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1. Materials

All chemicals and solvents were purchased from Sigma-Aldrich and used as-received.

2. Synthesis and Experimental Procedures

2.1 Synthesis and Purification of Oleate-Capped CdS QDs

We synthesized oleate-capped CdS QDs with R = 1.9 nm using a modified reported procedure.[1] We synthesized cadmium oleate from 99.99% trace metals grade cadmium oxide (0.27 g, 1.9 mmol) and 90% technical grade oleic acid (6.9 mL, 21.8 mmol) in 90% technical grade octadecene (15.0 mL, 46.9 mmol). We heated the mixture to 260 °C under an N_2 atmosphere with vigorous stirring until the mixture became clear, reduced the temperature to ~120 °C and opened the flask to the atmosphere while flowing with N_2 for ~30 minutes. To synthesize CdS QDs, we injected 4 mL of a 0.1 M solution of sulfur precursor, prepared by dissolving elemental sulfur (0.02 g, 0.63 mmol) in 90% technical grade octadecene (6.0 mL, 18.8 mmol), into 8 mL of cadmium oleate and 12 mL 90% technical grade octadecene. We allowed the nanoparticles to grow for 3 minutes at 260 °C under an N_2 atmosphere. We purified the oleate-capped CdS QDs by washing with 3:1 (v/v) acetone to QD solution and centrifuging at 3500 rpm for 5 minutes, discarded the supernatant and resuspended the QD pellet in hexanes. We then washed the QDs twice with 3:1 (v/v) methanol to QD solution, centrifuged as before, discarded the supernatant, and resuspended and stored the oleate-capped QDs in hexanes.

2.2 Synthesis of 2-Mercaptoethyl Phosphonic Acid (MEPA)

We synthesized 2-mercaptoethyl phosphonic acid (MEPA) by using a modified previously reported procedure.[2] We added NaH (0.8 g, 30 mmol) to triphenylmethanethiol (8.6 g, 30.8 mmol) solution in dry tetrahydrofuran (250 mL), yielding a yellow solution. We added (2-bromoethyl)phosphonic acid diethyl ester (5.1 mL, 28.1 mmol) and the mixture was stirred for 1 h, and quenched the reaction with H_2O (25 mL). We evaporated the resulting mixture to *ca*. 20 mL, added it to an extraction funnel containing H_2O (100 mL), extracted with of CH_2Cl_2 (3 × 150 mL), and dried the organic phase with Na_2SO_4. We concentrated the organic phase by rotary evaporation and triturated the resulting solid with Et_2O (20 mL) to obtain a white suspension. We cooled the mixture to −78 °C for 1h, filtered the suspension, washed the filter with cold Et_2O (−78 °C, 20 mL) and finally dried the product, (2-tritylsulfanylethyl)phosphonic acid diethyl ester (9.8 g, 78% yield). ^{1}H-NMR (500 MHz, CD_2Cl_2): 7.4 (m, 15H), 3.95 (m, 4 H), 2.65 (m, 2H), 2.35 (m, 2H), 1.2 (t, 6H).

We removed the trityl protecting group by dissolving the above-mentioned product in CF_3COOH (50 mL). We added Et_3SiH dropwise to the rapidly stirring solution until the yellow color was gone was gone and a white solid precipitated. Once the precipitate was removed via vacuum filtration, we evaporated the TFA solution to yield a colorless oil, transferred the oil to a flask equipped with a Dean-Stark trap (and condenser), and hydrolyzed in refluxing 5 M aq. HCl (150 mL) for 48 h. After cooling, we washed the aqueous layer with $CHCl_3$ (2×100 mL), and concentrated the aqueous solution by rotary evaporation. Finally, we purified the product by reverse-phase auto-column (C_{18}, basic H_2O 100%), concentrated the fractions by rotary evaporation and dried under high vacuum to obtain a white solid (2.0 g, 62% overall yield). ^{1}H-NMR (500 MHz, D_2O): 2.75 (m, 2H), 2.08 (m, 2H).

2.3 Ligand Exchange Procedure

We added 550 equivalents either of AEP or MEPA per QD as a 0.04 M basic solution (molar ratio KOH:AEP of 3:1) in MeOH to 6 mL of a $9 \cdot 10^{-7}$ M suspension of oleate-capped CdS QDs in hexanes. The addition of the 2-AEP induced the flocculation of the QDs. Rapid mixing of the suspension induced the precipitation of the QDs, and centrifugation at 9500 rpm for 5 min left the hexanes layer completely colorless. We removed the hexanes layer, and redispersed the pellet in 3 mL of water of the desired pH, controlled by addition of HCl or KOH.

3. Instruments and Methods

3.1. Ground-State Absorption and Photoluminescence Spectroscopy

We acquired ground-state absorption spectra on a Varian Cary 5000 spectrometer and we corrected the baselines of all spectra with neat solvent prior to measurement. We acquired all photoluminescence spectra with a Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon) with a 2 nm slit width and we diluted all the samples such that the absorbance at the excitation wavelength (350 nm for all the CdS QDs samples) was less than 0.1. All spectra were acquired at room temperature using either a 1 cm or 0.1 cm quartz cuvette.

We determined the concentration of QDs using the ground-state absorption and PL spectra and the extinction coefficient for CdS QDs reported in literature.[3] We used the sample of AEP-capped CdS QDs at pH 10.8 to calculate the yield for the phase transfer from hexanes to water and determined the yield as average of three replicates. We measured the relative quantum yield of AEP-capped CdS QDs using anthracene dissolved in ethanol (Φ = 0.27) as a standard.[4] The PL quantum yields were calculated according to equation (S1):

$$\Phi_x = \Phi_{st} \cdot \frac{I_x}{I_{st}} \cdot \frac{1 - 10^{-A_{st}(\lambda_{exc})}}{1 - 10^{-A_x(\lambda_{exc})}} \cdot \frac{\eta_x^2}{\eta_{st}^2} \qquad \text{(S1)}$$

where I is the integrated PL intensity, A is the absorbance at the excitation wavelength, η is the

refractive index of the solvent and Φ is the quantum yield. The index *x* denotes the sample, and the index *st* denotes the standard. The reported quantum yields are an average of three replicates.

3.2. Nuclear Magnetic Resonance Spectroscopy

We acquired ^{1}H-NMR spectra on a Bruker Neo 600 MHz spectrometer with a QCl-F cryoprobe using a solvent suppression pulse sequence, or on a Bruker Avance III HD 500 MHz spectrometer equipped with a TXO Prodigy probe. The sample temperature was set at 25 °C. Chemical shifts are reported in ppm using the solvent residual signal as an internal reference. For the quantitative 1D ^{1}H measurements, we acquired 16 scans per spectrum with a relaxation delay of 30 s. We used 1,4-dioxane as an internal standard and performed the measurements in triplicate.

We acquired 1D NOESY spectra with the Bruker's "selnog" pulse program. We chose the 180° selective excitation of the protons adjacent to the phosphonate of AEP. We set the mixing time to 300 ms, the relaxation delay to 2 s, and acquired 1000 scans per spectrum. We performed measurements of the spin-spin (T_2) relaxation times with the Carr-Purcell-Meiboom Gill (CPMG) pulse sequence.[5,6] The number of scans was 16 per spectrum with a relaxation delay of 30 s. The 90° (pw90) and 180° (pw180) pulse lengths were 10 and 20 μs, respectively. The echo time τ was 0.1 ms and the evolution time was calculated as (2τ + pw180) × (number of echo loops). All the peak integrals for the AEP-capped CdS samples are averaged over 3 experiments.

4. Supporting Figures and Tables

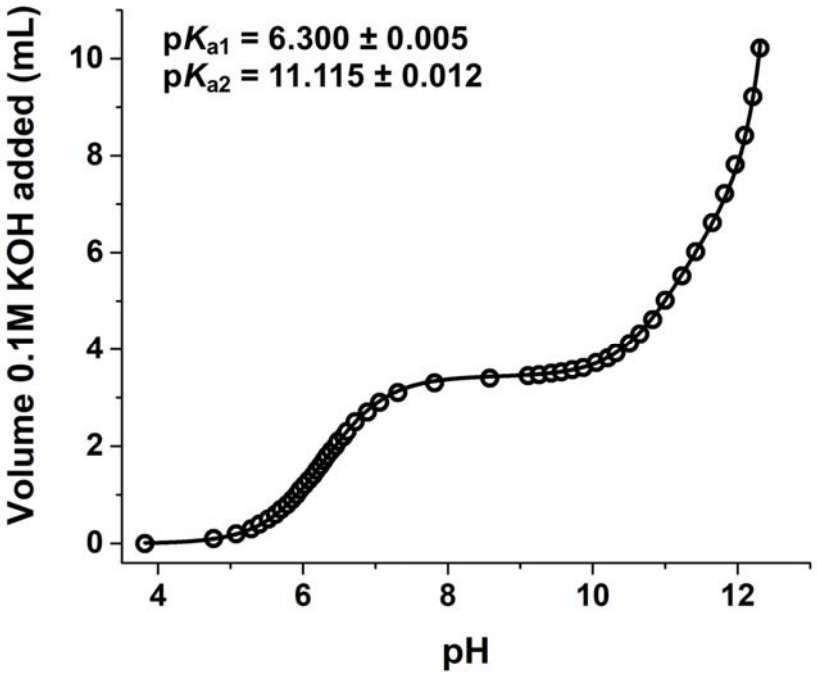

Figure S1. Titration of 3 mL AEP 0.1M in DI water with KOH 0.1M.

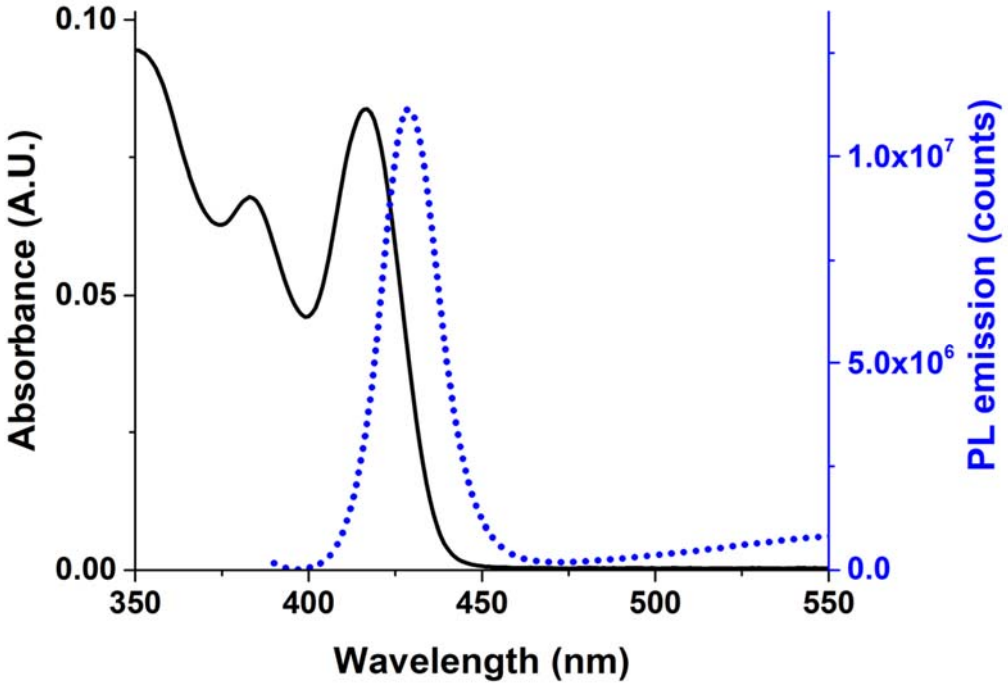

Figure S2. Ground state absorbance (black solid line, left axis) and emission (blue dotted lines, right axis) of oleate-capped CdS QDs in hexanes.

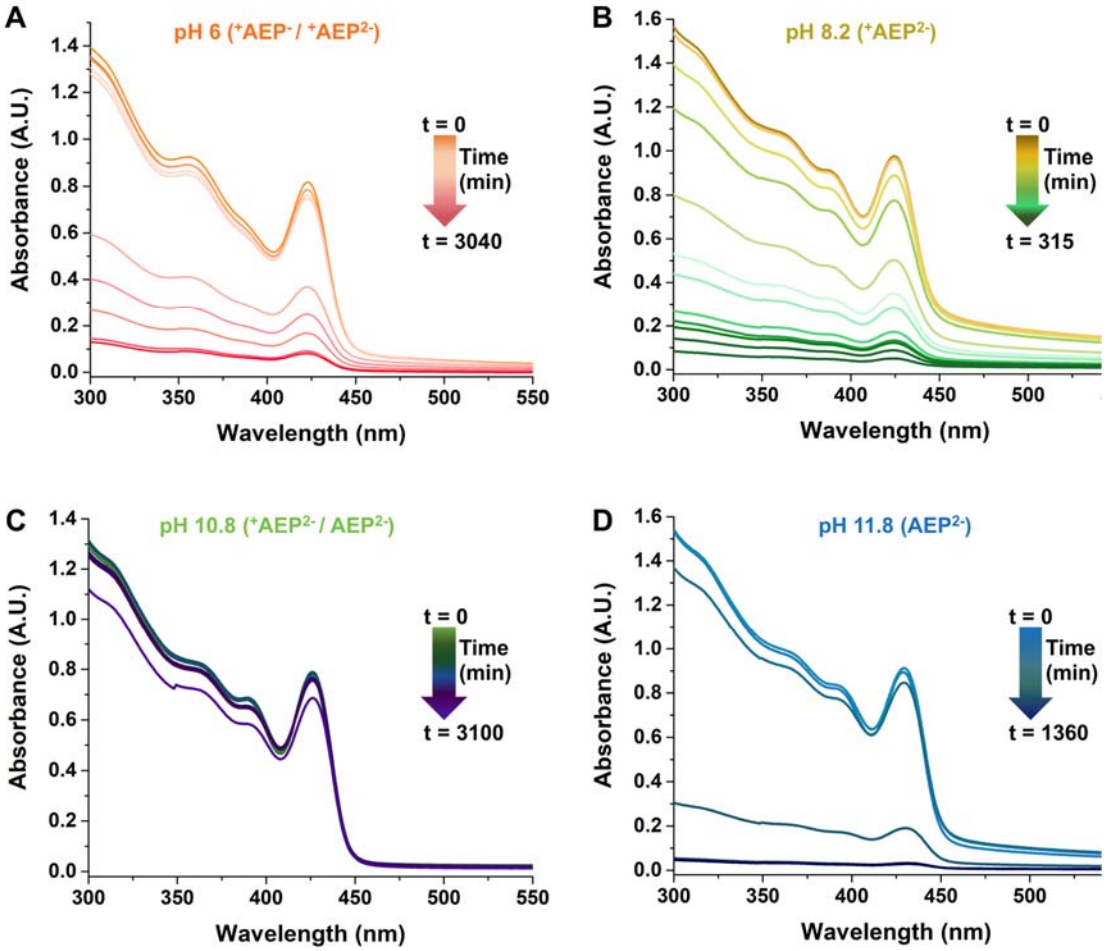

Figure S3. Ground state absorbance over time of AEP-capped CdS QDs capped at pH 6 (**A**), pH 8.2 (**B**), pH 10.8 (**C**) and pH 11.8 (**D**).

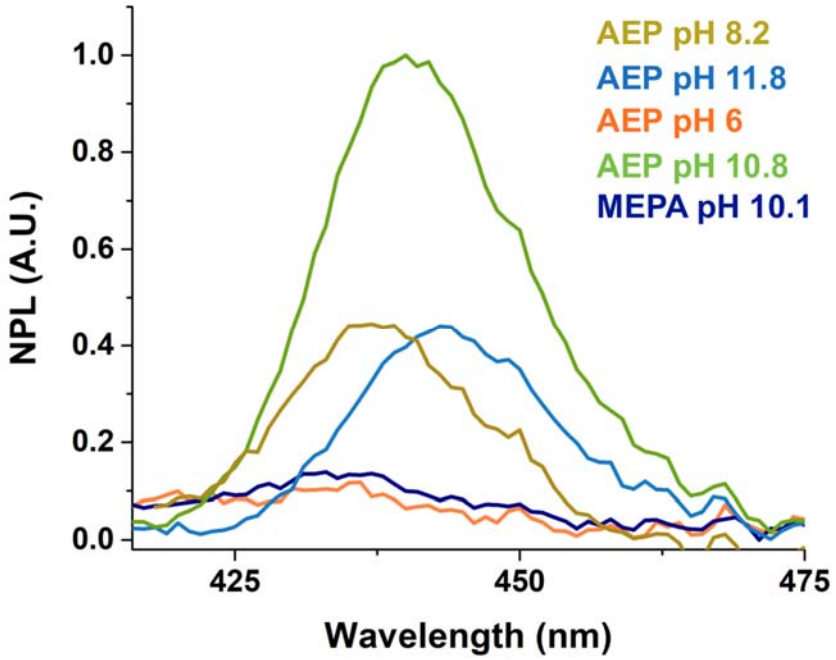

Figure S4. PL emission spectra of AEP-capped CdS QDs pH 6 (orange), pH 8.2 (dark yellow), pH 10.8 (green), pH 11.8 (blue) and of MEPA-capped CdS QDs at pH 10.1 (dark blue). The PL spectra have been scaled by their absorbance at the 350 nm excitation wavelength and normalized to the spectrum at pH 10.8. The PL QY of AEP-capped CdS QDs was 0.04% at pH 10.8 and 0.02% at pH 8.2 and pH 11.8. The peaks of AEP-capped CdS QDs at pH 6 and of MEPA-capped CdS QDs were not integrable.

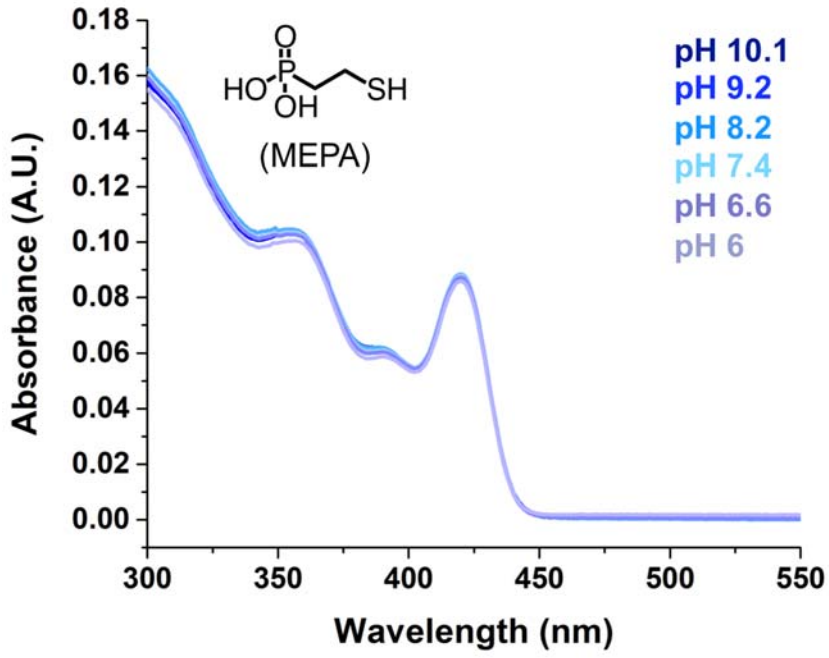

Figure S5. Ground state absorbances of 2-mercaptoethyl phosphonic acid (MEPA)-capped CdS QDs in water.

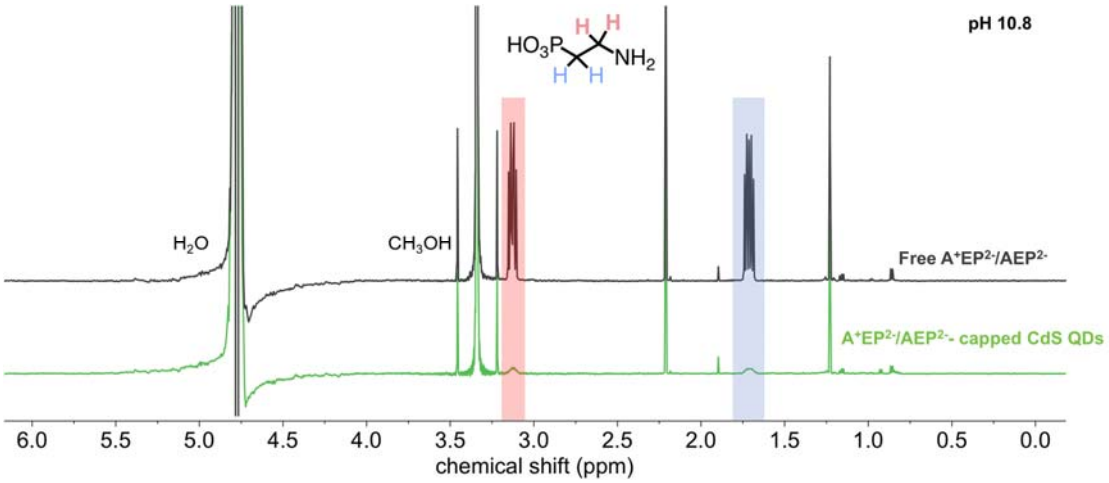

Figure S6. 600 MHz ^{1}H-NMR spectra of AEP-capped CdS QDs (green line) and AEP (grey line) at pH 10.8 in 80:20 (v/v) H_2O/D_2O (nt = 16, d1 = 30 s).

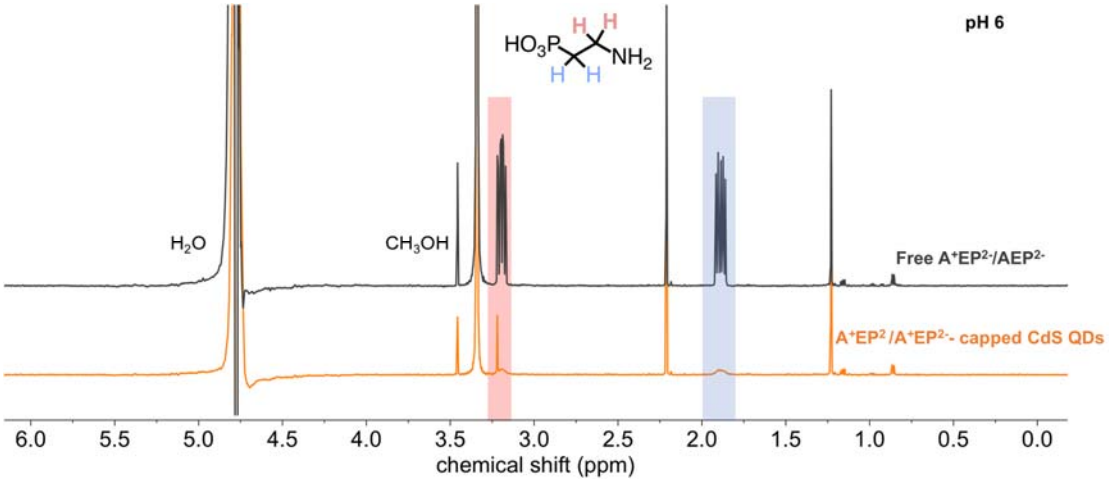

Figure S7. 600 MHz ^{1}H-NMR spectra of AEP-capped CdS QDs (orange line) and AEP (grey line) at pH 6 in 80:20 (v/v) H_2O/D_2O (nt = 16, d1 = 30 s).

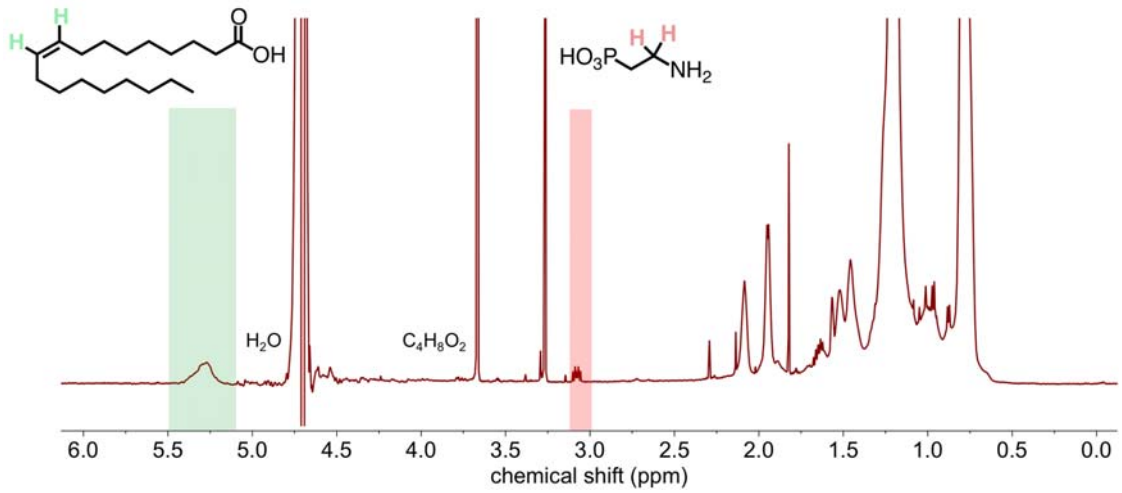

Figure S8. 600 MHz ^{1}H-NMR spectra of the supernatant of the AEP-treated sample after centrifugation (nt = 16, d1 = 30 s). The hexane layer is dried under N_2 flow and redispersed in 80:20 (v/v) H_2O/D_2O. The signal of the methylene protons adjacent to the amino group is integrated for quantitative ^{1}H measurements, as the signal of the methylene protons adjacent to the phosphonate group of AEP is buried beneath the aliphatic signals of oleate.

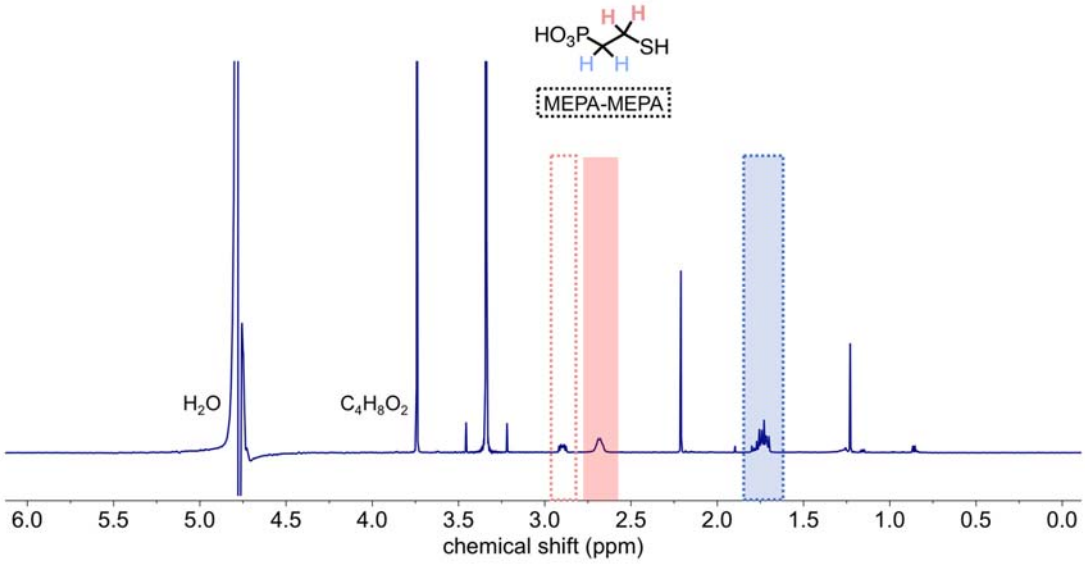

Figure S9. 600 MHz ^{1}H-NMR spectra of MEPA-capped CdS QDs at pH 10.1 in 80:20 (v/v) H_2O/D_2O (nt = 16, d1 = 30 s). "MEPA-MEPA" indicates the disulfide formed by the oxidation of MEPA in solution.

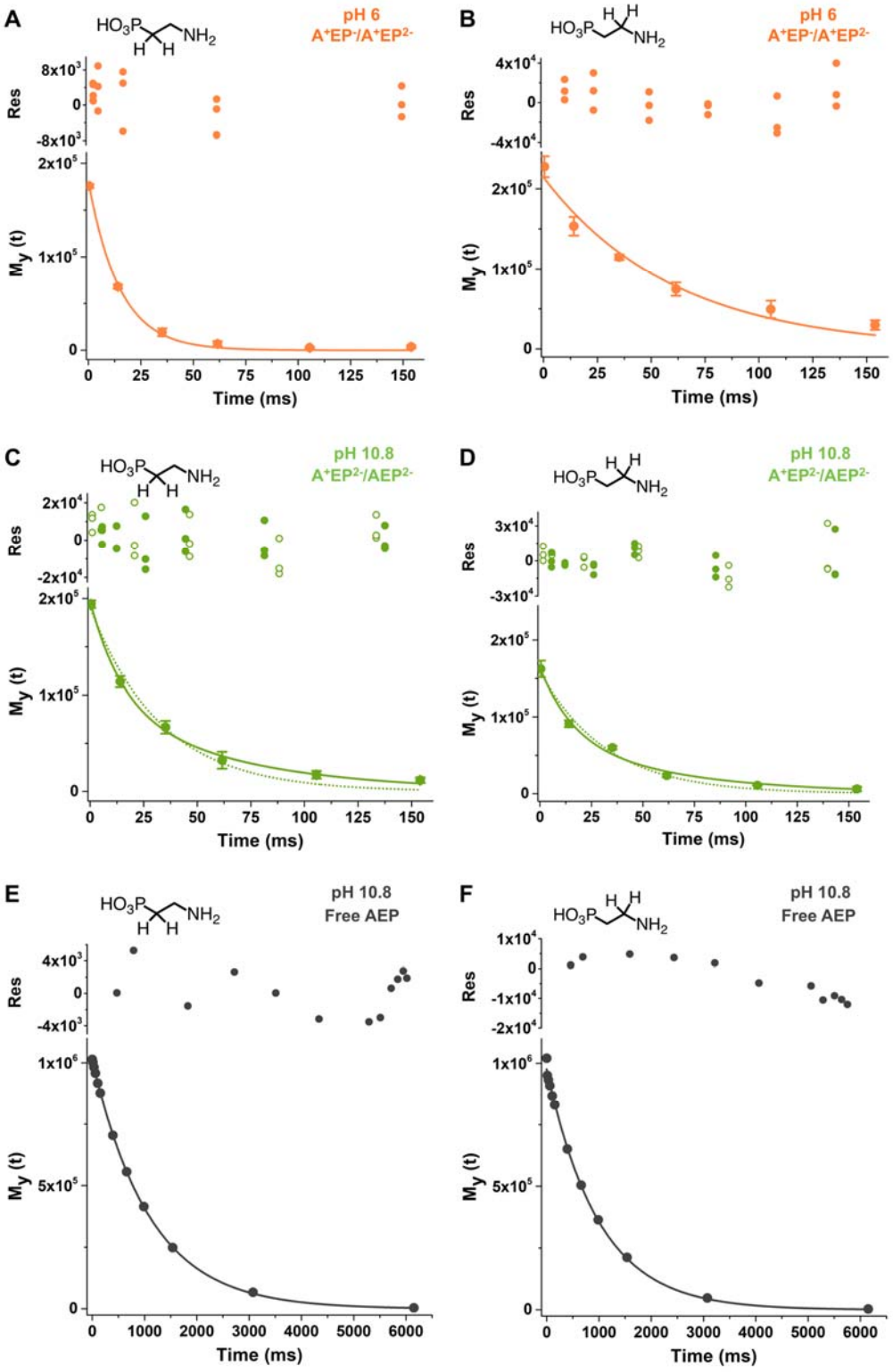

Figure S10. T_2 exponential decays and associated curve fits of resonances adjacent to the phosphonate group (**A**, **C**, **E**) and to the amino group (**B**, **D**, **F**) for AEP-capped CdS (**A – D**) and free AEP (**E, F**), and accompanying residuals, at the pH values indicated in the legends. Dashed lines are monoexponential fits; solid lines are biexponential fits. Open dots are residuals for monoexponential fits; solid dots are residuals for biexponenential fits. All peak integrals are averaged over three independently performed experiments on separate samples.

Table S1. Full-Width-at-Half-Maximum (FWHM) and theoretical homogeneous line broadening of the AEP peaks associated with protons adjacent to the phosphonate (H_α) and to the amine (H_β) in AEP-capped QDs (at pH 6 and pH 10.8).

	FWHM [a] **(Hz)**	**$1/(\pi T_2)$** [b] **(Hz)**
H_α AEP-QDs pH 6	36.3	21.4
H_β AEP-QDs pH 6	29.4	5.2
H_α AEP-QDs pH 10.8	34.1	9.6
H_β AEP-QDs pH 10.8	25.5	9.8

[a] Gaussian fitting. [b] T_2 value from monoexponential fit (see Table S2).
The homogeneous line width is smaller than the experimental FWHM indicating the heterogeneous nature of the resonances, which is in agreement with bound-ligand resonances previously reported.[7]

Table S2. Relaxation Times and Population of the AEP peaks associated with protons adjacent to the phosphonate (H_α) and to the amine (H_β) in AEP-capped QDs (at pH 6 and pH 10.8) and free AEP, from monoexponential[a] and biexponential fit[b].

	T_2[a] **(ms)**	**$T_{2\text{-HEAD}}$** [b] **(ms)**	**$M_{0,HEAD}$**[b] **($\times 10^3$)**	**$T_{2\text{-TAIL}}$** [b] **(ms)**	**$M_{0,TAIL}$**[b] **($\times 10^3$)**
H_α AEP-QDs pH 6	14.9 ± 0.6[c]				
H_β AEP-QDs pH 6	60.9 ± 5.9[d]				
H_α AEP-QDs pH 10.8	33.0 ± 2.5	14.9[e]	106 ± 19	64.1 ± 13.5	92 ± 16
H_β AEP-QDs pH 10.8	32.3 ± 2.6	15.7 ± 4.8	89 ± 16	60.9[e]	75 ± 16
H_α AEP	1100.5 ± 5.2				
H_β AEP	992.5 ± 27.1				

[c] $T_{2\text{-HEAD}}$. [d] $T_{2\text{-TAIL}}$. [e] Fixed value in the biexponential fit $M_{0,HEAD}$ and $M_{0,TAIL}$ indicate resonances adjacent to the headgroup and to the tailgroup, respectively.

5. References

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[2] B. E. W. Foster, G. J. Kearns, S. Goto, J. E. Hutchison, **2005**, *17*, 1542–1545.
[3] W. W. Yu, L. Qu, W. Guo, X. Peng, *Chem. Mater.* **2003**, *15*, 2854–2860.
[4] W. H. Melhuish, *J. Phys. Chem.* **1961**, *65*, 229–235.
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