

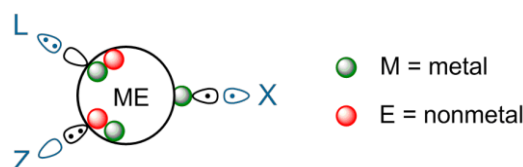
Carboxylic Acid Passivated Metal Oxide Nanocrystals, Ligand Exchange Characteristics of a New Binding Motif**

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Abstract: Ligand exchange is central in the processing of inorganic nanocrystals (NCs) and requires understanding of surface chemistry. Studying sterically stabilized HfO_2 and ZrO_2 NCs using ^1H solution NMR, IR and elemental analysis, this paper demonstrates the reversible exchange of initial oleic acid ligands for octylamine and self-adsorption of oleic acid at NC surfaces. Both processes are incompatible with an X-type binding motif of carboxylic acids as reported for sulphide/selenide NCs. We argue that this unexpected behavior stems from the dissociative adsorption of carboxylic acids at the oxide NC surface. Both proton and carboxylate moieties must be regarded as X-type ligands yielding a combined X_2 binding motif that allows for self-adsorption and exchange for L-type ligands.

Colloidal nanocrystals (NCs) are hybrid objects where the properties of core and surface both determine the characteristics of the entire NC. The surface is often capped by (in)organic ligands which determine the colloidal stability and the physical and chemical properties.^[1] As a result, NC surface chemistry, i.e., the understanding of and control over the ligand shell, has become one of the central themes in NC research.

The Covalent Bond Classification (CBC)^[2] provides an apt framework to describe NC-ligand binding.^[1a, 3] Ligands are defined as L-, X- or Z-type depending on the number of electrons that the neutral ligand contributes to the NC-ligand bond (2, 1 or 0 respectively). This classification is unambiguous^[4] and allows to label distinct NC-ligand model systems (Scheme 1). L-type ligands such as amines and phosphines are neutral donors of a free electron pair. In apolar solvents, they coordinate to surface metal ions of stoichiometric NCs to yield overall charge-neutral objects.^[5] Z-type ligands are neutral electron-pair acceptors (e.g., metal carboxylates) that bind to the surface anions of stoichiometric NCs.^[1a] In NC surface chemistry, X-type ligands are presented as negatively charged ligands (RCOO^- , OH^- , Cl^-) that bind to excess surface cations of non-stoichiometric NCs.^[1a, 6] Although this concept is correct, it is a too restrictive description as we argue in this paper. According to the original CBC, ligands must be classified in their neutral form. X-type ligands are thus formally regarded as radicals (Scheme 1).



Scheme 1. The Covalent Bond Classification (CBC) considers L-type ligands as Lewis bases, Z-type as Lewis acids and X-type as radicals.

Obviously, desorption or adsorption of L- and Z-type ligands involves the separation or combination of two neutral, closed shell moieties. In contrast, self-desorption of X-type ligands implies the formation of either radicals or charged species. The former process is generally unfeasible and the latter is thermodynamically unfavorable in apolar media due to the low dielectric screening. For the same reason, it would be impossible to exchange X-type ligands for L-type ligands. Anionic X-type ligands can only be traded for other anionic X-type ligands by the transfer of a proton or trimethylsilyl group.^[3, 6a, 6c, 7]

In contrast to CdSe NCs,^[6a] the surface of ZnO, TiO_2 , ZrO_2 and HfO_2 NCs can adsorb protons.^[8] In case of fatty acid capped ZrO_2 and HfO_2 NCs, we recently showed that both carboxylate and proton bind to the metal oxide NC surface.^[8d] This internal proton source could facilitate new exchange reactions, but evidence was lacking. In this paper, we investigate exchange and self-adsorption of oleic acid (HOAc) on HfO_2 and ZrO_2 NCs, benchmarked against oleate capped CdSe NCs. Our findings indicate that the dissociated carboxylic acid can be described as an X_2 ligand, i.e., a combination of a cationic X-type ligand (H^+) and an anionic X^- type ligand (RCOO^-). This new binding motif results in exchange characteristics comparable to that of L-type ligands.

HfO_2 , ZrO_2 and CdSe NCs were synthesized according to established procedures and HOAc was employed as ligand.^[9] HOAc can populate three different states; chemisorbed to the NC, physisorbed in the ligand shell and free in solution.^[6a] However, the ^1H NMR spectrum of a purified HfO_2 NC dispersion features only broadened signals of chemically bound HOAc (Figure 1A), i.e., no free or physisorbed acid is present in the sample. Upon addition of octylamine (Am), the alkene resonance changes and a new signal appears at a slightly lower chemical shift (Figure 1B). This is a mixed state resonance, the result of fast exchange between physisorbed and free HOAc, featuring a population averaged chemical shift and line width. This signal increases and sharpens with increasing Am concentration, indicating the growing contribution of the free state. However, the physisorbed contribution is still apparent from the negative $n\text{Oe}$ cross peaks, innate to bound states (Figure 1C).

Regarding the resonances of the amine, we focus on the $\alpha\text{-CH}_2$ of Am (2.3 ppm) since it is separated from the aliphatic signals of HOAc. Only a single resonance without fine structure is

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observed and this resonance clearly leads to negative nOe cross peaks (Figure 1C). From these two features we infer that Am is in fast exchange between a bound and a free state and only a time average is detected.^[10] The above results suggest that HOAc is displaced by Am.

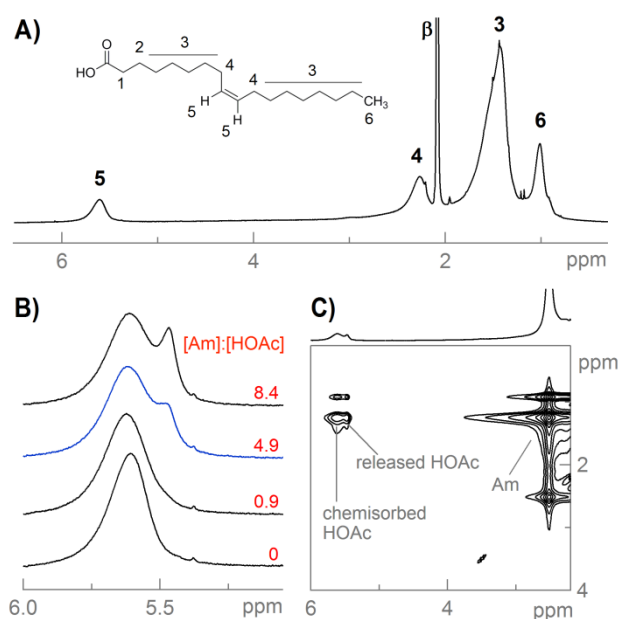


Figure 1. A) Bound HOAc (3-6) and toluene (β) are noted in the 1H NMR spectrum of a HfO_2 NCs dispersion in toluene- d_8 , $[HOAc] = 10.69 \text{ mol L}^{-1}$. B) Upon addition of Am the alkene resonance splits in two parts, bound and free acid. C) 2D NOESY spectrum of HfO_2 NCs + 8.4 eq of Am.

As reported by Owen et al. the addition of amines to oleate capped CdSe NCs releases coordinated $Cd(OAc)_2$.^[1a] Although no subtle changes in the alkene resonance were analyzed – probably due to the higher amine concentration – this raises the question as to whether our results with HfO_2 could be explained by a release of $Hf(OAc)_4$ instead of HOAc. We therefore repeated our titration with CdSe NCs, adding similar amounts of Am as with the HfO_2 NCs. Again, a sharper alkene resonance appears (Figure 2A). Since this signal features negative nOe cross peaks (Figure S1), we again attribute it to a mixed state resonance with, however, slightly different characteristics. The fraction of mixed state – the released species – is much larger for CdSe than for HfO_2 , as determined by deconvolution of the alkene resonance (Figure 2B), indicating a more effective ligand exchange for CdSe NCs. Furthermore, a comparison of the blue spectra in Figure 1B and 2A, both having a more or less equal amount of released alkene (Figure 2B), shows that the mixed resonance of CdSe NCs appears at lower chemical shifts and is more narrow. We conclude that the free state is more predominant in case of $Cd(OAc)_2$ release. Indeed, even a first hint of fine structure is observed for the mixed resonances in Figure 2A, innate to free molecules. Since $Cd(OAc)_2$ can be coordinated in solution by excess Am, it will populate less the physisorbed state due to steric hindrance. This behavior is not observed in the titration of HfO_2 NCs, indicating that the released species is not $Hf(OAc)_4$.

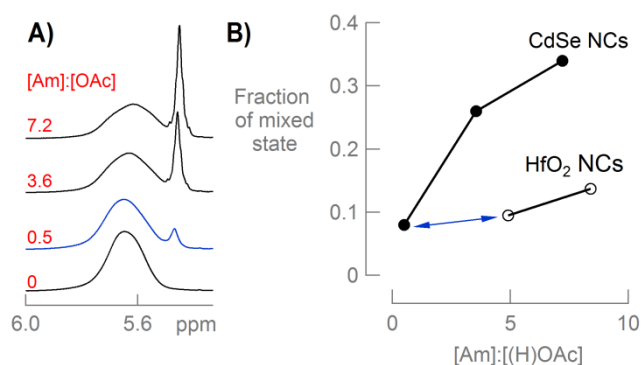


Figure 2. A) A new alkene resonance appears upon addition of Am to a CdSe NC dispersion in toluene- d_8 . B) Am releases a higher fraction of original ligand at CdSe NCs than at HfO_2 NCs.

To confirm the nature of the released species we combined IR, NMR and XRF analysis. Upon addition of Am to HfO_2 NCs, the expected carboxylic acid band at 1720 cm^{-1} is absent in the IR spectrum (Figure 3). However, released HOAc could be deprotonated by the excess of Am and form an ion pair. Indeed, the shape and position of the carboxylate peak (1570 cm^{-1}) of Am treated NCs is essentially the same as for a mixture of HOAc and Am.

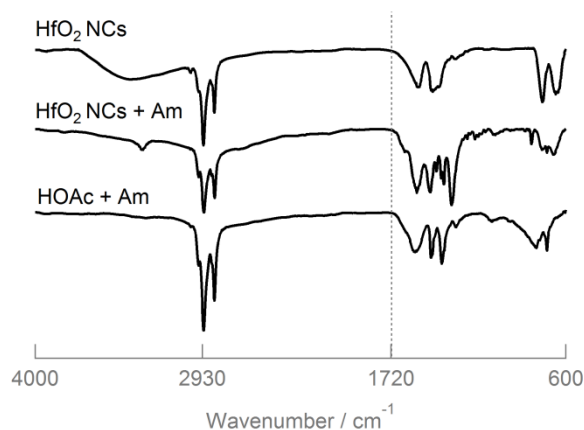
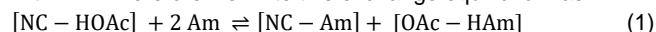


Figure 3. Carboxylic acid bands (1720 cm^{-1}) are neither observed in the FTIR spectrum upon addition of Am to HOAc capped HfO_2 NCs nor in a mixture of HOAc and Am.

However, IR does not allow to differentiate between the ion pair and $Hf(OAc)_4$. Therefore, we precipitated the Am treated NCs with methanol. After centrifugation, the supernatant was dried under vacuum and the resulting oil was dissolved in deuterated methanol and measured in NMR and XRF. An alkene resonance with fine structure was observed in the 1H NMR spectrum (Figure S2) indicating free species. The intensity of the resonance was comparable to the mixed state resonance in the titration experiment, confirming that we were able to quantitatively separate the NCs from the released species. In addition, no hafnium was detected by XRF analysis (Figure S3) so we finally conclude that the displaced species is HOAc and not $Hf(OAc)_4$.

Clearly, the exchange reaction is an equilibrium. In addition, the NOESY spectrum (Figure 1C) proves that Am has a bound state

and IR analysis showed that released HOAc forms an ion pair with Am. Therefore we write this exchange equilibrium as:



The reaction formally comprises 3 equilibria; oleic acid desorption (2), octylamine adsorption (3) and ion pair formation (4).



We calculated a reaction quotient of $2.0 \pm 0.6 \cdot 10^{-5}$ for the exchange reaction (1), confirming that carboxylic acids bind stronger to the NC surface than amines (calculation in SI). Importantly, the reaction quotient is only independent of amine concentration if equilibrium (4) is included (Figure 4A). This stresses the central role of the ion-pair formation in the exchange reaction.

Even more clear is the equilibrium's temperature dependence. We find that with increasing temperature equilibrium (1) is displaced to the left, i.e., less HOAc is removed from the surface by Am (Figure 4B). The exchange is therefore reversible and exothermic. If the exchange was regarded as a combination of only (2) and (3), it would be endothermic since amines bind weaker than carboxylic acids. However, reaction (4) is apparently sufficiently exothermic to render the whole exchange exothermic. Hence the identification of (4) as the main driving force of (1).

The same temperature dependence is observed for CdSe (Figure 4B). In that case, the driving force for exchange is most likely the exothermic coordination of octylamine to $\text{Cd}(\text{OAc})_2$,^[1a] rendering the overall reaction exothermic. This means that at high temperatures – typical for NC syntheses – the adsorption of amines is negligible compared to the binding of metal carboxylates or carboxylic acids.

Auto-desorption of HOAc (2) does not take place without external driving force. Even when the temperature was raised to 130 °C, no indication of free HOAc was observed in the NMR spectrum. However, we could demonstrate the reverse, auto-adsorption, by gradually adding excess HOAc to a HfO_2 NC suspension which was purified 5 times with acetone (Figure 5). The concentration of bound ligand increased with 17 % (at 0.4 eq HOAc excess). HOAc is thus capable of spontaneous dissociation on the oxide surface at 25 °C. The free adsorption sites probably emerged from the extensive purification. Indeed, DLS measurements (Figure S4) confirm that aggregates are formed during the purification, indicating ligand stripping. In contrast, HOAc does not display such binding behavior towards CdSe NCs.^[6a]

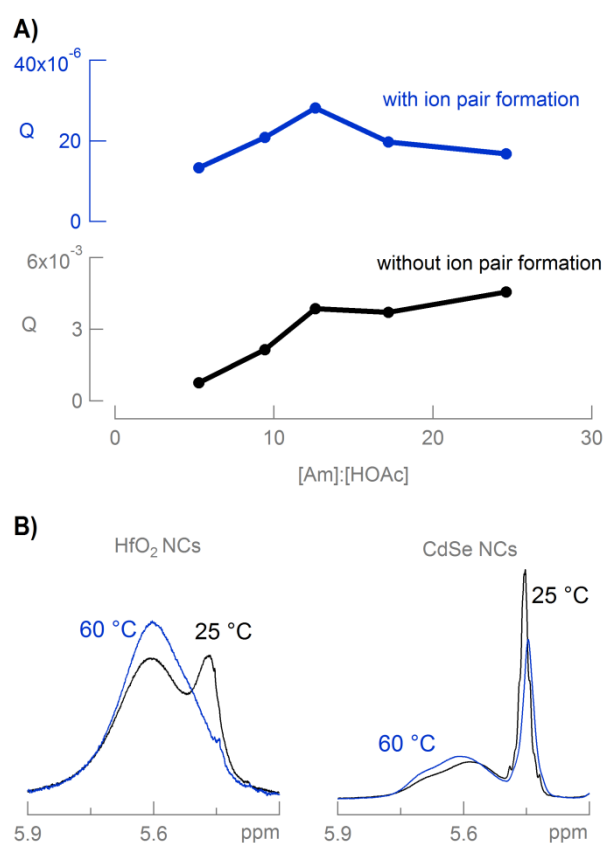


Figure 4. A) The exchange reaction quotient in function of amine concentration. B) Temperature dependence of the alkene resonance after titration with Am.

Scheme 2 summarizes the ligand exchange processes we observed at HfO_2 NCs. First, there is the exchange of carboxylic acids for amines, typical L-type ligands. Note that the driving force is the acid-base ion pair formation. Second, self-adsorption of HOAc on the HfO_2 surface was recognized.

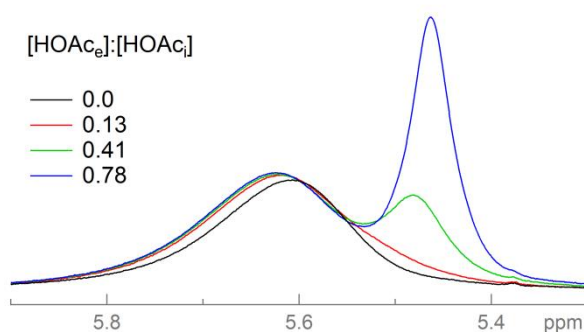
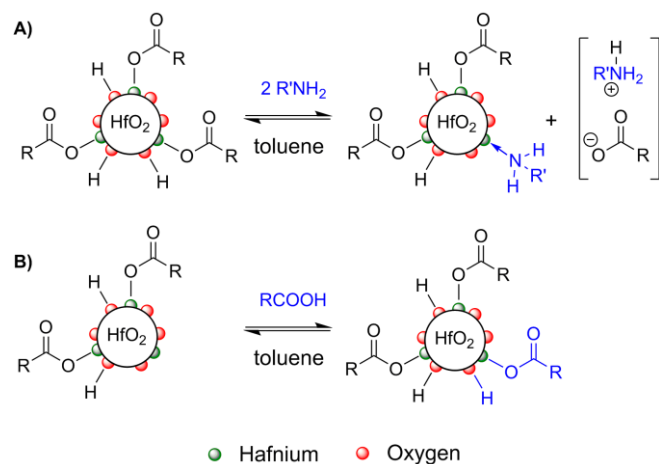


Figure 5. Change of the alkene resonance upon progressive addition of excess oleic acid, $[\text{HOAc}_e]$.

These reactions can be rationalized within the concepts offered by the CBC. An X-type ligand is a radical, which can either take an electron (anionic X-type, RCOO^-) or donate its own electron (cationic X-type, H^+) upon formation of an ionic NC-ligand bond. Hence, dissociative adsorption of carboxylic acids brings two X-type moieties on the NC surface, proton and carboxylate.

Opposite from a single X-type ligand, this overall charge neutral X_2 motif can be exchanged for L-type ligands, either by direct release of X_2 or by the formation of complexes such as the ion pair observed here.



Scheme 2. A) L-type alkylamines displace X_2 -type carboxylic acid B) Auto-adsorption of carboxylic acids at the HfO_2 NC surface.

To generalize these findings, we repeated the Am titration with ZrO_2 NCs capped with HOAc. Importantly, the ZrO_2 NCs were synthesized with a different precursor, leading to a crystal structure and initial surface chemistry different from the HfO_2 NCs.^[9c] Nevertheless, we observe the release of HOAc acid upon titration with Am (Figure S5), a result indicating that our model may apply to metal oxide NCs in general. Indeed, the ability to hold protons on the surface depends on the basicity of the anion rather than on the nature of the metal although the latter's influence cannot be fully excluded.

In conclusion, we have shown that octylamine releases oleic acid from HfO_2 and ZrO_2 NCs while cadmium oleate is released from CdSe NCs. The ligand exchange reaction is rendered exothermic and thus impeded at high temperature by the formation of an acid/base pair in case of oxides or a metal complex in case of CdSe. Finally, oleic acid features self-adsorption at the oxide but not at the CdSe NC surface. We argue that the exchange characteristics of carboxylic acids bound to metal oxide NCs result from their dissociative adsorption. The NC surface thus contains equal amounts of anionic and cationic X-type ligands, a binding motif we label as X_2 . Importantly, the X_2 -type binding brings about a new class of NC-ligand systems – stoichiometric NCs with overall neutral X_2 ligands – in addition to cation rich NCs with anionic X-type ligands and stoichiometric NCs with neutral Z- or L-type ligands. Our work indicates that this new NC-ligand class will be most relevant to understand to surface chemistry of metal oxide NCs in general.

Keywords: CdSe • Ligand exchange • Nanoparticles • NMR spectroscopy • Surface chemistry

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