Surface Sites and Ligation of Amine-capped CdSe Nanocrystals

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Abstract

The conversion of colloidal nanocrystals (NCs) into various applications is usually facilitated by designing and controlling their surface properties. A key strategy for tailoring surface properties is to modulate surface ligands. Amines, as L-type ligands, have been universally introduced into various surface modifications, promoting NCs synthesis, processing and performances. However, a full understanding of the nature of the amine-capped NCs surface has yet to be established, due to several challenges, such as the presence of various surface, subsurface and bulk sites along with the presence of surface dynamic. In this work, we addressed the issue on CdSe NCs, looking at both NC surface sites and the ligation of amine based on the combination of $^{113}\text{Cd}$, $^{77}\text{Se}$ and $^{15}\text{N}$ NMR spectroscopy, respectively. In particular, dynamic nuclear polarization (DNP) enhanced $^{113}\text{Cd}$ and $^{77}\text{Se}$ NMR allowed acquisition of high quality 1D spectra, thus enabling the identification of bulk and surface sites on different facets. Amines terminated sites on both Se-rich facets and nonpolar facets were resolved by $^{113}\text{Cd}$ 2D NMR spectroscopy, augmented with density function theory (DFT) calculations. In addition to directly bonding to surface sites, amines interaction through hydrogen-bonding with absorbed water and carboxylate surface ligands were further revealed by $^{15}\text{N}$ NMR. The insight into the complexity of amine-capped CdSe NCs surface and the characterization methodology developed in this work is an important step towards rational design, assessing surface modification as well as improving the processing of colloidal NCs towards their exploitation in various applications.
Introduction

Colloidal semiconductor nanocrystals (NCs) with sizes in the quantum confinement regime, are among the most widely studied class of nanoscale materials.\(^1\) They can be regarded as nanometer-sized fragments of the corresponding bulk single crystalline core stabilized with a monolayer of organic ligands. The confinement of electronic states within the core endows NCs with a high degree of tunability to the optical and electronic properties.\(^2\) Broadly, the absorption, luminescence properties, and the electronic charge carriers mobility can be finely modulated by the selection of chemical composition, size, and dimension of core.\(^3\) These characteristics have made NCs holding the promise of important advances in diverse applications, including light-emitting devices,\(^4,5\) photovoltaics,\(^6,7\) bioimaging,\(^8,9\) as well as catalysis\(^10,11\) to name but a few.

The properties, performances and resulting applications are also directly related to the properties of NCs surface.\(^12\) Due to their typical sizes of only few nanometers, a large fraction of the component atoms in a NC are at the surface. These atoms are usually incompletely bonded within the crystalline lattice, showing different electronic configuration from the atoms of the core crystal. Their distinct electronic energy states can trap electrons, quench fluorescence emission, and reduce charge transfer rates.\(^12,13\) In nearly all applications, these surface atoms need to be bonded to coordinating ligands. As a consequence, manipulating surface ligands was found to be an effective strategy to dictate the NCs’ surface structures and thus properties.

Starting from pristine synthesis\(^14,15\) of NCs, surface ligands play multiple roles ranging from enabling colloidal stability,\(^16,17\) controlling shapes/morphology,\(^18–21\) passivating the surface defects\(^22,23\) and acting as soft matter in the assembly of artificial solids.\(^14,15,24\) Furthermore, the ligands also affect the optical properties\(^25,26\) and solution processibility,\(^17,27,28\) and dictate the interfacial energy\(^29\) and charge transfer\(^30,31\) of NCs. The initial introduction of surface ligands occurs during the synthetic procedure.
In most applications, however, the native ligands are not sufficient to meet the requirements. To modify the surface properties, they are usually exchanged with specific functional ligands of different features in binding group or pendant structure to tune their ultimate properties and transpositions into applications.\textsuperscript{13} This highlights the significance of surface chemistry modification by post-synthetic ligand exchange.

Amines have been universally introduced as L-type ligands\textsuperscript{32} for surface modifications of NCs, boosting both synthesis\textsuperscript{20,33–35} and performances.\textsuperscript{36–39} For instance, amines have been used as coordinating solvents during the synthesis of both II–VI and III–V NCs leading to narrow size distributions in the early years,\textsuperscript{40} replacing the role of trioctylphosphine oxide (TOPO). The addition of excess amine ligands was also found to drastically promote the photoluminescence quantum yield (PLQY) of NCs.\textsuperscript{36} Besides, amines are usually used to stabilize anionic surfaces of NCs, facilitating surface reactions\textsuperscript{41} and controllable growth.\textsuperscript{42,43} Amines are also introduced to NCs for manipulating the surface stoichiometry which is associated with both colloidal stability and PLQY.\textsuperscript{44} Furthermore, amines are found to be an ideal class of ligands to promote the efficiency and operational lifetime of QLED devices.\textsuperscript{26}

Despite many significant advances in surface modification of NCs by utilizing amines, the detailed understanding on amine-capped NCs surface at the atomic level have been limited or rarely achieved. The lack of knowledge of the amine binding sites, binding modes and thus their binding strength can, not only hinder the rational design for surface modification, but also misestimate the reactivity of NCs surface for chemical processing in industry. Accessing the detail of NCs surface, especially for amines, is highly challenging because of their inhomogeneous and dynamically changing nature. For example, as shown in Figure 1, a CdSe NC can be regarded as a polyhedron with surface truncated by diverse and specific crystalline facets,\textsuperscript{45} though featuring a nearly spherical shape upon observation with most
transmission electron microscopes (TEM). Fundamentally, Cd-rich facets, Se-rich facets and nonpolar facets can be formed under different synthesis or processing procedures. These facets can possibly provide multitudes of binding sites for amines. In practice, most NCs systems usually interact with two or several types of ligands on the surface, which further complicates the situation.

Accessing the detail of NCs surface primarily relies on only a few analytical techniques, such as TEM,\textsuperscript{46–48} X-ray crystallography\textsuperscript{49,50} or photoelectron spectroscopy (XPS),\textsuperscript{51} mass spectrometry (MS)\textsuperscript{52,53} and nuclear magnetic resonance (NMR) spectroscopy.\textsuperscript{54,55} Among them, NMR is a key information-rich technique, which can achieve a high spectroscopic resolution to identify the chemical speciation of the surface as well as provide structural, conformational and dynamic information. In principle, it can be applied for resolving surface of NCs comprehensively because most NCs systems are composed of NMR active nuclei, such as $^{113}$Cd, $^{77}$Se, $^{207}$Pb, $^{31}$P, $^{17}$O, $^{13}$C, $^{15}$N, $^{1}$H, etc., ranging from inorganic surface fractions to organic ligands. However, solid-state NMR (SSNMR) intrinsically suffers from the low sensitivity of the relevant nuclei, such as $^{113}$Cd or $^{77}$Se. Recently, dynamic nuclear polarization (DNP) under magic angle spinning (MAS) has been shown to significantly enhance the sensitivity of SSNMR experiments at cryogenic temperatures by transferring the polarization from unpaired electron spins of exogenous polarizing agents to nuclear spins.\textsuperscript{56} Notably, dynamic nuclear polarization surface enhanced NMR spectroscopy (DNP-SENS)\textsuperscript{57,58} strategies have been developed to study nanoparticles; the use of an inert solid matrix, such as mesoporous silica,\textsuperscript{59} enables dispersion of nanoparticles and maintaining their proximity to the DNP polarizing agents within a glassy matrix at low temperatures. The DNP-based techniques do not only offer a better assessment of low natural-abundance nuclei present in NCs, but also enable the efficient implementation of multi-dimensional NMR experiments,\textsuperscript{60–62} which aid in resolving the NCs surface.

Here, we report a combined experimental and computational study on amine-capped NCs. Taking
CdSe spherical NCs (QDs) with tailored surface as a model system, DNP enhanced $^{113}$Cd and $^{77}$Se NMR experiments were performed to identify the bulk and surface sites. By means of $^{113}$Cd-${}^1$H cross polarization magic angle tuning (CPMAT) 2D experiments, amine-terminated sites from Se-rich surface and neutral surface were pinpointed. The origin of their featured $^{113}$Cd chemical shielding anisotropy (CSA) were further seized by calculations performed within the [Cd(SeH$_2$)$_x$(L)$_{4-x}$]$^{2+}$ (L: ligand) cluster models. Moreover, $^{15}$N NMR in combination with computational modelling including periodic density function theory (DFT) calculations revealed that the amines can, not only directly ligate Se-rich facets and nonpolar facets, but also interact with absorbed water on the surface through hydrogen bonding.

Results and discussion

Models under study: amines-capped CdSe NCs. In this work, we focus on alkylamine-capped CdSe NCs as prototypical systems of study. In order to encompass various cases of amine ligand bindings on NCs surfaces, different surface reactions were used to introduce amines into CdSe NCs systems. The stearate-capped CdSe quantum dots (spheroidal NCs), denoted as QD-St, were synthesized and purified according to reported procedures$^{63}$ as starting point for further surface reaction with amines. The surface of as-synthesized QD-St is expected to be Cd-rich considering that the only available surface ligands in the synthetic system were carboxylates (stearates). The average diameter of QD-St was ~3 nm, according to the TEM image shown in Figure S1. The corresponding ultraviolet-visible (UV-vis) absorption (Figure 2b) and PL spectra (Figure S2) further confirm the size and shape within a narrow distribution. Here, three different surface reactions were carried out on QD-St in order to introduce amines into tailored surfaces, respectively. All the samples were purified after reactions to remove excess ligands before further characterizations. Figure 2a depicts the reaction workflows of
QD-St. First of all, we performed a direct ligand exchange reaction on QD-St by adding excess dodecylamine (DAm) to prepare QD-St/DAm. The zinc-blende QD-St is expected to be dominated by Cd-rich facets (e.g., {100} and {111} facet) stabilized by carboxylate along with a small fraction of nonpolar facets (e.g., {110} facet), as discussed in previous studies. The Cd-carboxylates (Z-type ligand) on Cd-rich facets can be displaced through complexation with amines (L-type ligand). The removal of surface Cd moieties exposes the subsurface Se atoms, and forms the Se-rich facets probably coated by amines.

Second, prior to exchange with amines, carboxylate ligands on QDs were first completely replaced by thiolates. QD-St was exchanged with dodecanthiol (DSH) to produce QD-DS and then reacted with excess DAm to produce QD-DS/DAm. Compared with Cd-carboxylates, Cd-thiolates features much lower complexing capacity to amines. Using thiolates instead of carboxylates for termination, the Cd-rich facets can be maintained under reaction with amines, leaving only nonpolar facets capable of binding amine ligands.

Finally, QD-St was reacted with excess Se and DAm at 150 °C to convert the surface from Cd-rich to Se-rich state. Se-rich facets can be formed by growing an additional layer of Se atoms on top of QD-St surface. In this case, the Se atoms on Se-rich surfaces are expected to be protonated to keep neutrality and be solely coated by amines ligands; denoted QD-SeH/DAm.

The surface moiety changes of QDs during the amine modification can be monitored by the wavelength of the lowest absorption peak in UV-vis absorption spectra, shown in Figure 2b. In comparison with QD-St (abs. 550 nm), the absorption peak of QD-St/DAm blue-shifts to 545 nm, indicating the removal of surface Cd moieties. The absorption peak of QD-DS/DAm is maintained at 550 nm, consistent with the absence of changes for the surface moiety. An apparent red-shift of absorption peaks occurred in QD-SeH/DAm (abs. 573 nm), confirming the successful layer growth of
Se on QDs surfaces.

As the starting point of all the surface reactions with amines is QD-St, the carboxylates on surface can act as reaction descriptors and be tracked by solid-state $^{13}$C NMR spectra (Figure 2c). The carboxylate (COO$^-$) on QDs surface exhibits a typical $^{13}$C chemical shift of 185 ppm for QD-St. A residual COO$^-$ signal with a slight shift was observed in QD-St/DAm, indicating that amines cannot completely displace Cd-carboxylates on the surface. In other words, the surface of QD-St/DAm should include carboxylates coated Cd-rich facets. Note that the COO$^-$ signals are not observable in the spectra of QD-DS/DAm and QD-SeH/DAm, confirming the removal of carboxylate ligands from the surface. Figure 2d illustrates the corresponding solution-state $^1$H NMR spectra. The broadened resonances, especially the one at $\sim$2.7 ppm (which should be assigned to $\alpha$-CH$_2$ of DAm), support that all the observed amine ligands are bonded to the surface rather than being free. This assignment is further corroborated by the presence of asymmetric (3141 cm$^{-1}$) and symmetric (3229 cm$^{-1}$) N-H stretching signals in FT-IR spectra (Figure 2e). More interestingly, an additional signals at $\sim$ 3300 cm$^{-1}$ appears for QD-St/DAm, probably reflecting a more complex ligation of amines on surface.

The results above suggest that CdSe QDs displaying different facet compositions and thereby different preference of capping ligands have been prepared as expected. While carboxylate and thiolate ligands occupy Cd-rich surfaces, neutral electron donor amine ligands are expected to bind on nonpolar facets or protonated Se-rich facets. Therefore, with varying facet speciation and thereby specific ligand sets, one would expect these samples can serve as promising models for the studies in the following.

**Probing the NCs surface by $^{113}$Cd, $^{77}$Se and $^{15}$N CPMAS NMR.** As for the surface of amines-capped CdSe NCs, the surface Cd/Se sites and their corresponding ligation by amines can be opportunely explored by $^{113}$Cd, $^{77}$Se and $^{15}$N NMR, respectively. First and foremost, in order to investigate the surface sites of CdSe NCs by $^{113}$Cd and $^{77}$Se NMR, DNP enhanced cross polarization magic angle
spinning (CPMAS) experiments were carried out for signal enhancement. In this study, 1,1,2,2-tetrachloroethane (TCE), TEKPol, and meso-SiO$_2$ (pore size = 100 nm) were used respectively as solvents, radicals, and inert porous solid matrix for QDs DNP formulation.

Figure 3a illustrates the DNP enhanced $^{113}$Cd$\left\{{^1}H\right\}$ CPMAS spectra of CdSe QDs with different surface components, including QD-St, QD-St/DAm, QD-DS/DAm, and QD-SeH/DAm. All studied QDs have the same single-crystalline core, the internal core Cd atoms (bonded with four Se atoms), that can be readily assigned by the same isotropic $^{113}$Cd resonance signal at –65 ppm. Other signals observed in $^{113}$Cd NMR spectra are likely associated with surface Cd atoms. As a matter of fact, not only the $^{113}$Cd isotropic shifts, but also their CSAs are greatly impacted by different surface ligations of QDs, further confirming their assignment to surface species.

For QD-St, the $^{113}$Cd NMR signal centered at –330 ppm with the characteristic spinning sideband pattern (SSB) is assigned to the surface Cd atoms bonded to carboxylates, consistent with previous reports. Another $^{113}$Cd signal, slightly shifted ($\delta_{iso} = –350$ ppm) but with a much lower relative intensity, also appears in QD-St/DAm; it is due to surface sites associated with the displacement of Cd-carboxylate moieties on surface. The $^{113}$Cd NMR spectrum for QD-DS/DAm is dominated by a resonance at –35 ppm without a noticeable spinning sideband, which is attributed to the surface Cd sites bonded to thiolate ligands, as thiolates dominate the surface of this sample. This assignment can be also corroborated by the $^{113}$Cd NMR spectra of CdSe capped by pure thiolate ligands (QD-DS), as shown in Figure S3.

In QD-SeH/DAm, the surface $^{113}$Cd signal at –150 ppm with several spinning sidebands is observed. It should be related to the Cd atoms from Se-rich facets, considering that the Se-rich facets are dominated and solely capped by amines for this sample. In the case of QD-St/DAm sample, which is expected with same amine-capped Se-rich facets, the corresponding signal is possibly covered up by
the signal from Cd-carboxylates (δ = –350 ppm) with intense spinning sidebands. Notably, this $^{113}\text{Cd}$ resonance at -150 ppm is not found in QD-DS/DAm. The Cd signal associated with amine capped nonpolar facets are perhaps overlapped with the signal of core Cd, making it trackless in 1D spectra. Employing $^{77}\text{Se}$ NMR measurements to probe the surface Se sites can be complementary to $^{113}\text{Cd}$ NMR. The corresponding DNP-enhanced $^{77}\text{Se}\{^1\text{H}\}$ CPMAS spectra are shown in Figure 3b. Similarly, the $^{77}\text{Se}$ core signals are found at –523 ppm for all samples. The surface $^{77}\text{Se}$ signal are mainly centered at ~620 ppm. The sharp surface signal observed in QD-St is likely due to the isotropic environments for subsurface Se atoms under Cd-rich facets. Two shoulders around this main surface signal appear after exchange with the amines in QD-St/DAm. Noteworthy, whereas both of them appear, even more prominently, in QD-SeH/DAm, the upfield shoulder does not appear in QD-DS/DAm. We thus attribute the upfield side shoulder to Se atoms on Se-rich facets and the downfield shoulder to nonpolar facets; with the Se atoms probably interacting with surface amine ligands.

Following probing the surface sites, $^{15}\text{N}$ NMR experiments were implemented aimed at accessing the ligation of amine on surface. For purpose of balancing sensitivity and resolution, $^{15}\text{N}$ NMR experiments were performed on $^{15}\text{N}$ labeled dodecylamine capped CdSe QDs at room temperature. Figure 3c shows the $^{15}\text{N}\{^1\text{H}\}$ CPMAS NMR spectra. In general, the $^{15}\text{N}$ NMR spectra shows diverse resonances which vary between 32 ppm and 45 ppm. Comparing with the other two, the $^{15}\text{N}$ NMR spectrum of QD-DS/DAm is much simpler, which is in line with the fact that amine ligands are expected to be binding to nonpolar facets only. Two resonances centered at ~41 ppm (green) and ~39 ppm (blue) can be properly deconvoluted; both resonances should be assigned to amine ligands on nonpolar facets with possibly different ligation modes. On the basic of this assignment, the spectrum of QD-St/DAm can be deconvoluted into four resonances while the spectrum of QD-SeH/DAm can be deconvoluted into five NMR lines.
In QD-St/DAm, another two signals appear at ~43 ppm (orange) and $\delta_{\text{iso}} \approx 33$ ppm (pink). In addition, these signals can be also fitted with the same chemical shifts in the spectrum of QD-SeH/DAm with the additional of the resonance at ~45 ppm (grey). All these signals could be possibly correlated to the amine ligands on Se-rich facets, yet it is challenging to confidently assign them.

**Pinpointing the surface sites by DNP enhanced $^{113}\text{Cd CPMAT 2D experiments.** The 1D $^{113}\text{Cd}\{^1\text{H}\}$ or $^{77}\text{Se}\{^1\text{H}\}$ CPMAS NMR spectra have shown the capability to identify the bulk and surface sites with different ligand terminations. However, the characteristic large CSA of surface signals and insufficient MAS rates (e.g., 10 kHz at cryogenic temperatures), made it untenable to gain an unambiguous identification of surface sites solely from 1D NMR spectra due to the lack of resolution. Under limited MAS rates, 2D cross polarization magic angle turning (CPMAT) experiments enable correlation of isotropic chemical shifts to their spinning sideband manifolds (containing isotropic and anisotropic shifts) with promoted resolution than 1D spectra. Here, we performed DNP-enhanced 2D $^{113}\text{Cd}\{^1\text{H}\}$ CPMAT experiments for further identifying the various surface sites, as schemed in Figure 4(1a-4a). The corresponding 2D spectra are shown in Figure 4(1b-4b). Typically, the slices in indirect dimension correspond to pure isotropic shifts, while the spinning sideband patterns can be extracted from the direct dimension of 2D CPMAT spectra. Figure 4(1c-4c) illustrates the projected spinning sideband patterns and their fitting CSA parameters of $^{113}\text{Cd}$ isotropic shifts. For QD-St with dominated Cd-rich facets purely capped by carboxylates (Figure 4(1a)), it is not surprising that there are only two isotropic Cd resonances being resolved in Figure 4(1b). The signal $\delta_{\text{iso}} = -65$ ppm presenting small CSA ($\Omega = 77$ ppm) is assigned to core Cd while the signal at $\delta_{\text{iso}} = -327$ ppm with large CSA ($\Omega = 420$ ppm) is assigned to surface Cd bound to carboxylate ligands. In the case of QD-St/DAm, four isotropic $^{113}\text{Cd}$ resonances with various CSA are observed (Figure 4(2b)). The two upfield signals, at $\delta_{\text{iso}} = -327$ ppm and $\delta_{\text{iso}} = -227$ ppm (indicated by blue dash lines), are assigned to the surface Cd
carboxylates because of their similarly large $\Omega$ and asymmetric parameter ($|k| = \sim 0.1$). The new emerging Cd signal at $\delta_{\text{iso}} = -143$ ppm is associated with surface amine ligations. Finally, while the signal located at $-63$ ppm displays an isotropic chemical shift consistent with the core signals, this signal manifests more intensive spinning sidebands than the one in QD-St, indicating a larger CSA (vide infra for further comments). The QD-DS/DAm only shows two downfield $^{113}\text{Cd}$ signals (Figure 4 (3b & 3c)). One $^{113}\text{Cd}$ NMR signal located at $\delta_{\text{iso}} = -63$ ppm with observable spinning sidebands.

Another signal $\delta_{\text{iso}} = -34$ ppm should be attributed to the surface Cd sites of Cd-rich facets terminated by thiolates, as discussed above. Besides, in QD-SeH/DAm, two isotropic $^{113}\text{Cd}$ NMR signals can be resolved, as shown in Figure 4(4b & 4c). The signal $\delta_{\text{iso}} = -149$ ppm, which is consistent with the one observed in QD-St/Dam ($\delta_{\text{iso}} = -143$ ppm), should correspond to Cd atoms from Se-rich facets capped by amines because of their dominated fraction for this sample. Another signal is centered at $-63$ ppm, showing pronounced spinning sideband.

The core structure of QDs ought to be mostly immune to the surface reactions, hence the core Cd should be endowed with a similar and small CSA (as shown in Figure 4(1c)). In all the three amine-capped CdSe QDs samples, the presence of intense spinning sidebands of resonance at $-63$ ppm indicates that Cd atoms are in more asymmetric environments. This could be the case of the Cd atoms of subsurface layers which become more disorder after surface reactions. Besides, it is more reasonable to propose that the observed $^{113}\text{Cd}$ signal at $\delta_{\text{iso}} = -63$ ppm consists of two components (Figure 4(2c-4c)), including one with small CSA ($\Omega = 77$ ppm, orange) corresponds to core Cd, while another one with larger CSA ($\Omega = 249$ ppm, purple) is assigned to surface Cd atoms, likely associated with amines termination. Owing to its ubiquitous appearance in all studied amine-capped CdSe QDs, this surface signal should be rationally explained by Cd sites from nonpolar facets capped by amines.

**Understanding the $^{113}\text{Cd}$ NMR chemical shifts within CdSe NCs.** Although amine-terminated
surface sites from both Se-rich facets and nonpolar facets can be properly distinguished by 1D and 2D $^{113}$Cd NMR, it remains intriguing to know where the $^{113}$Cd chemical shifts and CSA are coming from within CdSe NCs. For example, it is surprising that the Cd atoms from core and amine-capped nonpolar facets share similar isotropic chemical shifts. To further validate the assignment of $^{113}$Cd NMR signals, DFT calculations were performed. While periodic chemical shielding calculation would be ideal for NCs with fine crystalline core structures, the $^{111/113}$Cd NMR chemical shifts are significantly influenced by spin-orbit coupling, making accurate periodic calculations not readily accessible. The binary semiconductor CdSe is an ionic crystal in which anionic Se$^{2-}$ and cationic Cd$^{2+}$ atoms are each coordinated tetrahedrally by four nearest neighbor atoms of opposite charge. We thus adopted model, a single cadmium ion in a tetrahedral environment, $[\text{Cd}(\text{L})_4]^{2+}$ (L: terminated ligand) to represent the local geometries as a function of the facets and different ligations as it was shown to be a robust approach to assess the change of electronic structure and NMR response. In the case of zinc blende CdSe QDs study, the surface Cd atoms on Cd-rich facets(e.g. $\{100\}$) should be coordinated by two Se atoms, while the Cd atoms of nonpolar facets(e.g. $\{110\}$) are coordinated by three Se atoms. For the Se-rich facets (e.g. $\{100\}$) and the core, the Cd atoms are coordinated to four Se atoms. In these models, the formal Se$^{2-}$ bound to Cd$^{2+}$ are replaced by SeH$_2$ while the other ligands L are CH$_3$COOH, CH$_3$CH$_2$NH$_2$ and CH$_3$CH$_2$SH, to form a $[\text{Cd(SeH}_2)_x\text{(L)}_{4-x}]^{2+}$ (x = 2, 3, 4) complex, as shown in Figure 5a.

Relative to the model of core Cd (with four Se coordination), the $^{113}$Cd $\delta_{\text{iso}}$ of thiolate terminated Cd-rich facets is downfield shifted. The Cd of nonpolar facets model terminated by amines exhibits nearly the same $\delta_{\text{iso}}$ as core Cd, albeit with larger CSA($\Omega$). Understandably, compared with core Cd, surface Cd coordinated by three Se atoms and one N atoms (model of nonpolar facets) demonstrate reduced asymmetry and hence pronounced CSA. With increasing N atom coordinated, the $\delta_{\text{iso}}$ of amine
terminated Se-rich facets model shifts upfield. Moreover, the $^{113}$Cd chemical shifts of carboxylate terminated Cd-rich facets model manifests even more deshielding. Overall, there is a good agreement between calculation and experimental results, as demonstrated in Figure 5b.

The trend of $^{113}$Cd chemical shift of different surface models for NCs can be understood by analyzing the contribution of chemical shielding (See Supporting Information). As the diamagnetic contribution is independent of chemical environments (Table S1), the $^{113}$Cd chemical shielding of [$\text{Cd(SeH}_2)_x(L)_4$]$_{2+}$ is determined by both paramagnetic ($\sigma_{\text{PARA}}$) and spin-orbit coupling contributions ($\sigma_{\text{SO}}$) (Figure 5a). Prominently, $\sigma_{\text{PARA}}$ become larger for the model of amines terminated nonpolar facet compared with core Cd, because one coordinated Se of Cd was replaced by N. While the corresponding $\sigma_{\text{SO}}$ decreased, explaining why their $\delta_{\text{iso}}$ are similar even if Cd adopted different coordination. For the model of amine terminated Se-rich facet, its increased $\sigma_{\text{PARA}}$ and $\sigma_{\text{SO}}$ lead to $\delta_{\text{iso}}$ shifted upfield. Moreover, the $\delta_{\text{iso}}$ of carboxylate terminated Cd-rich facet models (O coordinated Cd) is dominated by the dramatically increased $\sigma_{\text{PARA}}$, leading to an upfield shifts, compared with Cd with four Se coordination. The results above also suggest that the $^{113}$Cd chemical shift within CdSe NCs is mainly determined by the type and number of ligand terminations, rather than specific structures.

**Predicting the surface ligation of amine on CdSe NCs surface.** As discussed above, $^{15}$N NMR shows high spectral resolution, which can properly provide detailed information of surface amine ligands. To further uncover the ligation of amines at the surface, we resorted the detailed analysis with computational methods. First, to model the ligation of amines at the surface of CdSe NCs, three types of low-index facets of zinc-blend structure, namely {100}, {111} and {110} facet were considered. As shown in Figure S4-S13, we used slab models with supercells to simulate ideal facets of CdSe NCs and butylamine to represent long chain amines to reduce the computational cost. The periodic calculations of $^{15}$N NMR were then carried out on the optimized slab models by CASTEP. The
calculation results are shown in Figure 6a and compared with the experimental $^{15}$N chemical shifts observed in Figure 3c. For clarity, the corresponding periodic slab model structures are displayed by cluster model in Figure 6b-6e.

For Se-rich facet, we modeled protonated $\{100\}$ facet with amines at different coverages (5.4 nm$^{-2}$ and 2.7 nm$^{-2}$). Figure S4-S5 shows that amines tend to be protonated ($-\text{NH}_3^+$) and bonded to Se$^-$ on $\{100\}$ facet irrespective of ligand density. The corresponding calculated $^{15}$N chemical shift are 46 ppm and 45 ppm, respectively (Table S2). This is consistent with the experimentally observed $^{15}$N resonance at ~45 ppm. For nonpolar facets, we modeled $\{110\}$ facet with amines coverage of 3.9 nm$^{-2}$. The optimized structure is shown in Figure S8-S9. Amines are inclined to bond with Cd sites on $\{110\}$ facet directly, as demonstrated in Figure 6d. The calculated $^{15}$N NMR chemical shift is 40 ppm, which can be assigned to the observed signal at ~41 ppm. After considering coordination of amines on both Se-rich facet and nonpolar facet with different densities, there are still several observed signals yet to be assigned in $^{15}$N NMR spectra.

We thus decided to model the possible presence of water due to two main reasons. First, it has been previously shown that there is a large amount of bonded water molecules within the NCs interface, especially for carboxylate capped CdSe NCs studied in this work. Second, water, as a neutral electron donor, can also be likely exchanged with amines on surface or interact with amines via hydrogen bonding.

The model of amine terminated Se-rich $\{100\}$ and nonpolar $\{110\}$ facet with the present of water were constructed. The optimized structures are displayed in Figure S6-S7 and Figure S10-S11. On Se-rich $\{100\}$ facet, protonated amines ($-\text{NH}_3^+$) is apt to bond with water by hydrogen bonding (Figure 6c). The corresponding calculated $^{15}$N chemical shift was decreased to 42 ppm, compared to the water-free model (45 ppm). It properly matches observed $^{15}$N resonance at ~43 ppm in both QD-St/DAm and
QD-SeH/DAm, which are expected to be with Se-rich facets. For nonpolar \{11\} facet, amine ligation is quite different, as shown in Figure S5. Instead of directly bonding to the surface Cd sites, amine interacts with surface coordinated water through hydrogen bonding (Figure 6e); the corresponding calculated $^{15}\text{N}$ chemical shift (36-38 ppm, blue bar in Figure 6a) is in good agreement with the observed signal at $\sim$39 ppm.

In addition to Se-rich and nonpolar facets, water molecules are expected to be bonded to the carboxylate group of alkanoate ligands on Cd-rich surface; this type of absorbed water can also offer addition sites for amine interaction with the surface. Hence, we further estimated the amines and water on carboxylate terminated Cd-rich $\{111\}$ facets, the optimized structures are shown in Figure S12-S13. The calculated $^{15}\text{N}$ NMR chemical shift of amine interacting with one water bonding to carboxylate is 30 ppm (purple bar), which is in agreement with the one observed experimentally at $\delta = \sim$33 ppm. Note that this $^{15}\text{N}$ signal was only pronounced in QD-St/DAm (see Figure 3c), confirming its association with remaining carboxylates.

Overall, the combination of experimental and computational $^{15}\text{N}$ NMR have revealed that the surface ligation of amines can be quite complex and does not only correspond to the directly binding to surface sites on both Se-rich and nonpolar facets, but also be likely affected by the interaction with surface bonding water through hydrogen bonding even in the case of Cd-rich facets.

**Conclusion**

The combination of advanced NMR techniques with DFT calculations allow a comprehensive understanding of the surface of amine-capped CdSe NCs, from surface sites to specific ligations. DNP enhanced $^{113}\text{Cd}$ and $^{77}\text{Se}$ NMR have resolved the bulk and surface sites of CdSe NCs with varying facet compositions. On the basis of $^{113}\text{Cd}$ CSA, amine terminated sites from Se-rich facets and
nonpolar facets were determined by means of 2D $^{113}\text{Cd}$ CPMAT spectroscopy. The $^{113}\text{Cd}$ NMR signal of amine terminated nonpolar facets was found to share the same isotropic chemical shifts as bulk CdSe (core), making them indistinguishable in 1D NMR spectra. This (unexpected) similarities can be attributed to the distinct spin-orbit coupling contributions to $^{113}\text{Cd}$ chemical shifts, as shown by cluster DFT calculations based on $[\text{Cd(SeH}_2)_x\text{(L)}_{4-x}]^{2+}$ models. The detailed ligation of amines on the surface has been further revealed by $^{15}\text{N}$ NMR and periodic DFT calculations. It was shown that amine ligands can, not only be directly bonded to surface sites on both Se-rich and nonpolar facets, but also interact with surface adsorbed water through hydrogen bonding, even in the case of Cd-rich facets. These results provide insights into the complexity and the speciation of amine-capped NCs surfaces, which are expected to impact the development of rational and targeted design of surface modification and processing of colloidal nanocrystals for various applications.
Supporting Information

Details of computations and supplementary characterization results have been included in the supporting information.

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Notes

The authors declare no competing financial interest.

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Figure 1. The overview of CdSe NCs and the strategies for studying amine-capped CdSe NCs surface in this work.
Figure 2. (a) Schematic diagram of preparing CdSe QDs with different surface ligands, including QDs with stearate ligands (QD-St), QDs with mixture of stearate and dodecylamine ligands (QD-St/DAm), QDs with dodecanethiolate ligands (QD-DS), QDs with mixture ligands of dodecanethiolate and dodecylamine (QD-DS/DAm) and QDs with Se-rich surface coated by dodecylamine ligands (QD-SeH/DAm). Their (b) UV-vis absorption spectra, (c) solid-state $^{13}$C($^1$H) cross polarization magic angle spinning (CPMAS) NMR spectra, (d) 1H solution state NMR spectra, and (e) Fourier-transform infrared (FT-IR) spectra were shown respectively.
**Figure 3.** DNP enhanced (a)$^{113}$Cd$^1$H CPMAS and (b)$^{77}$Se$^1$H CPMAS spectra of QD-St (black line), QD-St/DAm (red line), QD-DS/DAm (green line) and QD-SeH/DAm (purple line). The spectra were collected at a MAS speed of 10 kHz and CP contact time of 8 ms. The spinning side bands are indicated by asterisks. The shoulders of $^{77}$Se NMR signal peaks are indicated by grey zone. (c) The $^{15}$N CPMAS NMR spectra of $^{15}$N enriched QD-St/DAm, QD-DS/DAm and QD-SeH/DAm samples. The spectra were collected at a MAS speed of 15 kHz and CP contact time of 2.5 ms. Individual signals are deconvoluted as Lorentzian peaks in each spectrum. Their isotropic chemical shifts were indicated.
Figure 4. (1a–4a) Schemes of the CdSe QDs with different surfaces, along with the corresponding DNP enhanced $^{113}$Cd CPMAT 2D spectra (1b–4b). These experiments were conducted at a MAS spinning rate 10 kHz. The $^{113}$Cd isotropic chemical shifts are indicated by dashing lines with different
colors. Corresponding rows were extracted from the CPMAT 2D spectra showing $^{113}\text{Cd}$ spinning sideband manifolds (black solid line) in (1c–4c). The indicated chemical shift anisotropic parameters were extracted by fitting the spinning sideband intensities. The spinning side bands are indicated by asterisks.
Figure 5. (a) The examples of \([\text{Cd(SeH}_2)_x(\text{L})_{4-x}]^{2+}\) model and their calculated chemical shielding contribution (\(\sigma_{\text{PARA}} \& \sigma_{\text{SO}}\)) are indicated. Different types of atoms is presented by ball with different colors: apricot (Cd), orange (Se), blue (N), red (O), yellow (S), grey (C) and white (H). (b) The comparison between the \(^{113}\text{Cd}\) CSA parameter (\(\delta_{\text{iso}} \& \Omega\)) which are determined by CP-MAT experiments and calculated by DFT calculation of \([\text{Cd(SeH}_2)_x(\text{L})_{4-x}]^{2+}\) model. The solid dots indicate the calculation data while crosses indicate experimental data. The isotropic chemical shift was referenced to core signal (\(\delta_{\text{iso}}=-63\) ppm).
Figure 6. (a) The comparison between the experimental and calculated $^{15}$N chemical shifts of amine capped CdSe NCs. The cluster extracted from the optimized structures: (b)-(c) Se-rich $\{100\}$ facet, (d)-(e) nonpolar $\{110\}$ facet and (f) Cd-rich $\{111\}$ facet.