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Short-Chain Alcohols Strip X-Type Ligands and Quench the Luminescence of PbSe and CdSe Quantum Dots, Acetonitrile Does Not

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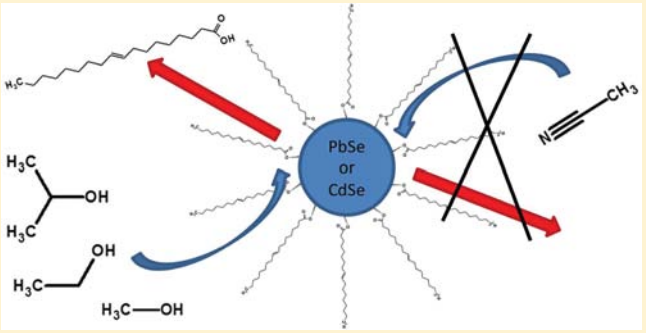
Supporting Information

ABSTRACT: The effect of short-chain alcohols and acetonitrile on the ligand shell composition and the photoluminescence quantum yield of purified PbSe and CdSe quantum dots is analyzed by solution NMR and photoluminescence spectroscopy. We find that short-chain alcohols induce the release of X-type carboxylate ligands with a concurrent reduction of the photoluminescence quantum yield, while acetonitrile does not. We interpret this difference in terms of the protic or aprotic character of both nonsolvents, where only the protic alcohols can provide the protons needed to desorb carboxylate ligands. We find similar differences between short-chain alcohols and acetonitrile when used as nonsolvents during the purification of crude synthesis products, a result stressing the importance of using aprotic nonsolvents for nanocrystal purification or processing.



INTRODUCTION

Colloidal semiconductor nanocrystals or quantum dots (QDs) are an outstanding example of the versatility and tunability nanomaterials can offer. By synthesis, they are formed as organic/inorganic hybrid materials featuring an inorganic, crystalline core surrounded by a shell or capping of organic ligands.[1,2] The core mainly determines the nanocrystals' physical properties, where, e.g., quantum confinement imparts tunability by size and shape.[3−5] The ligand shell on the other hand plays a central role in the interaction between nanocrystals and their surroundings.[6] This involves the stabilization of colloidal nanocrystal dispersions by steric hindrance and, by means of ligand exchange, the chemical functionalization of nanocrystals. In this way, nanocrystals can be tuned to interact specifically with analytes,[7−9] biomolecules,[9−11] other nanocrystals,[12] or surfaces.[13−15]

Over the last 5 years, various studies have addressed the chemistry of the organic/inorganic interface between the nanocrystal core and the ligand shell, where especially in the case of CdSe,[16−18] PbSe,[19,20] PbS,[21] and InP[22] very detailed studies have been published. This has led to a general picture where anionic moieties such as carboxylates or phosphonates bind as X-type ligands to the nanocrystal, which is itself usually cation rich. In the case of CdSe/carboxylate, it was shown that charge neutral nanocrystals are obtained from the combination of anionic X-type ligands and a cation-rich inorganic core,[17] suggesting a very simple interface consisting of carboxylate ligands only. In the case of PbS/carboxylate on the other hand, a more complex interface was demonstrated since the charge of the cation-rich core is balanced by a combination of X-type organic ligands and Cl^- ions.[21] For CdSe QDs synthesized in trioctylphosphine oxide (TOPO) as a coordinating solvent, additional L-type ligands like TOPO itself and trioctylphosphine selenide (TOPSe) have also been identified, which are however rapidly lost by successive purification steps.[18] Importantly, a number of studies indicate that this dilution-induced ligand loss does not occur with X-type ligands such as carboxylates or phosphonates since desorption requires a proton transfer step in this case.[17,18]

Apart from determining the interaction between a nanocrystal and its surroundings, various authors have shown that ligands also affect the physical properties of nanocrystals. The photoluminescence quantum yield (PLQY) of colloidal QDs is for example particularly sensitive to the ligand shell composition, where both PL enhancement and PL quenching have been reported.[23,24] In this respect, the quenching of the photoluminescence of CdSe QDs synthesized using TOPO as the coordinating solvent by short-chain alcohols such as methanol (MeOH) stands out since these are typically used as nonsolvents during the purification of colloidal QD dispersions.[23] Analyzing the same CdSe/TOPO system,

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Morris-Cohen et al. found that the PL quenching by adding MeOH during successive purification steps concurs with the loss of L-type hexadecylamine ligands, while the number of X-type alkylphosphonate ligands remained constant.[18]

In this paper, we take these observations as a starting point to analyze the interplay between typical nonsolvents—short-chain alcohols and acetonitrile—and the ligand shell composition and photoluminescence quantum yield for colloidal CdSe and PbSe QDs stabilized by X-type carboxylate ligands only. Such QDs typically result from hot injection syntheses that use non-coordinating solvents in combination with long carboxylic acids to dissolve metal cation precursors and stabilize the resulting QDs.[17,25−27] For both materials, we use solution ^{1}H NMR to monitor the changes in the ligand shell composition during the titration of well-purified dispersion with a nonsolvent and after successive purification steps starting from a crude reaction product. Making use of the unique capability of solution NMR to distinguish bound from free ligands,[17,28,29] both approaches show that short-chain alcohols induce the release of carboxylate ligands, while acetonitrile (MeCN) leaves the ligand shell untouched. Concomitantly, only the addition of alcohols eventually quenches the photoluminescence. Moreover, after excessive purification of PbSe and CdSe nanocrystals with MeOH as the nonsolvent, we observe the opposite process; i.e., the QDs release MeOH upon addition of excess oleic acid, which itself binds to the QDs. We thus interpret the different impact of short-chain alcohols and MeCN on the ligand shell in terms of an exchange reaction that requires a proton transfer between the nonsolvent and the carboxylate ligands. Hence, this work indicates that the use of aprotic nonsolvents like MeCN is strongly recommended during nanocrystal purification or processing when the ligand shell and the PLQY are to be preserved.

EXPERIMENTAL METHODS

PbSe Synthesis. Monodisperse colloidal PbSe QDs were synthesized by a modified high-temperature synthesis developed by Murray et al.[30] Lead oleate (PbOA, lead to oleic acid 1:4) and trioctylphosphine-selenium (TOP-Se, 1 M) or tributylphosphine-selenium (TBP-Se, 1M) precursors were prepared before the synthesis and stored under an inert atmosphere. By changing the growth temperature, different sizes of colloidal PbSe QDs were produced. In a typical PbSe synthesis, 26 mL of DPE was heated to a temperature 20 °C higher than the injection temperature, and 9.2 mL of PbOA was added. When the reaction mixture reached the desired injection temperature, 5.7 mL of TOP-Se or TBP-Se was injected, which further reduced the temperature to the preset growth temperature and started the reaction. For example, using injection of TOP-Se at 118 °C and growth at 108 °C with 6 min of the reaction time produced 4.5 nm PbSe QDs. The product was purified first by using butanol and MeOH as nonsolvents and toluene as solvent, respectively. The products for NMR and PL titration experiments were purified by two more precipitation/resuspension steps using MeOH and toluene. Synthesis, purification, and sample storage were done under an inert atmosphere. The QD concentration in suspension was determined from the QD absorbance spectrum, using the molar extinction coefficient at 400 nm.[31] NMR samples were prepared by drying a suspension of PbSe QDs under a strong nitrogen flow, followed by redispersing the nanocrystals in toluene-d_8. The ligand concentration was kept approximately constant between different samples and typically ranged from 1.2 to 1.5 μmol in a 650 μL NMR sample. To avoid oxidation of the PbSe QDs and any contamination from air during sample preparation and the titration experiments, the samples were prepared and titrated under an inert gas atmosphere.

CdSe Synthesis. An optimized version of the synthesis introduced by Jasieniak et al.[32] was used to produce monodisperse colloidal CdSe QD suspensions. Both cadmium oleate (CdOA, cadmium to oleic acid 1:10) and octadecene-selenium (ODE-Se, 0.1 M) precursors were prepared prior to the actual synthesis. The synthesis was performed under nitrogen atmosphere, and by varying the reaction time, different sizes of colloidal CdSe QDs were produced. In a typical synthesis, 10 mL of ODE and 950 μL of CdOA were mixed and degassed under nitrogen flow for 30 min, which was then continued for another 30 min at 100 °C. The reaction mixture was next heated to 260 °C where 3 mL of ODE-Se was injected. The growth temperature was set to 240 °C. As the reactivity of ODE-Se varies from batch to batch, a test synthesis with aliquots was done before synthesizing specific sizes of CdSe QDs. The product was first purified by using iPrOH and MeOH as nonsolvents and toluene as the solvent. The products for NMR and PL titration experiments were purified by three precipitation/resuspension steps in ambient using MeOH and toluene. The QD size and concentration were determined from the absorbance spectrum, where the QD size is given by the first exciton peak through a sizing curve, and the QD concentration is given by averaging the absorption at 340, 320, and 300 nm.[33] CdSe NMR samples were similarly prepared as PbSe NMR samples.

Solution ^{1}H NMR Spectroscopy. NMR tubes (5 mm) were used for all NMR experiments. For titration experiments, deuterated nonsolvents were used to suppress excess resonances arising from used nonsolvents. In a typical MeOH NMR titration experiment, ligand:nonsolvent molar ratios of 1:100, 1:300, 1:600, 1:1200, and 1:2400 were used, amounting to nonsolvent concentrations in the range 0.2−5.9 mol L^{-1}. The effect of other organic nonsolvents was studied by using a fixed ratio of 1:2400 (alcohols) or 1:1800 (MeCN). Addition of nonsolvents in these ratios was not observed to induce aggregation. Note that, in the titration of the samples, it was needed to initially add 1 μL of protonated nonsolvent to induce a signal. Molecular sieves were used to avoid water contamination from the protonated solvents. A typical QD concentration ranged in NMR experiments from 4 to 20 μM to obtain similar ligand concentration between different QD sizes. NMR data were collected using a Bruker DRX 500 spectrometer (^{1}H frequency of 500.13 MHz) equipped with a 5 mm TXI-Z (^{1}H, ^{13}C, ^{15}N) 3-channel probe (maximum Z-gradient strength of 0.556 Tm^{-1}) or a Bruker AVANCE II 500 spectrometer equipped with a 5 mm TXI-Z (^{1}H, ^{13}C, ^{31}P) 3-channel probe (maximum Z-gradient strength of 0.504 Tm^{-1}). The temperature was set to 298.15 K. Quantitative ^{1}H spectra were recorded with a 20 s delay between scans to allow full relaxation of all NMR signals. The quantification was done by using the Quantas software[17] based on the PULCON[34] (pulse-length-based concentration determination) approach. Macros for calibration and quantification were kindly provided by Dr. Richard Upton (GSK).

Optical Characterization. To avoid oxidation of PbSe QDs and water contamination, PbSe PL samples were prepared and titrated under an inert gas atmosphere, and high purity deuterated solvents were used. The PbSe QDs were dissolved to C_2Cl_4 for the PL titration experiments. The CdSe PL samples were prepared under ambient conditions as CdSe QDs are not sensitive to oxidation like PbSe QDs. High purity deuterated solvents were also used in the case of CdSe QDs to avoid water contamination, and the QDs were dispersed in toluene for the PL titration experiments. The absorption spectrum of the PL sample was recorded after each addition of nonsolvent to check for aggregation. The addition of nonsolvents in the ratios used for this work was not observed to induce aggregation. To obtain the desired optical intensity, the concentration of PbSe QDs was kept at ≈0.09 μM and for CdSe QDs at ≈0.05 μM. The different concentration of QDs used in PL and NMR experiments resulted in different ligand:nonsolvent molar ratios being used in these two experiments to work on similar nonsolvent concentrations. The steady state PL was measured using an Edinburgh Instruments FS920 PL setup and excited either at 380 nm (CdSe QDs) or at 500 nm (PbSe QDs) using a 500 W xenon lamp, coupled to a monochromator. The PL spectra were corrected for detector and grating efficiency.

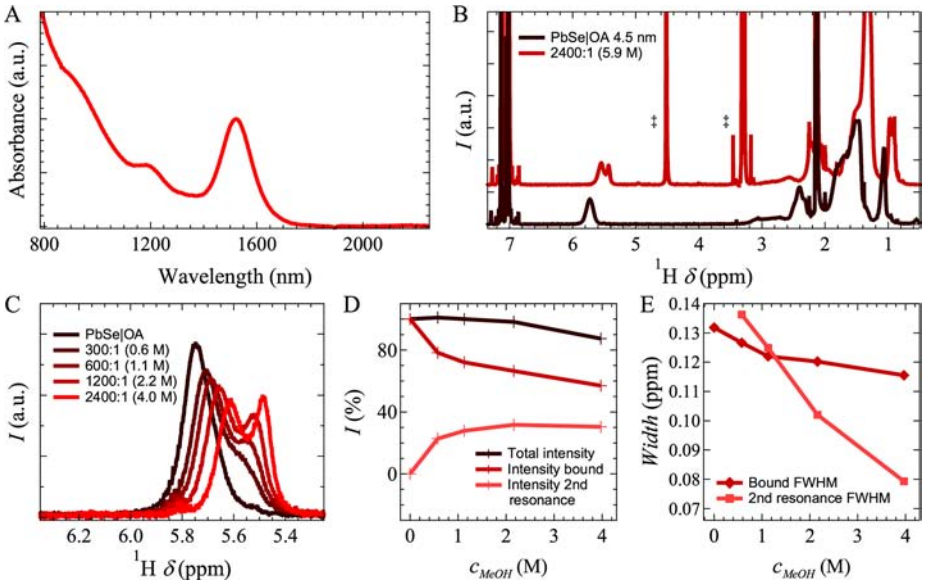

Figure 1. (A) Normalized absorption spectrum of 4.5 nm PbSe QDs in C_2Cl_4. (B) ^{1}H NMR spectra of PbSe QDs before (dark trace) and after (red trace) addition of MeOH-d_4. Sharp resonances in the red spectrum at ≈3.3 and ≈4.5 ppm can be assigned to MeOH (‡). (C) Zoom on the alkene resonance of bound oleate and the effect of MeOH-d_4 titration. (D) Peak intensity and (E) width of the oleate alkene resonances obtained from peak deconvolution.

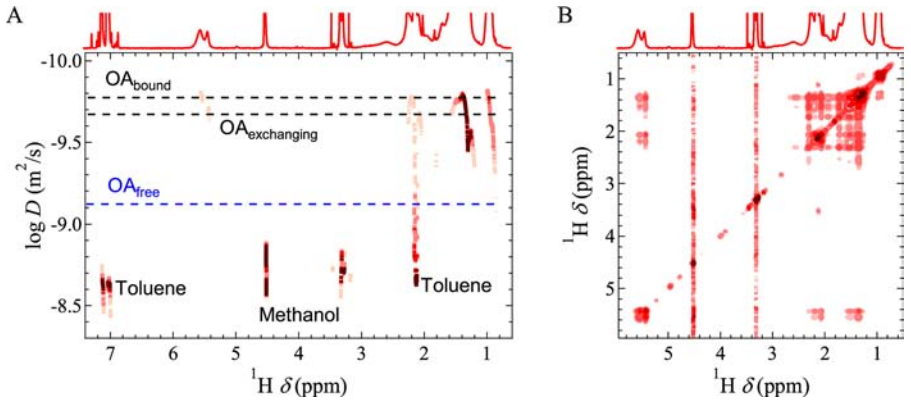

Figure 2. (A) Diffusion-ordered spectroscopy (DOSY) and (B) nuclear Overhauser effect spectroscopy (NOESY) spectrum of 4.5 nm PbSe QD suspension with excess MeOH. MeOH-d_4 was added in a 2400:1 nonsolvent:ligand ratio (≈5.9 M). In the DOSY spectrum, overlapping resonances of bound and exchanging cause streaking of the peaks along the diffusion axis, especially since a low cutoff is required to simultaneously visualize all relevant species.

RESULTS AND DISCUSSION

PbSe Quantum Dots: Methanol Titrations. Figure 1A shows the absorption spectrum of PbSe QDs (d = 4.5 nm) synthesized using lead oleate and TOPSe dissolved in diphenylether.[30] The ^{1}H NMR spectrum of this sample shown in Figure 1B (dark trace) only features the broad resonances typical for bound oleate ligands and the sharp resonances of residual toluene-d_8. The assignment of the resonances to the different protons of tightly bound oleate ligands is based on previous work by Moreels et al.[19] A particularly useful resonance is that of the alkene protons at ≈5.7 ppm since it is well resolved and separated from the region of both the aliphatic protons of bound oleate (0.5 − 3 ppm) and the aromatic resonances of residual toluene-d_8 (≈7 ppm). In what follows, we make use of this resonance to (1) quantify the amount of bound oleate in the NMR sample and (2) monitor any changes occurring with the bound oleate upon addition of nonsolvents.

The red trace in Figure 1B represents an overview ^{1}H NMR spectrum recorded after the addition of MeOH-d_4 in a 2400:1 nonsolvent:ligand ratio (≈5.9 M). As compared to the spectrum of well-purified PbSe QDs, the addition of MeOH adds an upfield-shifted second resonance to each bound oleate resonance. Focusing on the alkene resonance, Figure 1C illustrates in more detail how the oleate resonances evolve while increasing the MeOH concentration. Apart from the change in chemical shift related to the transition from toluene as a solvent to a toluene/MeOH mixture, peak deconvolution indicates that the initially broad resonance diminishes in intensity (Figure 1D) yet keeps its width to within ca. 10% (Figure 1E). On the other hand, the second resonance sharpens and gains intensity with increasing MeOH content. Moreover, the overall intensity of both resonances stays almost constant during the MeOH titration. Only at the highest MeOH concentration the overall intensity slightly decreases, possibly indicating the aggregation of some of the QDs. As shown in the Supporting Information, the additional resonances appear upon MeOH addition

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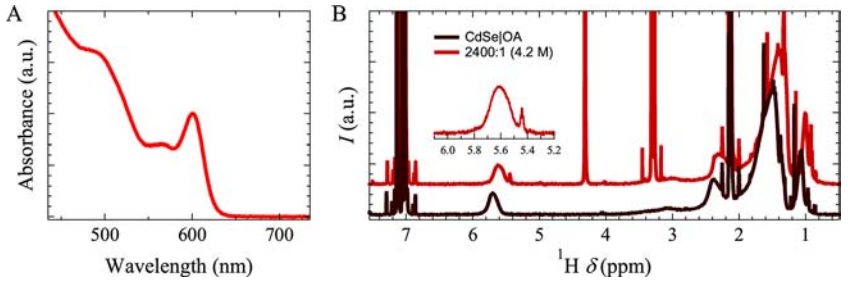

Figure 3. (A) Normalized absorption spectrum of 4.0 nm CdSe QDs in toluene. (B) ^{1}H NMR spectra of 4.0 nm CdSe QD suspension before (dark trace) and after (red trace) addition of MeOH-d_4. The inset shows a zoom of the alkene resonance after the addition, demonstrating release of oleate ligands by the spectrally upshifted second resonance.

regardless of the QD diameter, although their intensity is larger for smaller QDs.

Similar double resonances as observed here occurred upon titration of oleate-capped CdSe QDs with excess oleic acid.[17] In that case, the broad resonance was linked to tightly bound oleate, while the second resonance could be linked to oleic acid in fast exchange between a state of entanglement in the ligand shell and a freely dissolved state. Also here, the second resonance has all the features of this fast exchange. Figure 2A demonstrates that its diffusion coefficient is increased relative to bound oleate, yet well below the value expected for free oleic acid. Moreover, it features strongly negative NOE crosspeaks which is a characteristic of molecules interacting with the QDs (Figure 2B).[29] Taking into account that oleate ions are not soluble in apolar solvents and combining the results presented in Figure 1 and Figure 2, we thus conclude that the addition of MeOH induces the release of oleic acid from the ligand shell. The additional resonances are thus attributed to a pool of free oleic acid molecules in rapid exchange between a free and a bound physisorbed state.

CdSe Quantum Dots: Methanol Titrations. Figure 3A shows the absorption spectrum of CdSe QDs (d = 4.0 nm) synthesized using cadmium oleate and elemental selenium dissolved in octadecene.[32] As indicated in Figure 3B (dark trace), only the broad resonances typical for bound oleate ligands and the sharp resonances of residual toluene-d_8 are visible in the ^{1}H NMR spectrum of this CdSe QD dispersion.[17] In this case, addition of MeOH-d_4 leads to the appearance of sharp resonances, each occurring close to the bound oleate resonance (Figure 3B, red trace). For CdSe QDs of different sizes, very similar results are obtained (see Supporting Information). As compared to PbSe QDs, the intensity of the additional resonances is somewhat lower for the same amount of MeOH added, and their line width is more narrow; however, the presence of weak negative NOE cross peaks and the increased diffusion coefficient of the second resonance compared to bound oleate ligands (see Supporting Information) indicate that there is still exchange between a physisorbed and a free state. Hence, we conclude that also with CdSe QDs MeOH releases tightly bound X-type oleate ligands from the surface.

Ethanol, Isopropanol, and Acetonitrile Titrations. A straightforward explanation as to why MeOH can strip tightly bound X-type oleate ligands from PbSe and CdSe QDs is proton transfer from MeOH to oleate. This would result in the formation of a methoxide ion and the release of oleic acid, as summarized by the following reaction where RCOOH represents a carboxylic acid

$$\mathrm{MeOH} + \mathrm{RCOO-QD} \rightleftharpoons \mathrm{RCOOH} + \mathrm{MeO-QD} \quad (1)$$

Formally, one can rewrite this as a combination of three equilibrium reactions, which describe the breaking of the bond between a QD and a carboxylate (2), proton transfer between MeOH and the carboxylate (3), and the formation of a bond between a QD—having lost a carboxylate—and a methoxide (4)

$$\mathrm{RCOO-QD} \rightleftharpoons \mathrm{RCOO^-} + \mathrm{QD^+} \quad (2)$$

$$\mathrm{MeOH} + \mathrm{RCOO^-} \rightleftharpoons \mathrm{RCOOH} + \mathrm{MeO^-} \quad (3)$$

$$\mathrm{MeO^-} + \mathrm{QD^+} \rightleftharpoons \mathrm{MeO-QD} \quad (4)$$

Hence, if reaction 1 applies, one expects that the possibility of oleate removal depends on the protic or aprotic character of the nonsolvent, while the effect should be more pronounced with increasing nonsolvent acidity (reaction 3). One also sees that nonsolvents such as alcohols, which are considerably weaker acids than carboxylic acids, can still release oleate ligands provided that the alkoxide binds stronger to the QDs than the carboxylate (reaction 2 vs reaction 4). To investigate this, we extended the analysis to ethanol (EtOH) and isopropanol (iPrOH), two alcohols with a lower acidity than MeOH, and MeCN, an aprotic nonsolvent. Although having an acidity similar to MeOH, water was not considered in these experiments due to its low solubility in toluene. Since MeOH has a somewhat larger effect on PbSe QDs, we have studied the effect of EtOH and iPrOH on PbSe only, while MeCN was added to both PbSe and CdSe dispersions. In all cases, dry deuterated nonsolvents were added, and care was taken to prevent water contamination.

Figure 4A compares the alkene region of the ^{1}H NMR spectrum of 4.5 nm PbSe QDs after addition of equal amounts of (bottom) MeOH, (middle) EtOH, and (top) iPrOH. Clearly, in all three cases, alcohol addition induces the release of oleate ligands. Peak deconvolution shows that the intensity of the exchanging oleic acid resonance decreases in the order MeOH > EtOH > iPrOH (see Figure 4B), in line with the decreasing acidity constant. A striking difference is observed when MeCN is added to the QD dispersions. Neither with PbSe nor CdSe is the shell of bound oleate ligands affected since no change is observed in the bound oleate resonances up to MeCN additions of ≈ 3.5 M (see Figure 5A and Figure 5B). Clearly, this observation supports the initial assumption that proton transfer is an essential part of the mechanism leading to the observed release of oleate ligands from PbSe QDs.

A further indication of the different interactions MeOH and MeCN have with the ligand shell comes from the NOESY

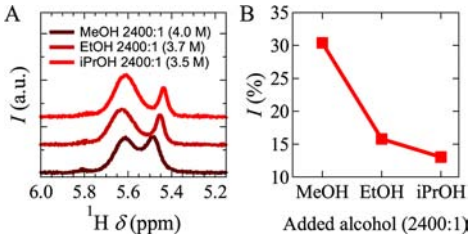

Figure 4. (A) Zoom of the alkene region of ^{1}H NMR spectra of a 4.5 nm PbSe QD suspension after addition of equivalent amounts of different alcohols. (B) Peak intensity of the second resonance is lower for EtOH and iPrOH, indicating that these release less oleate ligands than MeOH. The trend of the release is in line with the acidity constant of the added alcohol where MeOH has the highest acidity and the release is the strongest.

spectra shown in Figure 5C and E (PbSe) and Figure 5D and F (CdSe). After MeOH addition (100:1 ratio, ≈ 0.2 M), these show in both cases a clearly negative cross peak between the MeOH CH_3 resonance and the aliphatic protons of bound oleate (Figure 5C and D). The sharp nature of the MeOH methyl resonance shows its line width is dominated by the excess MeOH in the free state. The negative NOE therefore reflects a process where MeOH is exchanged between the free state and a state where it interacts with the QDs causing a transfer NOE cross-peak dominated by the bound state. On the other hand, no clear NOESY cross peak is observed between MeCN, added in identical amounts, and bound oleate (see Figure 5E and F and Supporting Information). We thus conclude that MeOH molecules spend on average more time interacting with the QDs than MeCN molecules do.

Nonsolvent Additions and Photoluminescence. Several authors have highlighted the relation between the composition of the ligand shell and the photoluminescence quantum yield (PLQY) of colloidal quantum dots.[23,24,35] Here, we study the influence of additions of short-chain alcohols and MeCN on the PLQY in view of their different impacts on the ligand shell. In the case of PbSe (Figure 6A), MeOH additions

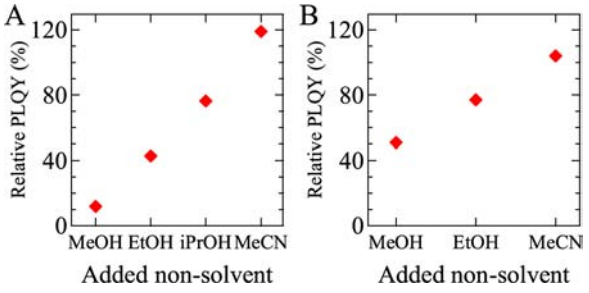

Figure 6. Relative PLQY of (A) 4.5 nm PbSe QDs and (B) 4.0 nm CdSe QDs after additions of an equivalent amount of alcohols and MeCN.

(100 000:1 ratio, ≈ 2.2 M) lead to an almost 10-fold reduction of the PLQY without inducing aggregation of the QDs. A similar albeit less pronounced reduction of the PLQY results from the addition of EtOH and iPrOH. Remarkably, an initial enhancement of the PLQY was observed after the additions of small amounts of short-chain alcohols (see Supporting Information). In contrast to alcohols, MeCN has little effect on the PLQY; addition of an amount equivalent to the alcohol addition even slightly increases the PLQY. A very similar

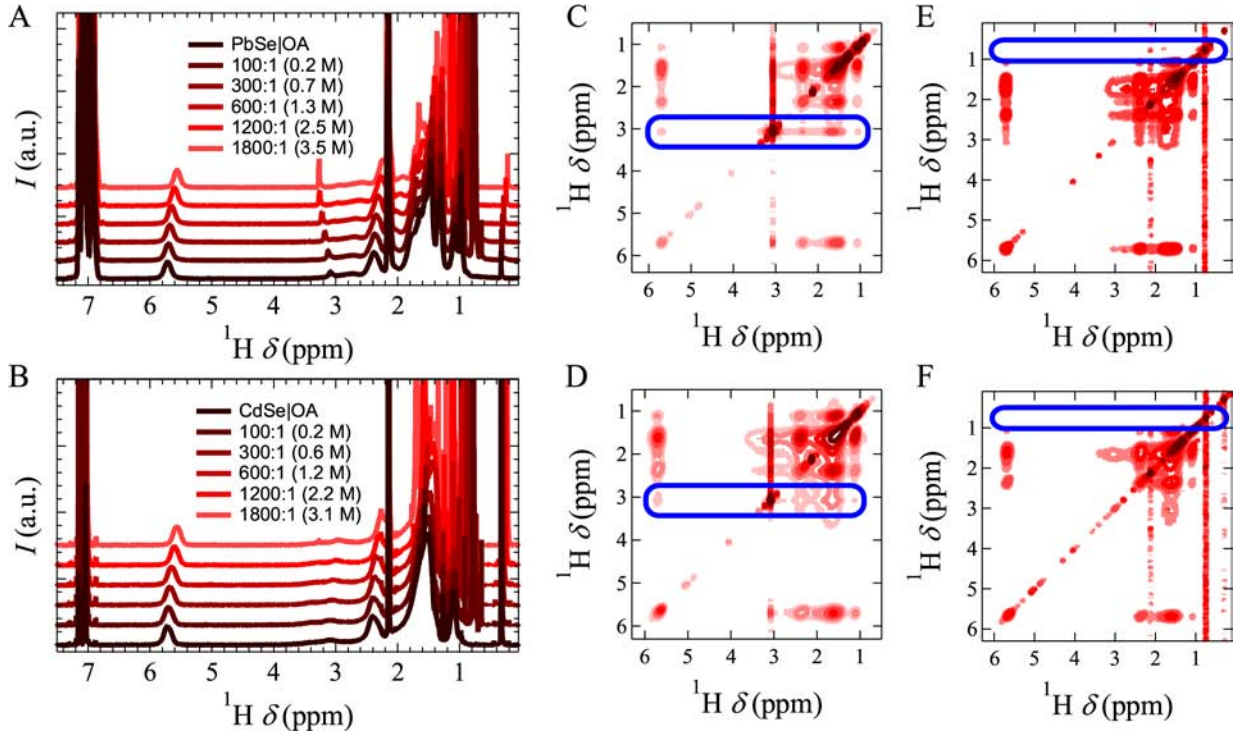

Figure 5. (A) MeCN-d_3 titration of 4.5 nm PbSe QDs. Residual MeOH is present at ≈3.1 ppm. The MeOH resonance is observed to shift and sharpen due to addition of MeCN-d_3, yet its intensity remains constant (see Supporting Information). (B) MeCN-d_3 titration of 4.0 nm CdSe QDs. NOESY spectra of (C) 4.5 nm PbSe QDs and (D) 4.0 nm CdSe QDs after addition of MeOH-d_4 in a 100:1 ratio (≈0.2 M), showing negative NOEs between MeOH and bound oleate (highlighted in blue). In contrast, addition of a similar amount of MeCN-d_3 does not lead to a measurable NOE cross peak with bound oleate for (E) PbSe or (F) CdSe QDs.

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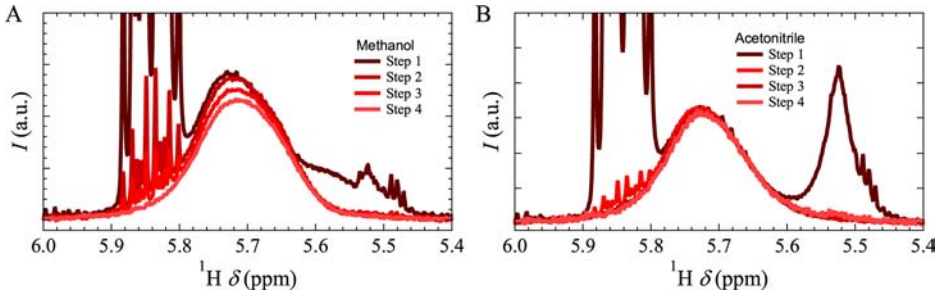

Figure 7. Alkene region of the ^{1}H NMR spectra of 4.2 nm CdSe QDs after every precipitation/resuspension step using (A) MeOH or (B) MeCN for precipitation.

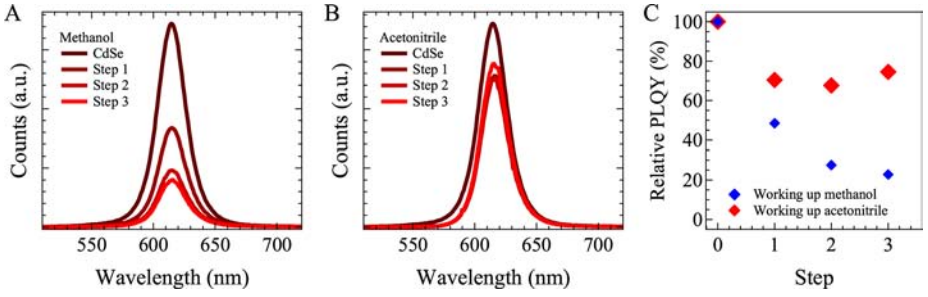

Figure 8. In PL the complete purification steps with (A) MeOH lead to a strong quenching of the PL of the CdSe QDs, whereas only the first precipitation/resuspension step with (B) MeCN lowers the relative PLQY of the QDs. (C) PLQY quenching curves obtained from peak integration.

picture follows from MeOH, EtOH, and MeCN additions to a dispersion of CdSe QDs (Figure 6B). Again, MeOH and EtOH reduce the PLQY, although not as drastically as with PbSe, while MeCN leaves the PLQY almost unchanged.

For a given material, ligand release and PL quenching by nonsolvent addition both increase from MeCN (no release, no quenching) to iPrOH, EtOH, and finally MeOH (strongest release, strongest quenching). This indicates that the loss of oleate ligands and PL quenching are strongly correlated. The initial enhancement of the PLQY, especially in the case of PbSe QDs, can arise from enhanced dynamics in the ligand shell, where the exchange between bound and free ligands would permit ligands to settle into previously unpassivated trap states. Alternatively, the initial increase in PLQY can indicate that not all oleate binding sites are equivalent and that the oleate ligands are most easily removed from sites where they contribute themselves to PL quenching. The heterogeneity in adsorption sites is further supported by the size effect on the oleate release, where in the case of PbSe QDs, ligands are more easily released when the QDs are smaller and thus have a more curved surface (see Supporting Information).

Analysis of Successive Purification Steps. The addition of nonsolvents to induce nanocrystal aggregation is a generally used method to purify QD dispersions after synthesis, where common nonsolvents are short-chain alcohols such as MeOH, EtOH, and iPrOH. Figure 7A shows the alkene region of the ^{1}H NMR spectrum of a CdSe dispersion after successive purification steps using MeOH and toluene as the nonsolvent and the solvent, respectively. The results of a similar experiment using MeCN as the nonsolvent are represented in Figure 7B. In both cases, the broad resonance of bound oleate can be clearly distinguished, while free oleic acid is still present after the first purification step (feature at 5.5 ppm) and traces of octadecene persist until the second or third step (resonances at 5.85 ppm). All spectra have been normalized to the QD concentration, such that peak intensities directly reflect concentrations.

Figure 7A indicates that the intensity of the bound oleate resonance decreases with successive purification steps when MeOH is used as the nonsolvent. Bound ligands are thus stripped from the QD surface, resulting in a reduction of the bound ligand density from an initial 4.1 nm^{-2} to a final 3.2 nm^{-2} after four purification cycles. On the other hand, use of MeCN does not reduce the intensity of the bound oleate alkene resonance, indicating that in this case the ligand density remains constant. Figure 8A and B shows photoluminescence spectra—normalized to the absorbance at 380 nm—recorded after these successive purification steps, again using either MeOH or MeCN. Also here, we find that the use of MeOH leads to a considerable loss of photoluminescence. In the case of MeCN on the other hand, 70−80% of the initial photoluminescence is preserved during the different purification steps (Figure 8C). We thus conclude that the results of the titration experiments are fully in line with the impact nonsolvents have on the ligand shell and the photoluminescence quantum yield during sample purification.

Surface Chemistry of Excessively Purified Quantum Dots. According to reaction 1, the stripping of OA ligands by MeOH should leave methoxide moieties at the QD surface, which can be released in turn by carboxylic acids. The OA loss upon excessive purification of QDs with MeOH provides us with an experimental system to verify this. Figure 9A shows the ^{1}H NMR spectrum (black) of a dispersion of PbSe QDs that were purified four times after synthesis. The spectrum clearly shows the alkene resonance of bound OA in the 5.6−5.8 ppm range and some left over MeOH at 3.07 ppm. As compared to a reference sample of doubly purified QDs from the same reaction mixture, the additional purification steps reduce the ligand density from 3.18 to 1.16 nm^{-2} (see Supporting Information). Upon addition of OA to this dispersion, we observe an increase of the intensities of both the bound OA and

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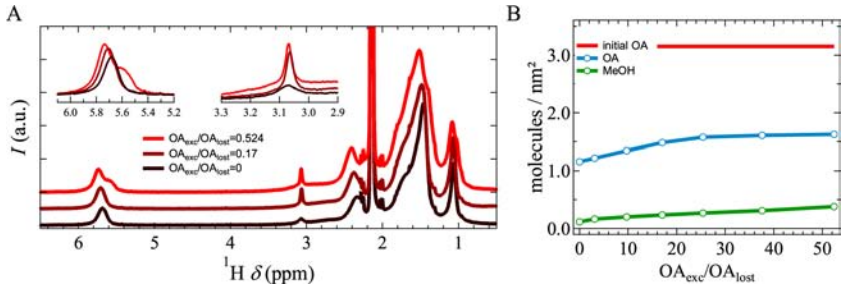

Figure 9. (A) ^{1}H NMR spectra obtained on 4.9 nm PbSe QDs purified four times with MeOH after the addition of different amounts of excess OA as indicated in the legend. The spectra are corrected for changes in concentration during the OA titration. The insets zoom in on the alkene region and the region around the CH_3 resonance of MeOH. (B) Amount of (blue) the bound OA alkene resonance and (green) the MeOH CH_3 resonance per nm^2 of QD surface area as a function of the ratio of excess OA and OA lost during the second and the fourth purification step. The red line gives the ligand density after two purification steps.

the free MeOH resonances; i.e., the excess OA binds to the PbSe QDs while releasing MeOH from the QD surface. In line with reaction 1, this indicates that exposure of QDs to MeOH leaves behind bound methoxide moieties—unobservable in ^{1}H NMR due to excessive line broadening—that can be re-exchanged for oleate moieties. As shown in the Supporting Information, similar results are obtained with CdSe QDs or when using technical MeOH. While for the forward reaction 1 a significant excess of MeOH is required, one sees in Figure 9A that MeOH is released in the backward reaction as soon as oleic acid is added, even in small amounts. This is a qualitative indication that the equilibrium in reaction 1 lies at the oleate/MeOH side, which is not surprising given the strong difference in acidity between oleic acid and MeOH.

The deconvolution of the different resonances of interest (bound and free OA, free MeOH) is difficult, yet it still leads to a reasonable estimate of the amounts of OA bound and MeOH released. As shown in Figure 9B, the initial ligand density (red line) is far from recovered by the binding of the excess OA added. Moreover, the amount of MeOH desorbed does not match the adsorbed excess OA. This indicates that excessive QD purification has more radical effects on the QD surface than a mere replacement of oleate by methoxide moieties. It appears that initial adsorption sites are lost, e.g., by surface oxidation or occupied by anionic species different from methoxide ions. Possibly, the latter involve hydroxide groups resulting from either residual water contamination—involved in a similar exchange reaction as 1—or condensation reactions between methanol and the carboxylic acid.

CONCLUSION

We exposed purified colloidal CdSe and PbSe QDs stabilized by oleate ligands to increasing amounts of nonsolvents including short-chain alcohols (MeOH, EtOH, iPrOH) and MeCN. Using ^{1}H NMR, we could demonstrate that short-chain alcohols strip these tightly bound X-type ligands from the QD surface, while MeCN does not. Using DOSY and NOESY spectroscopy next to ^{1}H NMR, the released ligands were observed to be in rapid exchange between a free and physisorbed state. We interpreted the different impact of these nonsolvents in terms of their protic or aprotic character, where only the protic alcohols can provide the proton needed to release a bound oleate ligand, leaving behind—in the case of MeOH—a methoxide moiety at the QD surface. This interpretation was supported by two observations. First, we found that the ligand release is less pronounced for alcohols with a smaller acidity constant. Second, after partially stripping oleate ligands by exposing QDs to MeOH, we observe the reverse reaction; i.e., oleic acid binds to the QDs while releasing MeOH.

Importantly, the ligand release induced by the addition of alcohols concurred with a considerable reduction of the photoluminescence quantum yield, which was not observed upon addition of MeCN. Since short-chain alcohols are commonly used in the purification of the crude reaction product of a nanocrystal synthesis, we studied the effect of sequential precipitation/resuspension steps with MeOH and MeCN on the ligand density and the photoluminescence of CdSe QDs. Combining NMR and photoluminescence spectroscopy, we found that purification with MeOH leads to a significant ligand loss and a concomitant quenching of the photoluminescence quantum yield to ≤20% of its initial value. On the other hand, no ligand release was observed with MeCN as the nonsolvent, while the photoluminescence quantum yield remained steady at ≥70−80% of its initial value during successive purification steps. Our results thus stress the significance of using aprotic nonsolvents for nanocrystal purification or processing.

ASSOCIATED CONTENT

Supporting Information

Provides more details on the NMR (^{1}H, DOSY, and NOESY) and PL spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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