 1.4, oil immersion, Olympus) down to a diffraction-limited spot on the sample. The estimated peak excitation power density is 60 MW/cm². The resulting fluorescence from the sample was detected by an avalanche photodiode (APD, Perkin Elmer SPCM-AQR-14). The APD output was analyzed by a time-correlated single photon counting (TCSPC) board (Becker&Hickel SPC 600). The fluorescence lifetime measurement has an instrument response function of 500 ps (FWHM). The QDs or QD-F27 complexes in heptane were dropped and dried on a glass cover slip and placed on a piezo scanner (Mad City Labs). Figure S2 shows a raster scanned single molecule fluorescence image of single QD-F27 complexes on glass, indicating well-separated single QDs.

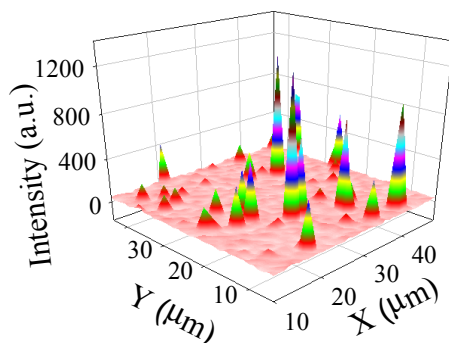


Figure S2. Raster scanned fluorescence image of single QD-F27 complexes (sample B') on a glass coverslip.

Nanosecond transient absorption spectra of Sample A and free QDs in solution

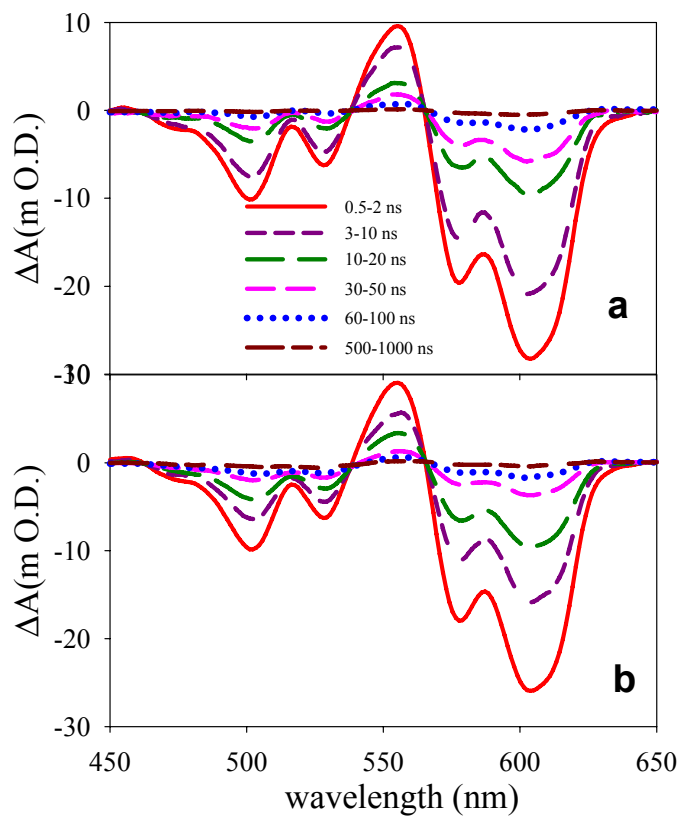


Figure S3. Transient absorption spectra at indicated delay times following 400 nm excitation of (a) free QDs and (b) QD-F27 complexes (sample A).

Subpicosecond transient absorption study of QD-F27 complexes

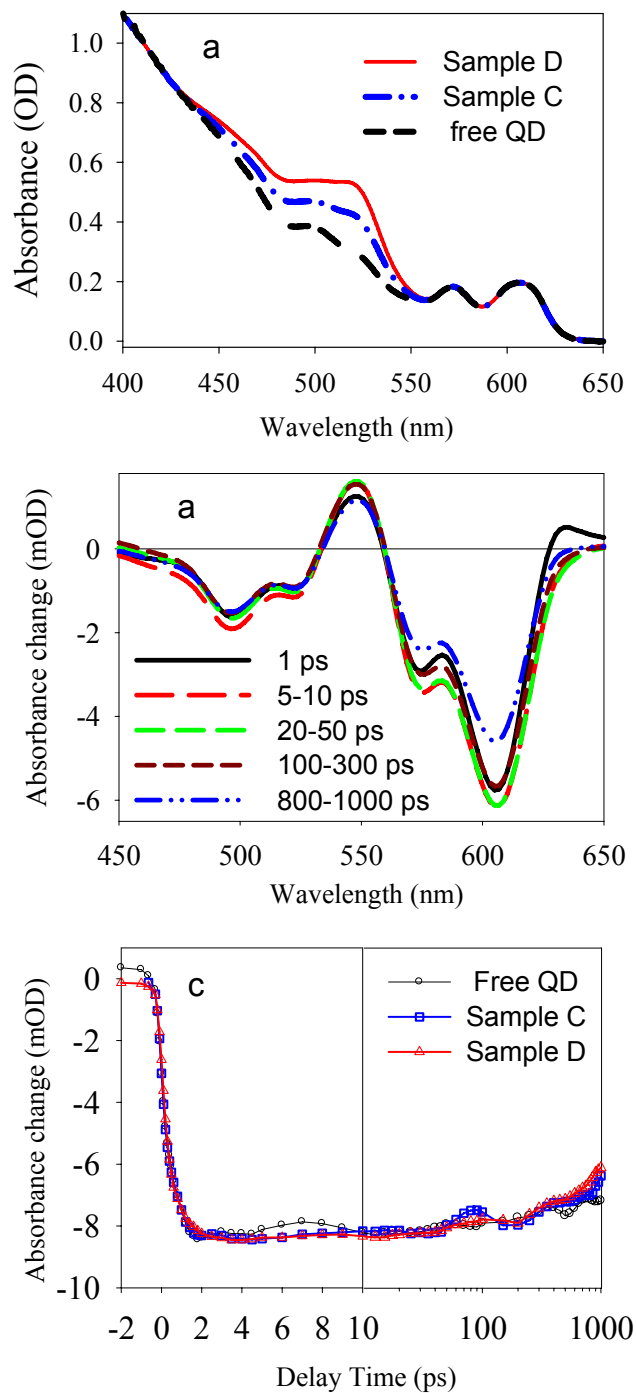


Figure S4 Femtosecond transient absorption study of QD-F27 complexes. a) UV-visible absorption spectra of free QD and QD-F27 complexes (sample C and D); b) Transient

absorption spectra of sample D at indicated delay times after 400 nm excitation; c) Exciton bleach recovery kinetics (monitored at 605 nm) of free QDs and QD-F27 complexes, indicating subpicosecond bleach formation and negligible bleach recovery in the < 500 ps time scale.

Estimate of QD 1S exciton oxidation and reduction potentials. The QDs used in this study have a first exciton peak at 605 nm. The energy of the electron and hole levels have not been directly measured, and they are estimated by the following procedure. These core/multi-shell structures were grown from CdSe cores with a first exciton peak at 574 nm. The radius of the CdSe core is estimated to be 1.8 nm by an empirical formula,¹ and 1.7 nm by a model that treats the electrons and holes as particles of effective masses of 0.13 and 0.45 m_0 (m_0 the free electron mass), respectively, confined in a finite spherical well.² From the calculated 1S electron, hole and exciton energy, the 1S exciton oxidation and reduction potentials in the CdSe core is determined to be -0.95 and + 1.05 V (SCE), respectively.³⁻⁵ Previous study of CdSe/CdS core/shell structures shows that the lowest energy conduction band electron is delocalized throughout the core and shell, whereas the valence band hole is localized in the core.^{6,7} We assume that in the quasi-type II core/multi-shell structure, the electron energy level is lowered while the hole level remains unaffected relative to the CdSe core. With these assumptions, the estimated 1S exciton oxidation and reduction potentials are -0.85 and +1.05 V (vs SCE), respectively, for the QDs used in this study.⁸

Reference

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