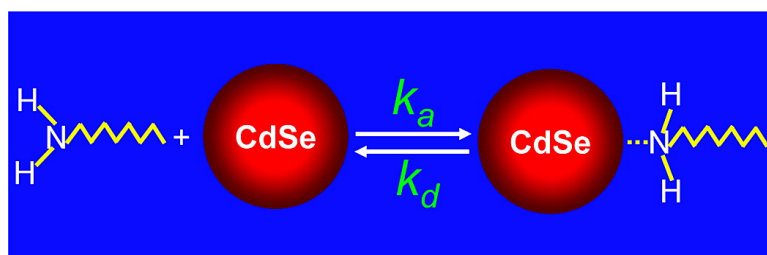Article

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Ligand Bonding and Dynamics on Colloidal Nanocrystals at Room Temperature: The Case of Alkylamines on CdSe Nanocrystals

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Abstract: With CdSe nanocrystals stabilized with very weak ligands (pyridine) as the starting materials, NMR techniques were applied to distinguish the bonded and free alkylamine ligands in an equilibrated adsorption/desorption system for the CdSe−amine nanocrystal−ligand pair. NMR and photoluminescence (PL) measurements were further correlated to identify the linear relationship between PL intensity and the surface ligand coverage of the amine-coated CdSe nanocrystals. For 3.5 nm CdSe nanocrystals and octylamine ligands, the chemical equilibrium constant (K) of the CdSe−amine nanocrystal−ligand adsorption/desorption process was found to be around 50−100, and the corresponding $\Delta_r G^o$ was calculated as 9.8−11.5 kJ/mol. With a proposed mathematic method, the corresponding chemical kinetic constants for the desorption (k_d) and adsorption (k_a) processes were measured to be 0.01 s^{-1} and 0.5 L mol^{-1} s^{-1}, respectively. K, k_d, and k_a obtained here are generally 2−4 magnitudes different from those estimated in literature. Analysis indicates that these constants are well consistent with the existing experimental observations.

Introduction

Surface organic ligands are well recognized as a key factor in synthesis and manipulation of colloidal nanocrystals.[1–3] Their integral role in the function of the nanocrystal−ligand complex, such as photoluminescence (PL) properties of semiconductor nanocrystals,[4–13] is also well-known. Furthermore, conjugation of biofunctional molecules onto colloidal nanocrystals solely relies on the properties of their surface organic ligands.[14] However, the bonding nature of organic ligands to the surface atoms of nanocrystals and the related bonding processes have

only marginally been studied. Typically, the bonding of nanocrystal−ligands can be described by its adsorption/desorption equilibrium constant, K, and the adsorption and desorption kinetic constants, k_a and k_d, respectively. K provides the thermodynamic feature of a nanocrystal−ligand system, whereas k_a and k_d proffer information of chemical kinetics and dynamics of the system. To our knowledge, it is quite difficult to accurately determine K, and the barrier for measuring k_a and k_d is even more daunting.[15,16]

Presently, CdSe nanocrystals are the most studied system for ligand chemistry.[3,4,15–19] Their size-dependent optical properties can be readily utilized as sensitive probes for studying bonding events of the surface ligands. For example, the optical properties of CdSe−amine nanocrystals−ligand system were used as the main probes for studying the ligand dynamics during the growth of the nanocrystals.[3] The dominating role of CdSe nanocrystals in the active field of quantum-confined semiconductor nanocrystals also requires such studies.

Recently, one report studied the nanocrystal−ligand bonding of CdSe nanocrystals coated with hydrophilic thiolate ligands in water, which utilized uncoated CdSe nanocrystals as the final

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state.[18] Also, several reports studied nanocrystal−ligand bonding at either room temperature[15,16,19] or growth temperatures[3] by using a system similar to that used in the related synthesis, namely CdSe−alkylamine nanocrystal−ligand system in nonaqueous solution. At present, the room temperature studies are the ones offering data for determining thermodynamic and kinetic constants.[15,16] In both cases, the studies were largely based on the enhanced PL of the nanocrystals by primary amines. However, these studies were all using CdSe nanocrystals coated with the original ligands obtained in the synthesis. As to be illustrated below, such nanocrystals biased the results so dramatically that they are not suited for quantitative studies.

Generally speaking, standardized protocols for the study of nanocrystal−ligand chemistry are mostly missing at this stage. An incomplete list of the problems for such studies includes the preparation of a proper nanocrystal sample for surface chemistry study, the distinction between free and bonded ligands, methods for monitoring bonding processes, and mathematic models for determining k_a and k_d. This work intends to explore these issues by quantitatively studying the model system—the CdSe−amine nanocrystal−ligand pair. We hope such studies shed new light on this important yet challenging subject, ligand and surface chemistry of high-quality colloidal nanocrystals.

Theoretical Preparation

Although general kinetic equations of adsorption and desorption are largely known, some special equations are needed for studying the related processes on nanocrystals by using their PL properties. These equations can be obtained with the following assumptions.

(i) Both adsorption and desorption are elementary steps expressed by eqs 1 and 2, respectively.

$$\text{Adsorption:} \quad M + L \rightarrow ML \qquad (1)$$

$$\text{Desorption:} \quad ML \rightarrow M + L \qquad (2)$$
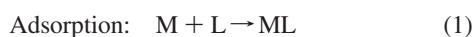
(ii) The surface bonding sites (M) on the surface of the nanocrystals in solution are the same as the ligands (L) and are indistinguishable by either their location or the surface ligand coverage on each nanocrystal.

(iii) A unique type of ligand is applied, and the interactions between the nanocrystals and any other molecules in the solution are negligibly weak in comparison to the nanocrystal−ligand (ML) bonding in study.

(iv) The processes occur under constant temperature and pressure.

(v) Chemical reactions other than the surface adsorption/desorption events, such as growth and dissolution of the nanocrystals, do not occur in the system.

(vi) The nanocrystals can be approximated as monodispersed sample (their size being d).

It should be noted that these assumptions are commonly seen in surface literature, such as when considering Langmuir isotherms. In fact, the experimental results of previous ligand-bonding studies seem to support the Langmuir adsorption mechanism for both semiconductor[15,16] and noble metal[20] colloidal nanocrystal systems. Some justifications of these assumptions are given in the Results and Discussion sections.

The reaction rates for reactions 1 and 2 are:

$$\text{Adsorption:} \quad (d[ML]/dt)_a = k_a[M][L] \qquad (3)$$

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$$\text{Desorption:} \quad (d[ML]/dt)_d = -k_d[ML] \qquad (4)$$

The average surface ligand coverage of the nanocrystals (Θ) can be calculated as:

$$\Theta = [ML]/([M] + [ML]) \qquad (5)$$

Because the number of bonding sites ($[M] + [ML]$) is constant for a given sample, eqs 3 and 4 become:

$$\text{Adsorption:} \quad (d\Theta/dt)_a = k_a(1 - \Theta)[L] \qquad (6)$$

$$\text{Desorption:} \quad (d\Theta/dt)_d = -k_d\Theta \qquad (7)$$

For the CdSe−amine nanocrystal−ligand system described here, PL intensity (I_{PL}) is often used as the probe for surface ligand coverage. In literature,[16] PL intensity and the surface ligand coverage of the nanocrystals are assumed to be linearly related (to be confirmed in this work):

$$I_{PL} = \alpha\Theta \qquad (8)$$

Here, α is a structural constant. Evidently, when $\Theta = 1$, I_{PL} should reach a theoretical maximum, $I_{PL,max}$. Therefore, the chemical meaning of α is $I_{PL,max}$ (eq 9).

$$\alpha = I_{PL,max} \qquad (9)$$

By substituting eqs 8 and 9 into eqs 6 and 7, the changing rates of PL intensity during adsorption and desorption processes are obtained.

$$\text{Adsorption:} \quad (dI_{PL}/dt)_a = k_a(I_{PL,max} - I_{PL})[L] \qquad (10)$$

$$\text{Desorption:} \quad (dI_{PL}/dt)_d = -k_dI_{PL} \qquad (11)$$

The desorption kinetic constant, k_d, can be determined experimentally. The following analysis is valid under two different bases. First, if the desorption process is an elementary step as assumed above, the analysis can be considered as a direct result of eq 11. Conversely, if the desorption mechanism is unknown and may involve multiple elementary steps, the following analysis should be considered as the determination of the observed k_d, more specifically $^{obs}k_d$. In the latter case, the following method for determining k_d still needs eq 8 to hold true (see some detail discussion about this below).

The specific experiment can be designed as follows. A tiny volume of nanocrystals with a given ligand coverage is rapidly injected into a large volume of pure solvent. This immediately enables the desorption process because the initial free ligand concentration in the pure solvent is 0. Thus, the adsorption rate should be 0 at the moment of injection. Following this, the PL spectra are recorded with the necessary time resolution, from which the temporal evolution function of PL, $I_{PL}(t)$, can be determined.

$$I_{PL}(t) = (a_0 + a_1t + a_2t^2 + a_3t^3 + \ldots) \qquad (12)$$

Here, eq 12 is the Taylor expansion of the time (t) dependence of I_{PL} where the constants, a_0, a_1, a_2, a_3,..., are the Taylor expansion coefficients. Specifically, a_0 is the PL intensity ($I_{PL,0}$), and a_1 is the first derivative of PL intensity ($(dI_{PL}/dt)_{d,0}$) at time $= 0$.

If the temporal evolution of PL intensity is determined with a reasonable time resolution, a polynomial fit of the data can be obtained by using common-office software, such as Microsoft Excel and Origin. At time $= 0$, one can then calculate k_d by using eq 13.

$$k_d = (\ln 2)/t_{1/2} = -(dI_{PL}/dt)_{d,0}/I_{PL,0} = -a_1/a_0 \qquad (13)$$

Equation 13 also provides the relationship between the half-life (or lifetime, $t_{1/2}$) and k_d of a desorption process. By definition, the half-life is the time needed for the nanocrystal ensemble to lose 50% of the surface ligands in a pure desorption process. It must be pointed out that eq 13 is based on the fact that, at time = 0, only the desorption process exists.

Evidently, eq 13 requires that desorption is a first-order process, which is true if it is an elementary step, as assumed above. If the mechanism is not known, the dilution experiment can be repeated with a series of initial concentrations of the nanocrystal—ligand complex. If a_1 and a_0 determined in such a series of dilution experiments are linearly related to each other, one can conclude that the desorption process is experimentally confirmed to be first-order in nature, and eq 13 is thus valid.

The adsorption kinetic constant, k_a, can also be calculated by using an algorithm similar to the one described above. Instead of nanocrystals coated with substantial ligand coverage, uncoated nanocrystals are used. These nanocrystals are rapidly mixed into a solution of suitably concentrated free ligands ($[L]_0$). In such an experiment, adsorption is the sole process at the initial time. A polynomial fit similar to eq 12 can then be applied for the temporal evolution of I_{PL} in the adsorption process, which shall identify the necessary polynomial coefficients, specifically a_0 and a_1. With these two coefficients, k_a can then be calculated from eq 10.

$$k_a = a_1/(I_{PL,max} - a_0)[L]_0 \qquad (14a)$$

and

$$k_a = a_1/(I_{PL,max}[L]_0) \qquad (14b)$$

Equation 14b accounts the fact that, in a pure adsorption process, the surface of the nanocrystals should have no ligands on it. This means that a_0—representing the initial PL intensity at time 0—should be 0. Again, eq 14 are formulated by assuming that the adsorption process is a first-order process against either of the two reactants, the free ligands or the bonding sites. As discussed for the measurement of k_d, this can be verified experimentally by performing the pure adsorption experiment with a series of nanocrsytal and/or ligand concentrations.

The equilibrium constant, K, can be obtained by performing experiments with both desorption and adsorption processes. Under such conditions, the total changing rate of the surface ligand coverage is the sum of two processes.

$$d\Theta/dt = (d\Theta/dt)_a + (d\Theta/dt)_d = k_a(1 - \Theta)[L] - k_d\Theta \qquad (15)$$

and

$$dI_{PL}/dt = k_a(I_{PL,max} - I_{PL})[L] - k_d I_{PL} \qquad (16)$$

Equation 15 is the general equation and eq 16 is the specific one if the experiments are monitored by the PL intensity, and eq 8 is satisfied. At equilibrium, both eqs 15 and 16 equal to 0. This gives us eqs 17 and 18.

$$K = k_a/k_d = \Theta_{eq}/[(1 - \Theta_{eq})[L]_{eq}] \qquad (17a)$$

$$\text{or} \quad \Theta_{eq} = K[L]_{eq}/(1 + K[L]_{eq}) \qquad (17b)$$

$$K = k_a/k_d = I_{PL,eq}/[(I_{PL,max} - I_{PL,eq})[L]_{eq}] \qquad (18a)$$

$$\text{or} \quad I_{PL,eq} = KI_{PL,max}[L]_{eq}/(1 + K[L]_{eq}) \qquad (18b)$$

It should be noticed that some of the parameters in eqs 17 and 18 must be equilibrium values, which are specified by the subscript eq. For PL-based experiments, eq 18 would be the

one to use. However, in this case, it becomes quite tedious to calculate $[L]_{eq}$ for every individual data point, so to simplify calculations, eqs 8 and 9 can be brought into eq 18 and solved under equilibrium conditions. The solution—eq 19—allows for a direct fitting of $[L]_0$ vs $I_{PL,eq}$.

$$[L]_0 = I_{PL,eq}/[K(I_{PL,max} - I_{PL,eq})] + \pi d^2[P]I_{PL,eq}/A_L I_{PL,max} \qquad (19)$$

By the definition above, $[L]_0$ is the initial ligand concentration used to obtain each data point in an isotherm; also, d, $[P]$, and A_L are the size of the nanocrystals, the nanocrystal concentration, and the cross section area of the ligands in its densely packed monolayer or single crystal, respectively. Equation 19, as opposed to eq 18b, uses $I_{PL,eq}$ as the x-axis. One can also solve $I_{PL,eq}$ from eq 19 and plot the data by using $[L]_0$ as the x-axis. However, the latter equation is mathematically much more complex. In addition, the two terms on the right side of eq 19 have a clear chemical meaning, that is, the free ligand contribution in the first term and the bonded ligand contribution in the second one. After fitting a series of data by using eq 19, one can readily obtain both K and $I_{PL,max}$ as the fitting variables.

It should be mentioned that because K, k_a, and k_d are associated with each other ($K = k_a / k_d$), one can calculate K from k_a and k_d determined by using the algorithms represented by eqs 13 and 14a, or vise versa. Furthermore, with the K value obtained in eqs 17−19, one can also calculate $\Delta_r G^o$ for the adsorption/desorption equilibrium by using eq 20.

$$\Delta_r G^o = -RT \ln K \qquad (20)$$

The special feature of eqs 13 and 14 is worth to be discussed further; they can be based on experimental results. Consequentially, they do not rely on either assumptions 1 or 2 made at the beginning of this section or a specific adsorption model. In other words, Langmuir-type adsorption is not a requirement for applying these relationships, and the adsorption and desorption processes do not need to be elementary reactions, either. Under such circumstances, the obtained k_a and k_d are observed kinetic constants. Also, because chemical equilibria do not require a clearly identified chemical mechanism, such experimental kinetic constants may still be applicable for calculations of K.[21] In this sense, eqs 13 and 14a offer a different pathway to study ligand chemistry for colloidal nanocrystals.

Still, the application of eqs 13 and 14 requires that the system satisfies eq 8, and the processes are first-order against each reactant (see above). However, if there exists another measurement that yields a defined relationship of surface ligand coverage, variations of eqs 13 and 14 can be formulated for the analysis of the experimental data. Furthermore, it is possible to formulate some algorithm for determining the reaction order and the kinetic constants simultaneously if the adsorption/desorption process is not a first-order process. For this work, eq 13 and 14 are sufficient as the data support first-order processes (see below).

Results

Surface preparation in studying nanocrystal—ligand bonding is as important as it is in any other branch of surface science. Generally, it is infeasible to study bonding events in vacuum, but it is possible to prepare the nanocrystals to be at a relatively

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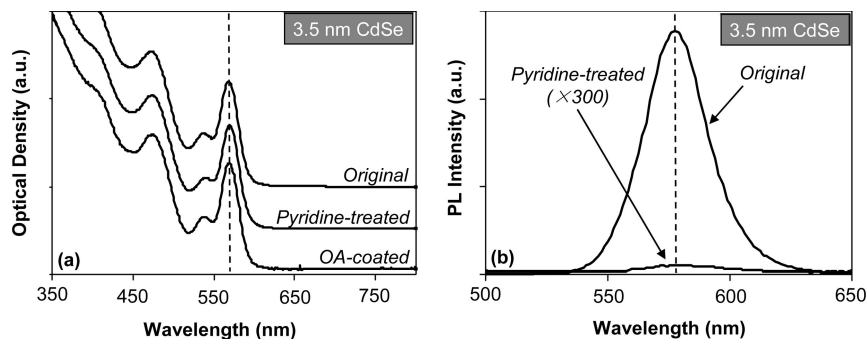
Figure 1. Optical properties of CdSe nanocrystals in different stages of surface treatment.

naked state. For CdSe and other chalcogenide nanocrystals, pyridine is known to offer a labile and reversible bonding with the surface cadmium ions.[15,22,23] Common organic ligands used in synthesis and for surface modification are Lewis bases, and their bonding strength can be roughly estimated by their ionization constants as a base, k_b. For instance, the k_b of pyridine is about 4−5 orders smaller than those related to the fatty amines used in this study. This substantial difference implies that the pyridine-treated CdSe nanocrystals can be considered as naked nanocrystals for relatively strong ligands, such as fatty amines and thiols.

The extremely weak bonding nature of pyridine, however, may cause oxidation and aggregation of the inorganic nanocrystals. Oxidation reduces the size of the nanocrystals and can thus be detected as a blue shift of the absorption and PL spectra.[24,25] To prevent oxidation, solvents used in the nanocrystal treatments were degassed or anhydrous solvents from the vendors. Other sources mentioned that a relatively high concentration of amine could etch CdSe nanocrystals, indicated by blue-shifted PL.[16] Opposite to this, aggregation causes a red shift of the spectra. Influences on aggregation and oxidation, which were found to often drastically distort the adsorption/desorption data, are summarized in the Supporting Information. The main solvent used in this work was chloroform, although most experiments were also repeated in hexanes (see Supporting Information and Experimental Section). In the latter case, the pyridine-treated nanocrystals were still stored in chloroform because of their good stability in chloroform.

The complete procedure for the preparation of pyridine-treated CdSe nanocrystals is presented in the Experimental Section. However, one crucial step is worth briefly mentioning. The first step for a complete replacement of the original ligands is to remove the majority of the free ligands in the nanocrystal stock solution. As we observed previously,[26] the extraction of free ligands by methanol from octadecene−hexane solutions is sufficient to achieve this goal yet gentle enough to prevent aggregation. This was a key step to ensure the complete removal of the original ligands by the following pyridine treatment. At present, the overall reproducibility of the sample preparation is about 90%.

The pyridine-treated nanocrystals should maintain the original optical spectra strictly (within 1 nm peak shift) to ensure no

oxidation, etching, and aggregation of the nanocrystals (see above). As shown in Figure 1, the contour and peak position of the absorption and PL spectra of this specific sample were the same in different stages. The PL brightness of the pyridine-treated nanocrystals, however, decreased by about four magnitudes, indicating at least 99.9% removal of the original ligands if eq 8 holds. Although the quenching of PL of CdSe nanocrystals by pyridine treatment indicates the removal of the original ligands, the mechanism could be either the fast dynamic and weak bonding of the pyridine or hole traps introduced by pyridine.[5]

The successful removal of the original ligands was further confirmed by ¹H NMR. Well-known in the field of colloidal nanocrystals, the NMR peaks of surface ligands are significantly broader than those of the corresponding free ligands.[22,27] Specifically, similar broadening was also reported for as-synthesized CdSe nanocrystals.[19] There are two models to explain this broadening.[22,27] One model assumes that the slow motion of the nanocrystals causes the broadening because of the quasi-solid state nature of the nanocrystals. The other model indicates that this broadening is a result of the inhomogenity of the chemical environment of the ligands on the surface of a nanocrystal. Although our results seem to support the inhomogenity broadening (see below), it is not a main concern in this work to distinguish the exact model. For quantitative calculations, we assume that the peak broadening of the surface ligands is a general phenomenon, and the degree of broadening is determined by a given nanocrystal−ligand system.

The NMR spectrum of a CdSe nanocrystal sample coated with the original ligands from synthesis is shown in Figure 2a. The two sharp peaks are from two solvents, chloroform (CHCl₃) at 7.27 ppm and acetone at 2.05 ppm. Although the broad features in the spectrum that range from 0.5 to 3 ppm can reasonably be associated with the surface ligands, it was impossible to match the spectrum with any of the potential ligands present in the original synthetic system. Very likely, it was a mixture.

Pyridine treatment removed the broad features in the 0.5−3 ppm spectral window (Figure 2b), although the CHCl₃ solvent peak and a very weak acetone peak were still present. Around 1 ppm, there are several sharp peaks from hexanes introduced for isolation of pyridine nanocrystals (see Experimental Section). The most-dominating features are the three very broad peaks of pyridine in the spectral window from 6.5 to 9 ppm. These spectral features confirmed the complete removal of the original

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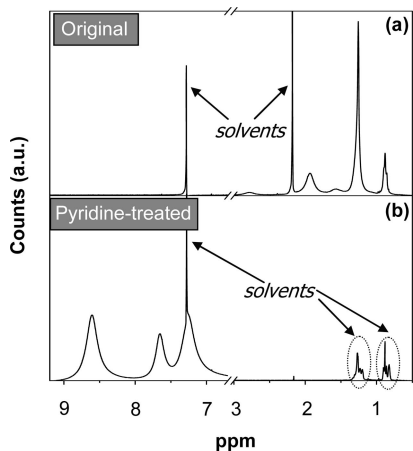
Figure 2. ^{1}H NMR spectra of the CdSe nanocrystals coated with the original ligands (a) and treated with pyridine (b). The samples were dispersed in CDCl$_3$.

surface ligands suggested by PL measurements (Figure 1, right panel). Indicated by the evidence below, the pyridine molecules are unlikely all bonded ligands, although the NMR peaks are broad.

Surface replacement of original ligands on CdSe nanocrystals grown by the original Cd(CH$_3$)$_2$-based route was systematically studied by Kuno et al. in the 1990s. Their study revealed that there always existed a small portion of the original ligands that could not be removed by any type of ligands under their conditions.[4] However, by using a different strategy for ligand exchange and different sources of CdSe nanocrystals (synthesized via greener methods), the removal of the original surface ligands down to the detection limit of NMR was demonstrated.[17,18] This indicates that the surface-ligand replacement is largely dependent on the chemical processes and also probably the source of nanocrystals.

The surface adsorption of fatty amines onto the pyridine-treated CdSe nanocrystals in D-chloroform (CDCl$_3$) was studied by NMR along with PL measurements. Octylamine (OA), a liquid fatty amine at room temperature, was chosen as the main target, although some other amines were also studied to a certain extent. The NMR spectra for the α-hydrogens of OA in the window between 2.5 and 2.85 ppm, along with the pyridine signals, are shown in Figure 3a for various amine concentrations. With no OA present in the solution, the broad pyridine peaks were the only detectable signals in the spectrum. Interestingly, the broad pyridine peaks are converted to sharp ones even when low concentrations of OA were present. This result first confirms that there is no noticeable adsorption competition between pyridine and amines, even if the amine concentration is very low. Second, it further supports that the broadening of the NMR peaks of surface ligands on nanocrystals is likely due to the diverse chemical environment of the ligands instead of the slow motion of the solid-like particles.[22,27] This phenomenon will be discussed in detail along with the line shape evolution of the NMR peaks associated with the OA ligands.

The NMR signals from the α-hydrogens of OA change gradually from a broad feature to three sharp peaks as the OA concentration increases from 4 to 100 mM. This gradual change is qualitatively reasonable. When a limited amount of OA was present, nearly all OA molecules were bonded onto the surface of the nanocrystals, indicated by a very broad feature. As the OA concentration increased, the concentration of the free ligands increased gradually. Eventually, when the free ligands became

dominant in the solution, the NMR spectrum should become similar to that of the free OA in the solution, meaning three sharp peaks for the α-hydrogen.

To quantitatively distinguish the broad peaks of bonded ligands from the sharp signals of the free ligands, it is necessary to have a standard for the bonded ones. We chose a sample with a substantially high nanocrystal concentration but a low total ligand concentration in comparison to the sample series in consideration (see Experimental Section). This reference sample, therefore, had a very low ligand coverage that was just sufficient for the nanocrystals to be soluble in the selected solvent system. Given the large K values reported in the literature[15,16] and found below, the free ligand concentration was assumed to be 0 for the reference sample. It should be noticed that this reasonable approximation slightly overestimates bonded ligands and underestimates free ligands in the solution. The NMR spectrum of the reference sample (black line in Figure 3b and c) was found to be even broader than that of the sample in Figure 3a with the same amine concentration (4 mM, the lowest amine concentration in the entire series). On the basis of this reference spectrum, one can then fit each NMR spectrum in the experiment series to determine the ratio between the bonded and free ligands (see examples in Figure 3b and c).

After the peak fitting, the supposed contribution from the free ligands (red line in Figure 3b and c) is not as sharp as those from the free ligands, although it is much sharper than the contribution from the bonded ones (black line in Figure 3 b and c). A possible reason is that the free ligands, especially at low ligand concentration, can actually feel the existence of the nanocrystals. The kinetics data reveal that, on average, 50% of the surface ligands of a nanocrystal would exchange once with the free ligands in solution in about 70 s. As a result, the free ligands in this nanocrystal−ligand system would experience a more diverse chemical environment within the NMR time scale (about 110 s for recording each spectrum) than that for the true free ligands without the presence of any nanocrystals. This diverse chemical environment results in significantly broadened peaks in a nanocrystal−ligand system.[27] Evidently, this effect should have a greater impact on the free ligands in the solution with a low initial OA concentration, which is consistent with the slightly broader red line in Figure 3b than that in Figure 3c. This very same argument can also be made for the pyridine-treated nanocrystals.

As a rather weak bonding ligand, it is difficult to imagine that all of the pyridine molecules in the pyridine−nanocrystal solution would bond to the nanocrystal surface. The likelihood is that all the pyridine molecules in the pyridine-treated nanocrystal solution would experience the bonding events within a very short time frame. In this way, nearly all pyridine molecules would be associated with the nanocrystals, although only a small portion of them would directly bond to the surface at a given moment. This dynamic picture is also consistent with the fact that all three pyridine peaks became as sharp as the peaks of free molecules (Figure 3a), even with a low OA coverage on the surface of the nanocrystals, as discussed above. When a small amount of strong and bulky amine ligands is bonded to the nanocrystal's surface, the extremely fast dynamics of the pyridine bonding must be greatly hindered, if not be completely stopped. As a result, the majority of pyridine molecules can no longer participate in the dynamic bonding events, and thus, behave like free molecules in the solution to yield sharp NMR signals.
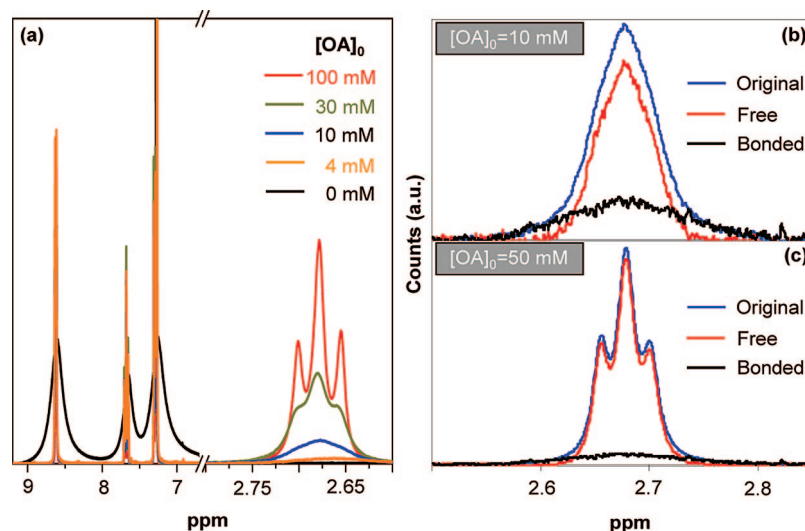
Figure 3. (a) ^{1}H NMR spectra of the pyridine treated CdSe nanocrystals (OD = 10) after equilibrium with a given concentration of OA. (b) and (c) Peak fitting of the NMR spectra in the spectral range related to the α-hydrogen of OA.
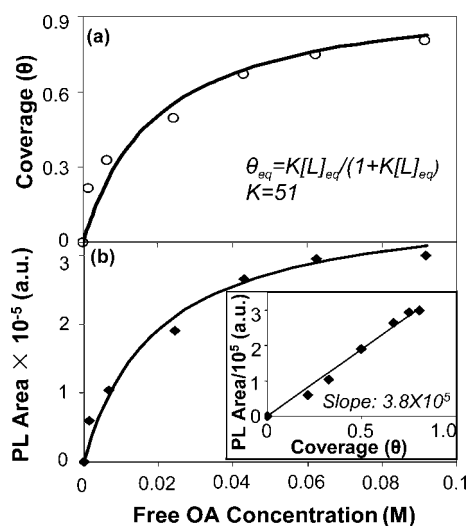

Figure 4. (a) OA surface coverage vs free OA concentration in the solution determined by the NMR method. The solid line is the fitting curve obtained with eq 17b. (b) PL area of the same sample series vs free OA concentration. The solid line is the fitting curve obtained with eq 18b. (Inset: linear relationship of PL area and surface coverage.)

The surface ligand coverage of the sample series shown in Figure 3 are plotted in Figure 4a by using the free amine concentration as the x-axis. Equation 17b, the famous Langmuir isotherm, was fit to the experimental data. The free- and surface-ligand concentrations were both calculated from the integrated areas of the corresponding components (Figure 3). The cross-section area (A_L) of each OA ligand used in the calculation of the total available bonding sites ([M] + [ML] in eq 5) was considered to be 0.18 nm^2, which is similar to the value found in the single crystals and dense monolayers of typical molecules with a long hydrocarbon chain.

The integrated PL intensity (PL area) of the same series of samples was also measured, and the results are plotted in Figure 4b. Clearly, the PL intensity and surface coverage—determined by the NMR method—follow a very similar trend. A good linear fit was obtained by plotting the PL intensity vs the surface ligand coverage (Figure 4b, inset). This linear relationship was repeatedly observed in our experiments indicating that eq 8 is a reasonable assumption. It should be pointed out that if

significant aggregation/oxidation was spotted by spectroscopy (see Supporting Information), the linear relationship was seriously distorted.

The linear fitting of PL area and surface ligand coverage, shown in the inset of Figure 4b, was forced to go through the origin. As a result, the points at relatively low surface ligand coverages were found to be generally below the linear fitting. By examining the NMR method discussed above, one could conclude that this is due to the overestimation of the bonded ligands of the reference spectrum. We assumed that all ligands in the reference spectrum were the surface ligands, which should contribute a small and systematic positive error for the surface coverage calculated by using this reference (see above). Nevertheless, this error seems to be quite small. Importantly, the $I_{PL,max}$, which equals the slope of the linear fitting, offered an excellent fitting of the experimental results in Figure 4b by using eq 18b.

Single molecular spectroscopy experiments have revealed that PL of CdSe nanocrystals either emit in a given intensity or exist at a dark state.[28] This intermittency has been repeatedly observed, although the exact mechanism is not yet clear. The linear relationship of PL intensity and ligand surface coverage (Figure 4b, inset) implies that the probability of the dark state of a CdSe nanocrystal should increase linearly upon reduction of the surface ligand coverage. From a dynamic viewpoint, a linearly decreasing PL intensity (Figure 4b, inset) is quite reasonable. Upon photoexcitation, different decay channels compete with each other. As the surface ligand coverage decreases, the number of the surface-trap states on a nanocrystal should increase linearly, and the related nonradiative decay should thus increase linearly as well.

As noted in the Theoretical Preparation section, the equilibrium constant, K, can be determined by using either NMR or PL data. The values determined for CdSe−OA nanocrystal−ligand complex with 3.5 nm nanocrystals were in the range of 50−100 for nanocrystals from different stock solutions and/or with different batches of pyridine treatment. This value is about 2−3 magnitudes smaller than that reported by Bullen and Mulvaney

(28) Nirmal, M.; Dabbousi, B. O.; Bawendi, M. G.; Macklin, J. J.; Trautman, J. K.; Harris, T. D.; Brus, L. E. *Nature* **1996**, *383*, 802–804.
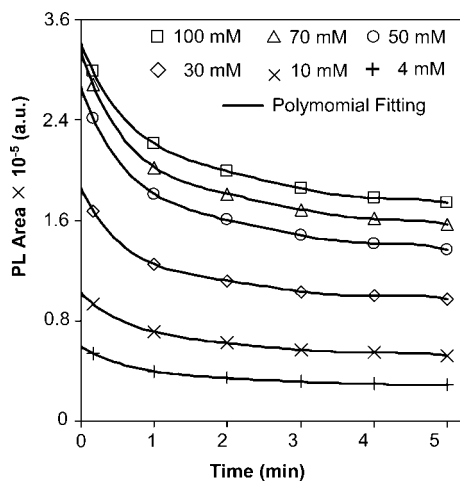
Figure 5. Temporal evolution of PL area by the addition of 30 μl of CdSe—OA solution (OD = 10, [OA] = 4 $\approx$ 100 mM) into 1.97 mL of pure CHCl₃. The solid lines are the polynomial fit of the experimental data for each reaction.

for the CdSe—amine system,[15] and it is about 3—4 magnitudes smaller than the estimated value reported by Munro et al. for the equilibrium constant between CdSe nanocrystals and the native amine ligands.[16] It should be pointed out that the cross-section area (A_L) for OA is also a factor affecting the K value. For instance, if A_L were chosen to be 0.20 nm², the K value would be 74 for the data series in Figure 4. This uncertainty caused by A_L still falls within the experimental values mentioned above. It should be noted, however, that bonding sites are more intrinsic to the system than the surface area for bonding. Here, we adopted the surface area as an average measure of the bonding sites because of the difficulty in exactly mapping the surface composition and structure. In fact, the average distance between Cd ions on wurtzite CdSe is about 0.4—0.5 nm, which matches reasonably well with the dense packing distance for alkyl amines.

Although the K values have been found to vary over a significant range, the corresponding $\Delta_r G°$ values are in closer proximity—between 9.8 and 11.5 kJ/mol—which seems to be reasonable in comparison to some values found in the literature for nanocrystal—ligand pairs with a strong interaction. For instance, the $\Delta_r G°$ of the adsorption/desorption equilibrium was found to be around 50 kJ/mol for gold—thiol nanocrystal—ligand pair[20] and 30 kJ/mol for CdSe—thiol nanocrystal—ligand pair. [18]

As pointed out in eq 19 and the related text, the most convenient way to obtain the K value from the PL data is to plot the initial free amine concentrations used to establish the adsorption/desorption equilibrium vs the integrated PL intensity. To demonstrate the feasibility of this method, the data shown in Figure 4b are replotted in Figure 2S (Supporting Information), and the fitting results are also provided.

The determination of the desorption and adsorption kinetic constants, k_d and k_a, relies on the temporal evolution of the PL intensity of a given sample (see eqs 13 and 14). To measure k_d, experiments were performed by placing a small volume of nanocrystal solution with a high particle concentration into a large volume of pure solvent (see details in Experimental Section). The PL spectrum of the diluted solution was recorded as soon as possible and continued for a certain amount of time. One series of data of nanocrystals with different surface ligand coverages is plotted in Figure 5. The polynomial fit of each reaction is also shown in the plot.
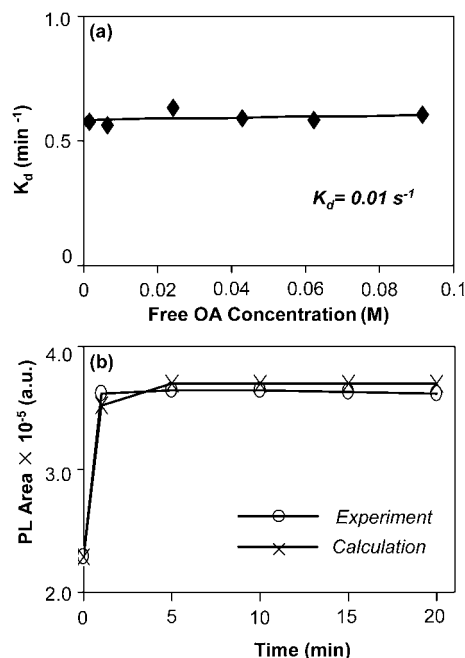

Figure 6. (a) k_d values obtained with different initial OA concentrations. (b) Experimental and calculated temporal evolution of PL upon the addition of amine (5 M, 20 μL) into 2 mL of CdSe solution.

Each of the polynomial fitting functions shown in Figure 5 can be applied to calculate the k_d value by using eq 13. The results shown in Figure 6a reveal that all of the six k_d values are nearly the same. The average value is 0.01 s⁻¹, and the corresponding half-life of desorption, $t_{1/2}$, is 70 s. This time scale is the fundamental reason why an accurate determination of k_d values is possible by using our simple experimental setup with a low time resolution. The k_d value calculated in Figure 6a for the CdSe—amine system, however, differs by about 2 magnitudes from the value estimated by Bullen and Mulvaney.[15]

As pointed out in the Theoretical Preparation section, the method for determining k_d values used here does not rely on the nature of the adsorption—desorption model. Instead, it is valid as long as the desorption process is a first-order process against the surface ligand coverage of the nanocrystals. The essentially identical k_d values for different samples shown in Figure 6a directly verify that the first-order nature exists in the current system. Thus, the method is valid.

Furthermore, the results in Figure 6a somewhat support the unique bonding-site assumption (the second assumption in the Theoretical Preparation section), which is a key assumption needed for the Langmuir model. The samples used to measure k_d varied from each other by close to 1 magnitude in terms of the initial surface ligand coverage. The similar k_d values in Figure 6a thus indicate that the desorption process of the amine ligands from the nanocrystal surfaces did not change with surface ligand coverage.

Although a similar method is also formulated to obtain the k_a value (see eq 14 and related text), our current experimental setup cannot offer a reasonable temporal resolution of the adsorption process. Another option is to calculate the corresponding k_a value from the K and k_d values determined above by using the relation $K = k_a / k_d$, which gives k_a being 0.50 L mol⁻¹ s⁻¹. Again, this value is quite small in comparison to the value estimated for a similar system.[15]

This calculated k_a value can be verified by using a simple experiment. As shown in Figure 6b, a rapid increase of the PL
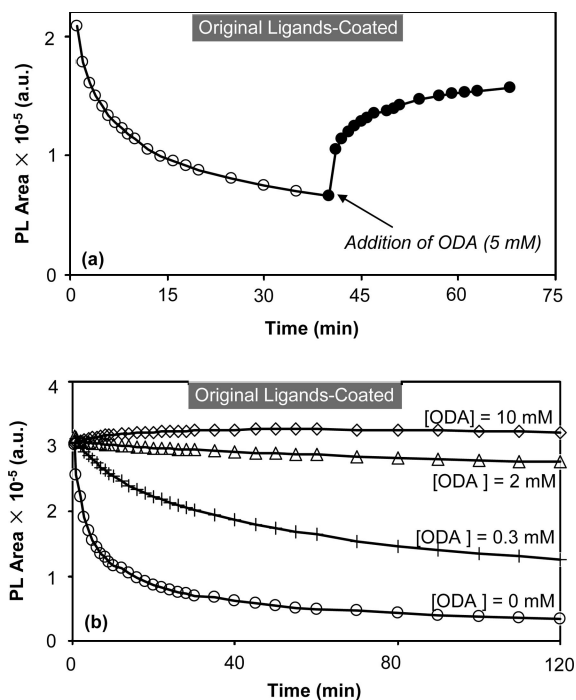
Figure 7. Desorption and adsorption properties of CdSe nanocrystals coated with original ligands (see text for detail).

intensity was observed when the concentration of the amines in the solution was suddenly boosted. As expected, this rapid increase was hard to temporally resolve by using our experimental setup. With the k_a and k_d values obtained above and the known amine concentrations, however, one can also calculate the adsorption curve for each experimental point by using the integrated form of eq 16 (see Supporting Information). A good match between the experimental and calculated curves is evidenced in Figure 6b.

Desorption and adsorption processes of CdSe nanocrystals coated with original ligands are illustrated in Figure 7 for comparison. Figure 7a illustrates the temporal evolution of PL brightness of the CdSe nanocrystals coated with the original ligands in a two-step experiment. First, a small volume of concentrated nanocrystal solution was injected into a large volume of pure solvent. This enabled an immediate desorption process, indicated by the gradual decrease of the PL intensity. At 40 min, a concentrated solution of octadecylamine (ODA)—supposedly the major ligands of the nanocrystals gained in the synthesis—was injected into the solution. This addition of the amine was equivalent to only 5 mM of initial free ligands in the nanocrystal solution. Although this concentration of ligands was very low in comparison to those shown in Figure 4, the PL intensity of the nanocrystals bounced back more or less to the original value before the desorption processes started.

The second set of experiments was performed by adding purified CdSe nanocrystals coated with the original ligands into ODA solutions with different concentrations (Figure 7b). The results indicate that saturation occurred when the amine concentration was a few millimolars, which is about 1−2 magnitudes lower than the saturation ligand concentration in Figure 4. In addition, when the ODA concentration was below 2 mM, the PL intensity decreased over time prior to reaching the equilibrium value, which indicates a process dominated by desorption. These results clearly reveal a significant surface coverage of the purified CdSe nanocrystals coated with the

original ligands. Consequently, only a small amount of ligands in the solution could bind onto the surface of the nanocrystals. This should significantly distort the adsorption/desorption data.

Overall, experiments with the nanocrystals coated with original ligands were much less reproducible than those using the pyridine-treated nanocrystals. It should also be pointed out that the exact saturation concentration of amines depended greatly on the degree of purification of the nanocrystal samples and is difficult to control.

Discussion

The substantial difference (2−4 magnitudes) of the K,[15,16] k_a, and k_d[15] values reported in the literature for the CdSe−amine nanocrystal−ligand system in comparison to what we obtained here is likely a result of the use of CdSe nanocrystals coated with the original ligands,[15] difficulty to distinguish free ligands from the bonded ones,[16] and lack of a reliable method for measuring k_a and k_d. In some cases, the nanocrystals were synthesized with different precursors/ligands, which may result in a different surface structure.

In those pioneer reports,[15,16] the initial PL intensity before the addition of amines was often more than 50% of the saturated values. In comparison, the pyridine treatment introduced here reduced the PL intensity of the original nanocrystals by at least 99.9% (Figure 1). Furthermore, the temporal evolution of the PL intensity of the nanocrystals in one of the reports did not show much decrease upon dilution by solvent.[15] These facts indicate significant amounts of free ligands in their starting materials, which would impact their PL-based measurements significantly (see Figure 7 and related text). In addition, the NMR results (Figure 2 and related text) reveal that the original ligands on the surface of the nanocrystals are likely more complicated than one composition. As a result, the surface adsorption process became complicated and could be better viewed as a surface-replacement process.

The mathematic algorithm (eqs 13 and 14) suggested in this work for the determination of the kinetic constants, k_d and k_a, seems to be quite practicable (see Figure 6 and related text). With a better time resolution, one could determine both k_d and k_a and calculate K. The time frame for measuring k_d in Figure 6a, as well as that for measuring k_a, was a few minutes instead of hours for a typical equilibrium-based experiment. Nanocrystal−ligand systems can be quite fragile, especially in the study of adsorption/desorption processes; thus, a short experimental time may offer a more reliable measurement of the constants. More importantly, as pointed out in the Theoretical Preparation section, this new method does not need to preassume an adsorption−desorption mechanism and can also be used for nonelementary reactions.

Semiquantitative understanding of the manipulation of nanocrystals by using K, k_d, and k_a, such as purification and surface-ligand replacement processes, can directly show the significance of surface-ligand chemistry. It can also illustrate the accuracy of these constants. For example, it was repeatedly reported that the surface amine ligands on CdSe nanocrystals could be readily removed in purification and dilution, which resulted in a significant decrease of PL brightness.[19,29] This particular process can be semiquantitatively explained by using the constants determined in this work.

A 3.5 nm CdSe nanocrystal fully coated with amines should have about 214 ligands on it, assuming A_L to be 0.18 nm². A

(29) Qu, L.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 2049−2055.

precipitation/decantation/redissolution cycle was usually performed with a particle concentration of 330 μM (see Experimental Section). This cycle would typically reduce the PL of the nanocrystals by approximately 50%, which means losing 50% of the ligands if eq 8 held roughly true. As a first-order approximation, one could reason that the decantation process in each cycle would remove the free ligands in the mother solution and force some of the bonded ligands to go into the fresh solvent upon redispersion to reach equilibrium between the bonded lignads on the nanocrystals and the free ones in the new solution. Upon 50% desorption of the bonded ligands in redissolution in the new solvent as mentioned above, the free ligand concentration in the solution was calculated to be around 35 mM by using the volumes from the Experimental Section. This value matched the free ligand concentration at equilibrium for the nanocrystals with 50% surface coverage reasonably well (see Figure 4a). Conversely, to make the nanocrystal solution with 100 μM of free amine estimated in a previous report,[16] each nanocrystal would lose less than one (0.3 in average) ligand in this specific example, which should not change the PL intensity upon redissolution and would thus be inconsistent with the experimental observation.

The typical lifetime for the desorption process, which is independent of both the ligand and particle concentrations and the surface ligand coverage (Figure 6a), was determined to be around 0.01 s^{-1} for typical samples. Provided that the desorption process was significantly slower than the adsorption process (comparing the desorption (Figure 5) with the adsorption (Figures 6b and 7) curves and related text), one could conclude that the ligand dynamics was determined by the desorption process. This means that about 50% of the surface ligands on a nanocrystal would be exchanged once with the free ligands in solution within about 70 s. This time scale should be sufficiently fast for the nanocrystals to lose PL brightness in a typical purification step, usually a few minutes.[19,29] Conversely, the $t_{1/2}$ of the desorption estimated by Bullen and Mulvaney,[15] around 4800 s, seems to be too long to allow a significant loss of ligands and decrease of the PL intensity in purification, even if losing ligands was thermodynamically feasible.

The 70 s lifetime calculated in the above paragraph by using the data reported in this work also provides an explanation for the experimental observations of ligand exchange. For instance, replacement of the surface amine ligands by the deprotonated thiols in methanol often occurred almost instantaneously.[17,18] Considering the significant barrier of the existing ligands, one could hypothesize that the desorption of the original ligands should play a rate-determining role in a ligand exchange process. Thus, the 70 s lifetime would be sufficiently fast to allow a rapid surface-ligand exchange process to occur.

The growth of high-quality nanocrystals undoubtedly relies on ligand dynamics.[3] In the growth of high-quality nanocrystals in nonpolar solvents, the processes are evidently kinetically controlled, which is the foundation for the size and shape control of the resulting nanocrystals. The ligand dynamics in the CdSe−amine nanocrystal−ligand system is on the minute time scale at room temperature as discussed above. This seems to be too slow to be noticeable for the growth of nanocrystals, which is consistent with the fact that the growth of CdSe nanocrystals with OA as ligands should be carried out under elevated temperatures.[3] Upon heating the system to the growth temperature range (140−360 °C), desorption events would be greatly accelerated, thus allowing the growth of the nanocrystals to occur in an appreciable rate. It should be pointed out that

although the k_d and k_a values obtained at room temperature could provide some perspective about the ligand dynamics at elevated growth temperatures, quantitative determinations of these kinetic constants at the corresponding temperatures would offer much more quantitative and precise guidelines for designing new synthetic strategies for high-quality nanocrystals.

Conclusion

Although surface chemistry of colloidal nanocrystals cannot usually be studied in vacuum, samples with properly prepared surfaces could still be made for quantitative studies, such as the pyridine-treated CdSe nanocrystals in the current work. In this study, the extremely large specific surface area of colloidal nanocrystals allowed the application of some routine analytic tools, such as solution NMR, in the surface chemistry studies. By combining these advantages, it was possible to distinguish the surface-bonded ligands from the free ones and identify the linear relationship between the surface coverage and the PL intensity of the samples. This provides the basis for the determination of the chemical equilibrium constant of the CdSe−amine nanocrystal−ligand pair, K. Furthermore, these experimental advantages coupled with some mathematical considerations (eqs 13 and 14) offered means to determine the related desorption and adsorption kinetic constants, k_d and k_a. In comparison with the values estimated in the literature,[15,16] these thermodynamic and kinetic constants are found to be substantially more consistent with the existing experimental observations. The results in this work are quite encouraging for more efforts to quantitatively and systematically explore the rich field of surface chemistry of colloidal nanocrystals. Such explorations shall uncover much needed knowledge for establishing reliable and rational strategies for growth, manipulation, and surface modification of high-quality nanocrystals.

Experimental Section

Materials. Octylamine (Aldrich), octadecylamine (Alfa), anhydrous pyridine (Aldrich), D-hexane (Alfa), D-chloroform (Alfa), D-methanol (Aldrich), acetone (EM Science), anhydrous hexanes (Alfa), methanol (EM Science), and anhydrous chloroform (Aldrich) were used without further purification. 1-Octadecene (ODE, Alfa) and hexane (EM Science) used in the purification of the original CdSe nanocrystals by extraction by using the hexane/methanol/ODE system were dried with Na.

The original CdSe nanocrystals in hexanes were supplied by NN-Labs and synthesized by using a procedure similar to that published previously.[29] The nanocrystals were purified by using the reported procedure to remove unreacted starting materials and side products.[26] The full width at half-maximum of the corresponding PL peak of the nanocrystals was about 25 nm, measured with an optical density (OD) of 0.1−0.2, and the absorption peak position was at about 568 nm (approximately 3.5 nm). All OD was measured at the first exciton absorption peak position with 1 cm cuvette in this work. For concentrated solutions, a proper dilution was needed to bring the OD down to a measurable value. For 3.5 nm CdSe, the extinction coefficient at the first exciton peak (568 nm) is 1.62 × 10^5 (L/mol cm),[30] which allows us to calculate the particle concentration.

Preparation of Pyridine-Protected CdSe Nanocrystals. The original nanocrystals, although purified by the standard procedure, still had a significant amount of the original ligands to maintain their bright PL. To remove the excess amine that remained in the original ligand-coated CdSe nanocrystal solution, approximately 2.5 mL of the original ligand-coated CdSe nanocrystals (OD = 35)

(30) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. *Chem. Mater.* **2003**, *15*, 2854–2860.

was extracted with 2.5 mL of methanol; the nanocrystals were dispersed in the hexanes layer, and the ligands were disperesed in the methanol layer. Chloroform (200 μL) and excess acetone (about 3:1 ratio to the extracted hexanes solution containing the nanocrystals) was added into the hexanes solution to precipitate the nanocrystals. The nanocrystals were isolated through centrifugation and decantation. The nanocrystal pellet on the bottom of the vial was redissolved in 2.5 mL of pure pyridine. For complete exchange, the nanocrystal/pyridine solution was sonicated for 1 h and placed in the dark overnight.

Excess hexanes were added to the nanocrystal/pyridine solution to precipitate the nanocrystals. The nanocrystal precipitate was isolated by centrifugation and decantation. This precipitate was redissolved in 0.5 mL of pyridine and sonicated for 30 min. After this second run of pyridine treatment, the CdSe nanocrystals were precipitated with 1 mL of D-hexane, isolated by centrifugation and decantation, and redissolved in 0.3 mL of pyridine by sonication for 5 min. The final pyridine-protected nanocrystals were isolated by precipitation with 0.5 mL of D-hexane, centrifugation, and decantation, and then, immediately dispersed into a defined volume of D-chloroform to make a solution (OD = 60) for NMR measurements.

After the first pyridine treatment, the nanocrystals might need to be separated by an extraction procedure by using the hexane/methanol/ODE system, if the nanocrystals could not be precipitated by hexanes. This extraction procedure was different from that described above. Typically, methanol (0.5−1.0 mL) was added into 2.5 mL of pyridine-treated CdSe nanocrystals diluted by 2.5 mL hexane, and then, about 2.5−5.0 mL of ODE was added to help the system form two phases. After removing the colorless nonpolar phase, the colorful methanol phase containing the nanocrystals stabilized by pyridine was isolated by precipitation with hexanes, centrifugation, and decantation for the following pyridine treatment.

If not for NMR study, it was unnecessary to use D-hexanes and D-chloroform. In the entire process, it was essential to avoid complete drying of the nanocrystals. Instead, the nanocrystal precipitates had to go to the next dissolution as soon as possible to avoid aggregation. It was found to be helpful to avoid unnecessary photoradiation in all the steps, although the entire procedure was not carried out in a dark room.

¹H NMR Measurements. ¹H NMR measurements were all carried out on a Bruker 300 MHz instrument. The typical volume of the solution was 600 μL.

The ¹H NMR spectrum of CdSe nanocrystals coated with the original ligands was obtained with samples treated differently from what is described above for the original nanocrystals prior to the pyridine treatment. Approximately 2.5 mL of original ligand-coated CdSe nanocrystals (OD = 35) was precipitated with excess acetone once and with D-methanol twice. This final precipitate was dissolved in D-hexane (OD = 50) for NMR measurements. To maintain a decent surface coverage and reflect the natural status of the nanocrystals more, it was necessary to carry out this purification process in a high concentration of nanocrystals. Additionally, purification with deuterium solvents helped minimize the solvent peaks, which are also sharp and thus dwarf the broad signal from the nanocrystals.

The ¹H NMR study of CdSe nanocrystals in desorption/adsorption processes was performed after the pyridine-treated nanocrystals were mixed with a given concentration of amine and equilibrated for at least 1.5 h. By using the sample with 100 mM OA as an example, the OA-coated CdSe nanocrystals were prepared by mixing 100 μL of the concentrated pyridine-treated CdSe nanocrystal solution in D-chloroform (OD = 60) with 500 μL of 120 mM free OA in D-chloroform in a NMR tube. Separate solutions were made for each targeted amine concentration, that is, 4, 10, 20, 30, 50, and 70 mM. The reference spectrum was made with 1.5−2 times the amount of the same pyridine-treated nanocrystals, although the total volume of the mixture was maintained at 600 μL (150 μL of the concentrated pyridine-treated nanocrystal

solution and 450 μL of 4.4 mM OA solution in D-chloroform). The OA concentration in this reference sample was 4 mM.

Desorption/Ddsorption of Amine Ligands. Desorption/adsorption of amine ligands onto CdSe nanocrystals coated with the original ligand was performed with the nanocrystals obtained from the supplier after one precipitation with excess acetone. The nanocrystals purified by using this simple procedure were redissolved in hexanes in a high concentration (OD = 40) as the stock solution for the PL studies. The desorption experiment in Figure 7a was performed by adding an aliquot of the stock solution into a pure solvent. After the solution was monitored for 40 min, a concentrated solution of ODA was swiftly injected into the solution to make the final ODA concentration right after the injection be 5 mM. The desorption experiments in Figure 7b were performed by adding the stock solution into 2 mL of ODA/hexane solution with different ODA concentrations (final OD = 0.2−0.3). The temporal evolution of the integrated PL intensity of the nanocrystals during the desorption/adsorption processes was recorded and normalized to the exact OD of each sample.

Adsorption of OA. Adsorption of OA onto the pyridine-treated CdSe nanocrystals was studied by using PL measurements. The pyridine-treated CdSe nanocrystals (freshly made) were precipitated from the mother solution in a glass cuvette and dissolved in the OA solutions in the concentration range from 4 to 100 mM. Alternatively, the pyridine-treated nanocrystals dissolved in chloroform with a high concentration could also be injected into the amine solution directly. The solvent used for the amine could be either chloroform or hexanes for the first option, and chloroform was used for the latter case. The final optical density was between 0.1 and 0.3. Temporal evolution of the PL intensity during the adsorption process of amine ligands was recorded. Sometimes, the adsorption process might be started with a sample going through a desorption process (Figure 6b) for a certain amount of time. In this case, the adsorption was initiated by adding a small volume of high concentration of amine into the existing nanocrystal solution. The temporal evolution of the integrated PL intensity of the nanocrystals during the desorption/adsorption processes was recoded and normalized to the exact OD of each sample.

Desorption of OA. Desorption of OA on the CdSe nanocrystals was studied with the OA-coated nanocrystals made by mixing OA and the pyridine-treated nanocrystals; this mixture was equilibrated for at least 1.5 h. The desorption process was initiated by adding the concentrated OA-coated nanocrystal solution into the corresponding pure solvent, typically 2 mL, and the final optical density was above 0.1 but below 0.3. The temporal evolution of the integrated PL intensity of the nanocrystals during the desorption processes was recorded and normalized to the exact OD of each sample.

UV−vis and PL spectra. UV−vis and PL spectra were recorded on an HP 8453 UV−vis spectrophotometer and Hitachi F-4500 fluorometer, respectively. The excitation wavelength for the PL measurements was 350 nm. For the temporal evolution of PL spectra, the nanocrystal samples were placed in the UV excitation only during the measurements. The OD for measuring the PL intensity was set above 0.1 but below 0.3. The PL intensity was identified to be linear in this OD range. All PL intensities reported, however, were normalized to OD = 0.3 for uniformity.

Supporting Information Available: Experimental results of the alternative fitting of the data in Figure 4b and effects of photo-oxidation. This material is available free of charge via the Internet at http://pubs.acs.org.

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