NMR Studies on the Phosphonic Acid Oxide Capping of Colloidal Semiconductor Nanocrystals

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Shape control of colloidal nanomaterials with a wurtzite crystal structure like CdSe and CdS can be attained by translating the intrinsic crystal anisotropy into an anisotropic growth kinetics. Especially in the presence of phosphonic acids like octadecylphosphonic acid (ODPA), it was found that when the reaction is under kinetic control, the crystals generally grow faster along the *c*-axis, leading to the formation of quantum rods.[1] This experimental result has been substantiated by theoretical calculations on the relative binding strength of different ligands, which confirmed that phosphonic acids bind more strongly than fatty acids, amines, phosphines or phosphine oxides to the CdSe surface, with a specific affinity for the $11\bar{2}0$ surfaces parallel to the *c*-axis.[2] In spite of their key role in the formation of anisotropic nanoparticles like quantum rods, [1,3,4] the interaction of phosphonic acids with CdSe nanoparticles, and especially their binding strength relative to other ligands has not been experimentally investigated so far.

Here, we use solution nuclear magnetic resonance (NMR) spectroscopy to analyze the binding of phosphonic acid to CdSe quantum dots (QDs). Especially in the case that free/bound exchange is slow with respect to the NMR time scale, solution NMR is a suitable technique for this purpose.[5,6] Resonances of bound ligands appear broadened and shifted with respect to free ligand resonances, which enables to identify and quantify the ligands. Moreover, additional information can be obtained using diffusion ordered spectroscopy (DOSY), where the resonances of the free and surface-bound ligands are separated along the diffusion dimension, or using Nuclear Overhauser Effect Spectroscopy (NOESY), where efficient cross relaxation is indicative of ligand/nanoparticle interaction.[5]

In this work, we apply both ^{1}H and ^{31}P-NMR to study ODPA capped CdSe nanocrystals. As a starting point, we present the results regarding CdSe QDs that are used as seeds in the growth of highly luminescent CdSe/CdS QRs.[4] Although the reaction mixture to synthesize these CdSe QDs is complex and includes other possible ligands such as TOP (trioctylphosphine) and TOPO (trioctylphosphine oxide),[4] ODPA could be identified as the only ligand adsorbed at the QDs, using ^{31}P-NMR. As shown in Fig. 1A the spectra of ^{31}P-NMR CdSe QDs in THF is broad. Indeed, after the addition of ODPA a sharp signal develops at 30 ppm, thus assigned to the free ligand. Moreover, upon extraction of the organic part of the sample, the remaining free molecules give rise to a single peak at *ca* 30 ppm coincident with the one found for ODPA. Taking into account that TOP has a resonance at -33 ppm and TOPO at 40 ppm in ^{31}P-NMR spectrum, we conclude that ODPA is the only ligand of these CdSe QDs. In Fig. 1B, the ^{1}H-NMR shows also broad resonances corresponding to bound ODPA. From the integral of the peak at 1.31 ppm and using a reference of known concentration, a concentration of ODPA of 59.5 mM was determined. This corresponds to 4.45 ligands/nm^2.

In order to get a further insight into the system, we added excess oleic acid (OA) to the ODPA capped CdSe QD suspension. OA can be easily monitored in NMR by means of the resonance of the alkene protons at around 5.5 ppm. Even with an excess of 8:1, only free OA is observed, as shown in Fig. 2A. This result was corroborated by NOESY and DOSY measurements. Alternatively, two ligand exchange procedures (ODPA→OA) were performed successively, by adding a 100-fold excess of OA and heating the sample up to 60 ºC. After this treatment, we find that the alkene resonance is composed of a broad and a sharp component, indicative of bound and free OA. Based on the integration of the resonance, we find an OA:ODPA ratio of only 1:12. When excess ODPA is added to this sample, ^{1}H-NMR reveals that the intensity of the sharp feature in the alkene resonance increases, while the broad resonance goes down (Fig. 2B). This indicates that OA desorbs and is most likely replaced by the added ODPA. From the trend of the titration (*see* inset Fig. 2B), it is expected that when the added ODPA reaches 4 mM, the OA is completely replaced, that is, one molecule of ODPA replaces on average 1.1 molecules of OA.

In conclusion, we find that OA is readily and quantitatively replaced by ODPA on CdSe QD surfaces, while the reverse process is extremely difficult, that is, the binding strength of ODPA to CdSe QDs is indeed several orders of magnitude higher than that of OA. This study constitutes the first step towards the understanding of ligand exchange in the different facets of QRs and consequently the mechanisms for rod growth.

References

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Figure 1 – A) ^{31}P-NMR of ODPA capped CdSe QDs, the same after addition of ODPA and also after extraction of the organic part of the sample (free ligands only). B) ^{1}H-NMR of ODPA capped CdSe QDs. For all spectra CdSe QDs (2.9 nm, [QD]=506 µM, d_8-THF).

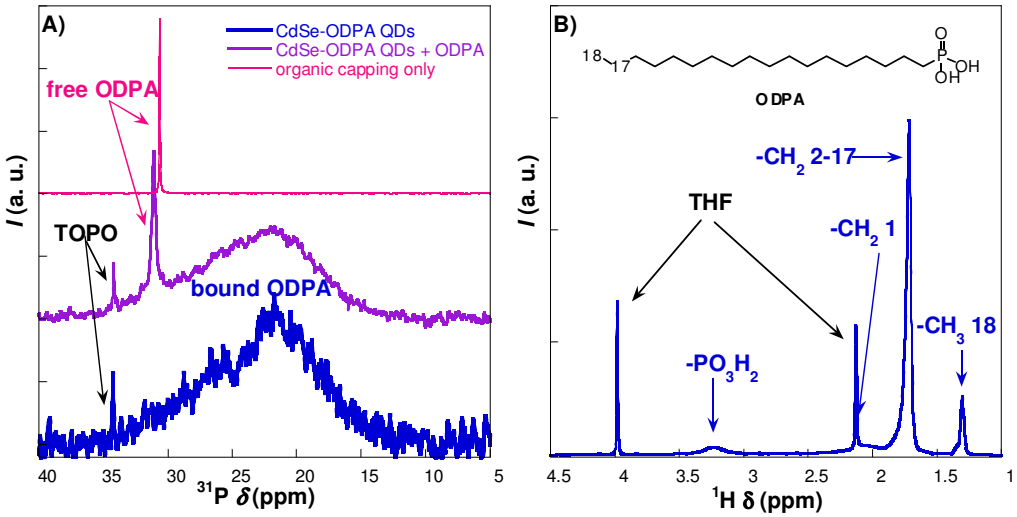

Figure 2 – ^{1}H-NMR spectra zoomed in the double bond region of OA. A) Addition of OA to ODPA capped CdSe QDs. B) Addition of ODPA to OA/ODPA capped CdSe QDs, *inset* intensity of the peak at 5.44 ppm in function of the concentration ratio added ODPA-bound OA.