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Electronic Supplementary Information

The Dynamic Surface Chemistry of Colloidal Metal Chalcogenide Quantum Dots

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Experimental Methods.

Materials.

All chemicals were of the highest purity available unless otherwise noted and were used as received. Lead oxide (PbO, 99.999%), Cadmium oxide (CdO, 99.5%), oleic acid (technical grade 90%), 1-octadecene (ODE, technical grade 90%), bis(trimethylsylil)sulfide (TMS, synthesis grade), were purchased from Sigma-Aldrich. Sulfur (S, 99%), and Selenium (Se, 99,99%) were purchased from Strem Chemicals. All solvents were anhydrous and were used as received.

Colloidal metal chalcogenide QD synthesis.

All QDs were synthesized in three-neck flasks connected to a standard Schlenk line setup under oxygen- and moisture-free conditions according to slightly modified, well-established recipes.[S1]

Colloidal CdS QDs.

In a typical synthesis yielding zinc-blende CdS QDs,[S2] 2 mmol of CdO were mixed with 6 mmol of oleic acid in 20 mL of ODE. The mixture was vigorously stirred and deaerated through repeated cycles of vacuum application and purging with nitrogen at about 120 °C. Then, the mixture was heated under nitrogen flow to above 200 °C to allow dissolution of CdO until the solution became colorless and optically clear, indicating the formation of cadmium(II)-oleate complex(es). The temperature was stabilized at 280°C. At this point, an aliquot of S precursor solution was swiftly injected and CdS QDs were allowed to grow for about 20 seconds. A stock solution of the S precursor had been previously prepared under inert atmosphere by dissolving 4 mmol of S in 12 mmol of oleic acid and 8 mL of ODE upon heating at 180 °C for a hour. The heating mantle was then removed and the reaction quenched by compressed air. After the synthesis, CdS QDs were transferred to a nitrogen-filled glove box. The QDs were repeatedly (three times, including the first step on crude product, are usually enough) precipitated using excess acetone (or methanol) and then redissolved in toluene. The QDs were stored at room temperature in a glove box for subsequent use as ~1 mM toluene solutions.

Colloidal CdSe QDs.

In a typical synthesis yielding zinc-blende CdSe QDs,[S3] 2 mmol of CdO were mixed with 6 mmol of oleic acid in 24 mL of ODE. The mixture was vigorously stirred and deaerated through repeated cycles of vacuum application and purging with nitrogen at about 120 °C. Then, the mixture was heated under nitrogen flow to above 200 °C to allow dissolution of CdO until the solution became colorless and optically clear, indicating the formation of cadmium(II)-oleate complex(es). The temperature was stabilized at 280°C. At this point, an aliquot of Se precursor solution was swiftly injected and CdSe QDs were allowed to grow for about 20 seconds. A stock solution of the Se precursor had been previously prepared under inert atmosphere by dissolving 4 mmol of Se in 12 mmol of oleic acid and 8 mL of ODE upon heating at 240 °C for ca. 2 hours. The heating mantle was then removed and the reaction quenched by compressed air. After the synthesis, CdSe QDs were transferred to a nitrogen-filled glove box. The QDs were repeatedly (three times, including the first step on crude product, are usually enough) precipitated using excess acetone (or methanol) and then redissolved in toluene. The QDs were stored at room temperature in a glove box for subsequent use as ~1 mM toluene solutions.

Colloidal PbS QDs.

In a typical synthesis yielding rock salt PbS QDs,[S4] 2 mmol of PbO (450 mg) and 6 mmol (1700 mg) of oleic acid were mixed in 10 g of ODE. The mixture was vigorously stirred and deaerated through repeated cycles of vacuum application and purging with nitrogen at about 80 °C. The mixture was then heated to above 100 °C to allow dissolution of PbO until the solution became colorless and optically transparent, suggesting the complete formation of lead(II)-oleate complex(es). The solution was cooled at 80 °C and repeatedly subjected to vacuum in the attempt of removing water eventually released upon lead(II)-oleate complex formation. The solution was then heated again under nitrogen flow and the temperature stabilized at 110°C. At this point, 1 mmol of sulfur precursor (bis(trimethylsilyl)sulfide; 210 μL) in 2 mL of octadecene was swiftly injected. The heating mantle was immediately removed and the resulting colloidal solution was allowed to cool to room temperature. After the synthesis, PbS QDs were transferred to a nitrogen-filled glove box. The QDs were precipitated using excess acetone (1:4 vol/vol), centrifuged at 4000 rpm and then redissolved in toluene. Two additional precipitation-redissolution cycles were performed by using methanol and toluene. An estimate of solvent volumes (about 4 mL of toluene to dissolve the QD pellet and 2 mL of methanol to precipitate the QDs) is crucial to obtain subtly purified QDs, although inherently empirical. The PbS QD size was varied by changing the amount of oleic acid (from two to sixteen equivalents) added to PbO, keeping constant its total concentration in the reaction flask; eventual dilution yields larger nanocrystals. Oleylamine (2 mmol) was added to the Pb-oleate precursor to obtain PbS QDs with diameters below 2.5 nm. Stock toluene solutions with concentration of ~ 1 mM were prepared and stored at room temperature in the glove box for subsequent use.

The Pb precursor was obtained by cooling down to room temperature the reaction mixture before the injection of the sulfur precursor and upon purification according to the same procedure described for the QDs, then followed by overnight drying under vacuum.[S5]

Materials Characterization.

Nuclear Magnetic Resonance Spectroscopy (NMR).

NMR analisys was performed with a Bruker Avance spectrometer operating at 700 MHz equipped with a Cryo-Probe optimized for ^{1}H observation on 0.1 mM solutions of colloidal ME QDs in hexane-d14, toluene-d8, dichloromethane-d2, chloroform-d, and dichlorobenzene-d4.

Optical Absorption Spectroscopy.

The optical absorption spectra of colloidal ME QDs were measured in suprasil quartz cuvettes with 1 cm path length and were recorded with a Varian Cary 5000 UV-Vis-NIR spectrophotometer.

Transimission Electron Microscopy (TEM).

TEM images of colloidal ME QDs were recorded with a Jeol Tem 1011 microscope operated at an accelerating voltage of 100 kV. Samples for analysis were prepared by dropping a QD solution onto carbon-coated Cu grids and then allowing the solvent to evaporate in a vapor controlled environment.

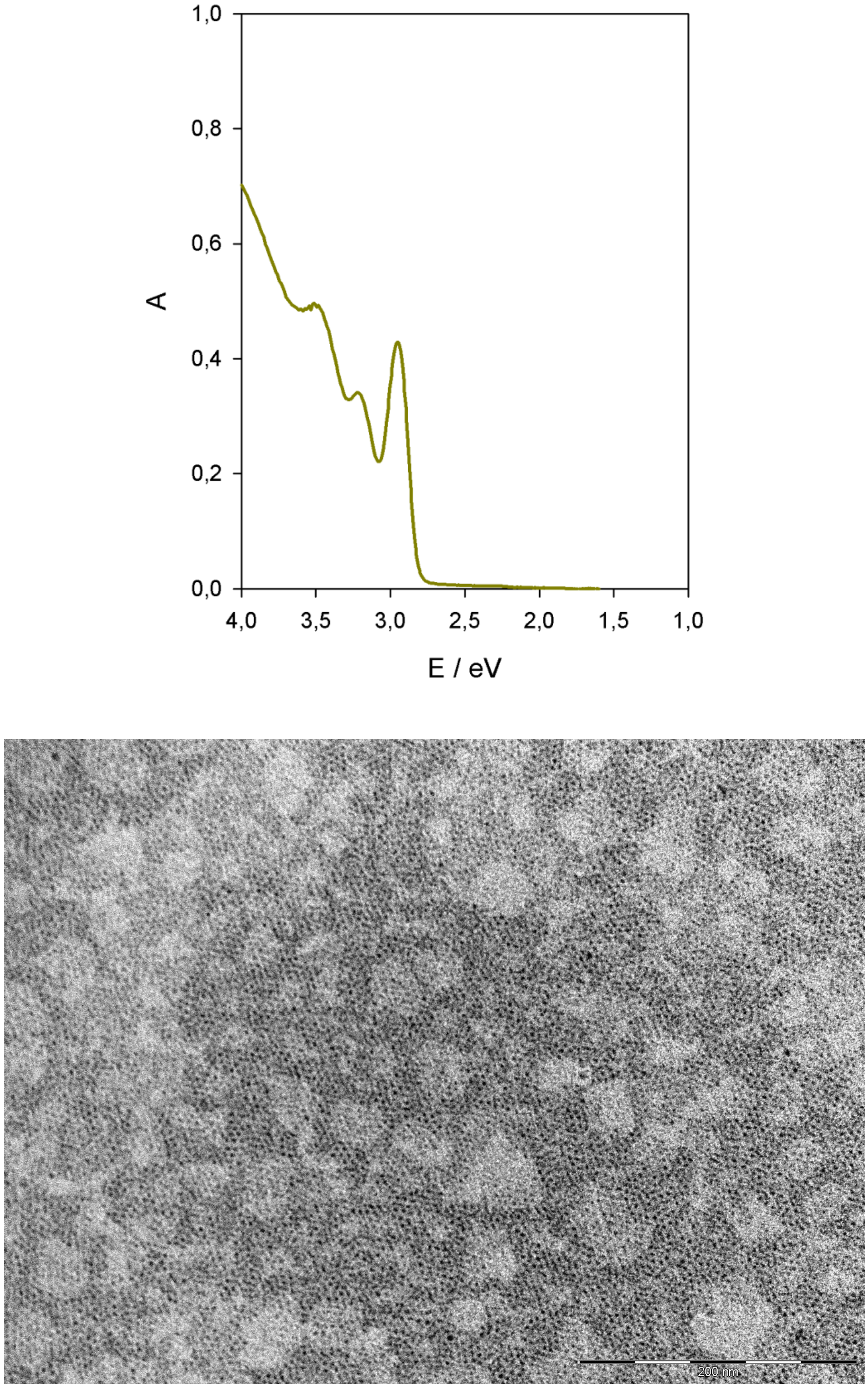


Figure S1. (top) absorption spectrum and (bottom) transmission electron microscopy image of as-synthesized CdS QDs with diameter of about 3 nm.

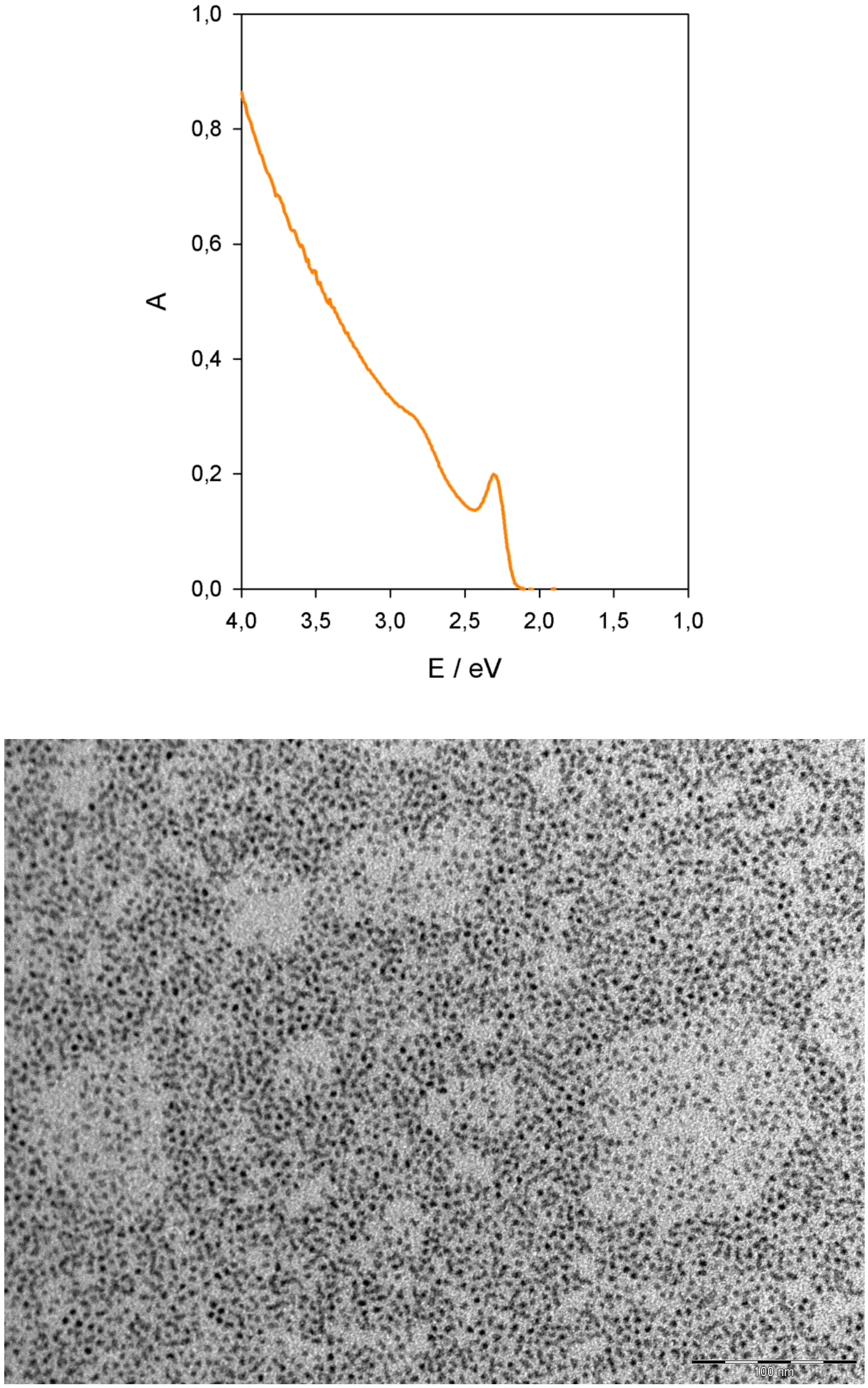


Figure S2. (top) absorption spectrum and (bottom) transmission electron microscopy image of as-synthesized CdSe QDs with diameter of about 3 nm.

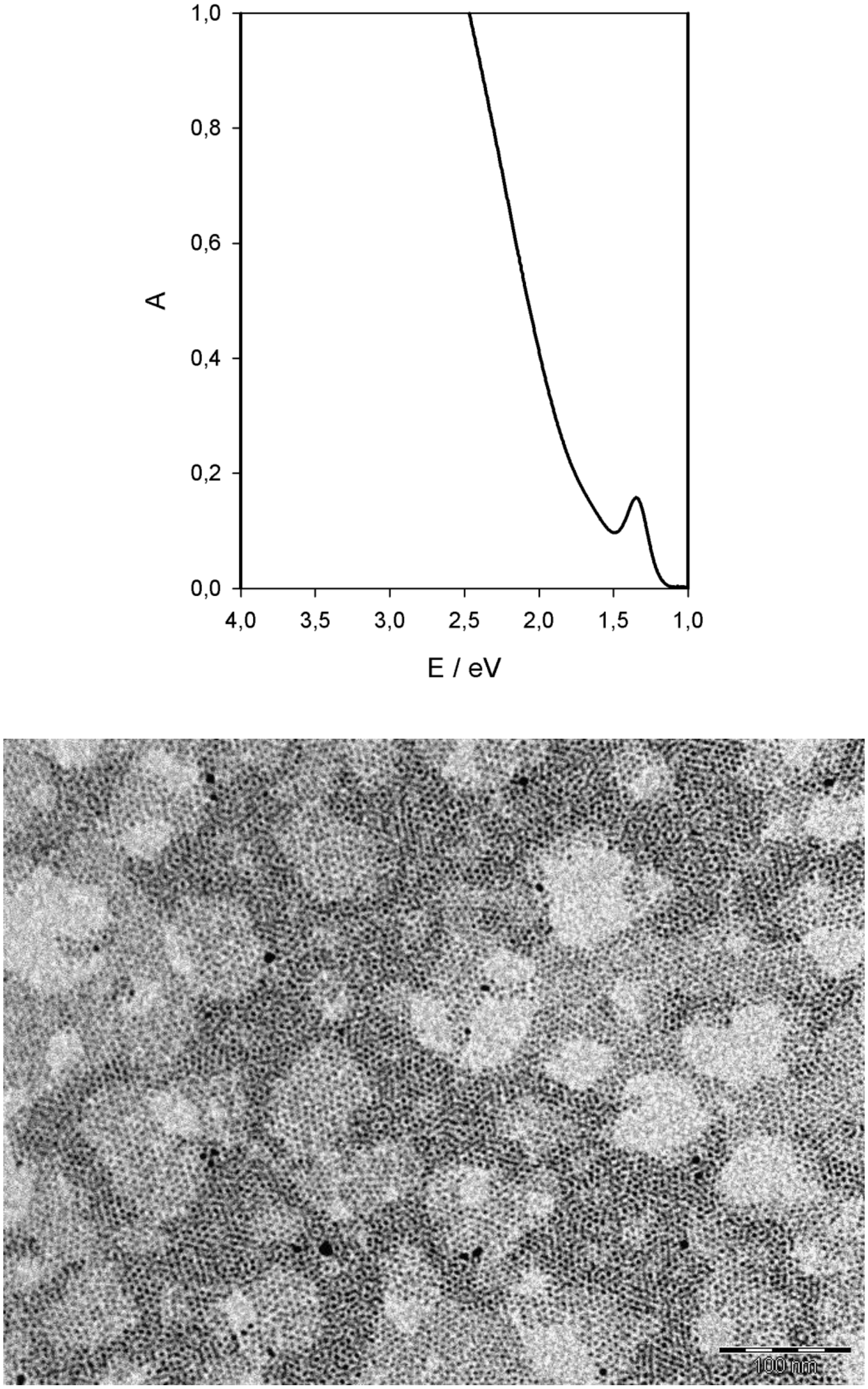
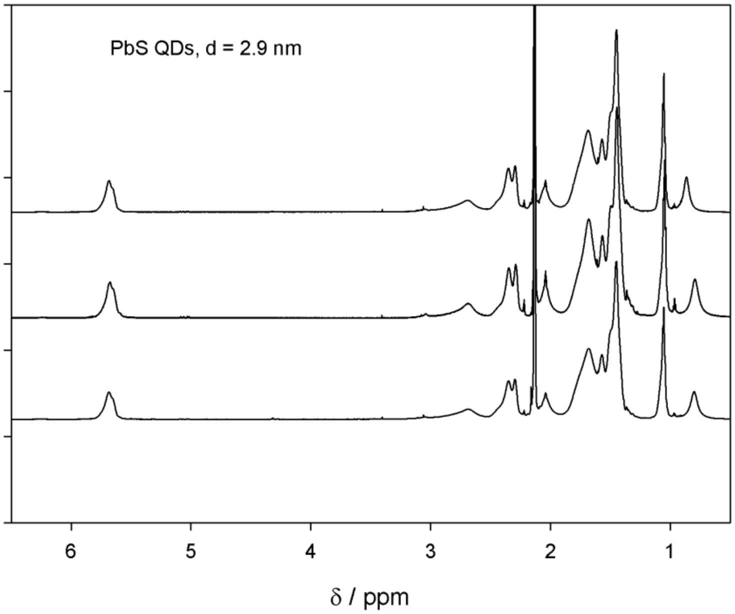


Figure S3. (top) absorption spectrum and (bottom) transmission electron microscopy image of as-synthesized PbS QDs with diameter of about 3 nm.



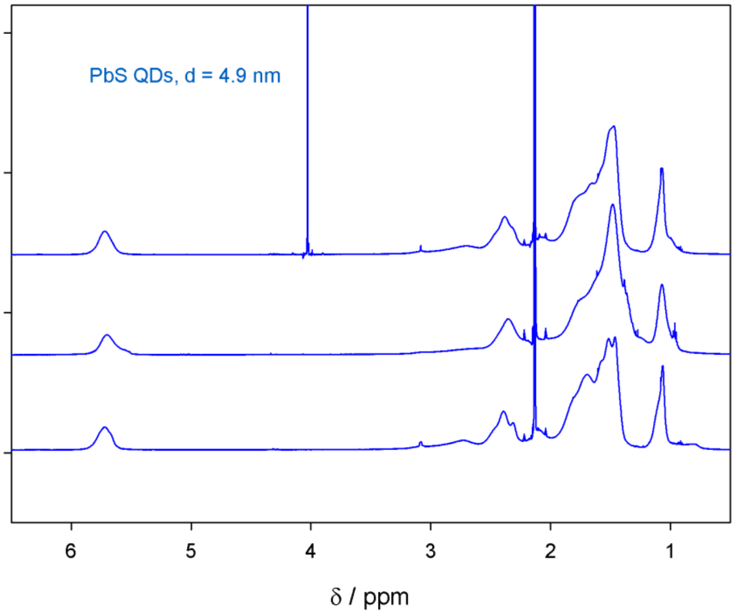


Figure S4. ^{1}H-NMR spectra of different batches of air-equilibrated 0.1 mM solutions of PbS QDs with diameter of about 3 nm (top) and 5 nm (bottom) in toluene-d8.

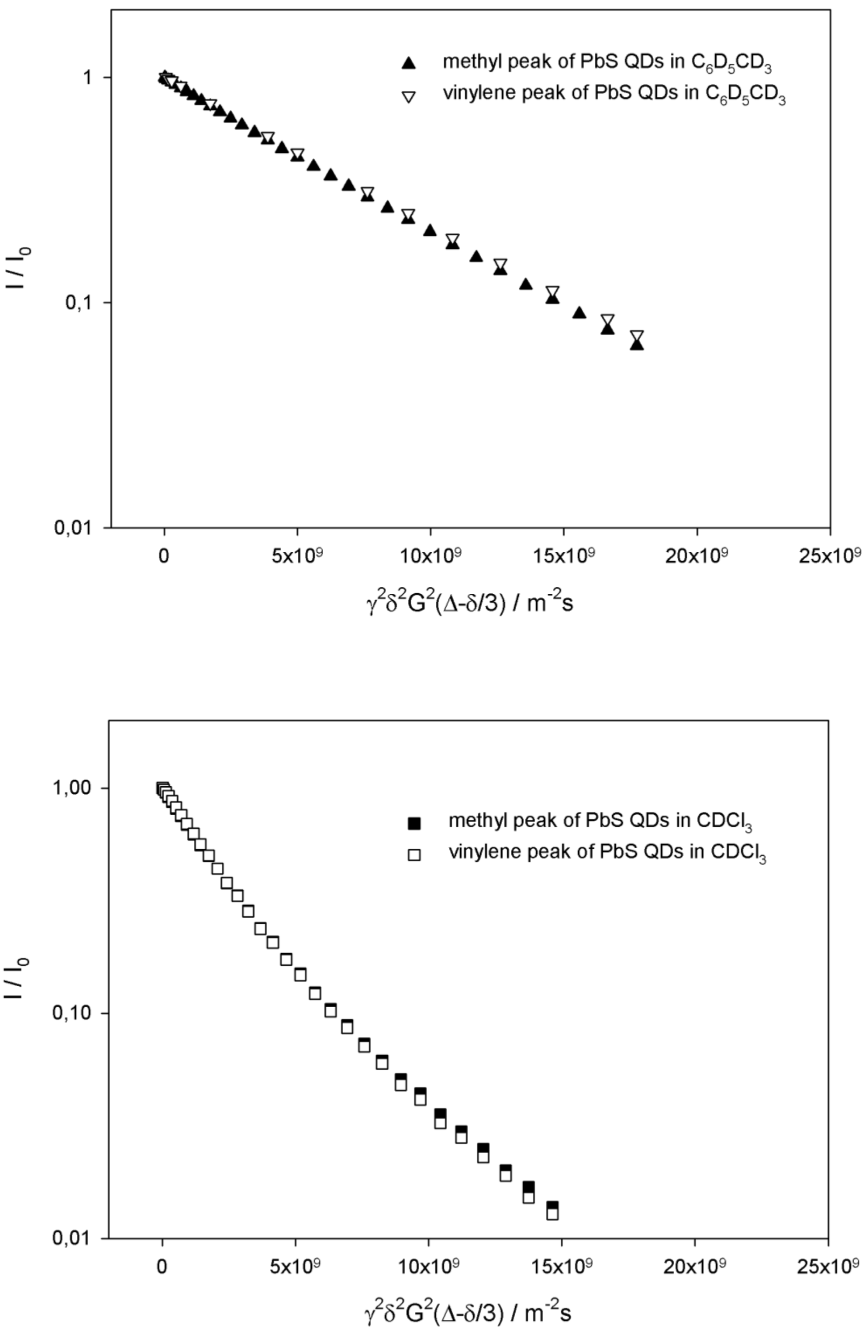


Figure S5. Stejskal-Tanner plots of air-equilibrated 0.1 mM solutions of PbS QDs with diameter of about 3 nm in (top) toluene-d8 and (bottom) chloroform-d as indicated in the corresponding panels, showing analogous decay with the pulsed field gradient for both vinylene and terminal methyl peaks.

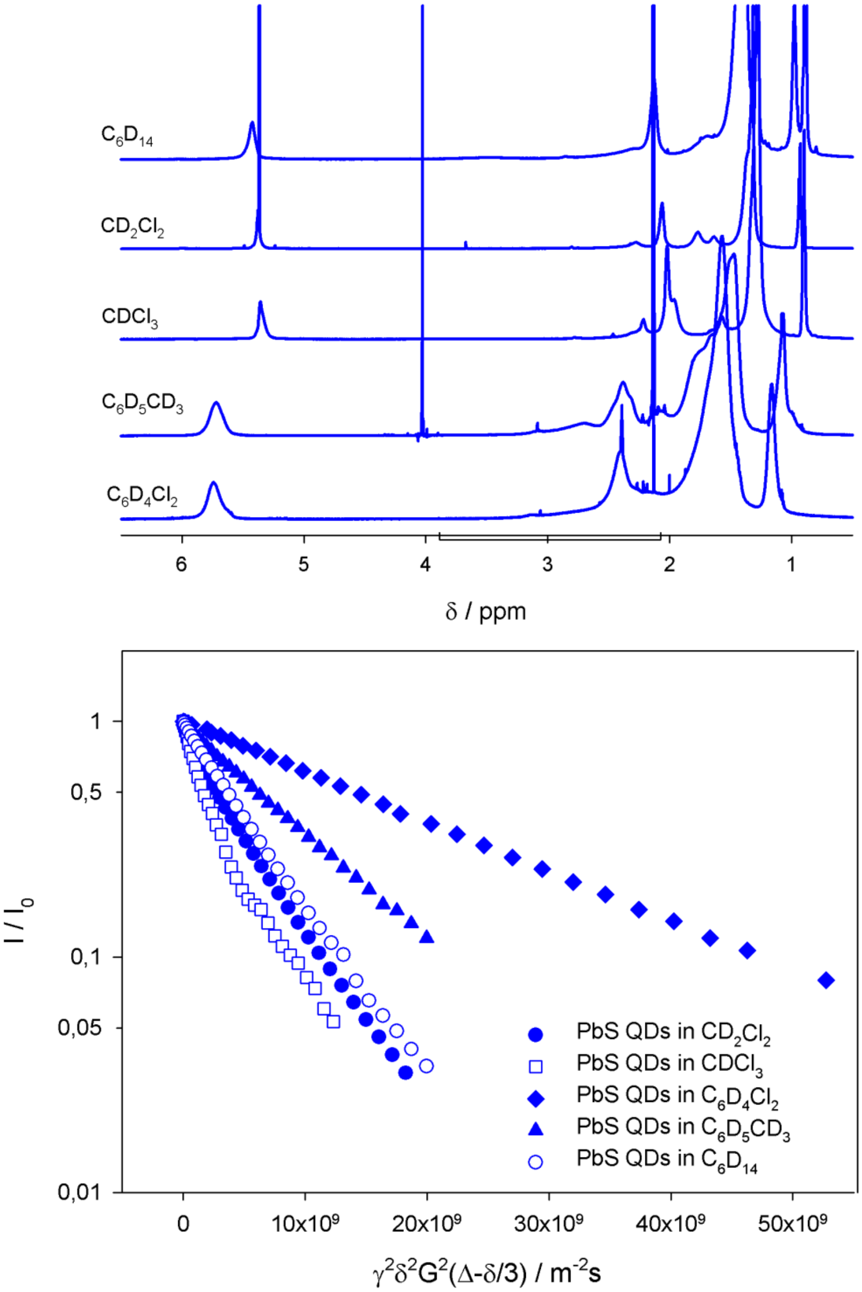


Figure S6. (top) ^{1}H-NMR spectra and (bottom) Stejskal-Tanner plots of air-equilibrated 0.1 mM solutions of PbS QDs with diameter of about 5 nm in hexane-d14, toluene-d8, chloroform-d, dichloromethane-d2, and dichlorobenzene-d4 as indicated in the corresponding panels.

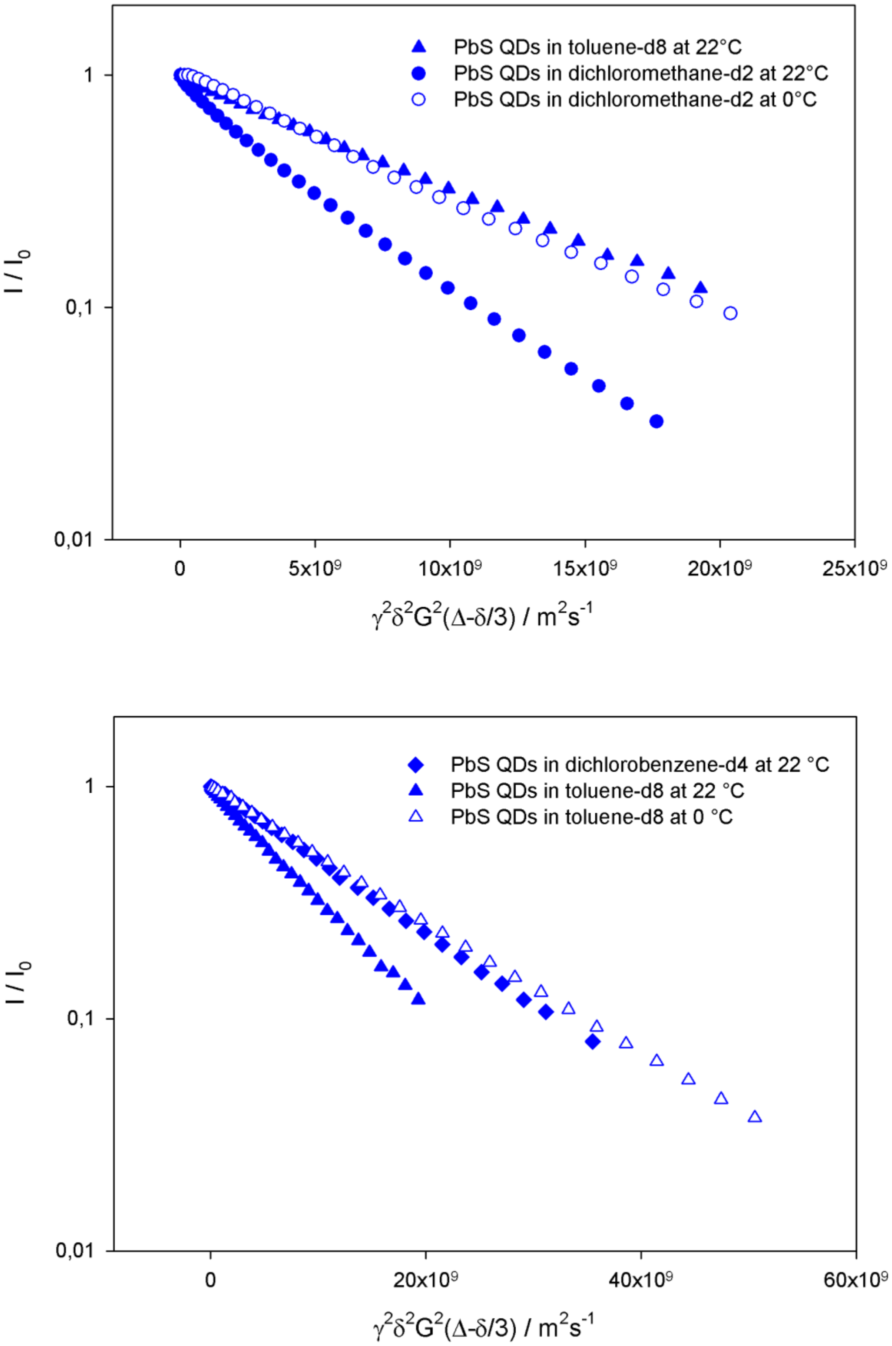
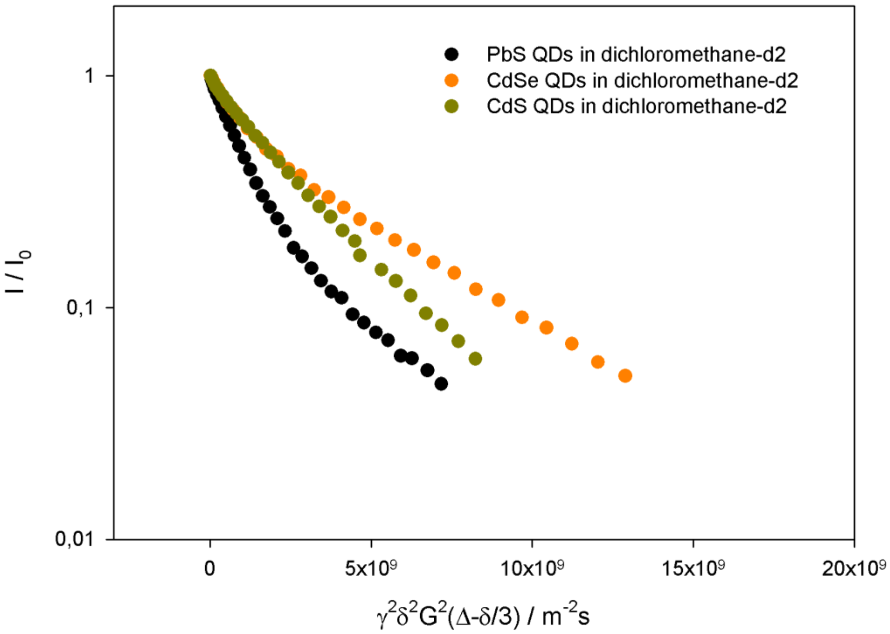


Figure S7. Stejskal-Tanner plots of air-equilibrated 0.1 mM solutions of PbS QDs with diameter of about 5 nm in (top) dichloromethane-d2 at different temperatures compared with toluene-d8 at 22 °C and (bottom) toluene-d8 at different temperatures compared with dichlorobenzene-d4 at 22 °C as indicated in the corresponding panels.



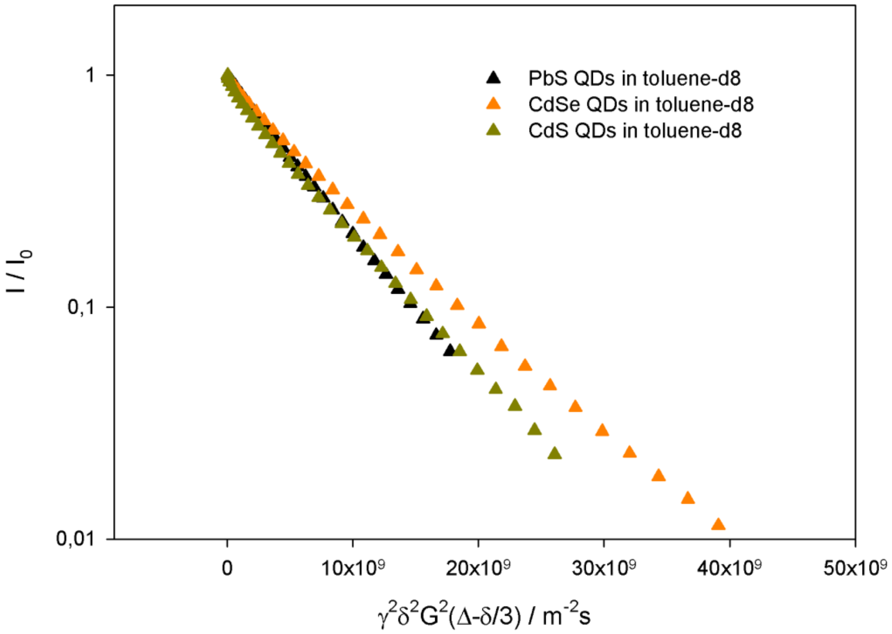


Figure S8. Stejskal-Tanner plots of air-equilibrated 0.1 mM solutions of ME QDs with diameter of about 3 nm in (top) dichloromethane-d2 and (bottom) toluene-d8 as indicated in the corresponding panels.

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Table S1. Values of the vinylene line width and apparent solvodynamic diameter for ME QDs in different solvents, as plotted in Figure 4.

	CdS QDs	**CdSe QDs**	**PbS QDs**
hexane-d14	$\Delta\nu$ = – d_{solv} = –	$\Delta\nu$ = 65 Hz d_{solv} = 5.1 nm	$\Delta\nu$ = 22 Hz d_{solv} = 4.9 nm
toluene-d8	$\Delta\nu$ = 78 Hz d_{solv} = 4.9 nm	$\Delta\nu$ = 110 Hz d_{solv} = 5.3 nm	$\Delta\nu$ = 50 Hz d_{solv} = 5.1 nm
chloroform-d	$\Delta\nu$ = 42 Hz d_{solv} = 4.3 nm (23 %) d_{solv} = 1.8 nm (77 %)	$\Delta\nu$ = 52 Hz d_{solv} = 4.9 nm (37 %) d_{solv} = 1.8 nm (63 %)	$\Delta\nu$ = 11 Hz d_{solv} = 4.4 nm (19 %) d_{solv} = 1.6 nm (81 %)
dichloromethane-d2	$\Delta\nu$ = 26 Hz d_{solv} = 4.2 nm (21 %) d_{solv} = 1.9 nm (79 %)	$\Delta\nu$ = 43 Hz d_{solv} = 4.8 nm (41 %) d_{solv} = 1.9 nm (59 %)	$\Delta\nu$ = 12 Hz d_{solv} = 4.0 nm (26 %) d_{solv} = 1.8 nm (74 %)
dichlorobenzene-d4	$\Delta\nu$ = 88 Hz d_{solv} = 5.3 nm	$\Delta\nu$ = 97 Hz d_{solv} = 5.9 nm	$\Delta\nu$ = 47 Hz d_{solv} = 5.2 nm

Table S2. Values of the vinylene line width and apparent solvodynamic diameter for PbS QDs with different diameters in both deuterated toluene and chloroform, as plotted in Figure 6.

	PbS QDs **in toluene-d8**	**PbS QDs** **in chloroform-d**
$d_{QD} = 1.9\ nm$	$\Delta\nu$ = 51 Hz d_{solv} = 3.8 nm	$\Delta\nu$ = 6.3 Hz d_{solv} = –
$d_{QD} = 2.9\ nm$	$\Delta\nu$ = 50 Hz d_{solv} = 5.1 nm	$\Delta\nu$ = 6.0 Hz d_{solv} = 4.4 nm (19 %) d_{solv} = 1.6 nm (81 %)
$d_{QD} = 3.5\ nm$	$\Delta\nu$ = 57 Hz d_{solv} = –	$\Delta\nu$ = 8.0 Hz d_{solv} = –
$d_{QD} = 4.4\ nm$	$\Delta\nu$ = 65 Hz d_{solv} = 6.4 nm	$\Delta\nu$ = 8.5 Hz d_{solv} = 5.4 nm (53 %) d_{solv} = 1.9 nm (47 %)
$d_{QD} = 4.9\ nm$	$\Delta\nu$ = 73 Hz d_{solv} = 7.3 nm	$\Delta\nu$ = 9.7 Hz d_{solv} = 5.7 nm (61 %) d_{solv} = 1.9 nm (39 %)
$d_{QD} = 6.7\ nm$	$\Delta\nu$ = 88 Hz d_{solv} = 9.9 nm	$\Delta\nu$ = 15 Hz d_{solv} = 7.4 nm (89 %) d_{solv} = 1.8 nm (11 %)

Supporting References.

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