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Utilizing Self-Exchange To Address the Binding of Carboxylic Acid Ligands to CdSe Quantum Dots

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Abstract: We use solution NMR techniques to analyze the organic/inorganic interface of CdSe quantum dots (Q-CdSe) synthesized using oleic acid as a surfactant. It is shown that the resulting Q-CdSe are stabilized by tightly bound oleic acid species that only exchange upon addition of free oleic acid. The NMR analysis points toward a two-step exchange mechanism where free ligands are initially physisorbed within the ligand shell to end up as bound, chemisorbed ligands in a second step. Importantly, we find that every ligand is involved in this exchange process. By addition of oleic acid with a deuterated carboxyl headgroup, we demonstrate that the bound ligands are oleate ions and not oleic acid molecules. This explains why a dynamic adsorption/desorption equilibrium only occurs in the presence of excess free oleic acid, which donates the required proton. Comparing the number of oleate ligands to the excess cadmium per CdSe quantum dot, we find a ratio of 2:1. This completes the picture of Q-CdSe as organic/inorganic entities where the surface excess of Cd^{2+} is balanced by a double amount of oleate ligands, yielding overall neutral nanoparticles.

1. Introduction

Ligands are a key constituent of sterically stabilized inorganic colloidal nanoparticles (NPs).[1] Especially with synthesis recipes that make use of noncoordinating solvents, the nucleation and growth of NPs are controlled by surfactants such as fatty acids, amines, or phosphonic acids that end up as ligands adsorbed at the NP surface.[2−4] While scientific research on the resulting semiconductor, metal, or metal oxide NPs was initially mainly oriented toward the physical properties of the inorganic core, interest in the organic ligand shell has shown a steady increase over the last 5−10 years. As far as synthesis is concerned, it was shown that specific ligand mixtures enable the formation of NPs with controlled shapes, like rods[4,5] or tetrapods.[4] After synthesis, ligands proved to enhance or quench the luminescence of semiconductor NPs or quantum dots (QDs).[6] Moreover, ligand exchange proved to be a powerful tool to achieve the homogeneous dispersion of NPs, both in liquids and in solids, and to tune the conductivity of NP assemblies.[7−10] Moreover, by means of specific bifunctional ligands, colloidal NPs can be turned into macromolecular building blocks to form, for example, linear NP chains,[11] and functionalization with biomolecules enables their use as specific biolabels or biosensors.[12−14]

The increasing importance of ligands and ligand exchange processes in the field of colloidal NPs has stimulated the application of a set of experimental techniques to analyze NP ligands, such as nuclear magnetic resonance spectroscopy (NMR),[15−28] infrared spectroscopy,[29] or photoluminescence

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spectroscopy.[30] NMR-based approaches have been especially successful in this respect, enabling the discrimination between bound and free ligands,[17] the identification and quantification of bound ligands, and the analysis of the adsorption isotherm[18] or the ligand exchange kinetics.[19] However, in spite of this growing range of analysis techniques, few studies have addressed the most fundamental aspects of the chemistry of the NP/ligand interaction. In the case of CdSe QDs (Q-CdSe) with tri-*n*-octylphosphine oxide and tri-*n*-octylphosphine ligands, X-ray photoelectron spectroscopy and NMR suggested the formation of a dative or dipolar bond.[31,32] Similar indications follow from solution NMR studies on Q-InP/TOPO[18] and Q-CdTe stabilized by dodecylamine (DDA),[19] which both demonstrate a dynamic adsorption/desorption equilibrium of ligands. On the other hand, for Q-CdSe stabilized with phosphonic acids, it was demonstrated that the ligands are anionic alkylphosphonate moieties rather than neutral phosphonic acids.[33] Apart from these studies, the question as to how ligands bind and pack at the nanocrystal surface remains unanswered for even the most widely used NP/ligand combinations.

Here, we report on the interaction between oleic acid (OA) ligands and colloidal CdSe QDs, which we see as a model system for colloidal NPs in general. Being used for the synthesis of metal,[34−36] metal oxide,[37−40] and semiconductor[2,41−44] nanocrystals, carboxylic acids like OA are a prominent class of NP ligands. CdSe, with its band gap covering almost the entire visible spectrum with changing size, is the most widespread semiconductor QD with applications in solar energy conversion,[45,46] light-emitting devices,[47,48] and bioimaging.[49,50] By means of solution NMR on zinc blende Q-CdSe synthesized using cadmium oleate and elementary selenium dissolved in octadecene (ODE), we demonstrate that the resulting Q-CdSe are stabilized by OA ligands. The 1D ^{1}H NMR spectra of these Q-CdSe|OA suspensions give no indication of exchange between a free and a bound state, meaning that the QDs are present in a ligand-free solvent as well-defined organic/inorganic entities. On the other hand, as soon as excess OA is added to the colloid, evidence of exchange between free and bound ligands is provided by a set of different NMR techniques. The NMR spectra are indicative of a two-step exchange process, where free ligands possibly get entangled in the bound ligand shell prior to their full incorporation as bound ligands. By addition of deuterated OA to a Q-CdSe|OA suspension, we can demonstrate that this self-exchange involves a proton transfer from a free OA molecule to a bound oleate ion. This explains why, in the absence of excess oleic acid, no adsorption/desorption equilibrium is established. Finally, using elemental analysis, we find a ratio between the number of ligands and the excess Cd^{2+} ions per QD of 2:1. This completes the picture of the CdSe|OA QDs as well-defined inorganic/organic entities, where the charge on the excess Cd cations is balanced by the anionic oleate ligands.

2. Experimental Section

2.1. CdSe QDs—Synthesis and Basic Characterization. CdSe nanocrystals where synthesized according to the procedure of Jasieniak et al.[51] A selenium stock solution was made by heating a mixture of Se powder (0.1263 g, 1.6 mmol, 99.999% Alfa Aesar) in *n*-octadecene (ODE, 16 mL, 90% Alfa Aesar) under nitrogen atmosphere at 195 °C for 2 h. Then the mixture was cooled to room temperature, resulting in a stable yellow transparent solution. For the nanocrystal synthesis, cadmium oxide (CdO, 0.36 mmol, 99.999% Strem), oleic acid (OA, 3.6 mmol, 90% Sigma-Aldrich), and ODE (12 mL) were mixed and degassed for 1 h at 100 °C under nitrogen, followed by heating to 250 °C until all CdO was dissolved. Next, the solution was heated to 265 °C, and the Se stock solution (3.6 mL) was injected. The temperature of the mixture dropped after injection, and the reaction continued at 235 °C for 11 min. After reaction, equal volumes of toluene and isopropanol were added, and the particles were precipitated by adding methanol. Afterward, the particles were further purified twice by resuspension in toluene and precipitation with methanol. After synthesis, the nanocrystals were characterized using UV/vis spectroscopy. Samples used for the quantitative determination of the ligand density were additionally analyzed by transmission electron microscopy (TEM). Concentrations were determined according to recently published UV/vis extinction coefficients.[52] For the sample used in the OA-d_1 exchange, the Cd/Se ratio was determined with Rutherford backscattering spectrometry (RBS).

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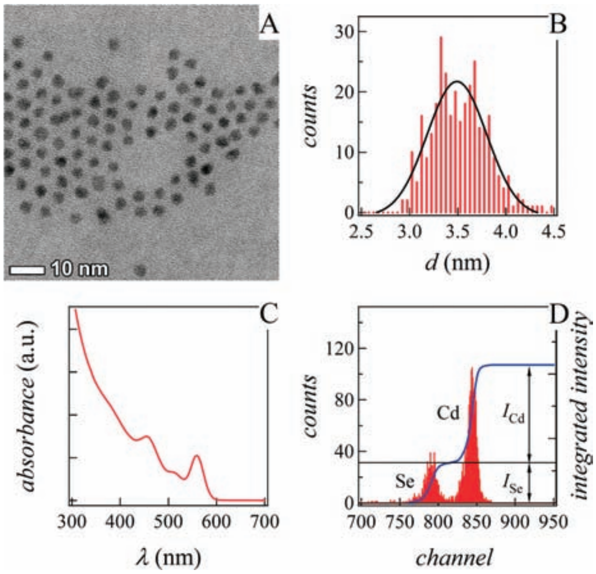

Figure 1. Characterization results for the Q-CdSe|OA sample used in the OA-d_1 exchange experiments. (A) TEM overview image. (B) Diameter histogram as obtained from a set of TEM overview images. (C) UV−vis absorption spectrum. (D) Rutherford backscattering spectrum indicating backscattering by Se and Cd. The red line indicates the measured scattering intensities as a function of energy, and the blue line is the integrated intensity from which the Cd/Se ratio is calculated.

2.2. NMR Analysis of CdSe QD Suspensions. Q-CdSe|OA NMR samples were prepared in deuterated toluene (99 atom % D, dried with 4 Å molecular sieve). To prevent moisture from entering the sample, the dispersion was transferred into an NMR tube with septum inside a glovebox flushed with N_2. All experiments were performed on a Bruker Avance DRX 500 spectrometer, operating at a ^{1}H frequency of 500.13 MHz and equipped with a 5 mm TXI probe with Z-gradient affording a maximum gradient strength of 0.5613 T m^{-1}. The temperature was set to 298.15 K. Additional information on the experimental settings is given in the Supporting Information.

3. Results and Discussion

3.1. Characterization of Q-CdSe. Figure 1 gives an overview of the materials properties relevant for this work of the CdSe QDs used. They are zinc blende CdSe nanocrystals,[52] typically having a diameter in the range of 3−3.5 nm, with a size dispersions of about 8%. Importantly, the CdSe QDs are nonstoichiometric. More specifically, the RBS spectrum (Figure 1D) obtained at the sample used in the OA-d_1 titration (see section 3.5) yields a Cd/Se ratio of 1.23 ± 0.03, a number which is in line with CdSe stoichiometries published in the literature.[52,53]

3.2. NMR Characterization of Purified CdSe Dispersions. Figure 2 shows a typical example of the 1D ^{1}H NMR spectrum we obtained with purified suspensions of 3−3.5 nm Q-CdSe in the concentration range of 1.5−60 μM. As outlined above, the Q-CdSe are made according the procedure of Jasieniak et al.,[51] where OA is the only ligand used, and precipitated twice with methanol prior to drying and dissolution in toluene-d_8. The spectrum is very similar to that of Q-PbSe|OA,[54] showing next to the resonances of the residual solvent and H_2O only broadened resonances that are slightly shifted relative to those of free OA.

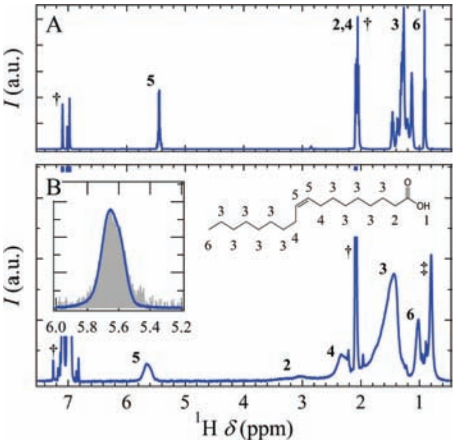

Figure 2. (A) One-dimensional ^{1}H spectrum of OA in toluene-d_8. (B) One-dimensional ^{1}H spectrum of a Q-CdSe suspension in toluene-d_8 (d = 3.0 nm, [Q-CdSe] = 40 μM). Next to the different protons of OA (labeled as indicated in the figure), we identify residual solvent resonances (†) and a proton pool related to H_2O contamination (‡). The inset shows an overlay of the alkene proton resonance at 5.65 ppm at a concentration of 50 μM (blue line) and after a 30-fold dilution down to 1.67 μM (gray background).

Using the NMR toolbox for NP ligand analysis (i.e., 1D ^{1}H, 2D ^{1}H−^{13}C HSQC, and diffusion ordered spectroscopy (DOSY) with 3.5 nm Q-CdSe), we find that these broadened resonances belong to OA that diffuses as a particle with a hydrodynamic diameter of 7.8 ± 0.1 nm. The different OA resonances can be attributed to the OA protons, as shown in Figure 2B, with for instance the characteristic resonance of the OA alkene protons at 5.65 ppm[54] (see Supporting Information). Since the measured hydrodynamic diameter corresponds to that of the Q-CdSe (3.5 nm core diameter + 2 × 2 nm ligand shell), we conclude that the broadened OA resonances come from tightly bound OA ligands, as in the case of Q-PbSe|OA.[54] This is in line with the presence of strong negative NOE cross-peaks (NOEs) between the OA resonances in the 2D NOESY spectrum (see Supporting Information). From the integration of the alkene resonance and the size and concentration of the Q-CdSe in suspension, we obtain an OA ligand density of 4.6 ± 0.4 nm^{-2} (see Supporting Information).

An element worth noticing is the absence of free ligand resonances in the 1D ^{1}H spectrum. A control experiment, where the concentration is reduced from 50 down to 1.67 μM, confirms that dilution changes neither the peak shape nor the peak position (Figure 2B). This indicates that dilution does not induce desorption, in contrast to, for example, Q-InP|TOPO.[17]

3.3. Ligand Self-Exchange. To investigate the possible interplay between bound and free OA, we progressively added OA to a Q-CdSe|OA suspension and systematically measured quantitative 1D ^{1}H spectra, diffusion coefficients, and NOESY spectra. Zooming in on the alkene resonance area, Figure 3A shows that addition of excess ligands generates a new and separate set of resonances, next to those of bound OA (OA_b). Again, the ^{1}H−^{13}C HSQC spectrum confirms that these are OA resonances, which we identify with excess OA (OA_e) (see Supporting Information). Both the line width and the chemical shift of the OA_e alkene resonance are between those observed for OA_b and free OA in the absence of NPs. In addition, Figure 3A demonstrates that, with increasing excess to bound OA ratio ($[OA_e]/[OA_b]$), both the chemical shift and the line width of the resonance tend toward the values expected for free OA. On the other hand, the OA_b alkene resonance stays put. Moreover, although its shape changes slightly after the first addition, its intensity remains constant (see Supporting Information), indicat-

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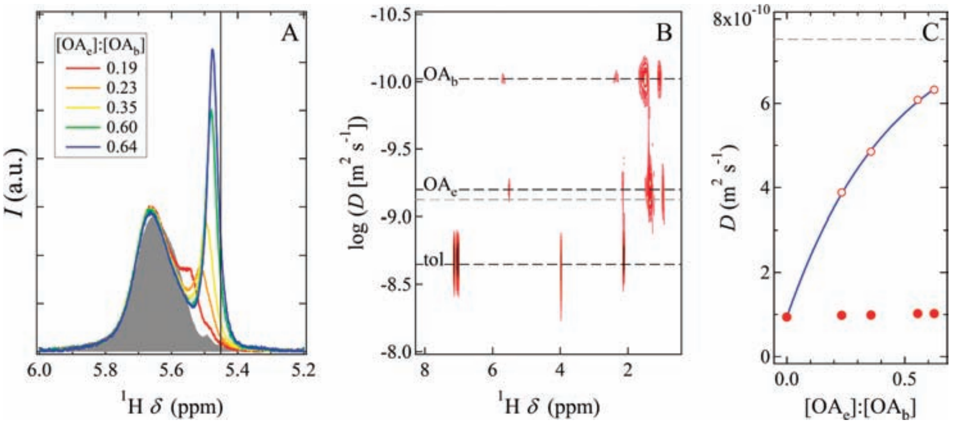

Figure 3. (A) Change of the alkene resonance upon progressive addition of free OA. The gray background is the alkene resonance measured in the original Q-CdSe|OA suspensions, while the vertical black line indicates the position of the alkene resonance of free OA. The different colors correspond to different [OA$_e$]/[OA$_b$] ratios. (B) DOSY spectrum of a Q-CdSe|OA suspensions with excess OA ([OA$_e$]/[OA$_b$] = 0.64). The black lines indicate the respective diffusion coefficients, and the gray line gives the diffusion coefficient of free OA in toluene (0.75×10^{-9} m^2 s^{-1}) as a reference. (C) Change of the diffusion coefficient related to the OA$_e$ (○) and OA$_b$ (●) resonance as a function of the [OA$_e$]/[OA$_b$] ratio. Again, the dashed line gives the free OA value as a reference. The blue line is a guide to the eye.

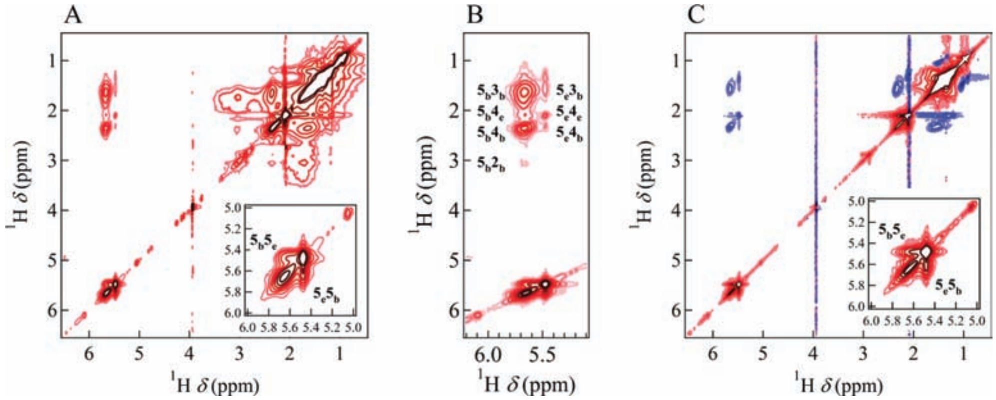

Figure 4. (A) NOESY spectrum of a Q-CdSe|OA suspension with excess OA. Negative NOE cross-peaks (red) involving the excess OA resonances are clearly visible. The inset shows a zoom of the alkene region, with an indication of the excess-bound cross-peaks 5$_e$5$_b$ and 5$_b$5$_e$ between the alkene protons. (B) Zoom on the NOE cross-peaks of the alkene protons with an indication of the different cross-peaks, where the numbers refer to the different OA protons as indicated in Figure 1 and the Supporting Information. (C) ROESY spectrum of the same suspension. Here the positive sign (blue) of all cross-peaks except 5$_e$5$_b$ and 5$_b$5$_e$ confirms that these are true NOE cross-peaks, while the negative sign (red) of the 5$_e$5$_b$ and 5$_b$5$_e$ cross-peaks conclusively establishes them as resulting from chemical exchange.

ing that the number of tightly bound OA ligands is not affected by the addition of excess OA. A similar picture results from DOSY measurements. The diffusion coefficient of OA$_b$ remains the same, while the OA$_e$ resonances yield a diffusion coefficient between that of bound and free OA (see Figure 3B). Again, the higher [OA$_e$]/[OA$_b$], the more the diffusion coefficient of OA$_e$ agrees with that of free OA (see Figure 3C), while the diffusion coefficient of the OA$_b$ resonance does not change.

The behavior of the OA$_e$ resonances in 1D ^{1}H and DOSY is typical for a species in fast exchange, for example, between a NP-associated and a free state as in the case of CdTe QDs stabilized by DDA.[19] With a chemical shift difference of at least 0.1−0.2 ppm and a 500 MHz NMR spectrometer, fast exchange means an overall exchange rate exceeding 300−600 s^{-1}. Remarkably, in the case of CdSe|OA, the rapidly exchanging species is observed together with a pool of bound OA, where NMR results are indicative of slow exchange, if any. We have analyzed this further by means of NOESY and rotating frame NOESY (ROESY), which are ideal techniques to pinpoint ligand/NP interactions.[19] Figure 4A shows the NOESY spectrum of Q-CdSe|OA with excess OA, measured at 100 ms mixing time. The OA$_b$ resonances are connected by strong and negative NOEs (e.g., 5$_b$2$_b$, 5$_b$3$_b$, and 5$_b$4$_b$ in Figure 4A) as expected for tightly bound Q-CdSe ligands.[11] Interestingly, the OA$_e$ resonances are similarly connected by negative NOEs (e.g., 5$_e$4$_e$ in Figure 4B). Together with the concentration-dependent chemical shift and diffusion coefficient of these resonances, this demonstrates that the underlying fast exchange process involves a state where OA molecules are also associated with the Q-CdSe.[19]

A cross-peak that deserves a closer look is the 5$_b$5$_e$ cross-peak between the alkene protons of the bound and the excess OA. While all other cross-peaks connect different proton species and must involve cross-relaxation at some point, this cross-peak connects the alkene protons on different molecular species. Such a peak can either originate from intramolecular cross-relaxation between the alkene protons of neighboring OA$_b$ and OA$_e$ molecules or result from the simple exchange of molecules between the pool of bound and excess OA. While NOESY cannot tell cross-relaxation from chemical exchange in the case at hand here, ROESY always can. Indeed, the ROESY experiment features oppositely signed cross-peaks for both processes, with chemical exchange cross-peaks having the same sign (negative) and NOEs demonstrating opposite sign (positive) with respect to the diagonal peaks.

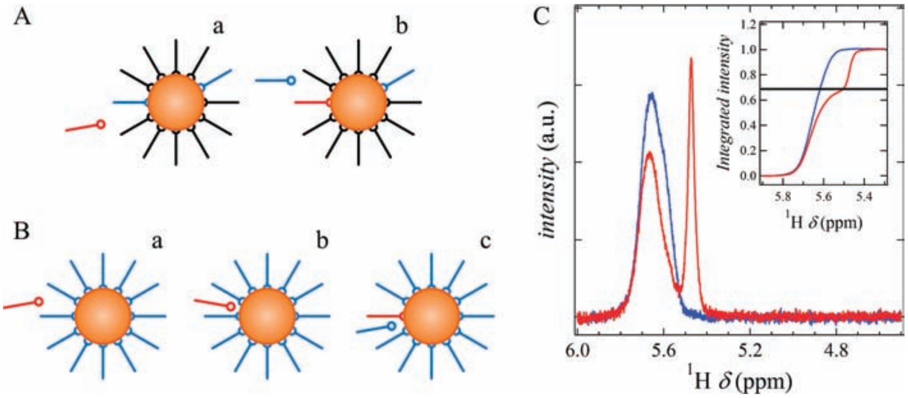

Figure 5. (A) Bound/free exchange process where only a few bound OA ligands (indicated in blue) are involved in the exchange. (B) Bound/free exchange reaction where all bound OA ligands can be exchanged in a two-step exchange process where free OA (a) first gets entangled in the ligand shell (b) to be fully integrated in the ligand shell in a second step (c). (C) Results of a titration with OA-d_2 having the alkene hydrogen replaced by deuterium. The inset shows the integrated intensities normalized to the initial OA intensity. The solid line indicates the expected reduction to 69% based on the fraction of OA-d_2 added ($[OA_e]/[OA_b] = 0.45$).

In contrast to all other cross-peaks, we find that the 5_b5_e cross-peak has the same sign in the ROESY spectrum as the diagonal peaks (Figure 4C). This means that it originates mainly from chemical exchange of OA molecules between the pools of bound and excess OA at a rate on the order of per second and not from cross-relaxation.[55]

The appearance of two different ligand states associated with the Q-CdSe is a novel observation. Initially, this might indicate that rapidly exchanging and tightly bound ligands are simultaneously present next to each other at the Q-CdSe surface but do not mutually exchange (see Figure 5A). In that case, the 5_b5_e cross-peak can only come from intermolecular cross-relaxation, and it should change sign in the ROESY spectrum, in contrast to our observations. Instead, the observation of chemical exchange in the ROESY spectrum tells us that the overall free/bound exchange is a two-step process, where a free OA ligand goes, for example, through an intermediate state of physical entanglement or physisorption with the ligand shell prior to its full incorporation as a chemisorbed ligand (see Figure 5B). The exchange of OA ligands between the free and the physisorbed state accounts for the fast exchange process involving OA_e, while the full incorporation of a physisorbed ligand in the ligand shell (i.e., the transfer to the OA_b pool) is slow on the respective NMR time scales. This two-step exchange provides the simplest description of the overall exchange behavior accounting for the occurrence of negative NOE cross-peaks that connect the OA_b and OA_e resonances involving different ^{1}H along the OA chain (e.g., 5_b4_e, 5_e3_b, and 5_e4_b in Figure 4B) and an exchange cross-peak coupling the alkene resonances of OA_b and OA_e.

From the 1D ^{1}H spectra, we have access to the ratio between bound and excess OA ($[OA_e]/[OA_b]$), and by means of the average diffusion coefficient (Figure 3C), we can derive the fraction of the excess OA in the physisorbed state ($OA_{e,phys}$) and the excess OA free in solution ($OA_{e,free}$). From these data, we calculate a ratio $[OA_{e,phys}]/[OA_b]$ of about 1:8, irrespective of OA_e concentration (see Supporting Information), indicating that the number of free ligands that get entangled in the ligand shell is limited, probably due to steric hindrance.

To confirm the conclusion that the exchange is a two-step process that involves every OA ligand bound to the QDs, we repeated the titration with OA(9,10)-d_2, a deuterated OA isotopomer where the alkene hydrogens are replaced by deuteriums. If the broad alkene resonance at 5.65 ppm would reflect or contain bound OA ligands not involved in any exchange, this titration should not change its intensity or shape. If all bound OA ligands are involved in the exchange, the intensity of the alkene resonance should go down proportionally to the amount of OA(9,10)-d_2 added while preserving the peak shape. Figure 5C shows that we indeed observe the second possibility, where upon addition of OA(9,10)-d_2 in a 0.45:1 ratio the OA_b alkene resonance is reduced to 69% (i.e., 1:1.45) of its initial value (black line).

3.4. Oleic Acid versus Oleate Ligands. Having established self-exchange between bound and excess ligands, the question arises as to what adsorption process we are looking at. Does it involve the formation of a simple dative or dipolar bond between OA and a free adsorption site (Figure 6A), or is the adsorbed species an oleate ion, which means that exchange involves the transfer of a proton between the adsorbing and the desorbing ligand (Figure 6B)? Because we have no access to the protons closest to the NP surface due to their too high transversal relaxation rate, we addressed this problem by adding deuterated OA (OA-d_1) instead of protonated OA to a Q-CdSe|OA suspension. In this case, deuterated means that the carboxylic acid hydrogen has been replaced by deuterium, hence OA-d_1. To be successful, water-free starting solutions are needed, and any water contamination during the experiment must be avoided. We typically worked with a 97−98% deuterated OA-d_1 stock solution and a suspension that was fully prepared under N_2 atmosphere. This suspension is split in three parts. A first part is analyzed as is to verify the absence of water and to determine the bound OA concentration. To the second part, OA-d_1 is added in a 10:1 ratio relative to the bound OA. The third part serves as a reference solution to which protonated OA is added, again in a 10:1 excess.

Figure 7A shows the spectrum of the Q-CdSe|OA used in this experiment. It shows no resonance attributable to water or exchanging protons (see Figure 1). The spectra after the addition of a 10.8:1 excess of 98.2% OA-d_1 and a 10:1 excess of OA are represented in Figure 7B. In both cases, a narrow resonance corresponding to the carboxylic acid protons of OA is observed. Relative to the alkene resonance, it attains an intensity of only 1.5% with OA-d_1. This value is far less than expected in the

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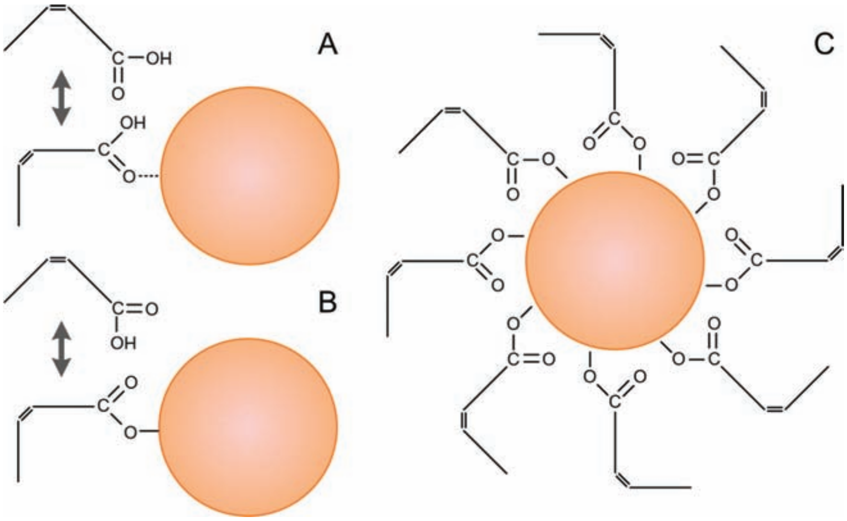

Figure 6. (A) Bound/free exchange reaction where free OA replaces bound OA, involving the breaking of a dipolar bond. (B) Bound/free exchange reaction where free OA replaces bound oleate, involving bond breaking and proton exchange. (C) Symbolic representation of the CdSe|OA model resulting from the OA-d_1 exchange. The QD is capped by oleate ligands.

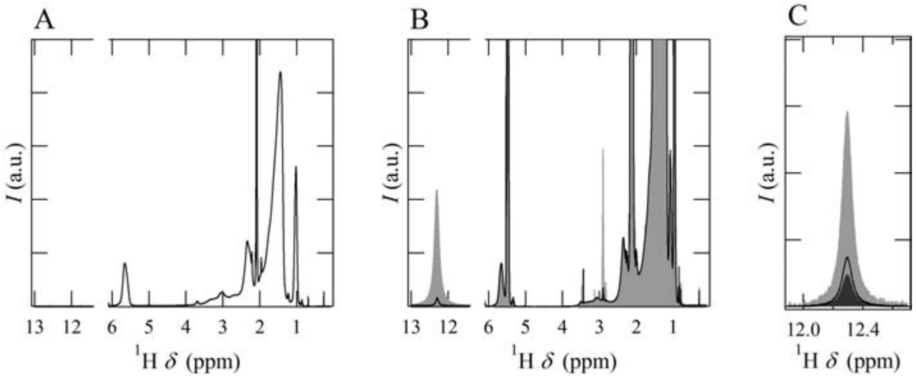

Figure 7. (A) One-dimensional ^{1}H spectrum of the Q-CdSe|OA suspension used in the OA-d_1 titration. The absence of the 0.5 ppm resonance confirms that the sample is water-free. (B) One-dimensional ^{1}H spectra recorded after the addition of excess OA-d_1 (black line, 10.8:1 ratio) and excess OA (gray background, 10:1 ratio). In both cases, a narrow resonance of the carboxylic acid protons is visible, albeit with a much lower intensity in the case of the OA-d_1 addition. (C) Comparison of the observed carboxylic proton resonance upon OA-d_1 addition (black line) with the expected resonance in case of an acid/acid exchange mechanism (light gray) and an acid/oleate exchange mechanism.

case of an OA−OA exchange mechanism (Figure 6A), which should lead to a ratio of 5.1% upon addition of OA-d_1 (Figure 7C). On the other hand, it corresponds closely to the intensities expected for the oleate/oleic acid exchange (Figure 6B), which should result in a ratio of 0.9% due to the limited OA-d_1 purity (Figure 7C). Since minute water contaminations are easily picked up in these experiments, we conclude that these results show that the exchange of bound ligands for free ligands does not release protons from the Q-CdSe surface. Clearly, this is a strong indication for a ligand shell made of oleate ions and not OA molecules, as shown in Figure 6C. This result is in line with the observed difference between dilution, which does not induce exchange, and titration with free ligands, which leads to a relatively fast self-exchange between bound and free ligands. In the latter case only, protons necessary to desorb the oleate ligands are provided and exchange is possible.

3.5. Overall Quantum Dot Stoichiometry. Like other binary semiconductor nanocrystals such as PbS and PbSe,[54,56] the zinc blende CdSe QDs made via a fatty acid based synthesis have an excess of cations. In the case of PbSe, it was demonstrated that this cation excess should be interpreted as a surface excess.[54] Having a Cd/Se ratio of 1.23 ± 0.03 (see Figure 1D), 3.50 ± 0.05 nm particles, a ligand density of 4.6 ± 0.4 nm^{-2}, and presuming spherical particles, we calculated that a single particle is composed of about 440 ± 5 Cd and 360 ± 5 Se atoms together with 175 ± 15 ligands. This implies a Cd_c^{2+}/OA^- ratio of 1:2.1 ± 0.4 (i.e., 1:2 within the error of the measurements).

4. Discussion

The idea of this study was to analyze the interaction between oleic acid and colloidal CdSe QDs as a model system for sterically stabilized colloidal nanoparticles in general. We found that, in purified Q-CdSe/OA dispersions, there is no indication of a dynamic adsorption/desorption equilibrium. In contrast to systems with TOPO[18] or amine-based ligands,[19] Q-CdSe/OA dispersions simply consist of QDs with tightly bound ligands and solvent. Importantly, such dispersions form an ideal starting point to analyze QD properties, such as their charging in apolar media,[57] their tendency to self-assemble,[58] or the link between

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the surface chemistry and their opto-electronic properties.[59,60] In addition, they enable the formation of high-quality mono- and multilayers of QDs, for instance, by Langmuir−Blodgett or Langmuir−Schaeffer deposition.[61]

The addition of excess OA to a purified dispersion establishes an adsorption/desorption equilibrium, and this self-exchange involves a proton transfer step between excess oleic acid molecules and bound oleate ions. This result clarifies the lack of a dynamic adsorption/desorption equilibrium in purified dispersions: if no protons are supplied to the oleate ligands, they will not come off. Owen and co-workers proposed a similar interpretation of their ligand exchange studies involving CdSe QDs stabilized by alkylphosphonate moieties.[33] However, the self-exchange with deuterated OA used in this work directly demonstrates the proton transfer step. Moreover, the suggestion of these authors that the anionic ligands balance the charges of the cation excess of the inorganic core is fully confirmed here, as we find a Cd_e^{2+}/OA^- ratio of 1:2. Importantly, this shows that dispersed CdSe|OA QDs are well-defined inorganic/organic entities. They have a stoichiometric inorganic core and a Cd-rich surface terminated by a dense shell of tightly bound oleate ligands, making them overall neutral NPs. In the case of Q-PbSe/OA, Moreels and co-workers reported a similar combination of a cation excess and a lack of a dynamic adsorption/desorption equilibrium in purified dispersions.[54] This indicates that the combination of a cation excess and anionic ligands might be a general theme for NPs synthesized using acidic surfactants that can be demonstrated for each particular case using solution NMR methods. On the other hand, a Pb^{2+} to ligand ratio of 1:1 was found in the case of Q-PbSe/OA. Hence, although the combination of anionic ligands with an excess of metal cations is probably widespread, not all charge balancing should necessarily come from the anionic ligands.

The fact that desorption of oleate ligands does not involve the breaking of a dative bond, yet corresponds to an acid/base equilibrium, provides an improved basis for the design of more powerful ligand exchange reactions and nanoparticle processing procedures. These are, for example, of fundamental importance for the development of highly conductive QD films for photovoltaic[62,63] or electronic applications,[58] where the original ligands need to be replaced by more conductive ones. Often, this is based on the exposure of QD films to short amines, hydrazine, or pyridine. However, replacing oleate ligands with ligands forming a dative bond is not trivial and may involve significant side reactions such as the release of Cd-oleate. Furthermore, QD surface and ligand chemistry form the starting point for biofunctionalization of colloidal QDs for use as biolabels. This requires the formation of a tightly bound ligand shell, preferentially with a small hydrodynamic radius.[14] Knowing that the supply of protons can initiate the release of ligands from the QD surface is of importance here, for example, to prevent ligand loss in the acidic environment of the endosomes. In this way, the determined exchange mechanism might give an inside view in the biodegradation of nanoparticle biolabels and lead to a better understanding of the segregation of these labels in in vivo applications. On the other hand, it may also be of use to achieve the triggered release of molecules from the QD surface.

To substantiate research into the surface chemistry of QDs, truly molecular modeling of surface/ligand interactions is needed. The reports that phosphonic acids induce the growth of CdSe and CdS quantum rods led, for example, to an extensive modeling effort to find the relative binding strength of ligands on particular surface facets.[64,65] Similarly, the interaction of amines with different PbS nanocrystal facets has been analyzed to understand the occurrence of facets other than (100) in colloidal PbS QDs.[66] However, such model calculations need well-defined starting points. In the case of CdSe|OA, this work makes clear that the starting point is oleate ligands in combination with a Cd^{2+} excess, and not oleic acid in combination with a stoichiometric NP, the combination so far analyzed in literature. Moreover, the concept of self-exchange by oleic acid shows a way of experimentally determining the relative binding strength of, for instance, fatty acids versus phosphonic acids, by monitoring the mutual replacement in situ using solution NMR. These experiments are currently underway in our laboratories.

5. Conclusion

By investigating a relatively common colloidal NP such as Q-CdSe|OA, we have shown that various key properties that make such a NP an organic/inorganic entity are experimentally accessible by solution NMR. This involves the identification and quantification of ligands, the nature of the ligand/QD bond, the overall stoichiometry of a colloidal QD, and the mechanism and kinetics of ligand self-exchange. Importantly, this self-exchange reaction involves a proton exchange between bound oleate ions and excess oleic acid. In many respects, this information enhances our fundamental understanding of the chemistry of nanoparticle surfaces and ligands, which has relevance to their applications in opto-electronics and biolabeling. Moreover, the techniques developed to obtain this information are relatively simple, combining established 1D and 2D ^{1}H NMR techniques with ligand self-exchange. Their application should provide a new experimental avenue to understand the organic/inorganic boundary of other and more complex nanoparticle/ligand systems.

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Supporting Information Available: Details on (1) the experimental conditions for NMR measurements, (2) the analysis of worked-up Q-CdSe by the NMR toolbox, (3) the excess oleic acid titration, and (4) the deuterated oleic acid addition. This material is available free of charge via the Internet at http://pubs.acs.org.

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