

## Supporting Information

### pH and Concentration Dependence of the Optical Properties of Aqueous Thiol-Capped CdTe Nanocrystals

R. Schneider<sup>a,d</sup>, F. Weigert<sup>a</sup>, V. Lesnyak<sup>b</sup>, S. Leubner<sup>b</sup>, T. Lorenz<sup>c</sup>, T. Behnke<sup>a</sup>, A. Dubavik<sup>b</sup>, J.-O. Joswig<sup>c</sup>, U. Resch-Genger<sup>a,\*</sup>, N. Gaponik<sup>b</sup>, and A. Eychmüller<sup>b</sup>

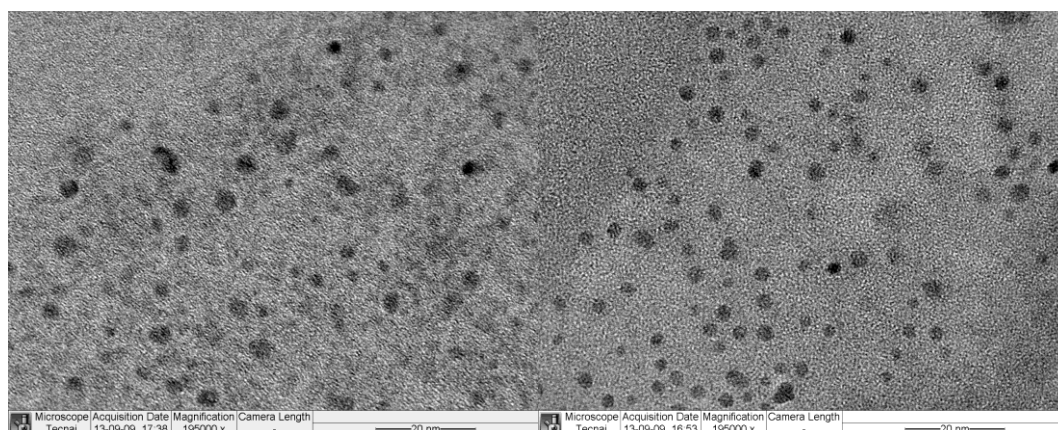
<sup>a</sup> Federal Institute for Materials Research and Testing (BAM), Richard-Willstätter-Str. 11, 12489 Berlin, Germany

<sup>b</sup> Physical Chemistry and Center for Advancing Electronics Dresden (CfAED), TU Dresden, Bergstr. 66b, 01062 Dresden, Germany

<sup>c</sup> Theoretical Chemistry, TU Dresden, Bergstr. 66b, 01062 Dresden, Germany

<sup>d</sup> Institute of Chemistry, University Potsdam, Karl-Liebknecht-Straße 24-25, 14476 Potsdam-Golm, Germany

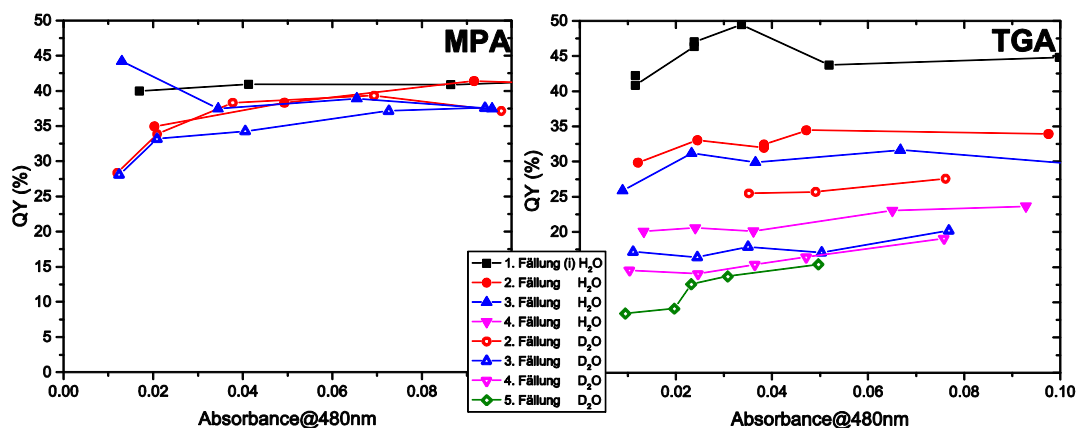
#### Transmission electron microscopy



**Figure 1S.** Transmission electron micrographs of TGA-capped T2 (left), and MPA-capped M2 (right) CdTe NCs.

#### Combined precipitation and dilution studies

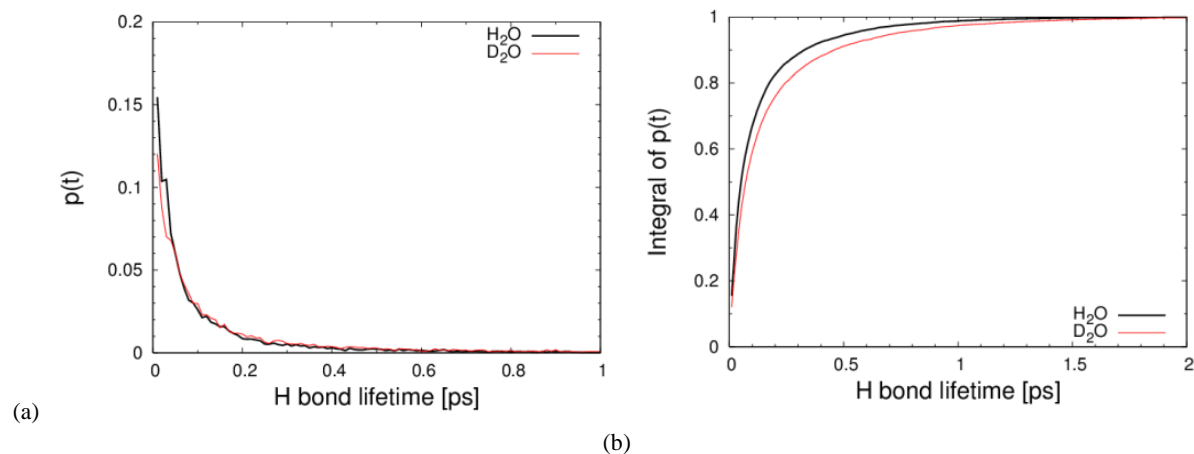
We performed dilution studies with the TGA- and MPA-stabilized CdTe NC colloids M2 and T2 after different precipitation steps, thereby varying the absorbance at the excitation wavelength between 0.01 and 0.10 and hence, the particle concentration in the range of  $1 \times 10^{-6}$  to  $1 \times 10^{-7}$  M. The changes in emission and PL QY resulting for both colloids are summarized in the main text in Figure 7 for an exemplarily chosen absorbance of 0.024 equaling a particle concentration of  $2.2 \times 10^{-7}$  M.



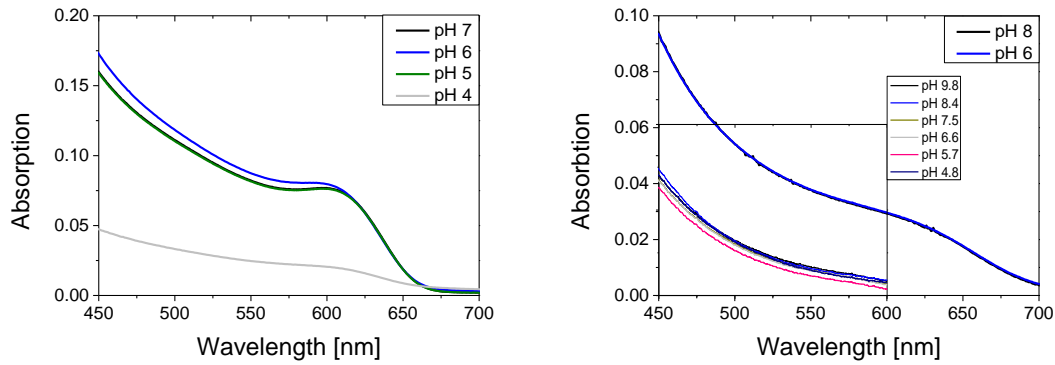
**Figure 2S.** PL QY of MPA- (left) and TGA- stabilized (right) CdTe samples as a function of SC NC concentration in H<sub>2</sub>O and D<sub>2</sub>O after different precipitation steps with EtOH. Excitation was at 480 nm, and the absorbance at  $\lambda_{\text{ex}}$  was varied between 0.01 and 0.1.

### Molecular dynamics simulations

Geometry optimizations of H<sub>2</sub>O and D<sub>2</sub>O (using density-functional theory) resulted in HO bond lengths of 0.974 Å, bond angles of 104.087°, and dipole moments of 1.847 D reflecting the chemical equivalence of the two molecules. The physical disparity is demonstrated in the vibrational frequencies, which are 1569/3713/3826 cm<sup>-1</sup> for H<sub>2</sub>O and 1148/2676/2805 cm<sup>-1</sup> for D<sub>2</sub>O, respectively. The molecular-dynamics simulations (using the density-functional tight-binding method) resulted in trajectories consisting of 3.000 frames each. During 30 ps, 14292 hydrogen-bond breaks were observed for H<sub>2</sub>O (100%) and 10426 for D<sub>2</sub>O (73%). The lifetime was calculated as time between two hydrogen-bond breaks and the probability function  $p(t)$  is a histogram of the resulting counts (see Figure 3S, panel a). The integral of  $p(t)$  as depicted in Figure 3Sb reveals more clearly that D<sub>2</sub>O shows slightly longer hydrogen-bond lifetimes.



**Figure 3S.** (a) Probability function of the hydrogen-bond lifetime and (b) integral of this probability.



**Figure 4S.** Absorption spectra of samples T2 (left) and M2 (right) at different pH values. The wavelength region for the pH experiment in the inset was chosen solely to calculate the PL QY.

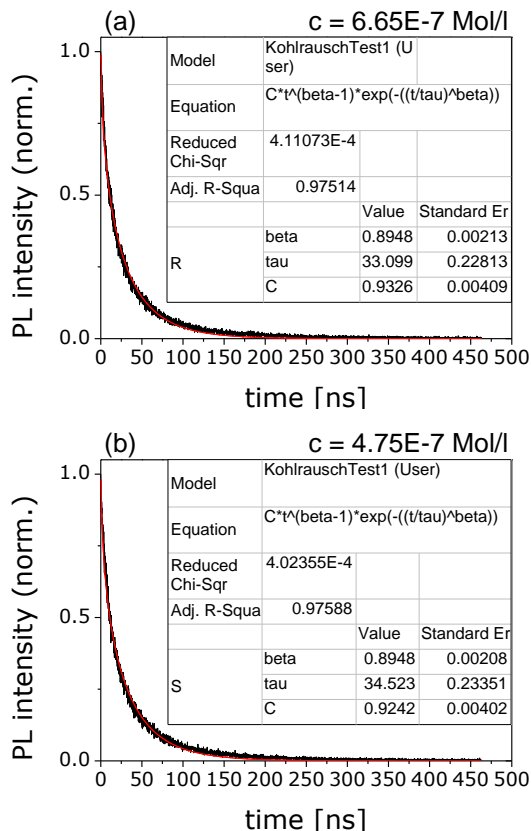
### Analysis of the PL lifetime data

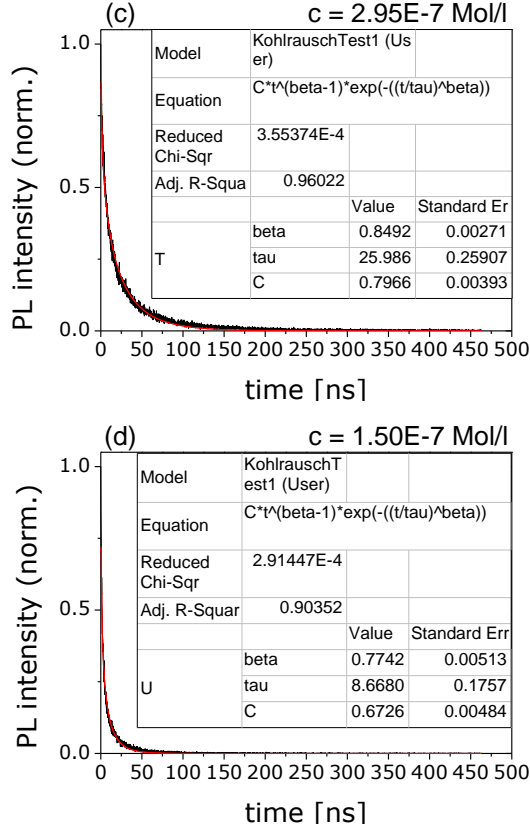
For PL decay, the stretched exponential function:  $\frac{n(t)}{n(0)} = \exp\left(-\left(\frac{t}{\tau_0}\right)^\beta\right)$  (eq. 1S)

can be transformed to  $I_{PL}(t) = C * t^{\beta-1} * \exp\left(-\left(\frac{t}{\tau_0}\right)^\beta\right)$ . (eq. 2S)

$n(t)/n(0)$  is the fraction of excited emitters after time  $t$ .  $\tau_0$  is an effective time constant,  $\beta$  is a constant between 0 and 1 and  $C$  is another constant.<sup>1-3</sup>

The lifetime decay curves were fitted using eq. 2S. The results are shown in Figure 5S together with the originally measured PL decay curves. The fit parameters and fit results are summarized in Table 1S.





**Figure 5S.** Stretched exponential fits of the PL decay curves shown in Figure 8 in the main article. Panels a-d correspond to the concentrations applied in the dilution experiments. The fit parameters are summarized in Table 1S.

**Table 1S.** Fit parameters (see equations 1 and 2) resulting from stretched exponential fit of lifetime decay curves from dilution experiments shown in Figure 8 in the manuscript and Figure 5S. The concentration of the SC NC resulting after sample dilution are given in the first row of the table.  $R^2$  provides a measure for the quality of the fit, with  $R^2$  of 1 indicating an excellent match being measured and fitted data.

SCNC Concentration	$R^2$	$\beta$	$\tau$	$C$
665 nM	0.975	$0.8948 \pm 0.0021$	$33.099 \pm 0.228$	$0.9326 \pm 0.0041$
475 nM	0.976	$0.8948 \pm 0.0021$	$34.523 \pm 0.234$	$0.9242 \pm 0.0040$
295 nM	0.960	$0.8492 \pm 0.0027$	$25.986 \pm 0.259$	$0.7966 \pm 0.0039$
150 nM	0.904	$0.7742 \pm 0.0051$	$8.668 \pm 0.176$	$0.6726 \pm 0.0048$

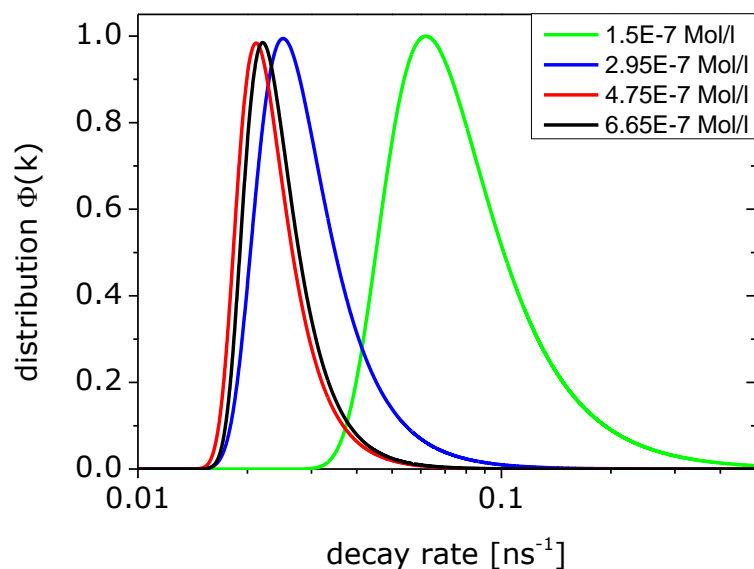
From the obtained fit parameters, the decay rate distribution probability function can be calculated according to the following equation (eq. 3S)<sup>1,3</sup>:

$$\phi(k) = \frac{a\tau}{\sqrt{2\pi\beta}} (k\tau)^{1-\frac{a}{2}} * e^{-(k\tau)^{-a}} \quad (\text{eq. 3S})$$

with  $a = \beta(1 - \beta)^{-1}$  and  $\tau = \tau_0(\beta(1 - \beta)^{\frac{1}{a}})^{-1}$ . Here,  $k$  equals the decay rate and  $\phi(k)$  the decay rate probability, respectively.

The decay rate distribution, calculated from the results of the fitting of the PL decays of the representatively chosen CdTe-MPA sample M3 upon dilution in  $D_2O$  at pD 6.4 (see Figure 8 in the manuscript), are summarized in Figure 6S. As follows from this figure, the increasing curvature of the PL decay curves in Figure 8 with decreasing SC NC concentration can be represented as a shift of the decay rate distribution of the SC NC ensemble to shorter lifetimes. This is tentatively ascribed to

an increase in the number of PL diminishing surface defects of all SC NC or less likely, to an increasing number of SC NC with a large number of surface defects, due to the desorption of surface ligands favored by dilution.



**Figure 6S.** Decay rate probability functions calculated from stretched-exponential fit parameters.

#### References

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2. A. Van Driel, I. Nikolaev, P. Vergeer, P. Lodahl, D. Vanmaekelbergh and W. Vos, *Physical review B*, 2007, **75**, 035329.
3. R. Saito and K. Murayama, *Solid state communications*, 1987, **63**, 625-627.