

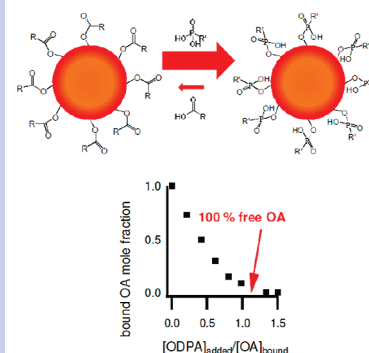
# Binding of Phosphonic Acids to CdSe Quantum Dots: A Solution NMR Study

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**ABSTRACT** We use  $^1\text{H}$  and  $^{31}\text{P}$  solution nuclear magnetic resonance spectroscopy to analyze the binding of phosphonic acid ligands to wurtzite CdSe quantum dots (CdSe QDs). CdSe QDs synthesized with phosphonic acids as a surfactant have a ligand shell composed of phosphonic acid and phosphonic acid anhydride moieties. Titrations of as-synthesized QDs with excess oleic acid do not induce desorption of phosphonic species, whereas titration of oleic-acid-exchanged QDs with excess phosphonic acid shows that the latter quantitatively replaces the oleic acid with a 1:1 stoichiometry. Both the stoichiometry of the oleic acid/phosphonic acid exchange interaction and the ratio between the Cd surface excess and the ligand density indicate that phosphonic acids bind as hydrogen phosphonates to the CdSe surface.

**SECTION** Nanoparticles and Nanostructures



In a hot injection synthesis, colloidal nanoparticles are made in a reaction mixture containing precursor species, solvent, and surfactants. These surfactants act as reagents during the reaction, and they stabilize the colloid by forming a molecular monolayer of ligands at the nanoparticle surface.<sup>1</sup> Among the commonly used surfactants, such as thiols, amines, phosphine oxides, or carboxylic acids, phosphonic acids ( $\text{RPO}(\text{OH})_2$ ) stand out. Being used in the synthesis of a variety of nanoparticles,<sup>2–7</sup> they are typically considered to be the strongest ligands, for instance, in the case of cadmium chalcogenide semiconductor nanoparticles or quantum dots (QDs).<sup>5</sup> Moreover, phosphonic acids are essential to the formation of quantum rods (QRs),<sup>8–12</sup> interesting nanostructures with anisotropic shape, and therefore have unique electrical and optical properties.<sup>13–15</sup>

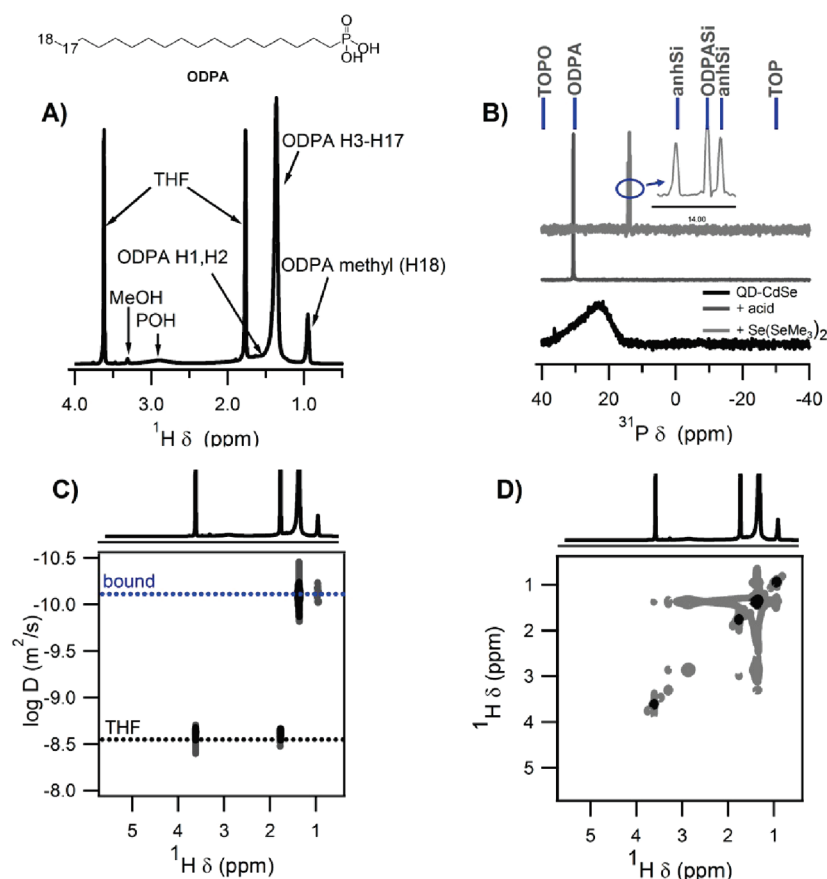
Density functional theory, ab initio calculations, and first-principles modeling calculations by Rempel et al.,<sup>16</sup> Pudzer et al.,<sup>17</sup> and Manna et al.<sup>18</sup> indicate that both properties are related: phosphonic acid ligands are more effective than phosphines, phosphine oxides, amines, and carboxylic acids in promoting anisotropic growth because they have a higher affinity and selectivity for the  $(11\bar{2}0)$  facet, parallel to the wurtzite (wz) CdSe  $c$  axis. Although it confirmed the experimental observations, this result was based on the assumption that the phosphonic acids bind as phosphonic acid molecules on CdSe surfaces. More recently, Owen et al. showed that phosphonic acid ligands are bound by the interaction of an anionic species with a surface  $\text{Cd}^{2+}$  ion and not as molecules.<sup>19</sup> However, these authors did not specify whether this anionic species concerned the hydrogen phosphonate  $\text{RPO}_2^-(\text{OH})^-$  (denoted as  $\text{ODPA}^-$  in the case of octadecyl hydrogen

phosphonate) or the phosphonate  $\text{RPO}_3^{2-}$  (denoted as  $\text{ODPA}^{2-}$  in the case of octadecylphosphonate). Because a detailed knowledge of the type of the bond formed by phosphonic acids with the crystal facets of wurtzite Cd chalcogenides is essential to understand its role as a ligand during synthesis as well as to manipulate these nanostructures by ligand exchange, further research on the interaction between phosphonic acids and CdSe quantum dots is mandatory.

Here we investigate the binding of phosphonic acids to wz-CdSe QDs, addressing both the type of bond and its binding strength relative to oleic acid (OA), a typical carboxylic acid ligand for CdSe QDs using  $^1\text{H}$  and  $^{31}\text{P}$  solution nuclear magnetic resonance (NMR) spectroscopy. Over the last 5 years,  $^1\text{H}$  NMR spectroscopy in particular has been introduced as a suitable technique for studying the capping of colloidal metal and semiconductor nanocrystals in situ, providing chemical and structural information on the ligands and on the ligand exchange.<sup>20–36</sup> Resonances of bound ligands appear broadened and shifted with respect to free ligand resonances, which frequently enables the identification of the ligands and the quantification of their concentration. Moreover, additional information can be obtained using diffusion ordered spectroscopy (DOSY), where the resonances of the free and surface-bound ligands are separated along the diffusion dimension,<sup>29,30,35</sup> or using nuclear Overhauser effect spectroscopy (NOESY), where efficient cross relaxation is indicative of ligand/nanoparticle interaction.<sup>35</sup> In contrast, solution  $^{31}\text{P}$

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**Figure 1.** (A)  $^1\text{H}$  NMR of a suspension of CdSe QD (545  $\mu\text{M}$ , 2.9 nm) dissolved in  $d_8$ -THF. (B)  $^{31}\text{P}$  NMR of the CdSe QD after digestion of the nanocrystals and extraction of the organic part of the sample (ligands only) and also after treatment with bis(trimethylsilyl)selenide. The blue lines mark the ppm values where free ODPA, TOP, TOPO, ODPA Si, and anhSi have their resonances in  $d_8$ -THF. (C) DOSY under the same conditions as those in part A. (D) NOESY under the same conditions; only the negative NOE cross peaks are shown.

NMR is seldom found in literature for characterization of nanocrystal ligands, mainly because of significant line broadening caused by the presence of more efficient relaxation pathways.<sup>3,19,27,37–39</sup> For instance, in the case of wz-CdSe QDs synthesized in the presence of TOP, TOPO, and phosphonic acids,<sup>19</sup> no clear assignment of the broad resonances observed in  $^{31}\text{P}$  NMR has been reported to date.

All NMR experiments are carried out with wz-CdSe QDs that are used as seeds in the growth of highly luminescent CdSe/CdS QRs. They are synthesized following the procedure previously published by Manna et al.<sup>40</sup> In brief, the solvent/surfactant mixture composed of trioctylphosphine oxide (TOPO), octadecylphosphonic acid (ODPA), and Se is delivered by hot injection of TOP-Se (trioctylphosphine selenide). The resulting CdSe QDs are purified by precipitating and resuspending them six times using toluene (first three times) and THF as solvents and methanol as the nonsolvent. An overview of their material properties is given in Figure 1S of the Supporting Information. Most importantly, they have an average radius of 2.9 nm, as calculated from the first exciton peak in the absorbance spectrum following the sizing curve of Jasieniak,<sup>41</sup> and a Cd:Se ratio of  $1.20 \pm 0.04$ , as measured using Rutherford backscattering spectrometry (RBS). NMR samples are made by resuspending dried CdSe QDs in  $d_8$ -THF.

$d_8$ -THF was used as the NMR solvent because the higher solubility of ODPA in THF as compared with toluene enables titration experiments based on the addition of excess ODPA; see below. Concentrations of CdSe QDs are obtained from the absorbance at 350 nm; see the Experimental Section for further details.

Figure 1A shows a  $^1\text{H}$  NMR spectrum of a 545  $\mu\text{M}$  dispersion of 2.9 nm CdSe QDs in  $d_8$ -THF. Apart from the resonances of residual THF, two pronounced resonances appear in the aliphatic region next to a broad resonance at  $\sim 3.0$  ppm and a small contamination at 3.3 ppm due to a residual amount of methanol ( $\text{CH}_3$  resonance). Because the synthesis is carried out in the presence of trioctylphosphine (TOP), TOPO, and ODPA, which all have their  $^1\text{H}$  NMR resonances in the aliphatic region, it is not possible to identify the actual ligands using the  $^1\text{H}$  spectrum. Therefore, we have also used  $^{31}\text{P}$  NMR (Figure 1B). The  $^{31}\text{P}$  spectrum of a CdSe QD dispersion shows a very broad resonance in the range 20–40 ppm. After dissolution of the dried QDs in aqua regia and extraction of the organic part of the sample,<sup>37</sup> the remaining free molecules give rise to a single peak at ca. 30 ppm in the  $^{31}\text{P}$  spectrum. Considering that TOPO, ODPA, and TOP have their  $^{31}\text{P}$  resonances at 40, 30, and  $-33$  ppm (Figures 2S, 3S, and 5S of the Supporting Information), this peak would

**Table 1.** Summary of the Ligand and Excess Cd Surface Densities As Obtained for As-Synthesized CdSe QD and CdSe QD after Ligand Exchange by Oleic Acid

	wz-CdSe as-synthesized	wz-CdSe OA exchanged
CH <sub>3</sub> nm <sup>-2</sup> integral	3.5 ± 0.2 nm <sup>-2</sup>	3.0 ± 0.2 nm <sup>-2</sup>
ODPA nm <sup>-2</sup>	1.3 nm <sup>-2</sup>	2.1 nm <sup>-2</sup>
ODPanh nm <sup>-2</sup>	1.1 nm <sup>-2</sup>	
OA nm <sup>-2</sup>		0.9 nm <sup>-2</sup>
excess Cd nm <sup>-2</sup>	1.5 ± 0.3 nm <sup>-2</sup>	1.5 ± 0.3 nm <sup>-2</sup>
excess Cd:CH <sub>3</sub>	1:2.3	1:2.0

correspond to ODPA, and we could conclude that ODPA is the only compound present after the acidic treatment of these QDs.

Considering the work of Owen et al.,<sup>19</sup> removal of the bound ligands can be accomplished by adding bis(trimethylsilyl) selenide. After some time, a part of the nanocrystals settles down in *d*<sub>8</sub>-THF, and sharp resonances are obtained in the NMR spectrum, which is indicative of the removal of the ligands promoted by the silanization of the bound oxygens. In particular, three sharp resonances characteristic of free molecules appear in the <sup>31</sup>P NMR spectrum that can be assigned to *O,O'*-bis(trimethylsilyl) octadecylphosphonic acid (ODPASi, 13.8 ppm) and the racemic and meso forms of *O, O'*-bis(trimethylsilyl)octadecylphosphonic acid anhydride (anhSi, 14.3 and 13.7 ppm).<sup>19</sup> Importantly, the phosphonic acid anhydride (ODPanh) is formed during synthesis as a byproduct of the reaction of trioctylphosphine selenium with Cd-ODPA<sup>32</sup> and not by the treatment with bis(trimethylsilyl) selenide.<sup>19</sup> Using a quantitative <sup>31</sup>P NMR experiment, the relative intensity of the three peaks is determined to be 0.8:1:0.8. Taking into account the fact that the anhSi has two phosphorus atoms, it follows that the ligand shell is composed of a mixture of ODPanh and ODPA with molar fractions of 0.45 and 0.55, respectively. After the dissolution of the nanocrystals in aqua regia, only ODPA is observed because the anhydride is hydrolyzed in acidic aqueous medium.

The <sup>1</sup>H NMR spectrum of ODPA and ODPanh are identical, except for the fact that the integral of the phosphonic proton should be half the value expected for ODPA. Therefore, even if the ligand shell is mixed, the comparison with the <sup>1</sup>H NMR spectrum of free ODPA (shown in Figure 4S of the Supporting Information) enables the attribution of all observed resonances, as indicated in Figure 1A. Note that bound ODPA can have phosphonic protons, which are proposed to give rise to the broad signal at 3.0 ppm. From the integral of the resonance at 0.91 ppm and using the Quantas artificial resonance (see the Experimental Section for details), we determined the concentration of ODPA units (ODPA and ODPanh) in the dispersion to be 47.8 mM. Therefore, we find on average 88 ODPA units per CdSe QD, which corresponds, as summarized in Table 1, to a ligand density of 3.5 ± 0.2 ODPA units per nm<sup>2</sup>, distributed over ODPA (1.3 nm<sup>-2</sup>) and ODPanh (1.1 nm<sup>-2</sup>).

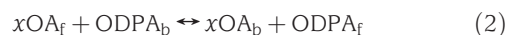
In the DOSY spectrum of a CdSe QD dispersion, two sets of resonances can be distinguished, with diffusion coefficients of (26.9 and 0.9) × 10<sup>-10</sup> m<sup>2</sup>/s, respectively. (See Figure 1C.) The first clearly corresponds to residual THF (and methanol if the

signal is boosted up), whereas the second is considerably smaller than the diffusion coefficient of 5.6 × 10<sup>-10</sup> m<sup>2</sup>/s we measured for free ODPA in THF (see the Supporting Information). Using the Stokes–Einstein equation with a THF viscosity of 0.456 mPa·s at 298.15 K,<sup>42</sup> we find that a diffusion coefficient of 0.9 × 10<sup>-10</sup> m<sup>2</sup>/s corresponds to a hydrodynamic diameter *d*<sub>H</sub> of 10.5 nm. This value is larger than expected for colloidal nanoparticles with a core diameter of 2.9 nm and an ODPA ligand shell with a thickness of 2 to 3 nm.<sup>27,33</sup> This enhanced reduction of the diffusion coefficient can be understood by considering the volume fraction  $\phi$  of the CdSe QD in solution. With the high concentrations used here, which are needed to record satisfactory <sup>31</sup>P NMR spectra, this amounts to ~10% if an ODPA chain length of 2.7 nm is assumed. In this case, nanoparticle/nanoparticle interaction leads to nonideal diffusion, and a diffusion coefficient at infinite dilution *D* can be obtained from the observed diffusion coefficient *D*<sub>obs</sub>, following<sup>43</sup>

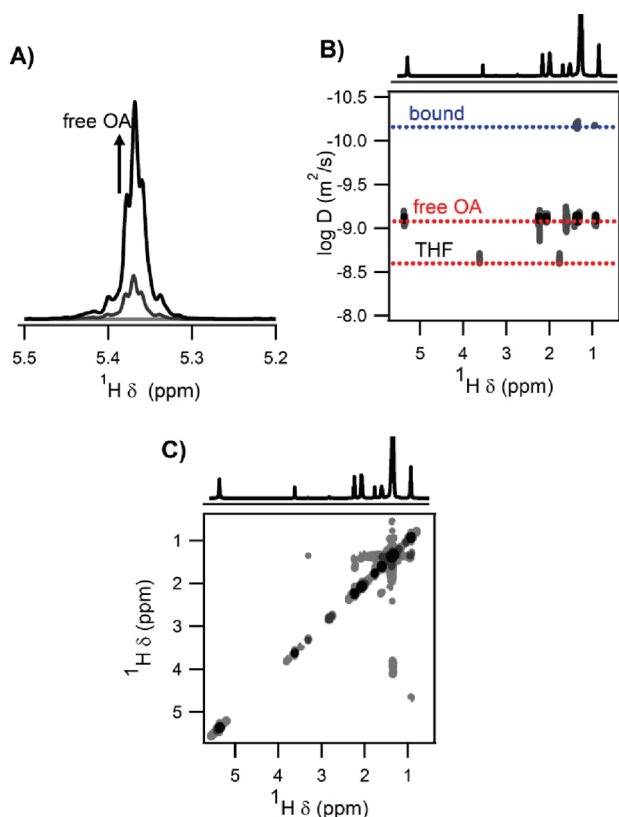
$$D = \frac{D_{\text{obs}}}{1 - 2\phi} \quad (1)$$

Following eq 1, *D* amounts to 1.1 × 10<sup>-10</sup> m<sup>2</sup>/s, yielding a *d*<sub>H</sub> of 8.4 nm, which agrees with the value expected for CdSe QD with an ODPA ligand shell. Hence, we attribute the second set of resonances to bound phosphonic species. This interpretation is corroborated by the NOESY spectrum, in which the resonances at 0.91 and 1.32 ppm feature the intense negative NOE cross peaks that are characteristic for bound ligands (Figure 1D).<sup>35</sup>

To obtain experimental information on the binding strength of the phosphonic species to the CdSe QD surface, we added a carboxylic acid (oleic acid, OA) to a dispersion of ODPA- and ODPanh-capped CdSe in THF. OA is a commonly used surfactant that binds strongly to CdSe QD surfaces and has the advantage that it can be easily monitored in <sup>1</sup>H NMR as the resonance of the alkene protons appears at ~5.37 ppm. (See Figure S10 of the Supporting Information.) Moreover, both OA and the phosphonic species are bound as ions to the CdSe QD surface, and an exchange reaction where one or more OA molecules replaces an adsorbed phosphonic ligand is possible (see eq 2), in which the subscript f stands for free molecules and b stands for bound species.



As can be seen in Figure 2A, the resonance of the alkene protons upon the addition of OA in a 5:1 OA:ODPA ratio (221 mM) to a CdSe QD/ODPA suspension is well resolved and does not show any perceptible broadening. This indicates that the added OA remains free in solution and does not bind to the QDs. In line with these results, the <sup>31</sup>P NMR remains unchanged after the addition of OA (results not shown). The DOSY spectrum (Figure 2B) features three different diffusion coefficients, corresponding to the residual solvent, bound phosphonic ligands, and free OA, respectively, without indication of bound OA. Moreover, the diffusion coefficient of OA (8.7 × 10<sup>-10</sup> m<sup>2</sup>/s) is comparable to the value determined for free oleic acid in THF (8.2 × 10<sup>-10</sup> m<sup>2</sup>/s, Figure S11 of the Supporting Information). In line with these results, we observe

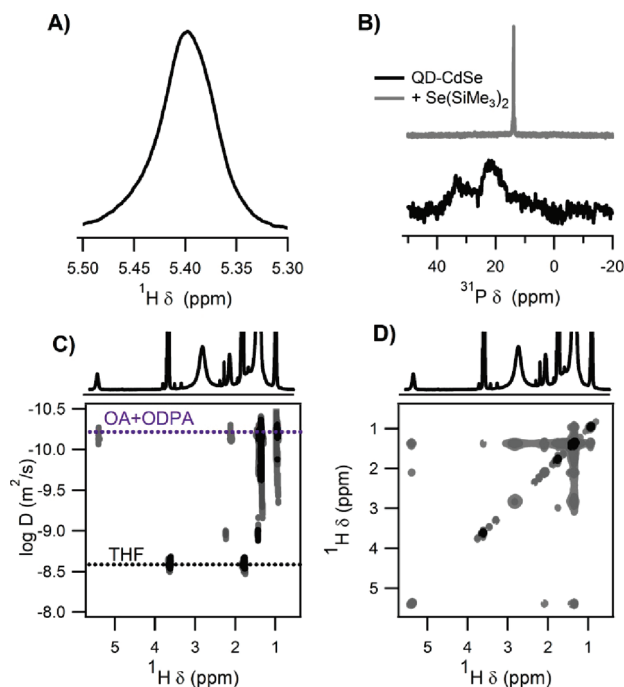


**Figure 2.** (A)  $^1\text{H}$  NMR of a suspension of CdSe QD ( $545\ \mu\text{M}$ ,  $2.9\ \text{nm}$ ) dissolved in  $d_8$ -THF after the addition of 46 and 221 mM oleic acid. Only the double bond region is shown. (B) DOSY of a suspension of CdSe QD ( $545\ \mu\text{M}$ ,  $2.9\ \text{nm}$ ) dissolved in  $d_8$ -THF after the addition of OA - 221 mM (OA:ODPA 5:1). (C) NOESY under the same conditions; only the negative NOE cross peaks are shown.

no negative cross peaks in the NOESY spectrum between the OA resonances (Figure 2C). Therefore, we conclude that within the limits of the NMR measurements there is no indication that the added OA replaces ODPA ligands bound to the CdSe QD surface, even if the OA concentration is increased to 221 mM.

To force the replacement of bound ODPA by OA, we dissolved as-synthesized, dried CdSe QD in OA and heated the resulting sample for 17 h to  $100\ ^\circ\text{C}$ . (See the Experimental Section for details.) After precipitating and resuspending the QDs, the resulting particles were then worked up as NMR samples in  $d_8$ -THF. Following this treatment, we find that the alkene resonance is broad, possibly indicating the presence of only bound OA (Figure 3A). On the basis of the integration of the alkene protons (OA double bond) and methyl protons (both OA and phosphonic species), we find an OA:ODPA ratio of about 1:2.4 with overall concentrations of 9.5 and 22.7 mM, respectively. Because the concentration of the sample is  $435\ \mu\text{M}$ , we calculate, as summarized in Table 1, an overall ligand density of  $3.0 \pm 0.2\ \text{ligands/nm}^2$  distributed over OA ( $0.9\ \text{nm}^{-2}$ ) and ODPA ( $2.1\ \text{nm}^{-2}$ ). This result points to the substitution of at least one ODPA unit by one oleate ligand.

The  $^{31}\text{P}$  NMR shows two broad resonances (Figure 3 B) in the same range as the very wide resonance previously found

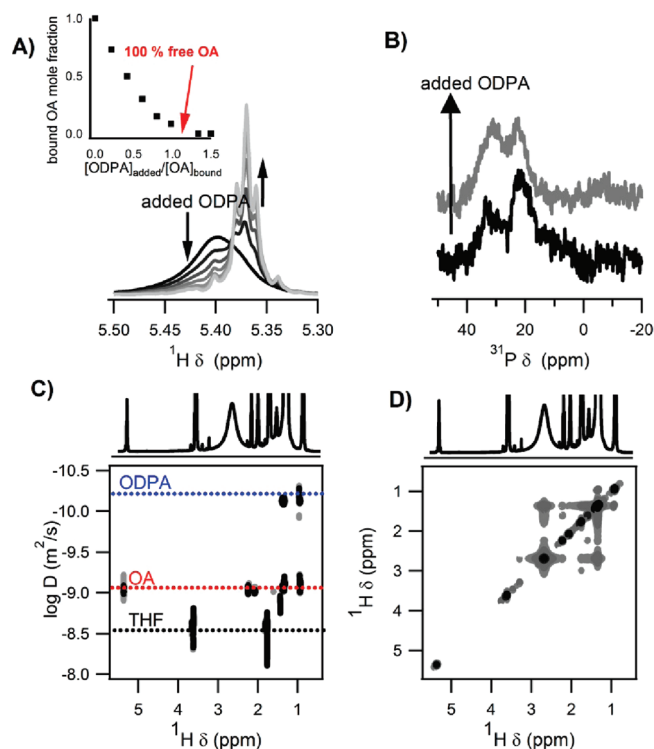


**Figure 3.** (A)  $^1\text{H}$  NMR zoomed in the alkene resonance of a suspension of CdSe QD ( $435\ \mu\text{M}$ ,  $2.8\ \text{nm}$ ) dissolved in  $d_8$ -THF capped with OA and ODPA ligands. (B)  $^{31}\text{P}$  NMR of the same suspension and also after treatment with bis(trimethylsilyl)selenide. (C) DOSY of the same suspension. (D) NOESY under the same conditions; only the negative NOE cross peaks are shown.

for the as-synthesized crystals (Figure 1 B). After the treatment with bis(trimethylsilyl)selenide,<sup>19</sup> only one resonance is now found at 13.8 ppm that corresponds to *O,O'*-bis(trimethylsilyl) octadecylphosphonic acid (ODPASe, Figure 1 B). Therefore, we have either substituted only ODPA or hydrolyzed ODPA to form the phosphonic acid during the process of ligand exchange in the presence of oleic acid. Because the density of ODPA ligands changes from  $1.3$  to  $2.1\ \text{nm}^{-2}$  after the OA treatment, clearly ODPA must be hydrolyzed during the ligand exchange process to readsorb partially as ODPA.

The DOSY spectrum (Figure 3C) shows one diffusion coefficient for OA with a value of  $0.8 \times 10^{-10}\ \text{m}^2/\text{s}$ , which agrees with the diffusion coefficient found for bound ODPA. Hence, we confirm the presence of OA in the bound state only. This is also in agreement with the NOESY spectrum (Figure 3D), which shows strong negative cross peaks, for example, the OA alkene protons at 5.43 ppm.<sup>35</sup>

Having QDs with a ligand shell that is a mixture of ODPA and OA at hand, we can further analyze the OA/ODPA exchange by the addition of free ODPA to the sample. Upon titration with excess ODPA, we find that the appearance of the OA alkene resonance changes. The broad peak decreases, whereas a new sharper resonance appears (Figure 4A). This indicates that OA desorbs and is most likely replaced by the added ODPA. Indeed, at each point of the titration, the alkene resonance can be decomposed in a linear combination of the totally bound OA (first spectrum) and the totally free OA (last spectrum after the addition of 1.5 equiv, 14.3 mM ODPA), and



**Figure 4.** (A)  $^1\text{H}$  NMR zoomed in the alkene resonance of a suspension of CdSe QD ( $435\ \mu\text{M}$ ,  $2.8\ \text{nm}$ ) dissolved in  $d_8$ -THF capped with OA and ODPA ligands upon the addition steps of ODPA from 0 to  $14.3\ \mu\text{M}$  final concentration (0 to 1.5 equiv). Inset: bound OA mole fraction as a function of the equivalents of added ODPA. (B)  $^{31}\text{P}$  NMR of the same titration upon the addition of 0 and 1.7 equiv of ODPA. (C) DOSY of a suspension of CdSe QD ( $435\ \mu\text{M}$ ,  $2.8\ \text{nm}$ ) dissolved in  $d_8$ -THF capped with OA and ODPA ligands after the addition of 1.7 equiv of ODPA ( $15.8\ \mu\text{M}$ ). (D) NOESY under the same conditions; only the negative NOE cross peaks are shown.

the fraction of bound OA thus obtained can be plotted as a function of the equivalents of added ODPA (inset Figure 4 A).

Interestingly, in Figure 3B, the  $^{31}\text{P}$  NMR spectrum of the exchanged CdSe QD is clearly constituted of two broad signals, and yet ODPA is the only phosphorus-containing ligand. Upon the addition of excess ODPA that substitutes the bound OA, the resonance at  $\sim 33\ \text{ppm}$  increases relative to the resonance at  $\sim 23\ \text{ppm}$ . A tentative interpretation of this result is that ODPA exhibits different  $^{31}\text{P}$  chemical shifts depending on the crystal facet it is adsorbed at. In addition to the presence of two species on the CdSe QD surface, this would explain the very considerable broadening of the  $^{31}\text{P}$  resonance for the as-synthesized CdSe QD (Figure 1 B). Moreover, it suggests that OA exchange is only possible on one of the facets of the wurtzite CdSe nanocrystals.

The trend in the inset of Figure 4 A constitutes evidence of a quantitative replacement of bound OA by ODPA, where every ODPA molecule added replaces bound OA until the QD surface is free of OA. This interpretation is corroborated by  $^1\text{H}$  DOSY and  $^1\text{H}$  NOESY. In both DOSY and NOESY, the OA resonances show all of the features of free OA, with a diffusion coefficient of  $9.7 \times 10^{-10}\ \text{m}^2/\text{s}$  and no negative NOE cross-peaks after the addition of excess ODPA to a concentration of

$15.2\ \text{mM}$ . (See Figure 4C,D.) By the trend in the inset of Figure 4 A, ODPA replaces all of the OA when an excess of ca. 1 equiv is added, meaning that approximately one OA ligand is replaced by one ODPA.

Returning to the OA/ODPA exchange in CdSe QDs, as expressed by eq 2, our experimental results indicate that the exchange equilibrium is strongly shifted toward the side of free OA and bound ODPA; that is, ODPA is the stronger ligand of the two. Because the stoichiometric coefficient  $x$  of this reaction is  $\sim 1$ , the exchange involves the replacement of OA, which binds as the oleate  $\text{OA}^-$  by the hydrogen phosphonate  $\text{ODPA}^-$ . This conclusion is also in agreement with the Cd/Se ratio of  $1.20 \pm 0.04$  found by RBS (see the Supporting Information). With  $2.9\ \text{nm}$  QDs, this ratio implies that an excess of Cd is found on the surface of the nanocrystals with a density of  $1.50 \pm 0.3\ \text{nm}^{-2}$ . With a density of phosphorous units of  $3.5 \pm 0.2\ \text{nm}^{-2}$ , it follows that we have one excess Cd species for two phosphorous units within the error of the measurement. (See Table 1.) Hence, overall neutral CdSe QD can be understood from a charge balance between ligands bound as  $\text{ODPA}^-$  and  $\text{ODPanh}^{2-}$  and excess Cd species with a formal charge of  $+2$ . After partial ligand exchange to OA, we have also reported that the total ligand density is  $3.0\ \text{nm}^{-2}$ . Again, this means that overall neutral CdSe QD results from a charge balance between the  $\text{Cd}^{2+}$  and the ligands, bound as  $\text{ODPA}^-$  and  $\text{OA}^-$ , respectively. Quantifying the equilibrium constant of the exchange reaction is more difficult. It requires the determination of the reaction quotient, yet the strong shift of the equilibrium toward bound ODPA renders it impossible to determine the concentration of all components together using solution NMR.

In conclusion, we have shown that the ligand shell of CdSe QDs synthesized in the presence of ODPA, TOP, and TOPO is constituted by 45% of the octadecylphosphonic anhydride and 55% of ODPA. The binding strength of the CdSe-ODPA bond strongly exceeds that of the CdSe-OA bond. In particular, OA is readily and quantitatively replaced by ODPA on CdSe QD surfaces, whereas the reverse process is only partially possible at elevated temperature. ODPA binds preferentially as a monodentate hydrogen phosphonate ligand ( $\text{ODPA}^-$ ), as indicated by the stoichiometry of the ligand exchange reaction and the charge balance between the  $\text{Cd}^{2+}$  excess and the bound ligands. In this way, this work provides the starting point for a better understanding of CdSe rod growth in the presence of phosphonic acids, from both experimental and theoretical perspectives.

## EXPERIMENTAL SECTION

**Materials.** CdO oxide (99.999%) and technical oleic acid (90%) were purchased from Sigma-Aldrich. Selenium powder ( $-200\ \text{mesh}$ , 99.999%) and tri-*n*-octylphosphine oxide (TOPO,  $\geq 98\%$ ) were obtained from Alfa-Aesar. Tri-*n*-octylphosphine (97%) was ordered from Strem Chemicals. *n*-Octadecylphosphonic acid (ODPA, 98%) was purchased from Epsilon Chemie, and bis(trimethylsilyl)selenide was purchased from ABCR. Methanol, tetrahydrofuran (THF), and toluene were all of quality "for synthesis" and were ordered from VWR.  $d_8$ -THF was purchased from Cambridge Isotope Laboratories.

**Synthesis and Characterization.** CdSe QD with mean sizes indicated in the Letter, were synthesized according to a procedure described in the literature.<sup>40</sup> The CdSe QD size and concentration were determined from the absorbance spectrum (Supporting Information) of a CdSe QD suspension, obtained by dilution of an aliquot of the NMR suspension. The nanocrystal diameter is given by the band gap,  $E_0$  (the first exciton peak), through the sizing curve of Mulvaney et al.<sup>41</sup> The QD concentration is calculated from Beer's law, using the absorbance at 350 nm and a molar extinction coefficient  $\epsilon_{350}$  obtained from the size-independent absorption coefficient at 350 nm<sup>41</sup>

$$\epsilon_{350} = 0.01685 \times d^3 \text{ cm}^{-1}/\mu\text{M}$$

**Determination of Cd/Se Ratio.** Samples for RBS are prepared by spincoating a small amount of CdSe QDs dispersed in chloroform (50  $\mu\text{M}$ ) on a Si substrate, hereby forming a close-packed thin film of thickness < 50 nm. RBS<sup>45</sup> experiments were performed using a 1.57 MeV  $^4\text{He}^+$  incident beam. The energy spectrum of the He particles scattered over an angle of 168° was determined. Given the significantly different masses of Cd (112.4) and Se (79.0), and the light substrate (Si,  $M = 28.1$ ), well-separated backscattering signals are obtained for the two metals. By normalizing their intensities by the Rutherford scattering cross section (essentially the  $Z^2$  dependence), an accurate value for the Cd/Se ratio nanoparticles can be derived.

**NMR Experiments.** We prepared NMR samples by drying a suspension of CdSe QD under a strong nitrogen flow, followed by redispersing the nanocrystals in  $d_8$ -THF. The OA partially exchanged samples were prepared by dissolving CdSe QD in 3 mL of OA ( $[\text{CdSe QD}] = 218 \mu\text{M}$ ) and heating the resulting sample for 17 h at 100 °C. The resulting CdSe QDs are purified by precipitating and resuspending them six times using toluene (first three times) and THF as solvents and methanol as the nonsolvent. Additions of bis(trimethylsilyl)selenide were always performed inside the glovebox and at least 50 equiv were added to ensure the formation of disubstituted species.

NMR data were collected using a Bruker Avance DRX 500 spectrometer ( $^1\text{H}$  and  $^{13}\text{C}$  frequency of 500.13 and 125.76 MHz, respectively) equipped with a 5 mm TXI probe or a 5 mm TBI probe (maximum Z-gradient strength of 0.556 T m<sup>-1</sup> for both probes). The latter was used to record  $^{31}\text{P}$  NMR spectra at 202.404 MHz. For the ODPa species, the  $T_1$  relaxation time and the 90° pulse length were separately determined. The quantitative  $^{31}\text{P}$  spectra were recorded using a 5 s interscan delay. This delay was calculated to allow over 96 % recovery of original magnetization when applying 30°  $^{31}\text{P}$  pulses. The temperature was set to 298.15 K. Quantitative  $^1\text{H}$  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<sup>44</sup> based on the PULCON<sup>46</sup> (pulse-length-based concentration determination) approach. Macros for calibration and quantification were kindly provided by Dr. Richard Upton (GSK). In the DOSY experiments, the gradient duration  $\delta$  and the diffusion delay  $\Delta$  were optimized for a signal decay of roughly 90 % at the maximum gradient strength. Typical values for  $\delta$  ranged from 900 to 2200 ms, and those for  $\Delta$  ranged from 100 to 200 ms, respectively. The gradient strength was varied from 2 to 95 %

of the maximum strength using a sine gradient shape. 2D NOESY spectra were recorded with a mixing time of 600 ms using typically 512 sampled indirect time domain points, consisting of 16 scans of 2048 sampled direct time domain points each recorded with a 2 s delay between scans. The spectral width of both dimensions was set at 11 ppm.

**SUPPORTING INFORMATION AVAILABLE** Additional information about the absorption spectrum of CdSe QDs and the spectra of ODPa and OA in  $d_8$ -THF. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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