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Physics and Chemistry of Nanostructures Group

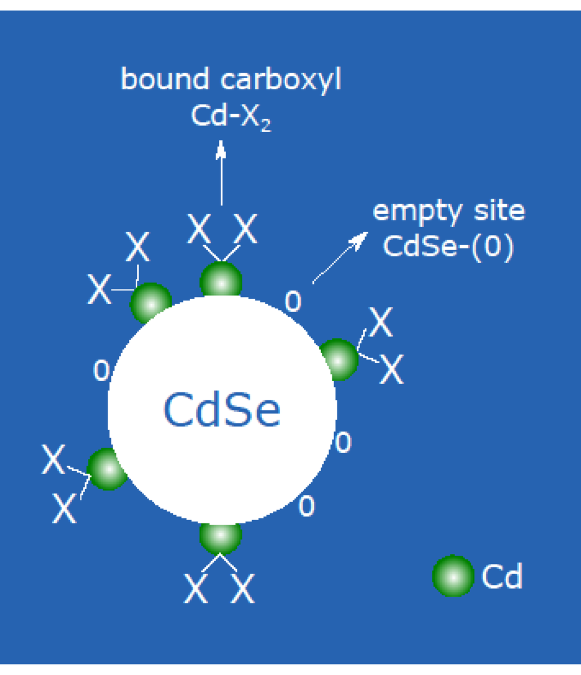
Influence of Ligand Shape and Steric Hindrance on the Composition of the Nanocrystal Ligand Shell

Kim De Nolf[1,2] | Jacek J. Jasieniak[3] | José C. Martins[4] | Zeger Hens[1,2]

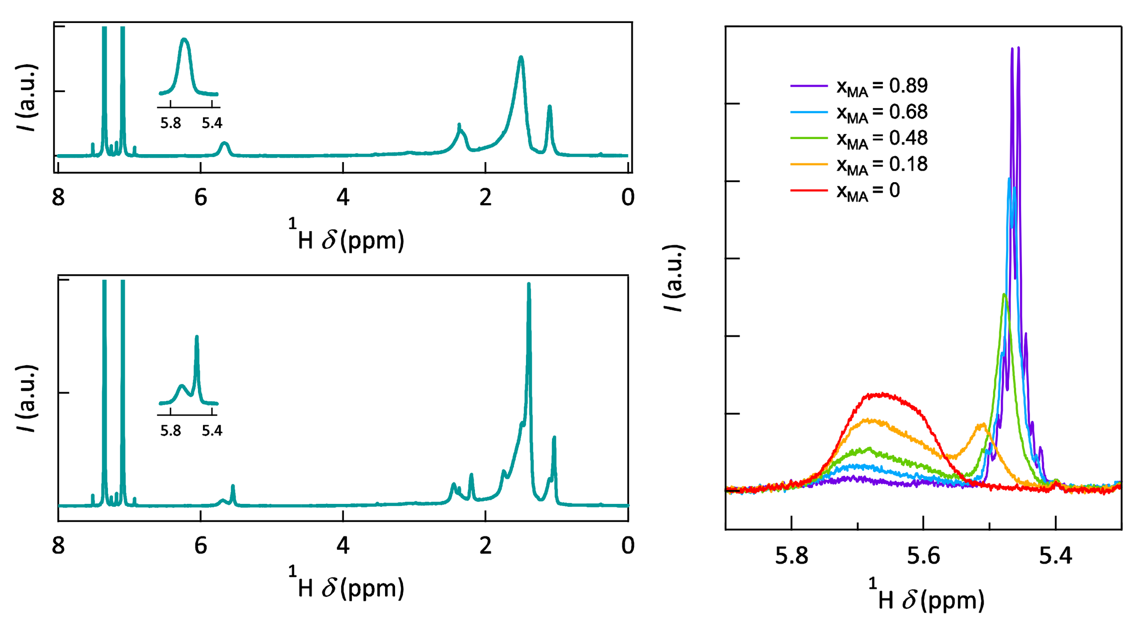
[1] Physics and Chemistry of Nanostructures, Ghent University
[2] Center for Nano- and Biophotonics, Ghent University
[3] CSIRO, Materials Science and Engineering, Clayton, Australia
[4] NMR and Structure Analysis, Ghent University

Introduction

Organic ligands play a key role in the synthesis of colloidal semiconductor nanocrystals or quantum dots. The functional group of those ligands ensures the binding to the nanocrystal surface, while the stability of the dispersion strongly depends on the interactions between the organic chains of the adjacent ligands. A number of studies already addressed the binding strength and the type of binding between the nanocrystal surface and the ligand yet none discuss the effect of the organic chain on the ligand exchange. By means of NMR spectroscopy, we examine the ligand shell composition of CdSe nanocrystals originally capped with oleic acid (OA), when exposed to linear and branched carboxylic acid.



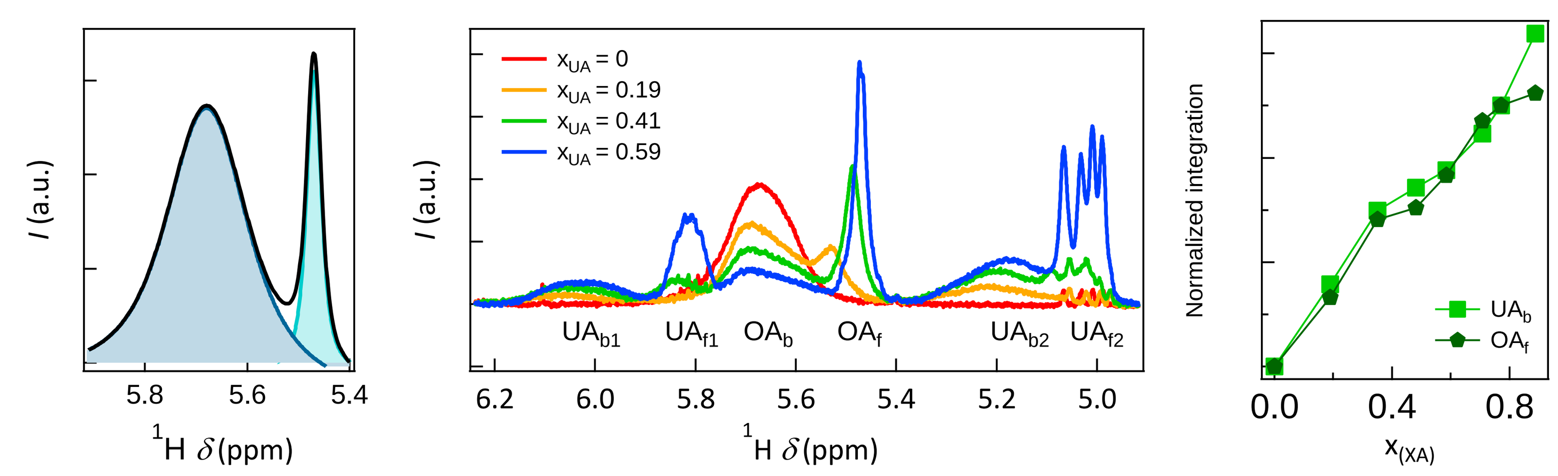
Addition of Carboxylic Acid



XA addition = all resonances obtain sharp twin peak.

Alkene signal has sharp shoulder = bound OA was released upon addition of the XA.

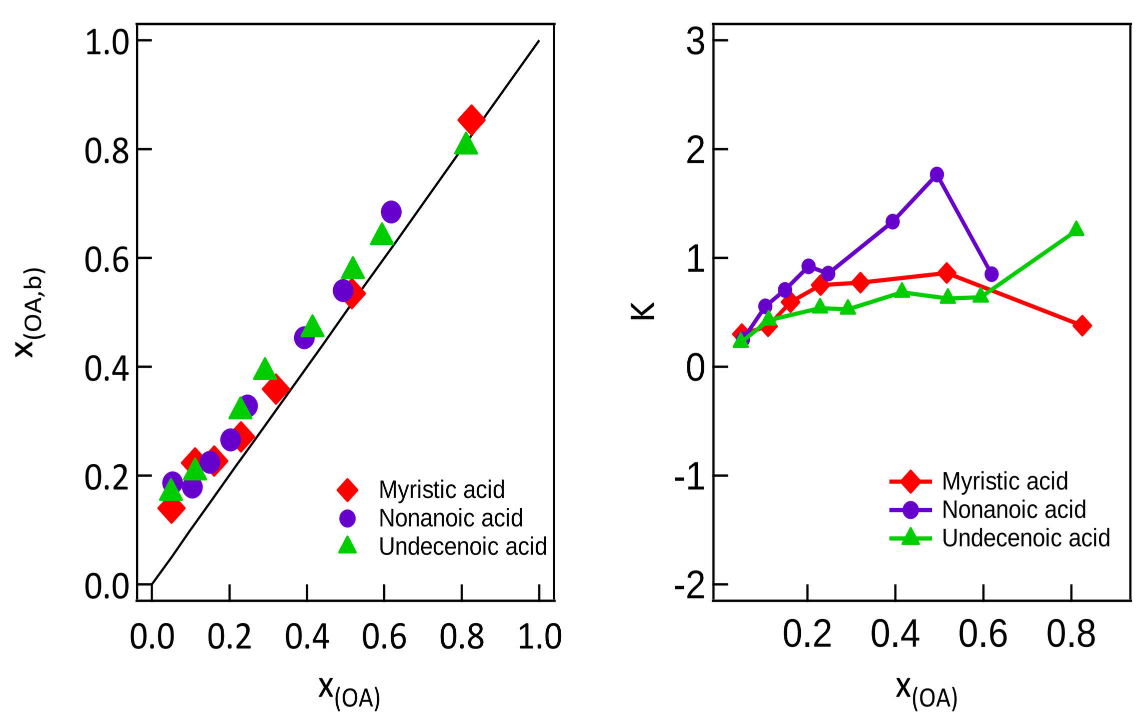
One-for-One Exchange



Undecenoic acid and oleic acid both have separate NMR features = easy monitoring

One-for-one exchange bewteen OA and UA: $n_{OA_f} \approx n_{UA_b}$

Linear Caroxylic Acid



$CdSe\text{-}CdOA_2 + 2HX \rightleftharpoons CdSe\text{-}CdX_2 + 2HOA$

OA fraction in dispersion ↓
= OA fraction in the ligand shell ↓

Composition of ligand shell
= Composition ligand mixture in solution

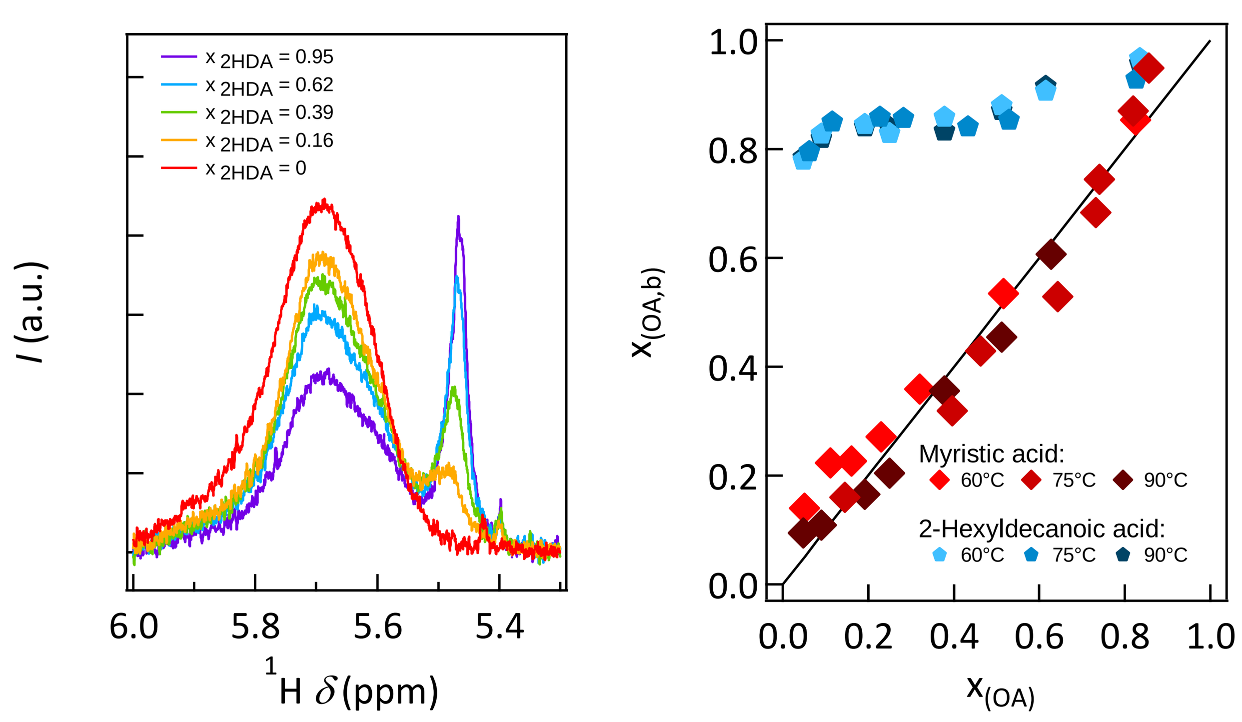
$$K = \frac{[\theta_{XA}]\,[HOA]}{[\theta_{OA}]\,[HXA]} \approx 1$$

K is cte → Ligand shell = ideal mixture of both ligands.

K ≈ 1 → $\Delta G^0 \approx 0$

Equilibrium is purely entopic

Branched Caroxylic Acid



$CdSe\text{-}CdOA_2 + CdSe\text{-}(0) + 2HDA \rightleftharpoons 2HOA + CdSe\text{-}HDA_2$

2-hexyldecanoic acid replaces no more than 25% of the oleic acid, even in high 2-HDA excess.

Exchange process: incoming ligand not only displaces oleic acid but also occupies additional space in the ligand shell to accommodate both aliphatic chains.

Conclusion

→ Regardless of chain length, the composition of the ligand shell closely matches that of the ligand mixture in solution

→ The ligand shell can be seen as an ideal mixture of both ligands

→ A mixed ligand shell can easily be prepared by adding a ligand mixture with desired composition to the nanocrystal dispersion.

→ A branched carboxylic acid is capable of replacing no more than 25% of the oleic acid, even in high 2-hexyldecanoic acid excess

→ 2HDA not only displaces oleic acid but also occupies additional space in the ligand shell to accommodate both aliphatic chains.

→ Results can be very useful in view of producing nanocrystals with lower ligand densities by means of synthesis with branched carboxylic acids.

NMR & structural analysis unit

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nb-photonics Center for Nano- and Biophotonics Ghent University

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