The capping of colloidal semiconductor nanocrystals: a ^{1}H NMR study on InP-TOPO

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Colloidal semiconductor nanocrystals in the range 1-10 nm are promising building blocks for future nanodevices since they show strong quantum confinement effects even at room temperature [1,2]. Colloidal semiconductor nanocrystals consist of an inorganic core, having the same crystal structure as the corresponding bulk semiconductor, surrounded by a shell of capping molecules. These cappping molecules have several functions. During synthesis, they limit the growth rate of the nanocrystals. This makes it possible to separate nucleation from growth, yielding monodisperse colloidal solutions. In addition, the capping prevents aggregation of the nanocrystal by steric stabilisation. After synthesis, the capping molecules determines the physical and chemical properties of the nanocrystals [2]. For instance, the capping may passivate surface states yielding nanocrystals with a high luminescence quantum yield or the capping molecules may contain functional groups that make it possible to bind nanocrystals to a substrate [3]. Capping engineering, i.e. capping a nanocrystal with molecules that give the nanocrystal a desired property, will be of importance for future work on colloidal semiconductor nanocrystals. This makes direct observation of capping molecules an important challenge.

In this contribution, we report on an NMR study on InP nanocrystals capped with TOPO molecules. Measurements on samples containing TOPO-capped InP nanocrystals show TOPO spectra that are considerably broadened relative to the free TOPO spectrum (see Fig. 1, bottom). This is related to the loss of rotational freedom of the capping molecules. However, since an exchange equilibrium between free and adsorbed TOPO is established, the spectrum remains a superposition of adsorbed and free TOPO. We have isolated the spectrum of bound TOPO by diffusion-ordered spectroscopy (DOSY). Since they make part of the nanocrystal system, adsorbed TOPO molecules diffuse much more slowly through the solution than free TOPO molecules. This makes it possible to rule out the free TOPO contribution to the spectrum by working with large enough diffusion times in the DOSY experiment (see Fig. !, top). DOSY measurements give access to the diffusion constant of the species under investigation. Using solutions of InP nanocrystals with different mean diameter, we find that the hydrodynamic radius obtained from the diffusion constant of the adsorbed TOPO molecules scales linearly with the nanocrystals. This confirms the attribution of the slowly diffusing part of the NMR spectrum to adsorbed TOPO molecules.

This work shows that it is possible to observe the TOPO capping of InP nanocrystals by hydrogen NMR and to distinguish TOPO molecules free in solution from TOPO molecules adsorbed on the nanocrystals.

References:

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Figures:

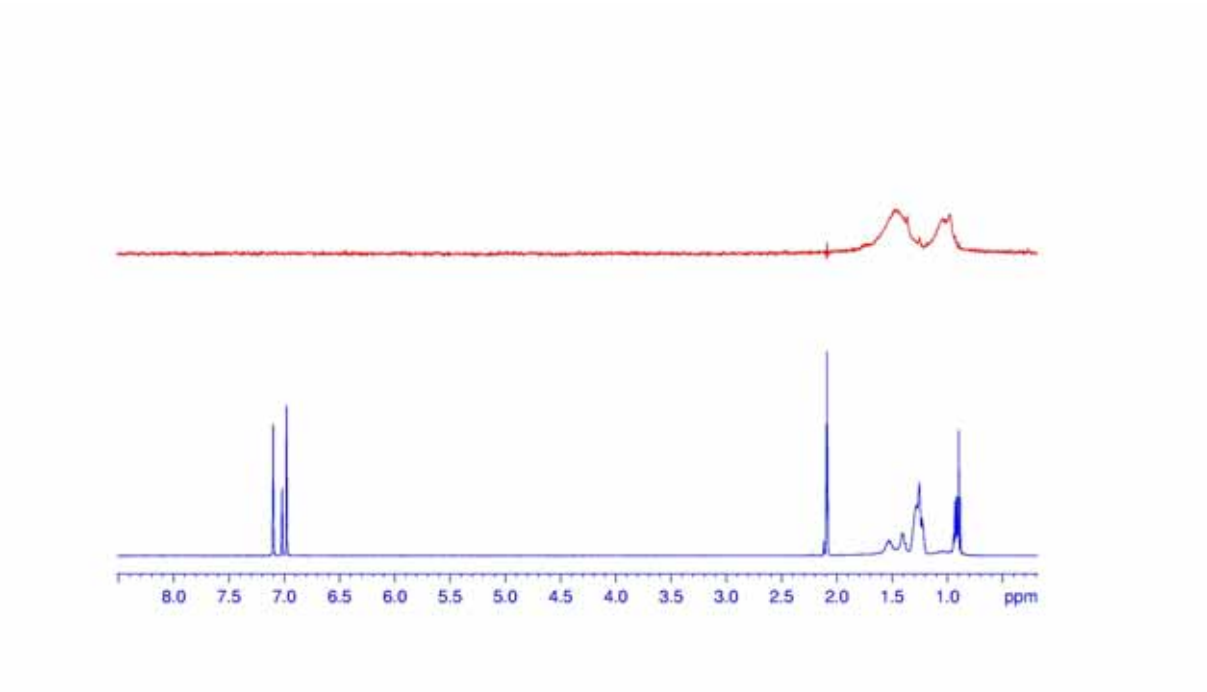

Figure 1: (Bottom): NMR spectrum of InP colloids dissolved in toluene. The toluene and TOPO signal are clearly visible (Top) DOSY spectrum of the same sample (diffusion time: 300 ms): only the broadened TOPO signal related to the adsorbed capping molecules remains. The vertical axis is different in both spectra.