

Solvents effects on charge transfer from quantum dots

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Sample preparation

In order to study the solvent effects on charge transfer in a quantum dot-dye molecule system, we attached methyl viologen (MV, Sigma-Aldrich) to octadecylamine capped CdSe quantum dots (QDs) with a diameter of 2.3 nm (NN-Labs). We added methanol (dropwise) to 12 mg of MV powder until the powder was completely dissolved, and then added this to a 0.01 mg/mL solution of QDs in hexane. This concentration corresponds to ~100 MV molecules per QD in solution. The control sample consisted of CdSe QDs also diluted to 0.01 mg/mL in hexane, but otherwise used as received.

In order to isolate the differences between the two techniques and probe the role of solvents in a charge transfer reaction, we performed photoelectron spectroscopy (PES) and transient absorption (TA) spectroscopy on the same samples, of both CdSe and the CdSe+MV complex. However, to acquire adequate signal in both experiments, different concentrations needed to be used. After the PES experiment, a portion of the remaining solution was concentrated (up to 10x) immediately before use in the TA measurement. Samples were concentrated by evaporating the hexane solvent under vacuum and redispersing in hexane to reach the desired concentration. TA measurements of samples of different concentrations (Figure S1) display similar kinetics, demonstrating the validity of comparing the solution phase TA and gas-phase PES experiments. TA samples were prepared and sealed under argon.

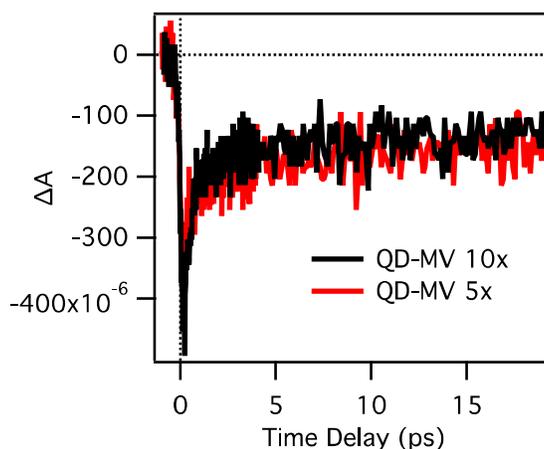


Figure S1. Comparison of the band edge transient absorption kinetics for 5x and 10x concentrated samples (0.05 and 0.1 mg/mL respectively) of CdSe nanocrystal-dye molecule complex (CdSe+MV). Concentration of the sample does not affect the excited state dynamics on the timescales studied here.

Two photon photoelectron spectroscopy

We utilized a nanoparticle aerosol source coupled to a velocity map imaging spectrometer (nanoVMI)¹⁻³ to perform PES on QDs. In the nanoVMI a hexane solution containing the QDs is aerosolized using a compressed gas atomizer (TSI). The atomizer creates micron sized droplets of solution, which dry as they travel through a gas line, leaving behind ~ 100 nm sized clusters of nanoparticles suspended in the gas phase. The nanoparticle aerosol beam is collimated to a width of ~ 500 μm by an aerodynamic lens⁴ (Aerodyne) and injected into the first vacuum chamber before passing through a skimmer into the differentially pumped VMI chamber, which is maintained below $\sim 5 \times 10^{-6}$ torr.

The QDs are excited by a 400 nm pump pulse (40 fs), and the resulting dynamics are followed via subsequent photoionization by a delayed 267 nm probe pulse (40 fs). Both pulses originate from a 1 kHz Ti:sapphire amplifier (KMLabs) at 800 nm, and are up-converted to the second and third harmonic in BBO crystals. The time delay between the two pulses is controlled using a mechanical delay stage (Thorlabs). The polarization of each beam is set parallel to the plane of the detector, and the fluence of the 400 nm pump beam is kept well below the single exciton limit (electrons excited in $<10\%$ of QDs). The photoelectrons are focused onto a micro-channel-plate-phosphor detector by three electrodes in an Eppink-Parker geometry⁵, and the photoelectron images are captured by a CCD camera. In order to improve the signal-to-noise ratio, the VMI was operated in spatial imaging mode^{6,7}, and therefore provided a measure of total photoelectron yield, but without energy resolution. Charge transfer between the CdSe QDs and attached MV molecules manifests as a decay in the total photoelectron yield. This decay is observed because an electron occupying the LUMO of MV is bound by 4.95 eV and therefore cannot be photoionized by the 4.65 eV probe pulse (Fig. 1a).

The pressure about the sample in the VMI chamber is $\sim 10^{-6}$ torr and, based on simple Langmuir relation, only about 10^{-6} layers of hexane molecules can cover the surface of the QDs⁸. Therefore, PES probes the quantum dot charge transfer processes in a hexane-free environment, as compared to liquid-phase transient absorption.

Slight differences between the PES and TA data can be seen before $t=0$. This is due to the excitation of 'hot electrons' in the PES measurement. In the PES experiment the 267 nm pulse can excite a hot electron to a high-lying conduction band state, and the electron can then be ionized by a subsequent 400 nm pulse, providing a non-zero photoelectron signal. This effect is not seen in the TA measurements since, in that case, the 465 nm probe excites electrons directly into the 1S(e) level. .

Transient absorption spectroscopy

The experimental setup used for TA measurements has been described previously⁹. Samples, concentrated as described above, were measured in 2 mm quartz cuvettes with constant stirring under 405 nm excitation. Pump powers were confirmed to be in the regime of single excitation per QD by comparing the kinetics under varying pump powers and noting the absence of Auger recombination kinetics. To determine the instrumental resolution (IRF) and t_0 , the point of maximum pump/probe temporal overlap, TA data was collected on a cuvette containing neat hexane^{10,11}. This data was collected immediately preceding measurements of the QD and QD-MV samples under identical experimental conditions, except that a higher pump power was used. Kinetic traces arising from impulsive stimulated Raman scattering in the neat hexane were fit to determine both t_0 and the IRF.

Fitting Procedure

We first fit the CdSe (without MV) dynamics, from both the TA and PES experiments, to a biexponential decay, where IRF is the instrument response function, and a and T are the amplitude and time constant, respectively, of the exponentials.

$$S = \text{IRF} \otimes (a_1 e^{-t/T_1} + a_2 e^{-t/T_2})$$

The data evidences a fast initial decay (T_2) and a slow component (T_1) corresponding to the long-lived excitonic state. The fit functions also take into consideration the instrumental resolution of the two experiments, which are fixed at their measured values. Indicated error ranges are extracted from the fitting function, parameters that are listed without errors were fixed at the indicated value. The T_1 value of 120 ps

was obtained from fitting a 20 ps TA data set, and then fixed for the fitting of the shorter time scale (2 ps) data sets.

	TA	PES
IRF (ps)	0.25	0.12
a_1 (%)	64 ± 1	64 ± 1
T_1 (ps)	120	120
a_2 (%)	36 ± 2	36 ± 5
T_2 (ps)	0.527 ± 0.05	0.415 ± 0.1

Table S1. Results from fitting a biexponential decay to the transient absorption and photoelectron spectroscopy kinetics of the control sample of CdSe.

The addition of MV introduces an additional decay, corresponding to charge transfer from the QD to the MV-LUMO. We characterized this decay by fitting the kinetic traces to a triple exponential decay.

$$S = \text{IRF} \otimes (a_1 e^{-t/T_1} + a_2 e^{-t/T_2} + a_3 e^{-t/T_3})$$

We fix two of the time components (T_1 and T_2) with the determined (Table 1) values from the CdSe fitting, and then fit for the third (T_3). We take this T_3 decay time to be indicative of the CdSe-MV charge transfer rate. The recovered T_3 values are very close to the instrument response functions of the TA and PES experiments, leading to the large errors in the fit value.

	TA	PES
IRF (ps)	0.25	0.12
a_1 (%)	25 ± 5	9 ± 1
T_1 (ps)	120	120
a_2 (%)	30 ± 11	47 ± 14
T_2 (ps)	0.525	0.415
a_3 (%)	45 ± 9	44 ± 4
T_3 (ps)	0.223 ± 0.070	0.100 ± 0.150

Table S2. Results from fitting a triple exponential decay to the CdSe+MV kinetics from transient absorption and photoelectron spectroscopy. Values listed without errors were fixed in the fitting.

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