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Insights into the Structural Complexity of Colloidal CdSe Nanocrystal Surfaces: Correlating the Efficiency of Non-Radiative Excited– State Processes to Specific Defects

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ABSTRACT: II-VI colloidal semiconductor nanocrystals (NCs), such as CdSe NCs, are often plagued by efficient non-radiative recombination processes that severely limit their use in energy-conversion schemes. While these processes are now well-known to occur at the surface, a full understanding of the exact nature of surface defects and of their role in deactivating the excited states of NCs has yet to be established, which is partly due to the challenges associated with the direct probing of the complex and dynamic surface of colloidal NCs. Here, we report a detailed study of the surface of cadmium-rich zinc-blende CdSe NCs. The surfaces of these cadmium-rich species is characterized by the presence of cadmium carboxylate complexes (CdX₂) that act as Lewis acid (Z-type) ligands to passivate undercoordinated selenide surface species. The systematic displacement of CdX₂ from the surface by N,N,N',N'-tetramethylethylene-1,2-diamine (TMEDA) has been studied using a combination of ¹H NMR and photoluminescence spectroscopies. We demonstrate the existence of two independent surface sites that differ strikingly in the binding affinity for CdX₂ and which are under dynamic equilibrium with each other. A model involving coupled dual equilibria allows a full characterization of the thermodynamics of surface binding (free energy, as well as enthalpic and entropic terms), showing that entropic contributions are responsible for the difference between the two surface sites. Importantly, we demonstrate that cadmium vacancies only lead to important photoluminescence quenching when created on one of the two sites, which allows a complete picture of the surface composition to be drawn where each site is assigned a specific NC facet locale, with differing CdX₂ binding affinity and non-radiative recombination efficiencies.

1. INTRODUCTION

Colloidal semiconductor nanocrystals (NCs) share the fascinating electronic, optical, and chemical properties that characterize crystalline semiconductor materials, but with an explicit, and often strong, dependence on the dimensionality of the crystallite.^{1,2} These chemical species, which can now readily be prepared efficiently through a variety of solutionphase approaches, are particularly well-suited for a host of applications – photosensing,³⁻⁵ solid-state lighting,^{4,6-9} photovoltaics,^{3-5,10,11} bio-imaging,¹²⁻¹⁴ or photo-catalytic transformations,¹⁵⁻²¹ to name but a few – that rely on the extraction of work, of one form or another, from electronically-excited NCs. Such energy-conversion schemes necessarily require control over the energetic configuration of NC electronic structure as well as the ability to limit undesired excited-state relaxation pathways that lead to direct energetic losses by rapid excitonic recombination. Unlike bulk semiconductors, where non-radiative processes generally arise at localized lattice defects (vacancies, impurity doping, dislocations...)²² that are not generally found in NCs due to unfavorable energies of formation,²³ non-radiative relaxation in NCs generally originate at the surface of the crystal.^{24,25} At least from a structural point of view, the molecular objects that we refer to as "nanocrystals" are as much characterized by those atoms that are regularly organized in space (the so-called core atoms), than by those that are found on their surfaces and which often amount to a significant part of the total mass of a single NC. Importantly, surfaces can significantly impact the desirable electronic properties associated with the NC core

atoms, most notoriously by providing low-lying electronic states that lead to efficient non-radiative excitonic recombination pathways.^{1,25-32} One approach to circumvent these processes consists in growing inorganic shells properly chosen so as to electronically insulate the NC core from its surface;³³⁻³⁷ this 'potential barrier' approach, which has proven extremely powerful in the utilization of NCs for photoemission applications, cannot be easily extended to instances where charge-carriers need to be exchanged across the NC surface. In principle, the detrimental contribution of surfaces can be mitigated by providing adequate termination of the surfaces by ligating species that push the surface electronic states far from the lowest delocalized excited-state energy,^{1,24,25,30} and indeed the literature is replete with empirical approaches that lead to various levels of improvement of the photoluminescence quantum yield (PLQY),^{30,38-43} the main metric by which the efficiency of nonradiative recombination processes is generally quantified. An important issue that severely limits the development of rational approaches to control the behavior of NC surfaces is the complexity of their structure, which varies not only from NC to NC, but also from facet to facet or even from site to site.44-48 Furthermore, surface-bound species are often labile and/or mobile, and thus exhibit complicated dynamical variations across complex free-energy landscapes multiple nearly-equivalent minima.^{27,49} Detailed with and quantitative structural surveys of NC surfaces are consequently notoriously challenging tasks to accomplish even for the simplest cases and using state-of-the-art analytical probes.^{29,42,48,50-61} highlighting the challenge of experimentally



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Scheme 1. Surface exchange processes involving two Lewis-basic surface sites, B₁ and B₂, with different binding affinities to a generic CdX₂ Lewis-acidic moiety.

relating specific surface defects to non-radiative loss mechanisms, which is one of the main objectives of the present contribution.

We present here a detailed investigation of the surface of CdSe NCs, one of the most studied materials of its class.^{29,32,60-76} We specifically focused our attention to zinc-blende (cubic) CdSe NCs obtained from carboxylate precursors; these materials have a non-stoichiometric cadmium-rich composition, which arises from the presence of neutral cadmium carboxylate (CdX_2) complexes on the NC surfaces. A valuable model to describe the surface of these NCs has been formulated by Owen and collaborators,^{42,52,58,77} whereby these CdX_2 complexes are considered as Lewis acid acceptors (Z-type ligands in the Covalent Bond Classification, CBC)^{78,79} that bind to unpassivated surface selenide sites (Se²⁻), yielding stable surfaces and likely playing an important role in favoring the zinc-blende morphology during the growth process. These surface-bound CdX₂ complexes can be displaced by simple (Lewis) acid/base exchange reactions taking the following general form:

$$B + L - CdX_2 \implies B - CdX_2 + L$$
 (1)

where B represents a generic Lewis-basic site at the surface of the CdSe NCs (sometimes referred to as a "dangling bond") and L is a soluble Lewis base (L-type ligand in the CBC).^{78,79} The displacement of CdX₂ from the surface induces a strong reduction of the PLQY, betokening enhanced non-radiative relaxation to surface states that have been associated to holetrapping processes.^{29,32}

Using the general ligand exchange process given in eq. (1), we demonstrate the existence of at least two types of sites at the surface of zinc-blende CdSe NCs (Scheme 1). We show that the two types of site not only differ strikingly in their binding affinity to CdX_2 complexes, but also lead to very different non-radiative mechanisms. The thermodynamical analysis of the surface binding and the photoluminescence spectroscopy data allows a detailed model of the surface composition to be proposed, along with a direct correlation between surface

morphology and the ensemble photodynamical behavior of CdSe NCs. Our results directly support the proposal that Cd vacancies on (100) facets are efficient trapping centers,^{29,32} but also provide a wider context by allowing a direct quantitative estimate of the overall (ensemble) PLQY of CdSe NCs from the knowledge obtained in this study about the thermodynamic stability and prevalence of specific surface defects.

2. EXPERIMENTAL SECTION

2.1.Chemicals. Cadmium nitrate tetrahydrate (Cd(NO₃)·4H₂O, 98%), oleic acid (90%), octadecene (ODE, 90%), N,N,N',N',tetramethylethylene-1,2-diamine (TMEDA, 99%), myristic acid (>99%), ferrocene (Fc, 98%) were purchased from Sigma Aldrich. Ethyl acetate (HPLC grade), toluene (ACS grade), sodium hydroxide (>98%), anhydrous methanol (HPLC grade) were purchased from Macron Fine Chemicals. Pentane was purchased from Fisher Chemical. d-toluene was purchased from Cambridge Isotope Laboratories (CIL). Ethyl acetate was degased by bubbling nitrogen for 2 h and dried over molecular sieves for at least two days prior to use. Oleic acid was degased through 3 cycles of vacuum/purge with nitrogen and kept under nitrogen atmosphere just prior to use. Ferrocene was recrystallized from methanol solutions. Toluene and pentane were dried using an alumina distill columns. TMEDA was stored in the glovebox and taken out for sample preparation. Other chemicals were used as received.

2.2. Synthesis of Cadmium Myristate. Cadmium myristate was prepared by adapting a literature protocol. 80 4.63 g (15 mmol) cadmium nitrate tetrahydrate is weighed and transferred to a 500 mL beaker with 150 mL anhydrous methanol. The mixture was sonicated until all cadmium nitrate was dissolved, and the solution was transferred to a 250 mL addition funnel. Separately, 1.2 g (30 mmol) crushed NaOH, 6.85 g (30 mmol) myristic acid and 1.5 L anhydrous methanol were added to a 2 L flask; the mixture was heated in water bath at 40 °C for 2 min, then sonicated until a single phase solution of sodium myristate is formed. The solution was then transferred to a 2 L round bottom flask with a stir bar, and positioned over a magnetic stirrer. The cadmium nitrate solution was then added into the sodium myristate solution over the course of 3 h, under stirring. The resulting cadmium myristate was then filtered and washed five times with anhydrous methanol (200 mL) and air-dried for 24 h, then crushed and transferred to a 250 mL round bottom flask, and finally sealed and dried under vacuum for 24 h at 50 °C. The yield was about 82%. Product was characterized using melting point, ¹H NMR and IR spectroscopies.

2.3. Synthesis and Purification of CdSe NCs. Cadmium selenide was prepared following literature protocols.⁸¹ 5.67 g (10 mmol) cadmium myristate, 1.11 g (10 mmol) selenium dioxide powder and 630 mL octadecene were placed in a 1 L three-neck round bottom flask equipped with a water condenser. The flask was degassed in three cycles of 20 min each, then heated to 240 °C over 7 min. Heat was maintained until the desired size was reached, which was checked by taking the absorption of a diluted aliquot of the reaction suspension (vide infra). Heat was consequently removed and 10 mL (32 mmol) of degassed oleic acid were injected over 20 min while the flask was allowed to cool down back to room temperature, followed by continuous stirring for 15 h under nitrogen flow. Octadecene was then removed by vacuum (50-70 mTorr) distillation at 130 °C, after which 20 mL dry toluene was added to the dark red concentrated and impure NCs suspension, which was finally transferred into four test tubes and centrifuged for 20 min at 6000 rpm.

The supernatant was transferred in 1 mL portions into test tubes, and 10 mL ethyl acetate was added to each tube to precipitate the NCs. After centrifugation at 6000 rpm, the supernatant was removed and the NCs resuspended in 1 mL of pentane; the entire cleaning cycle was repeated four times. Finally, 10 mL ethyl acetate was added to each test tube (with only the particles), followed by sonication for 15 s. The test tubes were then centrifuged (6000 rpm) and the supernatant removed. The NCs were dried over nitrogen for 24 h, and then

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suspended in *d*-toluene to make a 85.8 μ M stock solution of NCs, as assessed by UV-Vis spectroscopy, following the empirical calibration curve established by Mulvaney et al.⁸²

2.4. Optical Spectroscopy. Absorption spectra are collected on an OLIS17 UV/vis/NIR spectrometer in 1 nm increments, using 1 cm pathlength quartz cuvettes. Spectra were measured in toluene after the toluene background was subtracted. Continuous wave (CW) photoluminescence (PL) measurements were performed using a 0.55 m focal length spectrometer (iHR550, f/6.4, 150 grooves/mm grating blazed at 500 nm) equipped with a CCD detector (Horiba Symphony II nitrogen cooled deep depleted CCD), and exciting at 450 nm using a tungsten lamp coupled to a 0.32 m focal length monochromator (Horiba iHR320, f/4.1, 600 grooves/mm grating blazed at 500 nm). PLQY were measured with an absolute PL quantum yield spectrometer (Hamamatsu Quantasaurus, C11347), using toluene suspensions prepared as described below and exciting at 400 nm.

2.5. Sample Preparation for ¹H Nuclear Magnetic Resonance (NMR) and Photoluminescence Spectroscopies. Toluene solutions of TMEDA were prepared to cover a range of concentrations from 0.01 M to 6.7 M (neat TMEDA). Mixtures of CdSe NCs and TMEDA in d-toluene were prepared, each containing 600 µL of 85.8 µM CdSe NCs ([CdSe NC] = 78 μ M), 30 μ L of a given TMEDA solution ([TMEDA] varying from 0.1 mM to 273 mM, or about 1:1 to 1:3500 CdSe NC:TMEDA ratios) and 30 µL of 4.2 mM ferrocene solution ([Fc] = 0.19 mM); each sample was allowed to equilibrate after mixing by waiting 30 min prior to measurements.⁴² ¹H NMR spectra were collected on an Agilent DDR2 500 MHz NMR spectrometer equipped with 7600AS 96 sample auto-sampler running VnmrJ 3.2A, using a 45° pulse angle / 10 s relaxation time sequence and 32 scans (see SI for more details). Spectra were analyzed using MestreNova (Mestrelab Research S.L.) and Igor Pro 7.05 (Wavemetrics). Samples for photoluminescence (PL) spectra were prepared by diluting 30 µL aliquots from each NMR sample to 2 mL with toluene. Equilibrated samples of CdSe NCs with various amounts of TMEDA exhibit surprisingly sustained stability for colloidal materials: the same samples measured over 8 months apart (stored in the glovebox) exhibited the same surface coverage (as measured by ¹H NMR), PLQY, and absorption spectra, showing no change in the average size, surface composition, or concentration of suspended NCs.

2.6. Ligand Concentration and Surface Coverage Calculations. The integration of terminal methyl (-CH₃) peak at 1 ppm in ¹H NMR each spectra was recorded and referenced to the integration of the ferrocene protons at 4 ppm, allowing for the calculation concentration of total carboxylate ligands. From charge compensation considerations, the number of cadmium carboxylate complexes (CdX₂) is half



Figure 1. Absorption (solid) and photoluminescence (dashed) of 3.8 nm CdSe NCs $(1 \pm 0.1 \ \mu\text{M})$ before (black) and after (red) addition of TMEDA (3.6 mM), illustrating the impact of displacing CdX₂ complexes from the surface of CdSe NCs.

that of the carboxylate ligands. The ligand coverage was then calculated from the number of cadmium carboxylate ligands per NC (concentration of ligands divided by concentration of NC) and the surface area of the NC, assuming spherical shape (as confirmed by TEM). Although the surface coverage involves a mixture of both oleate and myristate species, both types of ligands behave identically with regard to exchange reactions,⁸³ which we further confirmed by NMR by monitoring terminal methyl protons (which account for both types of carboxylates) as well as vinylic protons (which belong only to oleate ligands). Specific ligand exchange reactions were monitored subsequently by monitoring exclusively the vinylic peaks. Residual protonated carboxylates (oleic or myristic acid) were observed by displacement of ethane with diethyl zinc added to isolated and cleaned NC samples (assuming there are no other sources of protons); the integration of the ethane ¹H NMR peak suggested that these species form at most 10% of the total carboxylate population, which is consistent with values reported by Chen *et al.*⁶¹ This puts at ~5% the overestimation of the cadmium coverage values reported herein. Further details are given in Supporting Information and below.

3. RESULTS AND DISCUSSION

3.1. CdX₂ Displacement from CdSe NCs. The absorption and photoluminescence spectra of a clean suspension (that is,



Figure 2. (a) ¹H NMR Spectra of 3.8 nm CdSe NCs (78 μ M in *d*-toluene) in presence of different concentrations of TMEDA (10 points are selected, values in mM listed on the right-hand side). (b) Zoomed-in spectra (from panel (a)) between 5 and 6 ppm showing the bound (B) and free (F) cadmium carboxylates (CdX₂). (c) Total number of CdX₂ units per CdSe NC (gray squares), number of CdX₂ units bound to the surface of CdSe NCs (red circles), and number of CdX₂ units displaced by TMEDA from the surface of CdSe NCs (blue circles).

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without free ligands; vide infra) of 3.8 nm CdSe NCs are shown in Figure 1 (data for 3.0 and 4.1 nm are also given in SI). Upon addition of 3,500 equivalents of TMEDA per NC, the PLQY drops by more than two orders of magnitude, from 10% to <0.1%, which is associated with the displacement of CdX_2 complexes in solution (eq. (1)), which can be quantified by ¹H NMR.⁴² The overall ¹H NMR spectra of 3.8 nm CdSe NCs, with and without TMEDA, are presented in Figure 2(a). Given the nature of these colloidal NCs (zinc blende CdSe NCs capped with oleate/myristate surfactants see Experimental Section and SI for more details), these spectra give a detailed account of the surfactants bound to the surface of the NCs, as well as of any organic species freely diffusing in solution. Of particular interest are the integrated intensities of bands associated with specific ligands, as they allow a direct evaluation of the NC surface densities of these species to be evaluated. Direct comparison of the integrated intensity of terminal methyl (-CH₃) groups, located at 1 ppm in Fig. 2(a), with an internal standard (ferrocene), yields a value of 190 ± 4 carboxylate (X⁻) ligands per NC, corresponding to $95 \pm 2 \text{ CdX}_2$ complexes per NC for the 3.8 nm CdSe NCs sample shown in Fig. 2. This value corresponds to a surface coverage of 4.2 ± 0.6 carboxylate nm⁻², or, equivalently, 2.1 ± 0.3 CdX₂·nm⁻², a value close to the largest coverage of CdSe NC by carboxylates reported in the literature. Furthermore, the ¹H NMR spectrum of as-prepared CdSe NCs indicates that, prior to the addition of TMEDA, all carboxylate species are quantitatively bound to the surface, without any measurable trace of unbound carboxylate species. This is indicated by the single broad feature around 5.7 ppm, better seen in the zoomed-in perspective of Fig. 2(b), which is assigned to the vinylic protons of surface-bound oleate ligands. Upon addition of TMEDA to the CdSe NCs suspension, the integrated intensity of this broad feature decreases, concomitantly with the increase of a sharp feature $[TMEDA] = [L] + [L-CdX_2] (mM)$ 200 300 0 100 0 10

at 5.47 ppm, which is readily assigned to carboxylate species that are unbound from the surface of CdSe NCs (hereby labeled "free").^{64,84-86} Importantly, as shown in Fig. 2(c), the decrease in intensity from the broad band is exactly matched by the increase in the integrated intensity of the sharp band, consistent with the assignment of a single species (the carboxylate ligands) being exchanged dynamically under the influence of the TMEDA species. The nature of this equilibrium was discussed in great details previously⁴² as a Ltype ligand-induced displacement of surface-bound cadmium carboxylates (CdX₂) complexes into solution, as shown in a general form by eq. (1), where the soluble Lewis base (L) was chosen here to be N,N,N',N'-tetramethylethylenediamine, TMEDA, shown in Scheme 1 (we note that formally TMEDA, a bidentate donor, would be referred to as a L₂ ligand and the resulting free complex as CdL_2X_2 in the CBC;^{78,79} we use the shortcut notation throughout here). The CdX₂ complex behaves as a Lewis acid (Z-type ligand) and eq. (1) thus describes the Lewis acid/base exchange of a Z-type ligand (the cadmium carboxylate complex) between two Lewis base groups: (i) the surface of the NC (B) and (ii) TMEDA (L). Interestingly, the trends in Fig. 2(c) suggest that the simple relation given by eq. (1) cannot account fully for this dynamical exchange: whereas almost a third of the surfacebound CdX₂ can be displaced upon addition of 10 mM of TMEDA (about 125 equivalents per NC here), the further addition of over 250 mM of TMEDA has a much reduced impact overall, bringing the total CdX₂ displacement to 40% of the initial value. This general feature is observed for all samples we investigated, irrespective of the NC size (SI). We show below that this behavior can be readily explained by invoking the existence of two separate CdX₂ binding sites at the NC surface, each with their own free energy of binding and role in deactivating the excited state of CdSe NCs.

3.2. Analysis of the Ligand-Exchange Equilibrium. We



Figure 3. (a) TMEDA titration of 3.8 nm CdSe NCs (78 μ M in *d*-toluene), modeled with eq. (11) (black dashed line). The top axis is a transformation of the ratio φ reported on the bottom axis (eq. (13), and represents the total TMEDA concentration in solution (note the non-linear scale). The right axis is a reciprocal transformation of the left axis, showing the number of bound CdX₂ units per NC. (b) Calculated number of vacant sites at the surface of the 3.8 nm CdSe NC sample, for each type of site, B₁: blue, B₂: red, all sites: black. The data for the total number of open sites, equivalent to the number of CdX₂ ligands that are removed from each surface site as a function of added TMEDA, is shown by the orange circles. The top axis is linearly scaled to represent the TMEDA concentration in total equivalents of CdX₂ complexes. (c) Same data/calculated curves as panel (b), but for a wider range of TMEDA concentrations and on a logarithmic scale. The largest magnitudes shown here correspond to unrealistically large concentrations, and are shown here for discussion purposes. The two arrows indicate the TMEDA concentrations (Figure 4) where conducted (blue arrow: 2 mM, red arrow: 274 mM).

begin by describing quantitatively the equilibrium involving a single type of surface sites (B), which can be either open (vacant) or occupied by a CdX_2 complex, itself being involved in a dynamic exchange between the free Lewis base (L) and the Lewis-acidic surface site (B), as given by eq. (1) above. The equilibrium constant for this equilibrium is given by:

$$K_{eq} = \frac{\left\lfloor \mathbf{B} - \mathbf{C} \mathbf{d} \mathbf{X}_{2} \right\rfloor \left\lfloor \mathbf{L} \right\rfloor}{\left\lfloor \mathbf{B} \right\rfloor \left\lfloor \mathbf{L} - \mathbf{C} \mathbf{d} \mathbf{X}_{2} \right\rfloor} = \frac{\left\lfloor \mathbf{B} - \mathbf{C} \mathbf{d} \mathbf{X}_{2} \right\rfloor}{\left\lfloor \mathbf{B} \right\rfloor} f$$
(2)

where as an approximation molarities are invoked instead of activities. We note that eq. (1) describes the binding of the CdX₂ complex onto the NC surface, which is the reversal of the displacement process monitored in Fig. 2; as shown below, this form yields simpler equations to describe quantitatively the equilibrium process; this convention will be kept throughout the study, where larger equilibrium constants are associated with stronger NC-CdX₂ bonds (*i.e.* less easily displaced by TMEDA). The parameter ϕ in eq. (2) designates the ratio of unbound ("free") *vs.* bound TMEDA:

$$f = \frac{\begin{bmatrix} L \end{bmatrix}}{\begin{bmatrix} L - CdX_2 \end{bmatrix}} = \frac{\begin{bmatrix} L \end{bmatrix}_0}{\begin{bmatrix} L - CdX_2 \end{bmatrix}} - 1$$
(3)

and is a quantity directly obtainable from NMR data such as that presented in Fig. 2 ($[L]_0$ is the total concentration of TMEDA). The total number of binding sites per NC, *N*, is given by the sum of occupied and vacant (open) sites:

$$N = \frac{\left[\mathbf{B} - \mathbf{C} \mathbf{d} \mathbf{X}_{2}\right] + \left[\mathbf{B}\right]}{\left[\mathbf{N}\mathbf{C}\right]}$$
(4)

Combining equations 2 and 4 yields an equation to describe the equilibrium process in terms of directly measurable quantities:

$$\frac{\left\lfloor \text{NC} \right\rfloor}{\left\lfloor \text{B} - \text{CdX}_2 \right\rfloor} = \frac{1}{N} + \frac{1}{N \cdot K_{eq}} f$$
(5)

Eq. 5 shows that a plot of [NC]/[B-CdX₂] (the inverse of the number of bound CdX₂ complexes per NC, directly obtained from the NMR data in Fig. 2(b)) *vs.* ϕ should yield a line of slope $(N \cdot K_{eq})^{-1}$ and intercept N^{-1} . Figure 3(a) reports the same data shown in Fig. 2(c) for the 3.8 nm CdSe NCs using the formalism of eq. (5). Consistent with the conclusion drawn above in Section 3.1, the data shows two different regimes, each converging to linear trends in the limits of small and large TMEDA concentrations. Obviously, the assumption of a single binding site is too restrictive, and a more sophisticated equilibrium model involving two types of surface sites is

needed to describe the data in Figure 3(a). We note that the two equilibria are not well separated, which implies that both equilibrium regimes are coupled to each other (at least in the intermediate region) and need to be considered simultaneously.

As above, we define these exchange reactions as being associative in terms of the CdX_2 complex, and use the labels B_1 / B_2 and B_1 -CdX₂ / B_2 -CdX₂ to distinguish the two types of open (vacant) and occupied surface sites, respectively:

$$B_1 + L - CdX_2 \implies B_1 - CdX_2 + L$$
(6a)

$$B_2 + L - CdX_2 \rightleftharpoons B_2 - CdX_2 + L$$
(6b)

The equilibrium constants for each exchange reaction are given by:

$$K_{1} = \frac{\begin{bmatrix} B_{1} - CdX_{2} \end{bmatrix} \begin{bmatrix} L \\ \end{bmatrix}}{\begin{bmatrix} B_{1} \end{bmatrix} \begin{bmatrix} L - CdX_{2} \end{bmatrix}} = \frac{\begin{bmatrix} B_{1} - CdX_{2} \end{bmatrix}}{\begin{bmatrix} B_{1} \end{bmatrix}} f$$

$$K_{2} = \frac{\begin{bmatrix} B_{2} - CdX_{2} \end{bmatrix} \begin{bmatrix} L \\ \end{bmatrix}}{\begin{bmatrix} B_{2} \end{bmatrix} \begin{bmatrix} L - CdX_{2} \end{bmatrix}} = \frac{\begin{bmatrix} B_{2} - CdX_{2} \end{bmatrix}}{\begin{bmatrix} B_{2} \end{bmatrix}} f$$
(7a)
(7b)

The analysis of ¹H NMR does not allow us to distinguish between the two types of sites (B₁ and B₂), as the deconvolution of free and bound cadmium carboxylates peaks yields only the total concentration of TMEDA-bound CdX₂ species, [L-CdX₂], as well as the total concentration of surface-bound CdX₂ species, [B-CdX₂]:

$$\begin{bmatrix} B - CdX_2 \end{bmatrix} = \begin{bmatrix} B_1 - CdX_2 \end{bmatrix} + \begin{bmatrix} B_2 - CdX_2 \end{bmatrix}$$
(8)

The total number of surface sites, N_{tot} , is given by:

$$N_{tot} = N_1 + N_2 = \frac{\left[B - CdX_2\right] + \left[L - CdX_2\right]}{\left[NC\right]}$$
(9)

where we assume full coverage of the surface in the absence of TMEDA (*vide infra*). The coupled exchange reactions given by eqs. (6a-b) are fully described by the following equation, which invokes the same two observables as eq. (5) above ([NC]/[B-CdX₂] vs. φ):

$$\frac{\left[\operatorname{NC}\right]}{\left[\operatorname{B}-\operatorname{CdX}_{2}\right]} = \frac{f^{2} + \left(K_{1} + K_{2}\right) \cdot f + K_{1} \cdot K_{2}}{\left(N_{1} \cdot K_{1} + N_{2} \cdot K_{2}\right) \cdot f + N_{tot} \cdot K_{1} \cdot K_{2}}$$
(10)

Interestingly, we note that the two limiting linear regimes observed at small and large [TMEDA] in Fig. 3 can be directly extracted from eq. (10) above:

Table 1. CdSe NC surface-related data, obtained from analysis of TMEDA titration experiments, T = 293.15 K.

NC Diameter ^a (nm)	N_1	N_2	K ₁	<i>K</i> ₂	$N_{ m tot}{}^{ m b}$	[NC] ^b (µM)	[CdX ₂] ^c (mM)	Surface coverage (CdX ₂ /nm ²)
3.0 ± 0.2	23 ± 1	34 ± 3	1.0 ± 0.3	$(9\pm5) imes10^2$	57 ± 2	80 ± 2	4.6 ± 0.3	2.1 ± 0.3
3.8 ± 0.2	34 ± 2	61 ± 4	0.9 ± 0.3	$(7\pm4)~\times10^2$	95 ± 2	78 ± 2	7.4 ± 0.7	2.1 ± 0.3
4.1 ± 0.3	43 ± 4	78 ± 6	0.6 ± 0.3	(3 ± 1) $ imes10^2$	121 ± 2	78 ± 2	9.4 ± 0.2	2.2 ± 0.2

^a From lowest excitonic transition energy in the absorption spectrum, using the calibration curve of ref. 81.

^b From total excitonic absorption cross-section, using the calibration curve of ref. 81.

^c From ¹H NMR data of the as-prepared CdSe NCs, assuming no intrinsic vacancies; *q.v.* Experimental Section for further details.

Table 2. Thermodynamic parameters for surface-bound CdX_2 exchange with TMEDA of CdSe NCs, T = 293.15 K.

NC Diameter (nm)	ΔH ₁ ^a (kJ·mol ⁻¹)	Δ <i>H</i> ₂ ^a (kJ·mol ⁻¹)	ΔS ₁ ^b (J·mol ⁻¹ ·K ⁻¹)	ΔS_2^{b} (J·mol ⁻¹ ·K ⁻¹)	ΔG1 ^c (kJ·mol ⁻¹)	ΔG_2^{c} (kJ·mol ⁻¹)
3.0 ± 0.2	11 ± 2	14 ± 4	38 ± 10	106 ± 21	0.0 ± 0.7	-17 ± 2
3.8 ± 0.2	8 ± 2	13 ± 1	26 ± 10	99 ± 10	0.3 ± 0.8	-16 ± 2
4.1 ± 0.3	10 ± 5	13 ± 4	30 ± 22	92 ± 17	1.2 ± 1.4	-14 ± 1

^a from the van 't Hoff analysis presented in Fig. 4; ^b from $DS = (DH - DG) \cdot T^{-1}$, using ΔH and ΔG from this Table.

^c from $DG_n = -R \cdot T \cdot \ln K_n$, using K_n from Table 1.

$$\lim_{f \to 0} \left(\frac{[\text{NC}]}{[\text{B} - \text{CdX}_2]} \right) = \frac{1}{N_1 + N_2} + \frac{K_1 + K_2}{(N_1 + N_2)K_1 \cdot K_2} \cdot f^2$$
(11a)

$$\lim_{f \to \infty} \left(\frac{[\text{NC}]}{[\text{B} - \text{CdX}_2]} \right) = \frac{K_1 + K_2}{N_1 \cdot K_1 + N_2 \cdot K_2} + \frac{1}{N_1 \cdot K_1 + N_2 \cdot K_2} \cdot f^{-1}$$
(11b)

The data in Fig. 3 has been fitted to eq. (10) using a non-linear regression analysis, yielding values for N_1 , N_2 , K_1 , and K_2 that are listed in Table 1.

The good agreement between the model and the observed experimental data validates the assumption that each site on the surface interacts independently from each other, as strongly correlated surface binding would not be well modeled by eq. (10) above. Importantly, different CdSe NC sizes are equally well described by the model, and the relevant parameters for each NC size are listed in Table 1. On the other hand, the good agreement between the sum $N_1 + N_2$ obtained from the nonlinear regression analysis and the value N_{tot} extracted from the NMR quantitation analysis should not be regarded as indicative of the validity of the model, as the model is itself designed to yield such a good agreement: the sum $N_1 + N_2$ is related to the y-axis intercept, which is experimentally related to the value N_{tot} obtained from the NMR data, see eq. (11) above for $\varphi = 0$. Rather, a subtle point related to this issue is the question of the validity of the assumption that there are no vacant sites prior to displacement of CdX₂ by TMEDA: as vacancies in our study are never probed directly per se, it is not strictly possible to verify this assumption, although we can evaluate the possible impact that their presence would have on the exchange dynamics. Given the large difference between K_1 and K_2 , it is clear that under equilibrium, any intrinsic vacant site would have to exist as a B₁ site. As a consequence, neglecting the presence of intrinsic vacant B₁ sites in our model artificially boosts the value of the K_1 equilibrium constants, that is, the mass action of each equivalent of TMEDA in eq. (6a) is effectively reduced. Consequently, the K_1 values reported in Table 1 can be regarded as upper-bound values for the actual equilibrium constants, to the extent that intrinsic B_1 vacancies, present in the as-prepared NC samples, would need to be taken into account. A more detailed analysis is presented in Section 3.5 below, allowing an estimate of the fraction of vacancies in the as-prepared samples and of the actual equilibrium constant K_1 . It is sufficient for now to regard the values N_1 and K_1 listed in Table 1 as effective parameters that describe accurately the equilibria of eqs. (6a,b).

With the values of the equilibrium constants and site densities in hand, a useful analysis of each separate equilibria can be obtained, for instance by relating directly the occupancy of each surface site to the ratio φ , or, equivalently, to the total amount of TMEDA added, *cf*. eq. (13):

$$\frac{\begin{bmatrix} B_i \end{bmatrix}}{\begin{bmatrix} NC \end{bmatrix}} = \frac{N_i \cdot f}{f + K_i} \qquad i = 1,2$$

$$\begin{bmatrix} L \end{bmatrix}_0 = \frac{N_{tot} \left(f^3 + f^2\right) + \left(N_1 K_2 + N_2 K_1\right) \left(f^2 + f\right)}{f^2 + \left(K_1 + K_2\right) f + K_1 K_2} \begin{bmatrix} NC \end{bmatrix} \quad (13)$$

The displacement of the CdX_2 complexes from the CdSe NC surfaces is plotted separately for each individual site (B₁ and B₂) in Figure 3(b), showing clearly that full displacement of CdX_2 from the B₁ surface sites is effectively achieved at around 50 mM of added TMEDA, corresponding to about 650 equivalents per NC. Comparatively, less than 10% of the B₂ sites are vacant under identical conditions; as shown in Fig. 3(c), there is not any physically realistic scenario under which TMEDA could displace all of the CdX₂ complexes from the B₂ sites, as concentrations higher than the density of pure liquid TMEDA being required.

Close inspection of the data in Table 1 reveals a few interesting facts. First, the apportionment of each type of site appears fairly regular across all sizes, with a rough 2:3 ratio between N_1 and N_2 , although we note that this likely depends



Figure 4. Temperature dependence of the equilibrium constants K_1 and K_2 for 3.8 nm CdSe NCs, expressed in the van 't Hoff formalism. Blue circles: [TMEDA] = 2 mM; red circles: [TMEDA] = 273 mM; the error bars are at most as large as the circles shown here. The black dashed lines are linear least squares fitted curves ($R^2 = 0.885$ for K_1 and $R^2 = 0.830$ for K_2).

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Table 3. Comparison of the thermodynamic binding stability of CdX_2 on the $B_2 vs$. B_1 surface sites of CdSe NCs.^a

NC Diameter (nm)	Δ <i>H</i> ₂₋₁ (kJ·mol ⁻¹)	ΔS ₂₋₁ (J·mol ⁻¹ ·K ⁻¹)	ΔG ₂₋₁ (kJ·mol ⁻¹)
3.0 ± 0.2	3 ± 4	68 ± 23	-17 ± 2
3.8 ± 0.2	5 ± 2	73 ± 14	-16 ± 2
4.1 ± 0.3	3 ± 5	62 ± 28	-15 ± 2

^a Data referenced to eq. (15), $\Delta X_{2-1} = \Delta X_2 - \Delta X_1$; T = 298.15 K.

sensitively on sample preparation conditions, and NCs prepared by different approaches, or those with much smaller superficial coverage than those reported here, might not exhibit the same trend. Second, whereas equilibrium constants for a given type of sites generally appear to decrease with increasing sizes, the accuracy of the analysis does not allow for firm conclusions to be raised concerning the precise size dependence of these parameters. Furthermore, we note that from a free energy perspective (Section 3.3), there is not a significant difference across the range of values reported for a given site. A much more critical observation stemming from this analysis, and a general feature common to all samples (beyond the existence of two distinct surface sites), is the fact that the equilibrium constants for the binding of CdX₂ on each of the two surface sites differ by about 2-3 orders of magnitude, *i.e.*, $pK_1 \sim 0$ and $pK_2 \sim -2$. This points to a significant difference in the free energy of binding CdX₂ between B_1 and B_2 , which we address specifically in the next Section.

3.3 Thermodynamics of Surface Site Binding. To probe further into the specific nature of the two different types of surface sites, temperature-dependent ¹H NMR studies were conducted as a way to modulate the equilibrium of the CdX_2 exchange reactions and extract the enthalpic contribution to the overall free energy of each exchange process. For each NC sizes, two TMEDA concentrations were selected, each corresponding to a regime where one of the two exchange reactions dominates the overall equilibrium. These two

regimes are highlighted with arrows for the 3.8 nm CdSe NC sample in Fig. 3(c). In each regime, and for all NC sizes investigated here (see SI), NMR studies indicate that the TMEDA-induced displacement of surface-bound CdX₂ becomes more efficient the lower the temperature, indicating that this process is exothermic ($\Delta H < 0$) or, in the framework established above, that eqs. (6a,b) represent endothermic processes ($\Delta H > 0$). A quantitative estimate of the enthalpy of reaction can be obtained from a van 't Hoff analysis of the temperature-dependent equilibria:

$$\frac{d\ln K_{eq}}{d\left(T^{-1}\right)} = -\frac{DH}{R} \tag{14}$$

Figure 4 reports the temperature-dependent exchange equilibria data obtained from NMR in the formalism of eq. (14). The behavior of $\ln K vs. T^1$ over the whole temperature range investigated (roughly 40 K above and beyond room temperature) is linear, indicating that the enthalpy change is nearly temperature-independent over this range, as expected for the simple ligand exchange processes under consideration. The enthalpy change for each exchange reaction is thus directly related to the gradient of each fitted line in Fig. 4. The Gibbs free energies for each process are directly obtained from the equilibrium constants in Table 1, which then directly yields the corresponding entropic changes; the thermodynamic quantities for eqs. (6a-b) extracted from such van 't Hoff analyses are reported in Table 2 for three different CdSe NCs sizes.

Although the thermodynamic data in Table 2 is referenced to TMEDA (more precisely, to differences between state functions of the TMEDA-CdX₂ complex and uncoordinated solvated TMEDA), a direct comparison between the binding stability of CdX₂ to $B_1 vs. B_2$ sites can be obtained by subtracting the two reactions in eqs. 6a and 6b, yielding the following overall equilibrium:

$$B_1 - CdX_2 + B_2 \rightleftharpoons B_1 + B_2 - CdX_2$$
(15)

which is independent of the nature of the Lewis base species used to displace the CdX_2 complexes; the thermodynamic



Figure 5. (a) PL intensity of 3.8 nm CdSe NCs ($\sim 1.0 \pm 0.1 \mu$ M), with varying amounts of TMEDA (0 -3.6 mM). Inset: PL spectra of the same samples. Intensities have been normalized to the integrated PL intensity of the CdSe NCs-only sample (I_0), after baseline subtraction and correction for dilution effects. (b) Quantification of the TMEDA-induced CdSe NC PL quenching, reported as the Stern-Volmer ratio, I_0/I . (c) CdSe NC PL quenching efficiencies of each type of vacancies, as induced by displacement of CdX₂ by TMEDA. The dashed lines are linear least squares fitted curves, constrained to the initial quenching region. The PL quenching correlates well with the creation of vacancies on the B₂ sites.

Table 4. (CdSe NCs	Photolumines	cence and	Stern-Volmer	· Analysis l	Data.
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NC Diameter (nm)	$K_{\scriptscriptstyle SV}^{\scriptscriptstyle { m B}_1}\left({ m M}^{\scriptscriptstyle -1} ight)$	$K_{SV}^{\mathbf{B}_2}\left(\mathbf{M}^{-1}\right)$	$\frac{K_{SV}^{\mathrm{B}_2}}{K_{SV}^{\mathrm{B}_1}}$	PLQY _{bright} ^a (%)	PLQY _{dark} ^b (%)	P _{dark} ^c (%)	Observed PLQY (%)	Predicted PLQY ^d (%)
3.0 ± 0.2	0.22 ± 0.04	170 ± 20	800 ± 200	17 ± 2	0.1 ± 0.1	0.4	16 ± 3	16 ± 2
3.8 ± 0.2	0.18 ± 0.02	53 ± 4	290 ± 40	14 ± 2	0.3 ± 0.3	1.0	10 ± 2	13 ± 2
4.1 ± 0.3	0.11 ± 0.03	12 ± 1	150 ± 60	22 ± 5	2 ± 1	2.0	12 ± 2	22 ± 5

^a Calculated PLQY of a NC without a B₂ vacancy, eq. (19); ^b Calculated PLQY of a NC with a single B₂ vacancy, eq. (20); ^c Probability that a NC has a single B₂ vacancy; ^d Overall calculated PLQY = $(1 - P_{dark}) \times PLQY_{brieht} + P_{dark} \times PLQY_{dark}$.

parameters relevant to eq. (15) are listed in Table 3. The data in Table 3 shows directly that the difference in the enthalpic terms associated with the equilibrium of the B_1 and B_2 sites is not only quite small, but also opposite to the thermodynamic stability associated with the B_2 -CdX₂ complex. Indeed, as written, eq. 15 is a slightly endothermic reaction, demonstrating, somewhat surprisingly, that the large thermodynamic stability of the B_2 -CdX₂ complex relative to the B_1 site analog is intrinsically an entropic effect; further insight into the origin of this effect will be provided in Section 3.5, along with a discussion of the nature of the B_1 and B_2 sites in terms of the specific surfaces of zinc-blende CdSe NCs.

3.4. Impact of Specific Surface Vacancies on PL Efficiency. With the knowledge of the energetics of CdX_2 surface binding in hands, we proceed to analyze the impact that the displacement of this group from the NC surfaces has on the excitonic photoluminescence (PL). As shown in Figure 5(a), the addition of TMEDA to CdSe NC suspensions dramatically impacts the PL intensity, an indication that efficient nonradiative recombination processes are becoming operative in the presence of TMEDA.^{29,42} Quantitatively, the PL quenching efficiency is better characterized through the Stern-Volmer formalism, whereby the reciprocal of the PL intensities, normalized to the PL intensity in the absence of the quencher (I_0), as reported in Figure 5(b):

$$\frac{I_0}{I} = 1 + K_{SV} [Q] \tag{16}$$

where [*Q*] is the quencher species concentration and K_{SV} is a constant characterizing the efficiency of the PL quenching process; from the onset of the Stern-Volmer data for TMEDA presented in Fig. 5(b), $K_{SV} = (57,000 \pm 1,000) \text{ M}^{-1}$. Of course TMEDA is not itself the direct PL quenching species, but rather acts indirectly by creating CdX₂ vacancies on the NC surfaces that are active trap centers, presumably as efficient hole trapping species.^{32,42} As the impact of TMEDA on the displacement of CdX₂ has been fully characterized above, a direct connection between the PL efficiency (which is indirectly reporting on the presence of trap centers) and the

 $\begin{array}{c} & & & & \\ & & & \\$

Scheme 2

precise composition of the NC surface can be made, as presented in Fig. 5(c). This figure clearly indicates a strong correlation between the overall PL quenching and the creation of B₂ sites vacancies: comparatively, the removal of CdX₂ species from B₁ sites does not appreciably quench the NC PL (the rise of the Stern-Volmer ratio at large B_1 displacement values is actually due to the concomitant creation of B_2 vacancies). From the values of the Stern-Volmer constants extracted from the onset of each regime, the efficiency of a B₂ vacancy is estimated to be nearly 300 times larger than that of a B₁ vacancy: $K_{SV} = 0.18/CdX_2$ for B₁ vs. 53/CdX₂ for B₂ (Table 4). This stark contrast between the two types of vacancies underlines that not all surface defects are necessarily equivalent, even for such defects that are in appearance quite similar (here, CdX₂ vacancies). Furthermore, although the overall stability of the B₂-CdX₂ complex overwhelmingly surpasses that of the B1-CdX2 (making B2 vacancies much rarer species under equilibrium conditions), the creation of even a single B₂ vacancy leads to a greater impact on the PL quenching (by over one order of magnitude) than would occur from the removal of every CdX_2 group bound to B_1 sites. Ultimately, the brightness of CdSe NCs is exceedingly sensitive to B_2 vacancies, and without the strong thermodynamic stability of CdX₂ complexes bound to these sites, the use of Cd-based Z-type ligands to passivate undercoordinated Se sites would unlikely be a successful strategy to mitigate non-radiative recombination processes.

Interestingly, a systematic trend between the quenching efficiency of single vacancies and the average NC diameter is observed, whereby smaller NCs are most efficiently quenched by each surface defects (Table 4); the same trend is also observed in the ratios between the Stern-Volmer constants for the two sites. The magnitude of the effect, which does not scale directly with the surface-to-volume ratio, might possibly indicate enhanced coupling to the surface states in more strongly quantum confined systems; a quantitative evaluation

Table 5. CdSe NCs Surface Areas and Ligand Coverage.

NC Diameter (nm)	$\frac{S_{tot}}{(\mathbf{nm}^2)}^{\mathbf{a}}$	$\frac{S_{100}}{(\mathrm{nm}^2)}^\mathrm{b}$	$\frac{S_{111}}{(nm^2)}^c$	/ ^{eff} d (nm ⁻²)	N _{1,tot}
3.0 ± 0.2	28 ± 3	13 ± 1	15 ± 4	1.5 ± 0.4	47 ± 2
3.8 ± 0.2	45 ± 3	23 ± 1	22 ± 4	1.5 ± 0.3	69 ± 4
4.1 ± 0.3	53 ± 5	29 ± 2	24 ± 7	1.8 ± 0.5	75 ± 7

^a Surface area of the equivalent sphere; ^b Calculated using eq. (17); ^c $S_{111} = S_{tot} - S_{100}$; ^d $\int_{111}^{eff} = N_1 / S_{111}$.

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3 We note finally that the PLQY of isolated NC samples 4 (following repeated ethyl acetate/pentane 5 crashing/resuspension cycles) are always markedly higher than 6 for the same samples in the TMEDA/free CdX₂ mixtures (see 7 SI). Interestingly, an analysis of the surface coverage after 8 isolation shows a concomitant increase in the surface coverage 9 which follows precisely the trend observed for the NC/TMEDA/free CdX₂ mixtures (see SI), suggesting that NCs 10 before and after isolation are behaving identically, provided 11 proper correction for the change in the surface coverage. This 12 also suggests that TMEDA does not impact the PLQY of CdSe 13 NCs, as there are not significant differences observed between 14 samples with very high concentrations of TMEDA and those 15 after isolation. The increase in the surface coverage for 16 isolated NCs is likely attributable to a reduction of the 17 solubility of the TMEDA-CdX₂ complex in the non-18 polar/polar solvent mix, which drives the rebinding of the cadmium complex onto the surface. 19

3.5 Microscopic Nature of the Surface Sites of CdSe NCs. Some insights into the potential microscopic nature of each of the two surface sites, B_1 and B_2 can be obtained from the results presented above. As has been recognized, ^{25,27,29,32,70,87} the different crystal previously facets of semiconductor NCs often exhibit strikingly different behaviors regarding the stability of surface-bound species (ligands or adatoms) and the generation of specific surface defects for excited-state energy-trapping processes. The surface of zincblende CdSe NCs is generally described in terms of the two most stable facets, namely the (100) and (111) facets.^{28,32,88,89} The (100) facet exposes two-coordinated species, either Se or Cd; the idealized "selenium-rich" (100) facet thus presents rows of Se²⁻ ions, each with two lone pairs located in sp² hybrids. The (111) facets by contrast expose species that are 3coordinated to the underlying lattice atoms; the idealized "selenium-rich" (111) facet thus presents arrays of Se²⁻ ions each with a single lone pair pointed perpendicular to the facet plane (Scheme 2). Although the (100) facet is atomically sparser than the (111) facet:

$$l'_{100} = \frac{2}{a_0^2} @ 5.4 \text{ atoms} \times \text{nm}^{-2}$$

 $l'_{111} = \frac{4\sqrt{3}}{3a_0^2} @ 6.2 \text{ atoms} \times \text{nm}^{-2}$

where a_0 is the lattice constant of zinc blende CdSe (0.608 nm),⁹⁰ the (111) facet has a lower density of "dangling bonds", and recent studies have suggested that CdX₂ vacancies created on (100) facets of cadmium-rich CdSe NCs lead to the introduction of electronic states in the bandgap that can efficiently trap photo-generated valence-band holes on surface Se²⁻ ions.^{29, 32} Following this hypothesis, we assign the B₂ sites (the highly efficient PL quenching sites) to vacancies on (100) facets. Given the large driving force to displace any CdX₂ complexes from B₁ sites onto B₂ vacancies, it is reasonable to assume that, at equilibrium, the (100) facets must be fully covered with CdX₂ complexes, a proposal which is also implied by the Stern-Volmer analysis presented above, where even a single vacancy on the B₂ sites would yield a PL quantum yield (PLQY) < 1/50, much lower than the observed

PLQY of the as-prepared samples studied here (avg. PLQY ~ 13%). The total (100) surface area, S_{100} , is thus simply calculated from:

$$S_{100} = \frac{N_2}{I_{100}/2} \tag{17}$$

where λ_{100} is the atom density of the (100) facet (the factor of 2 arising from the fact that only half of the (100) facets are Seterminated and able to coordinate CdX_2). The calculated total area for the (100) and (111) facets are listed in Table 5; interestingly, the ratio of the (100) vs. (111) areas obtained from this assumption is close to unity, which is consistent with the observed spherical morphology (among the isomorphic Archimedean solids, this specific shape falls in between that of the ideal truncated octahedron and the cuboctahedron). Following on our initial assumption that the B_2 sites correspond to vacancies on the (100) facet, we assign the B_1 sites (initially bound to N_1 CdX₂ complexes) to vacancies on the (111) facet. Since the total surface of each NC sample can be directly estimated from the average diameter, a direct quantification of the surface coverage for the (111) facets can be obtained, as given in Table 5. The surface coverage of the (111) facets (measured in CdX₂ units) is lower than the theoretical maximum, $I_{111}/2 @ 3.1 \text{ nm}^{-2}$, which is expected given the low overall ligand coverage listed in Table 1. In spite of the relatively large number of (111) sites that remain unpassivated, it is likely that these sites are actually sterically hindered, suggesting that the CdX2 coverages reported here are perhaps actually close to the effective maximum that can be achieved for the specific carboxylates and NC shapes under consideration in this study. Importantly, as discussed above, these unpassivated sites - assigned here as B₁ vacancies - do not significantly impact the brightness of the NCs, minimizing the detrimental impact of the low (111) facet coverage. With an estimate of the surface spanned by the (111) facets in hand, the number of B_1 sites that are not initially ligated by CdX_2 , which was neglected in the analysis before, can now be evaluated:

$$N_{1,tot} = \frac{I_{111}}{2} \times S_{111}$$
(18)

where, as above, we acknowledge that only half of the surface apportioned to (111) facets is Se-terminated. These values are listed in Table 5, showing that there are many B₁ vacancies on these as-prepared NC samples; an estimate of the role that these vacancies might play in the photoluminescence of these "pristine" CdSe NCs is presented in the next Section. As mentioned in Section 3.2 above, neglecting the presence of these B_1 vacancies effectively magnifies the values of K_1 obtained therein; using the values of $N_{1,tot}$ listed in Table 5 to analyze the data in Figure 2 leads to values of K_1 that are practically identical for all three sizes: $K_{1,corr} = 0.23 \pm 0.03$. This actual value, which is 3-5 times smaller than the effective values listed in Table 1, likely provides a better estimate of the actual affinity of the B_1 sites – that is, undercoordinated (111) selenide sites - toward CdX₂ ligation. We note here that although we treat surfaces as uniform distributions, it is possible, and perhaps likely, that specific locales over each surfaces (say edges or corners) play a dominant role in defining the ligand exchange kinetics and/or the efficiency of the recombination processes. Given the likely high mobility of

surface ligands over the whole surface of a NC and our inability to distinguish specific surface sites beyond the two types (B_1 and B_2) identified here, we limit our analysis to the attribution of the chemical and photophysical behavior of surface defects as mean values over the two main crystallographic facets.

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The conclusion that the (100) facets are fully covered is consistent with the highly organized nature of these facets, which lend themselves well to full packing of the CdX₂ ligands. On the other hand, as each carboxylate is required to bridge two Cd atoms, the (100) faceting can only accommodate half of the carboxylate ligands that are associated with a full Cd coverage; this "enrichment" of Cd²⁴ on the selenide-rich (100) surface balances the net negative charge of these facets, which likely provides a large amount of the driving force favoring the (100) faceting of these zincblende nanocrystals (everything else being equal, and prior to reconstruction, (100) facets are always less stable than (111) facets in diamond-like structures).⁹¹ Overall charge neutrality can be maintained by the transfer of an equal amount of carboxylates onto the opposite Cd-rich surfaces, which not only provides a mechanism to passivate the 3-coordinated cadmium atoms in the absence of L-type ligands, but also reduces the net positive charge of these facets. Overall, the results presented herein allow to develop a clearer representation of the schematic dual exchange reaction scheme used in the Introduction (Scheme 1), where the B_1 and B_2 sites are localized on specific facets.

Correlating 3.6 Specific Facet Vacancies with Photoluminescence Quantum Yields: Dark vs Bright NCs. In Section 3.4, we correlated how vacancies generated on each of the two specific sites, B_1 and B_2 , affected the photoluminescence efficiency. Having now in hand a better microscopic description of the nature of each of these sites, we complete this study by correlating the proposed surface composition of zinc-blende CdSe NCs with their observed photoluminescence behavior. Although we found in Section 3.4 that $B_1/(111)$ vacancies are not as effective as $B_2/(100)$ vacancies in quenching the PL of CdSe NCs, we were also led in Section 3.5 to postulate the existence of a rather large number of $B_1/(111)$ vacancies that are present in the asprepared samples (that is, before the deliberate displacement of CdX₂ complexes by TMEDA). As a consequence, assuming that each of these vacancies provides the same types of nonradiative relaxation pathways than those we found for $B_1/(111)$ vacancies generated by the action of TMEDA, we can readily estimate the starting PLQY of such as-prepared NCs (which we label here as "bright" NCs, to distinguish with "dark" NCs we will soon discuss):

$$PLQY_{bright} = \frac{1}{1 + K_{SV}^{B_1} \left(N_{1,tot} - N_1 \right)}$$
(19)

where the difference between $N_{1,tot}$ (Table 5) and N_1 (Table 1) corresponds to the number of $B_1/(111)$ vacancies per NC, and we assume that a NC without any vacancies would possess unity PLQY. The estimated PLQY_{bright} obtained from eq. (19) are listed in Table 4, and qualitatively compare well with the observed PLQY of each samples, although being systematically larger. One additional contribution to the PLQY of CdSe NCs might arise from the presence of $B_2/(100)$ vacancies. Although such vacancies cannot be predominant given the free energy cost, any NC with even a single of these vacancies would have a significantly lower PLQY than NCs with only $B_1/(111)$ vacancies, and would properly be described as a "dark" NC compared to the ensemble. The probability that a $B_2/(100)$ vacancy is found, P_{dark} can be calculated from the equilibrium of eq. (15), using the number of $B_1/(111)$ vacancies and the revised equilibrium constant K_1 (~ 0.2) obtained in Section 3.5; the calculated values for P_{dark} are listed in Table 4, and are all found to be on the order of 1% for the different NC sizes sampled here. The photoluminescence of these "dark" NCs can be obtained from the Stern-Volmer analysis data of Section 3.4:

$$PLQY_{dark} = \frac{1}{1 + K_{SV}^{B_1} (N_{1,tot} - N_1 + 1) + K_{SV}^{B_2}}$$
(20)

where for simplicity only the case of single $B_2/(100)$ vacancy per NC is treated (the probability that a NC is found with more than one vacancy is lower than 0.1% in all cases). The values listed in Table 4 show that photoexcited "dark" CdSe NCs are at least ten times less likely to radiatively recombine than their "bright" counterparts, with smaller NCs presenting the most striking dark/bright contrasts. It is important to point out here that the distinction made here between "dark" and "bright" NCs is likely not linked to the ubiquitous "blinking", or PL intermittency, phenomenon exhibited by most NC materials,^{26,92} as the "dark" PLQY values calculated here are still too large to sufficiently explain that phenomenon. Recent studies have suggested that PL blinking is probably linked to electron trapping processes that lead to delayed PL on long timescale:93-9 such electron trapping processes, the microscopic origin of which is still under debate, are not taken into account here, but perhaps explain partly the remaining discrepancy between the PLQY values we simulate and the observed ones. At any rate, we emphasize emphatically here that the proposed model of the overall PLQY discussed in this Section should not be taken too literally given the complexity of the actual problem. Rather, these results should be taken as representing part of the puzzle: inasmuch as the specific surface sites we uncovered here do exist on CdSe NCs, there will be unavoidable non-radiative losses associated with these; using an objective assessment of the actual prevalence of each site vacancy leads to qualitative agreement with the observed PLQY, suggesting that our estimate of the non-radiative recombination efficiencies of each type of site and of the surface composition are reasonably accurate. In this case, whereas full coverage of the Se-rich (100) facets appears critical to limit efficient non-radiative absolutely recombination in zinc blende CdSe NCs, for carboxylatecapped species the (100) facets rarely exhibit vacancies, and it is the low coverage of the (111) facets that effectively dictates the relatively low PLOY of the as-prepared materials.

5. CONCLUSIONS

In summary, we have demonstrated a direct correlation between specific surface defects and non-radiative recombination processes occurring at the surface of cadmiumrich zinc-blende CdSe NCs. The model developed here provides for the first-time direct evidence for the specificity of different crystalline facets with regards to the free-energy changes associated with the binding of cadmium carboxylate complexes, allowing for a detailed account of the distribution

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1 of these species over the different facets. These results provide 2 insights into the complexity of the surface of CdSe NCs, 3 which are expected to impact the development of targeted 4 designs of efficient NC systems for energy-conversion 5 applications. 6 **ASSOCIATED CONTENT** 7 8

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

> Additional NMR data, PL quenching, data analysis for all sizes of nanoparticles, nanoparticle characterization, XRD, TEM, and FTIR (PDF)

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Table of Content Figure

















