## **Supporting Information**

# Ligand Dynamics on the Surface of CdSe Nanocrystals

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#### A further analysis of the binding configurations.

(100) facets. Bridging/chelating mode 1-2-1 (**Figure S1.1**). Most oleates chelate a Cd atom, while one of their oxygens bridges between the chelated and the neighbor Cd. In this way two oxygens compensate the absence of Se atoms in the crystal lattice, optimizing oleate packing on the surface. One oxygen for each oleate, however, is out of lattice and sits on top of Cd in an unstable position. This binding is therefore not rigid and oleates assume, different conformations, such as the 2-2-1 (**Figure S1.2**) and 1-1-0 (**Figure S1.4**) binding modes, for brief intervals.



Sometimes oleates were observed breaking the ordered ligand arrangement and assuming positions

perpendicular to the  $\sigma_{yz}$  mirror planes oriented towards (111). The binding mode in these cases was found to be 2-2-0 (**Figure S1.6**): both oxygens bridge neighbor Cd atoms without chelating any of them. Fluctuations of carboxylate are strongly correlated among the same planes, with neighbor oleates likely to assume same binding modes and resulting in global moves that appear concerted.

(111) facets. Binding is distributed among the different modes. A binding mode was found only in this facet: the chelating/bridging 1-3-1 (**Figure S1.3**), in which an oxygen atom is in a lattice site.

(111) facets. The most straightforward way to visualize this peculiar type of binding is considering that Cd<sub>2</sub>(oleate) are created following a simple mechanism: i) Cd atoms initially diffuse to (111) either from sub-surface layers or from (111) facets; ii) an oleate molecule jumps on the defects and stabilize it. The diffusion of oleates on (111) hence primarily occurs as a collective motion of Cd<sub>2</sub>(oleate), i.e. two Cd atoms move on the surface with the oleate molecule attached to them. Cd<sub>2</sub>(oleate) then fluctuates between 1-2-1 and 1-1-0 binding modes.



**Fig. S2** Breakdown of the evolution of Se-2c states on the NC model at 500K. (a) Representation of the variation of the density of Se-2c states over the average lifetimes of the MD replicas. (b) Representation of the evolution of the decay of Se atoms to Se-2c over the course of the MD replicas. (c) Two examples of the evolution of the coordination of Se atoms located on edges/vertices of the model.

#### The role of temperature in the dynamics of Se-2c.

In their most common practical applications<sup>1–3</sup>, CdSe NCs are exposed to external perturbations that cause the local heating of the systems, as well as other side processes (i.e. surface reconstruction and creation of defects). We investigated the behavior of our NC models at higher temperatures by extending the final state of the replica MD for 1 µs at 298K and 1 atm. Thereafter,

the temperature of the simulation was brought to 500K in 20 ns and the dynamic behavior of the system was simulated at that temperature for an additional 480 ns. For statistical analysis, the initial 20 ns of these last 500K simulation were discarded.

Surface reconstructions and ligand diffusion were found to be higher at 500K, resulting in less ordered ligands and in overall higher ligand density, particularly on (111) facets. Additionally, more atoms were found in Se-2c states at 500K, and Se-2c states were generally found along all the simulation. Their densities, shown in **Figures S2**, show the presence of short-spanned excitation and reconstruction processes (**Figure S2.a**) at 500K characterized by overall high densities (**Figure S2.b**) and variable coordination numbers (**Figure S2.c**). Both local rearrangements and global reconstructions were enhanced by the higher temperature: globally, Se-2c states were shorter because quickly compensated by the global reconstructions. This behavior suggests the necessity to account for the effect of the increased number of excited states in future technological applications, as the number of defects is directly correlated to the stability of the NC models. In addition, the timespans of their relaxation at room temperature were found to be relatively long at higher temperatures, suggesting that any strategy aimed at the elimination of these defects would occur more effectively at lower temperatures.

### References

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