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Reaction chemistry and ligand exchange at cadmium selenide nanocrystal surfaces

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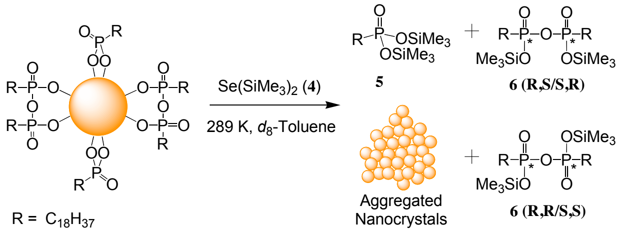
Chemical modification of nanocrystal surfaces is fundamentally important to their assembly, their implementation in biology and medicine, and greatly impacts their electrical and optical properties. However, it remains a major challenge owing to a lack of analytical tools to directly determine nanoparticle surface structure.[1] Early nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS) studies of CdSe nanocrystals prepared in tri-*n*-octylphosphine oxide (**1**) and tri-*n*-octylphosphine (**2**), suggested these coordinating solvents are datively bound to the particle surface.[2] However, assigning the broad NMR resonances of surface-bound ligands is complicated by significant concentrations of phosphorus-containing impurities in commercial sources of **1**, and XPS provides only limited information about the nature of the phosphorus containing molecules in the sample.

More recent reports have shown the surface ligands of CdSe nanocrystals prepared in technical grade **1**, and in the presence of alkylphosphonic acids, include phosphonic and phosphinic acids.[3] These studies do not, however, distinguish whether these ligands are bound datively, as neutral, L-type ligands, or by X-type interaction of an anionic phosphonate/phosphinate moiety with a surface Cd^{2+} ion.[4] Answering this question would help clarify why ligand exchange with such particles does not proceed generally as expected based on a L-type ligand model.[5] By using reagents with reactive silicon-chalcogen and silicon-chlorine bonds to cleave the ligands from the nanocrystal surface, we show that our CdSe and CdSe/ZnS core-shell nanocrystal surfaces are likely terminated by X-type binding of alkylphosphonate ligands to a layer of Cd^{2+}/Zn^{2+} ions, rather than by dative interactions. Further, we provide spectroscopic evidence that **1** and **2** are not coordinated to our purified nanocrystals.

We synthesized 3 - 6 nm CdSe nanocrystals by reacting tri-*n*-octylphosphine selenide with anhydrous cadmium-*n*-octadecylphosphonate prepared from dimethylcadmium and *n*-octadecylphosphonic acid (**3**) in **1** at 315 ˚C. ZnS shells were grown on these cores by reacting zinc-*n*-octadecylphosphonate with bis(trimethylsilyl)sulfide under similar conditions. Both **1** and **3** were recrystallized prior to use and shown to be free of phosphorus-containing impurities with NMR spectroscopy. To ensure the purity of the nanocrystal product, removal of remaining cadmium- and zinc-*n*-octadecylphosphonate, insoluble coordination polymers,[6] was accomplished by their depolymerization and dissolution with octylamine, followed by fractional precipitation of the nanocrystals (see Supporting Information).

^{1}H-NMR spectra of purified nanocrystals in d_8-toluene showed broad resonances for methylene groups (δ = 1.3 – 4.0 ppm) and methyl groups (δ = 0.9 – 1.0 ppm) in a ratio of ~17:1 representative of octadecyl chains (Figure S1). Additionally, a broad resonance of low intensity is visible between δ = 7.8 – 9.2 ppm, which we tentatively assign to a low concentration of acidic hydrogens present in the ligand shell.[7] A $\{^{1}H\}^{31}$P-NMR spectrum of a concentrated sample (278 mg/mL) showed a broad bimodal resonance from δ = 10 – 40 ppm reminiscent of the spectrum published by Bawendi and coworkers, and originally interpreted to be characteristic of surface-bound **1** and **2** (Figure 1). Neither the ^{1}H nor the $\{^{1}H\}^{31}$P-NMR spectrum showed sharp resonances that might arise from "free" surfactant molecules.

Scheme 1. Cleavage of alkylphosphonate ligands with **4**.



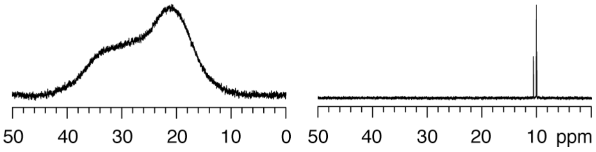


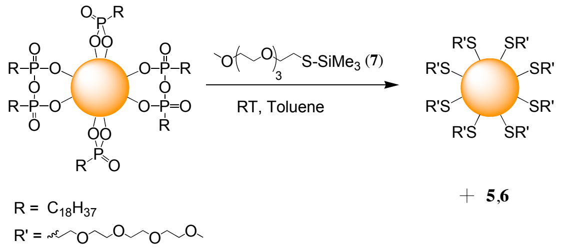
Figure 1. $\{^{1}H\}^{31}$P NMR spectra of 167 mg of as prepared CdSe nanocrystals in 0.6 ml d_8-toluene (left), and the reaction between CdSe nanocrystals and **4** in d_8-toluene (right).

Removal of these surface-bound ligands was accomplished by adding bis(trimethysilyl)selenide (**4**) to a solution of the CdSe nanocrystals in d_8-toluene. Shortly after addition (10 - 60 minutes) the sample became turbid and the nanocrystals then slowly settled out of solution. NMR spectra of these solutions immediately after mixing are dramatically sharpened due to release of the surface-bound ligands (Figure 1). In particular, three sharp resonances characteristic of "free" small molecules appeared in the $\{^{1}H\}^{31}$P-NMR spectrum that we assign to *O,O'*-bis(trimethylsilyl)octadecylphosphonic acid (**5**) and a mixture of racemic and meso *O,O'*-bis(trimethylsilyl)octadecylphosphonic acid anhydride (**6**) (Scheme 1). Similar reactivity was observed with bis(trimethylsilyl)sulfide. Both mass spectrometry and an independent synthesis of these reaction byproducts confirm our assignment (see Supporting Information).

The presence of the *n*-octadecylphosphonic acid anhydride in the ligand shell likely arises from reaction of **3** with trioctylphosphine selenide during the synthesis of CdSe, rather than as a byproduct of the ligand cleavage reaction.[8] This is further supported by the observation that increasing amounts of **6** relative to **5** are cleaved from nanocrystals synthesized in reactions run to higher conversion of the cadmium and selenium nanocrystal precursors.

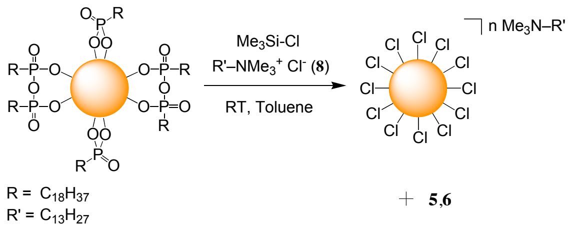
The reactivity of the silicon-selenium and silicon-sulfur bonds and the stability of the newly formed silicon-oxygen bond presumably provide the driving force for this reaction, and led us to attempt a similar ligand cleavage with a trimethylsilyl-protected thiol. In this case however, by reacting *S*-trimethylsilyl-2,5,8,11-tetraoxatridecane-13-thiol (**7**) with the nanocrystals, a thiolate is exchanged for the phosphonates as shown in Scheme 2. Addition of **7** to a d_8-toluene solution of the CdSe nanocrystals resulted in rapid disappearance of the broad ^{31}P-NMR resonance of the starting material, quenching of the nanocrystal fluorescence, and the appearance of **5** and **6** as described above, but did not result in nanocrystal aggregation.[9] The appearance of a broad resonance for the bound thiol in the ^{1}H NMR spectrum was also evident ($\delta = 3.2 - 4.5$ ppm). Removal of the solvent *en vacuo*, and washing the residue with anhydrous hexane produced nanocrystals that are soluble in polar solvents like water, methanol and chloroform. A ^{1}H NMR spectrum of the newly derivatized nanocrystals in d_8-toluene showed that 85% of the surface ligands are derived from **7** and 15% from octadecyl chains (Figure S9).[10] Analysis of the hexane-soluble portion with ^{1}H and $\{^1H\}^{31}$P-NMR spectroscopy and ESI-TOF mass spectrometry showed the presence of **5** - **7** but no ^{31}P NMR resonances for **1** and **2**.

Scheme 2. Conversion of alkylphosphonate to thiolate ligands with TMS-protected thiol **7**.



Encouraged by our nanocrystal derivatization experiments with trimethylsilyl bound chalcogenides **4** and **7**, we sought to exchange the alkylphosphonate ligands for chloride ligands. Adding anhydrous cholortrimethylsilane to a toluene solution of nanocrystals, results in rapid particle aggregation. Repeating this experiment in a mixture of toluene saturated with anhydrous tridecyltrimethylammonium chloride (**8**), however, prevented nanocrystal aggregation.[11] Removal of excess **8** by centrifugation and subsequent fractional precipitation with hexane gave nanocrystals that are soluble in toluene and chloroform. $\{^1H\}^{31}$P-NMR spectroscopy of the reaction byproducts in d_8-toluene showed the presence of **5** and **6**, while a ^{1}H-NMR spectrum of the nanocrystals showed resonances characteristic of the tridecyltrimethylammonium ion (Scheme 3). Repeating this experiment with CdSe/ZnS core-shell particles resulted in a 25% decrease in the fluorescence quantum yield.[12]

Scheme 3. Chloride termination with Me_3Si-Cl and **8**.[a]



[a] The number of chloride ligands on the particle surface is equal to the number of Cd-phoshphonate linkages transformed to chloride ligands, plus the number of adsorbed chlorides anions from **8**, denoted n above.

XPS of the Cl-functionalized nanoparticles made soluble with **8** was performed to demonstrate binding of chloride to the nanoparticle surface. Binding energies of Cl 2*p* electrons are sensitive to their coordination environment with reported values for tetraalkylammonium chloride salts of 196 eV, while $CdCl_2$ shows Cl binding energies of 199 eV.[13] XPS analysis of our chloride-terminated nanocrystals dropcast on a gold substrate showed Cl binding energies of 199 eV with no contribution below 198 eV, ruling out the presence of significant amounts of “free” **8** (Figure 2).

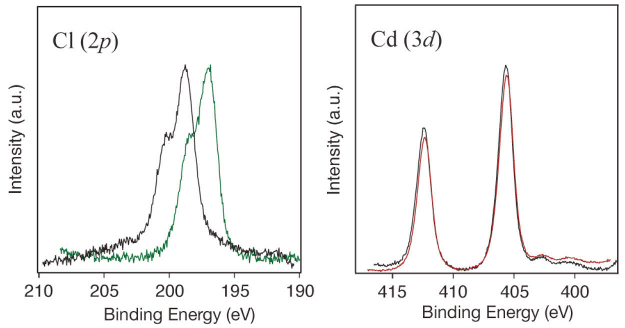


Figure 2. XPS of chloride-terminated CdSe nanocrystals (—) (Scheme 3), **8** (—), and underivatized nanocrystals (—). Au 4*f* binding energies of the substrate were used as an internal reference.

The facile ligand cleavage and exchange reactivity of the trimethylsilylchalcogenides and chlorotrimethylsilane presented above suggests that our nanocrystal surfaces may be terminated by X-type binding of anionic alkylphosphonate moieties to Cd^{2+} ions on the crystal surface. This hypothesis is best supported by a model where a layer of excess cadmium ions bind to the Lewis basic selenide surface sites of the CdSe core and are charge balanced by the phosphonate ligand. Previously reported Rutherford backscattering experiments also concluded that CdSe nanocrystals contain excess Cd ions on their surfaces.[14] This conclusion, however, does not strictly follow from these ligand cleavage experiments, since a control experiment showed free phosphonic acid (**3**) and its anhydride also produce **5** and **6**, respectively, on reaction with **4**.

To further investigate the nature of the binding between **3** and the nanocrystal surface, we studied the direct reaction of our CdSe nanocrystals with thiols. Addition of 2-methoxyethanethiol (**9**) or its long chain counterpart 2,5,8,11-tetraoxatridecane-13-thiol (**10**) to the CdSe nanocrystal sample resulted in minimal changes to the resonances for the surface-bound octadecyl chains in the ^{1}H NMR, though a broad resonance ($\delta = 3.2 - 4.5$ ppm) appeared upfield of the free thiol.[15] Repeated precipitation from toluene by addition of hexane furnished nanocrystals that retain the broad signature of the bound thiol ($\delta = 3.2 - 4.5$ ppm) *as well as the starting octadecylphosphonate ligands* in an approximate 1:1 ratio (Figure S10). No sharp lines indicative of “free” surfactant molecules were visible. Additionally, the nanocrystal fluorescence was immediately quenched upon addition of **9** and **10.** Both observations indicating that the thiol binds the nanocrystal surface. Repeating this experiment in the presence of added triethylamine, however, resulted in rapid ($t < 10$ minutes) sharpening of the aliphatic resonances in the ^{1}H-

NMR spectrum. At the same time two sharp resonances in the $\{^1H\}^{31}P$-NMR spectrum (δ =16.6, 26.1 ppm) appeared that we assign to the conjugate base of octadecylphosphonic acid and octadecylphosphonic acid anhydride.[16]

This indicates **10** will only displace the alkylphosphonate ligands upon deprotonation by triethylamine suggesting that anionic alkylphosphonate moieties are bound to excess cationic cadmium sites, rather than by a simple dative interaction. Accordingly, the incoming thiol must convert the alkylphosphonate ligand to an equivalent of phosphonic acid in order to displace it from the nanocrystal and form a Cd^{2+}-thiolate interaction. The lack of this reactivity in the absence of added base, likely arises from the greater pKa of thiols, which remain preferentially protonated over the alkylphosphonate oxygen. By adding triethylamine, however, the bound thiol can be deprotonated by the external base driving formation of a surface Cd-thiolate and displacement of a triethylammonium octadecylphosphonate salt.

In addition to X-type octadecylphosphonate binding, adsorption of thiols to our nanocrystal surfaces, without displacing the octadecylphosphonate ligands, suggests nanocrystal surfaces also contain L-type coordination sites. This helps explain why our chloride-terminated nanocrystals are soluble in the presence of tetraalkylammonium chloride salts, and the numerous reports that amines, phosphines, and thiols can change nanocrystal growth kinetics, solubility and optical properties.[17]

This picture of a CdSe nanocrystal surface is particularly interesting in light of recent single crystal X-ray structures of monolayer-protected Au clusters.[18] Those results complement our model in the sense that the Au cluster can be described as a Au core with a surface layer of Au(I)-thiolate. In our model, the nanocrystal is composed of a CdSe core with a surface layer of Cd-X where X is a phosphonate, thiolate or halide ligand. Though similar X-type surface ligation has been observed in the single crystal X-ray structures of cadmium-thiolate terminated cadmium-chalcogenide clusters,[19] it is unclear whether this description of II-VI nanocrystal surfaces is general. This model likely applies widely to II-VI nanocrystals grown in the presence of excess Lewis-acidic metal-phosphonates, -carboxylates, especially when the product nanocrystals contain excess M^{2+}.[14] However, it remains an open question whether nanocrystals grown in the absence of X-type surfactants or with chalcogenide-rich surfaces can be stabilized exclusively by dative interactions.[20]

These results shed new light on the chemistry and reactivity of CdSe nanocrystal surfaces, and in particular, indicate that ligand exchange reactions ought to be designed with the need to balance charges between the surface Cd^{2+} layer and the incoming ligand. Preliminary studies suggest similar chemical reactivity of other II-VI semiconductor nanocrystals. The conclusion that alkylphosphonate ligands are bound via X-type interaction with Cd^{2+} will not only influence the development of more powerful surface exchange reactions but will allow for more sophisticated understanding of how ligands and surfaces control the optical and electrical properties of nanocrystals. Furthermore, the ability to convert the alkylphosphonate ligands to other X-type ligands, like chloride, will undoubtedly have a significant impact on the electrical properties of these nanocrystals. Studies of these effects are underway in our lab.

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Supporting Information Available: Experimental conditions for nanocrystal growth and cleaning, synthesis of **5**, **6**, and **7**, and the NMR spectra discussed above. This material is available free of charge via the Internet at http://pubs.acs.org.

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[7] Assuming this resonance corresponds to the acidic hydrogen of an octadecylphosphonic acid ligand bound to the nanocrystal accounts for only one hydrogen per 11.5 ± 2 % of the octadecylphosphonate moieties. Additional work is required to unequivocally assign this resonance.

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[9] The reaction of 7 with CdSe/ZnS core-shell particles was slower ($t_{1/2} > 12$ hr).

[10] The relative integrals of the methylene and methyl resonances (1:17) from the remaining aliphatic chains showed that they are composed of octadecyl chains.

[11] Adding **8** to our nanocrystals resulted in a ~5 nm shift of the fluorescence maximum.

[12] All reactions of chlorotrimethylsilane with nanoparticles were conducted with two equivalents relative to the number octadecyl chains in the sample as determined by ^{1}H-NMR spectroscopy. Addition of *excess* chlorotrimethylsilane results in etching of the CdSe particles, as evidenced by a blue-shifting of their absorption and fluorescence spectra, as well as a decrease in quantum yield of the CdSe/ZnS core-shell samples.

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[15] A small concentration (< 10%) of free surfactant ligands appeared upon the addition of **5**, that rapidly reached equilibrium. Surprisingly, heating this sample to 100°C for 16 hours made little difference to these spectra. Further experiments to probe this reaction are underway, and will be reported elsewhere.

[16] The important resonance structures of the dianionic form of octadecylphosphonic acid anhydride show that this moluecule, unlike **6**, is not chiral. Similarily, its protonated form shows a single line spectrum as a result of rapid hydrogen ion exchange between the P-OH and P=O functionalities (see Supporting Information). Similar chemical shifts were reported in Ref. 3a.

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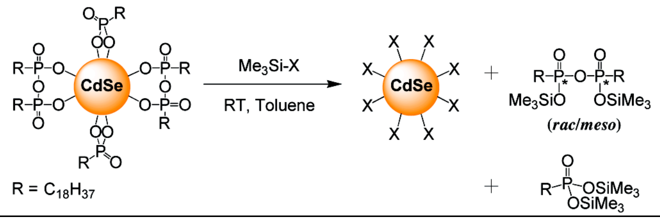

The surface chemistry of cadmium selenide nanocrystals, prepared from tri-*n*-octylphosphine selenide and cadmium octadecylphosphonate in tri-*n*-octylphosphine oxide, was studied with ^{1}H and $\{^1H\}^{31}P$ NMR spectroscopy as well as ESI-MS and XPS. The identity of the surface ligands was inferred from reaction of nanocrystals with Me_3Si-X (X = -S-$SiMe_3$, -Se-$SiMe_3$, -Cl and -S-$(CH_2CH_2O)_4OCH_3$)) and unambiguous assignment of the organic byproducts, *O,O'*-bis(trimethylsilyl)octadecylphosphonic acid ester and *O,O'*-bis(trimethylsilyl)ocatdecylphosphonic acid anhydride ester. Nanocrystals isolated from these reactions have undergone exchange of the octadecylphosphonate ligands for -X as was shown by ^{1}H NMR (X = -S-$(CH_2CH_2O)_4OCH_3$) and XPS (X = -Cl). Addition of free thiols to as prepared nanocrystals results in binding of the thiol to the particle surface and quenching of the nanocrystal fluorescence. Isolation of the thiol-ligated nanocrystals shows this chemisorption proceeds without displacement of the octadecylphosphonate ligands, suggesting the presence of unoccupied Lewis-acidic sites on the particle surface. In the presence of added triethylamine, however, the octadecylphosphonate ligands are readily displaced from the particle surface as was shown with ^{1}H and $\{^1H\}^{31}P$ NMR. These results, in conjunction with previous literature reports, indicate that as prepared nanocrystal surfaces are terminated by X-type binding of octadecylphosphonate moieties to a layer of excess cadmium ions.