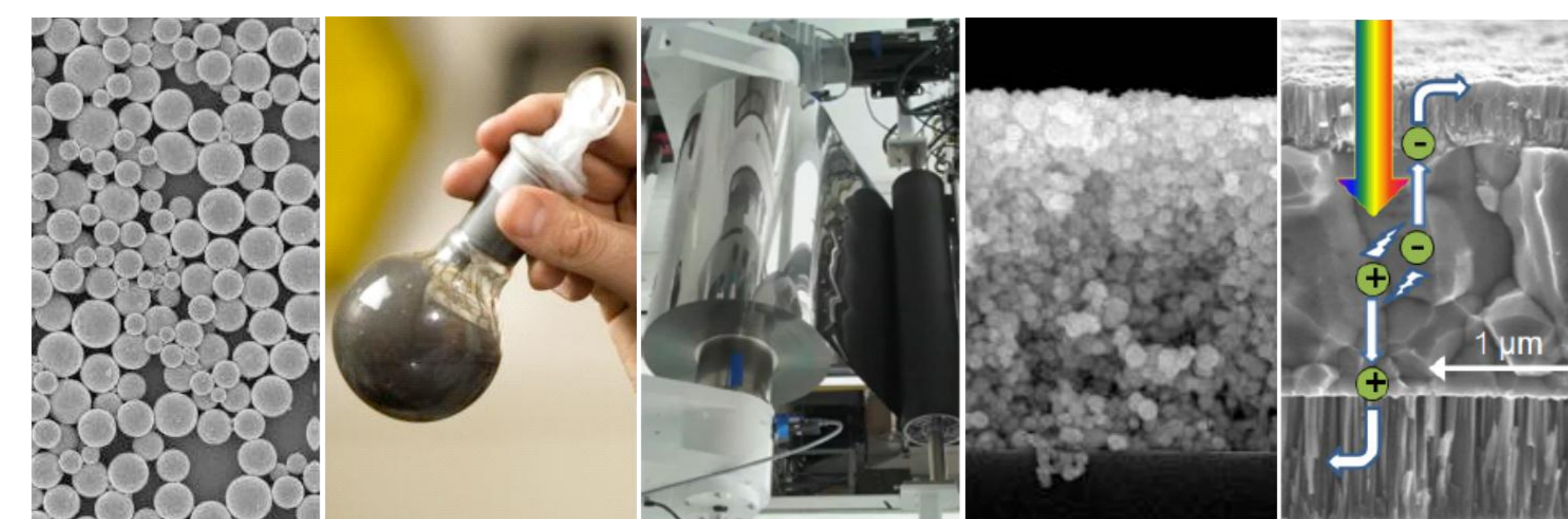
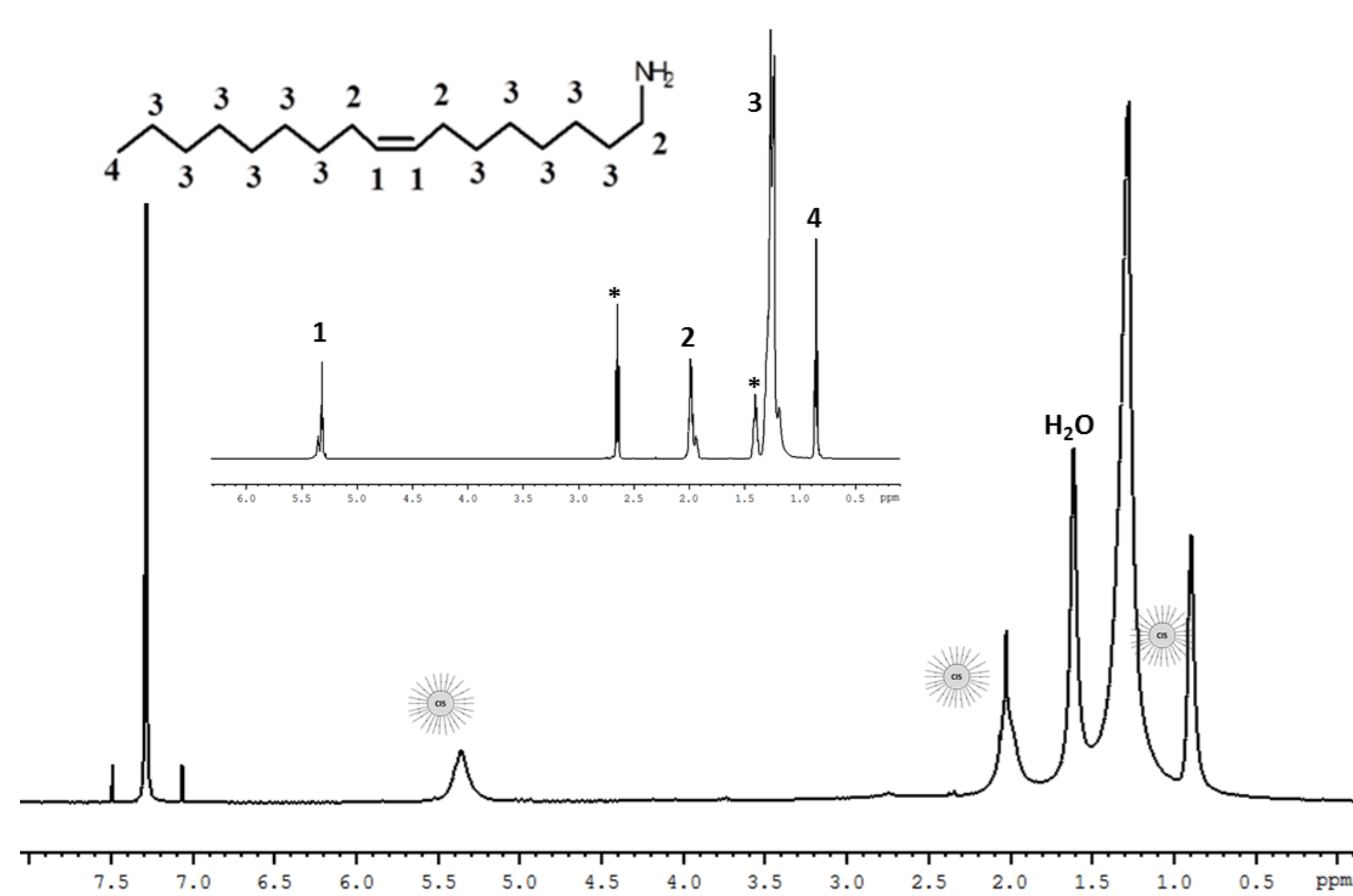


When studying colloidal nanoparticles (NPs) with NMR, we focus on the ligands that surround them. Used during synthesis to control nucleation and growth, they end up as a monolayer covering the NP surface and stabilizing the NP colloidal suspension [1]. After synthesis, they can be exchanged to other ligands to change the properties of the suspension or to improve certain characteristics [2], making the suspensions interesting for solar cell applications. In the last few years NMR techniques have been developed that can give a molecular view on the NPs from the ligands' point of view, both in a qualitative and quantitative way. Using this 'NMR toolbox' different NPs and ligands have already been investigated [2-4]. Here, a system of CupperIndiumSulfide (CIS) NPs synthesized using oleylamine as stabilizing ligand was studied.



Flowchart of the synthesis and processing of colloidal NPs that are integrated in a solar cell.



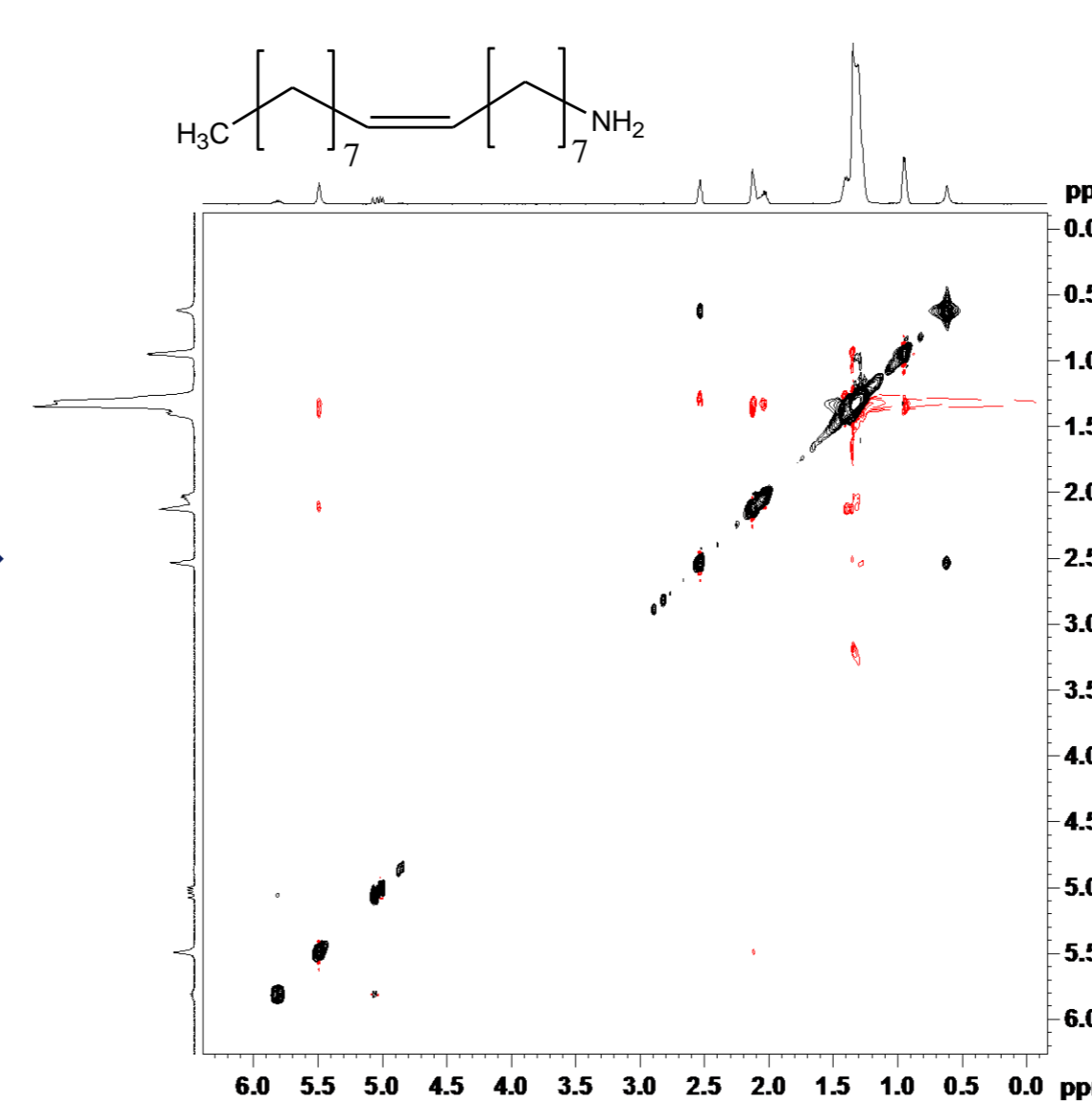
1D proton NMR of oleylamine coated on CIS NPs and a reference spectrum of oleylamine free in solution, recorded in CDCl₃ at 500 MHz, 25°C.

Ligands that are bound to a NP with a radius of app. 8 nm, have a molecular motion that is strongly determined by the NP. Thus, their 1D ¹H NMR signals are broadened compared to those of the ligand free in solution.

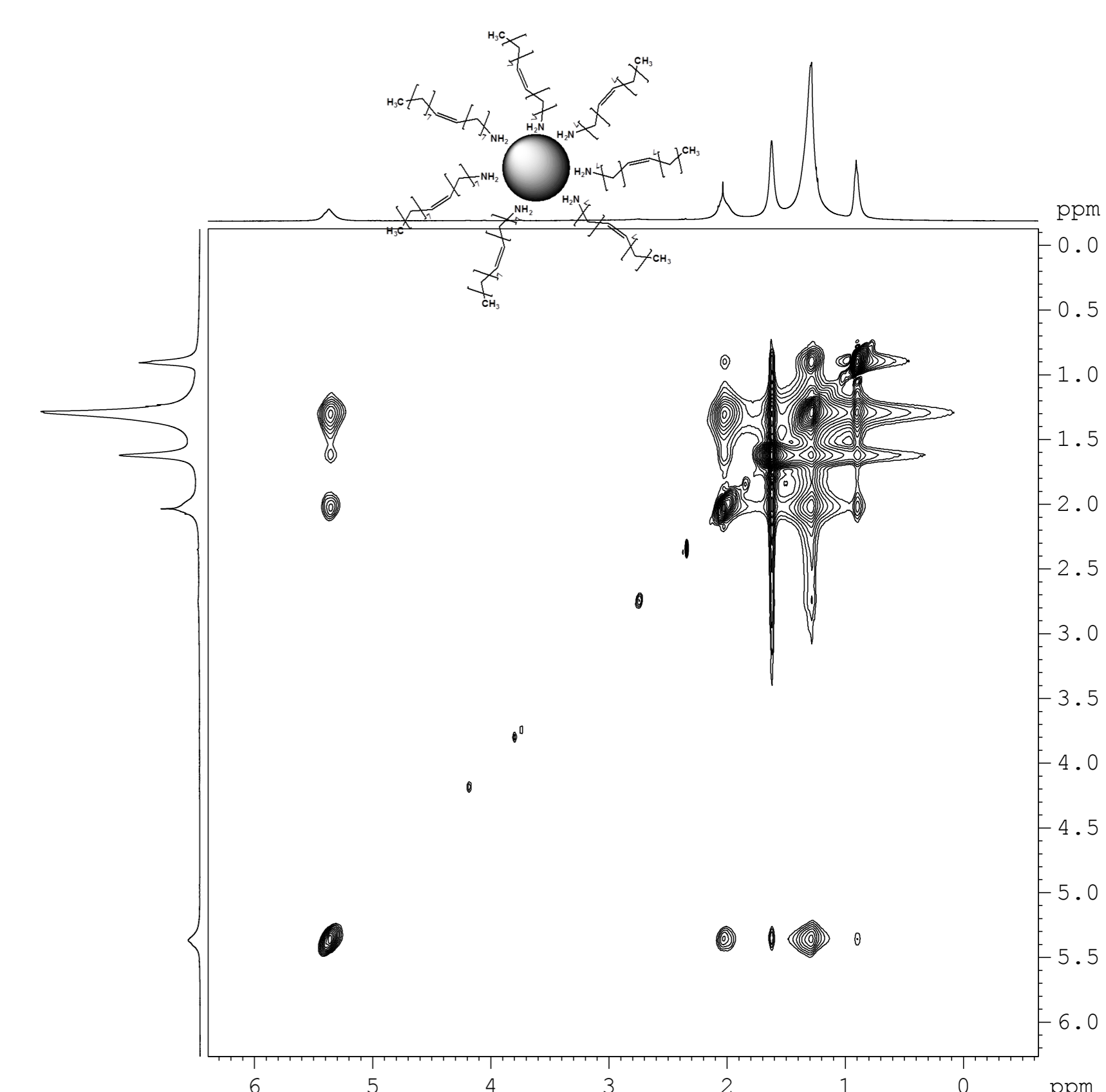
$$\text{ligand density} = \frac{[\text{ligands}]/[\text{NPs}]}{\text{surface area}}$$

With NMR we can also measure quantitatively, determine the concentration of bound ligand and calculate the ligand density. For the CIS NPs with oleylamine ligands in chloroform this is typically 3 ligands/nm².

Bound ligands have strong negative nOe's in the 2D NOESY spectrum, free ligands have small positive nOe's.



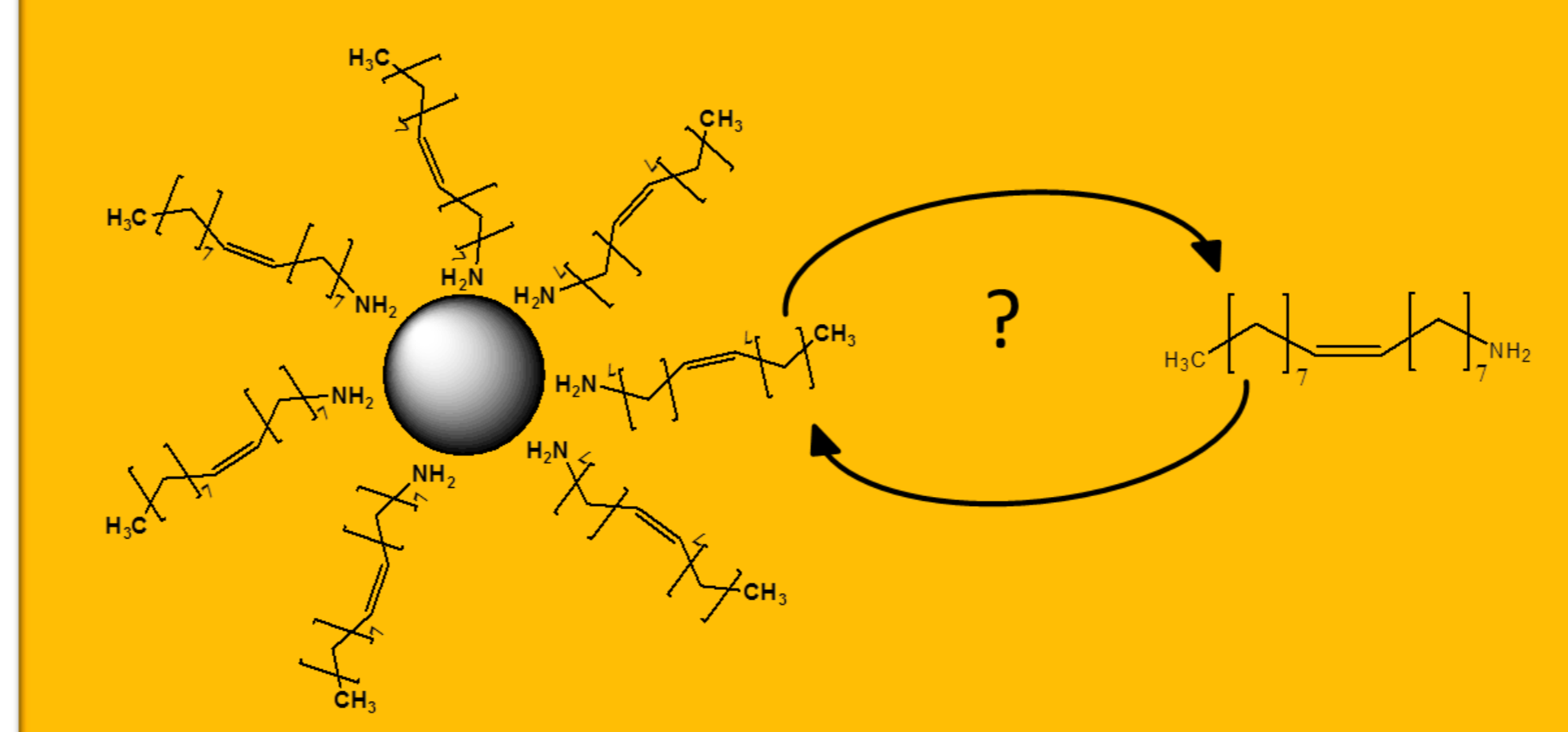
2D NOESY spectrum of oleylamine, small positive nOe's, recorded in CDCl₃ at 500 MHz, 25°C.



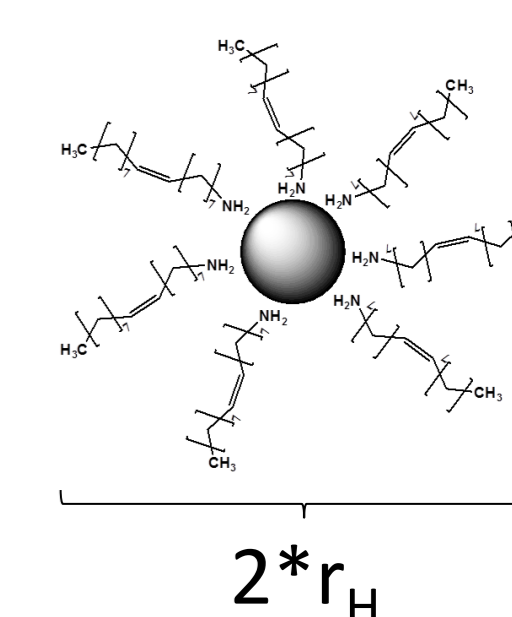
2D NOESY spectrum of colloidal CIS NPs with oleylamine ligands, strong negative nOe's, recorded in CDCl₃ at 500 MHz, 25°C.

Studied system

CIS NP with oleylamine ligands in chloroform



An important parameter of the colloidal NPs is their hydrodynamic radius r_H , this is the sum of the radius of the core and the surrounding ligands.

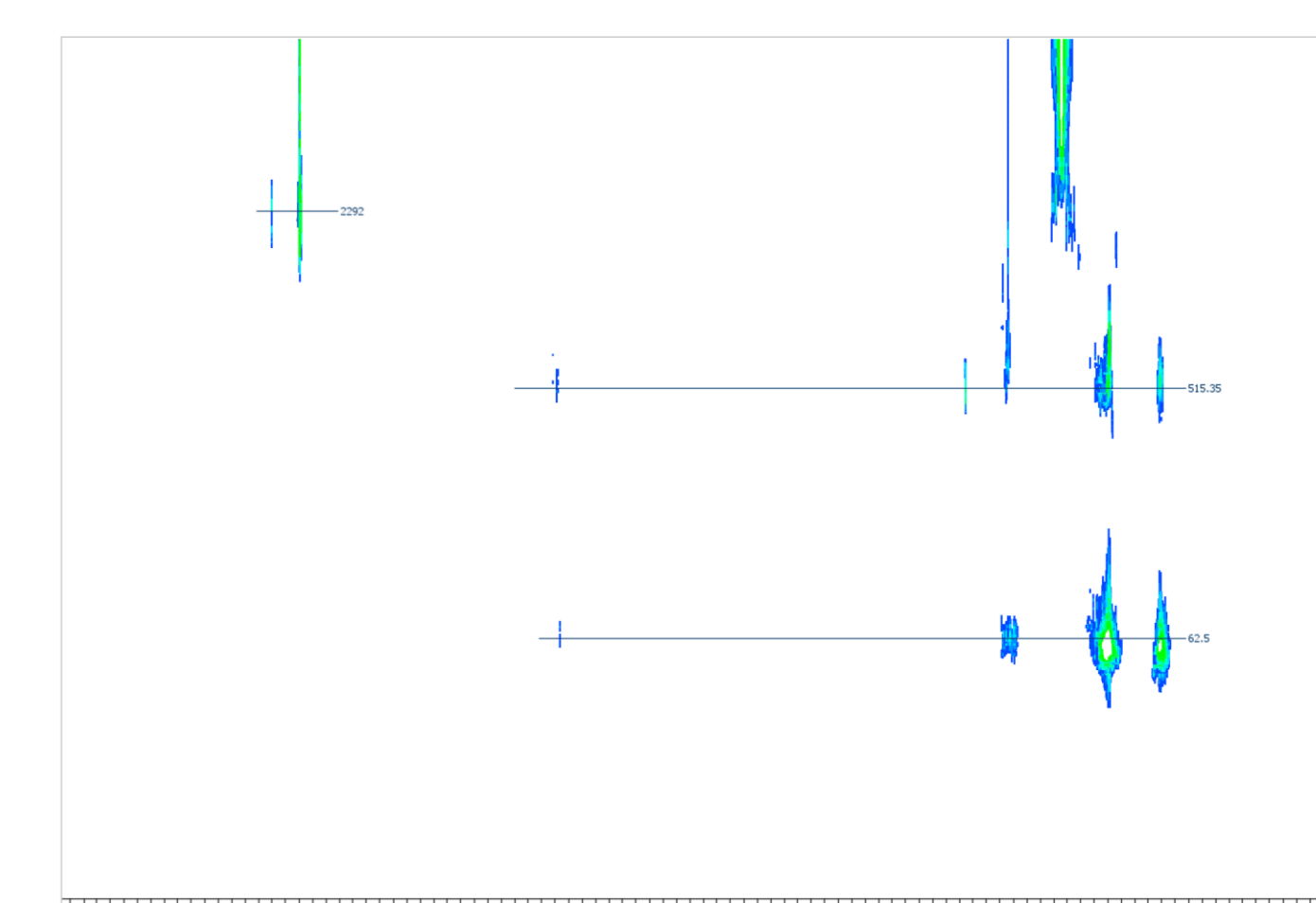
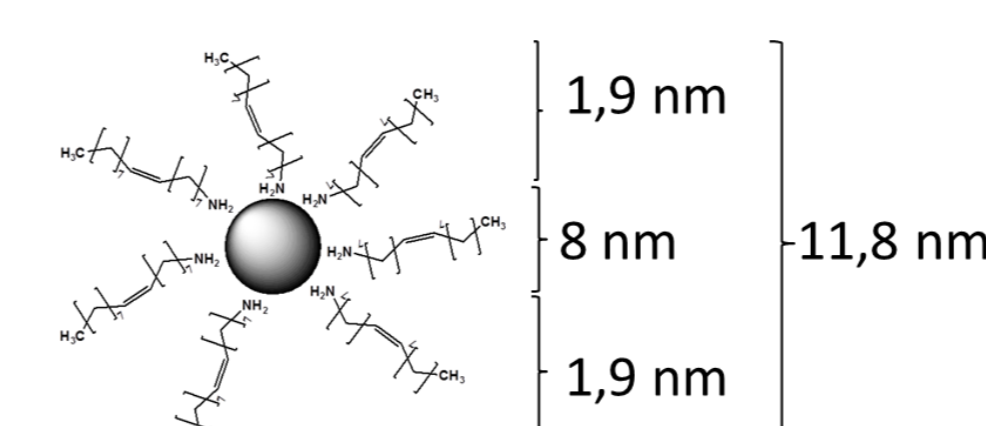


With 2D DOSY NMR we can determine the diffusion coefficient (D) of the different species in a mixture. Tightly bound ligands will diffuse together with the NP they are bound to. Fast exchanging ligands will have a D that is a weighted average between the free (NB) and bound (B) ones.

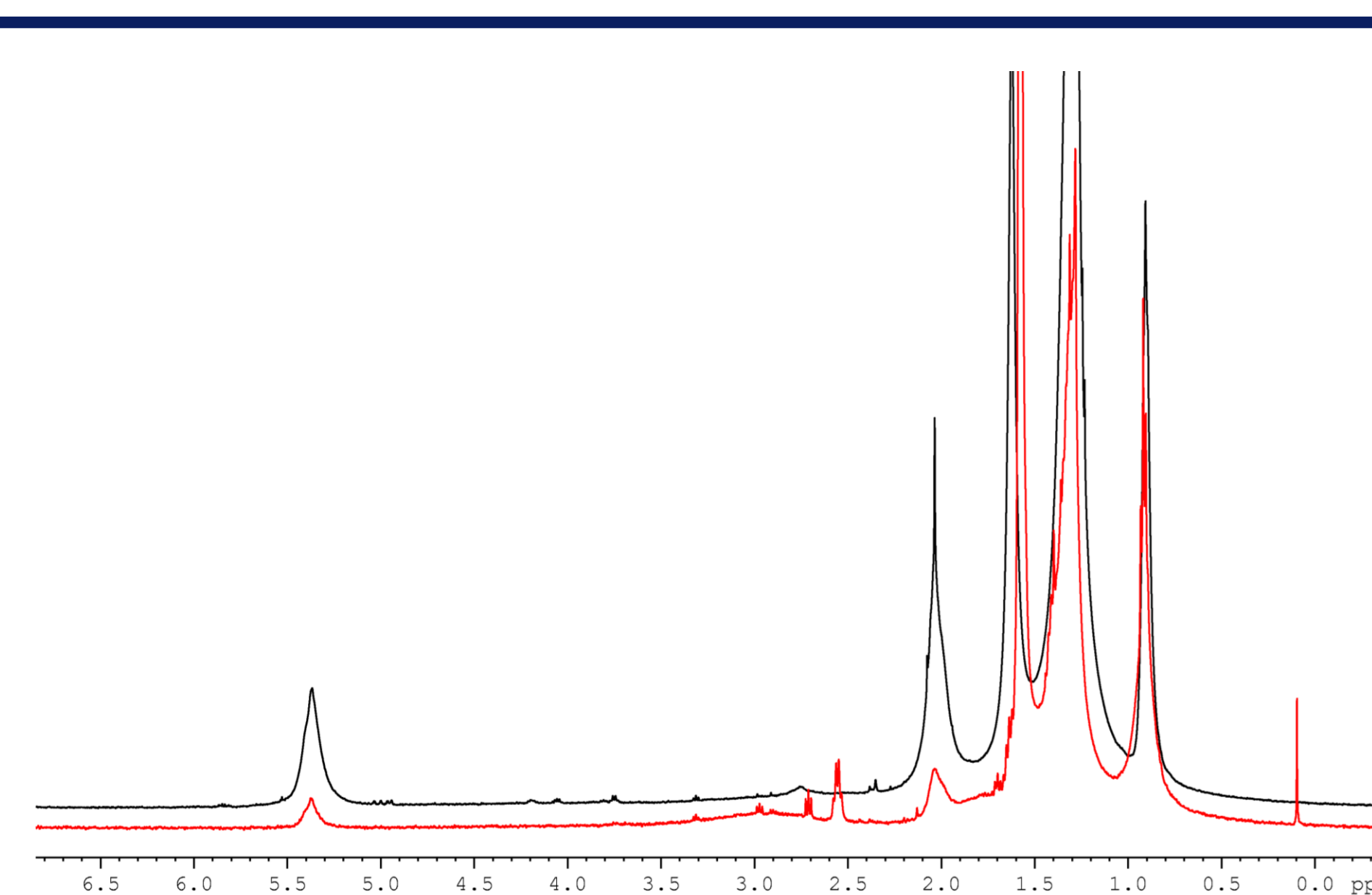
$$D_{obs} = x_{NB}D_{NB} + x_B D_B$$

In this system, oleylamine is tightly bound to the CIS NP. With the diffusion coefficient obtained for the bound ligands, r_H can be calculated according to the Stokes-Einstein equation.

$$r_H = \frac{k_B T}{6\pi\eta D} = 5,9 \text{ nm}$$

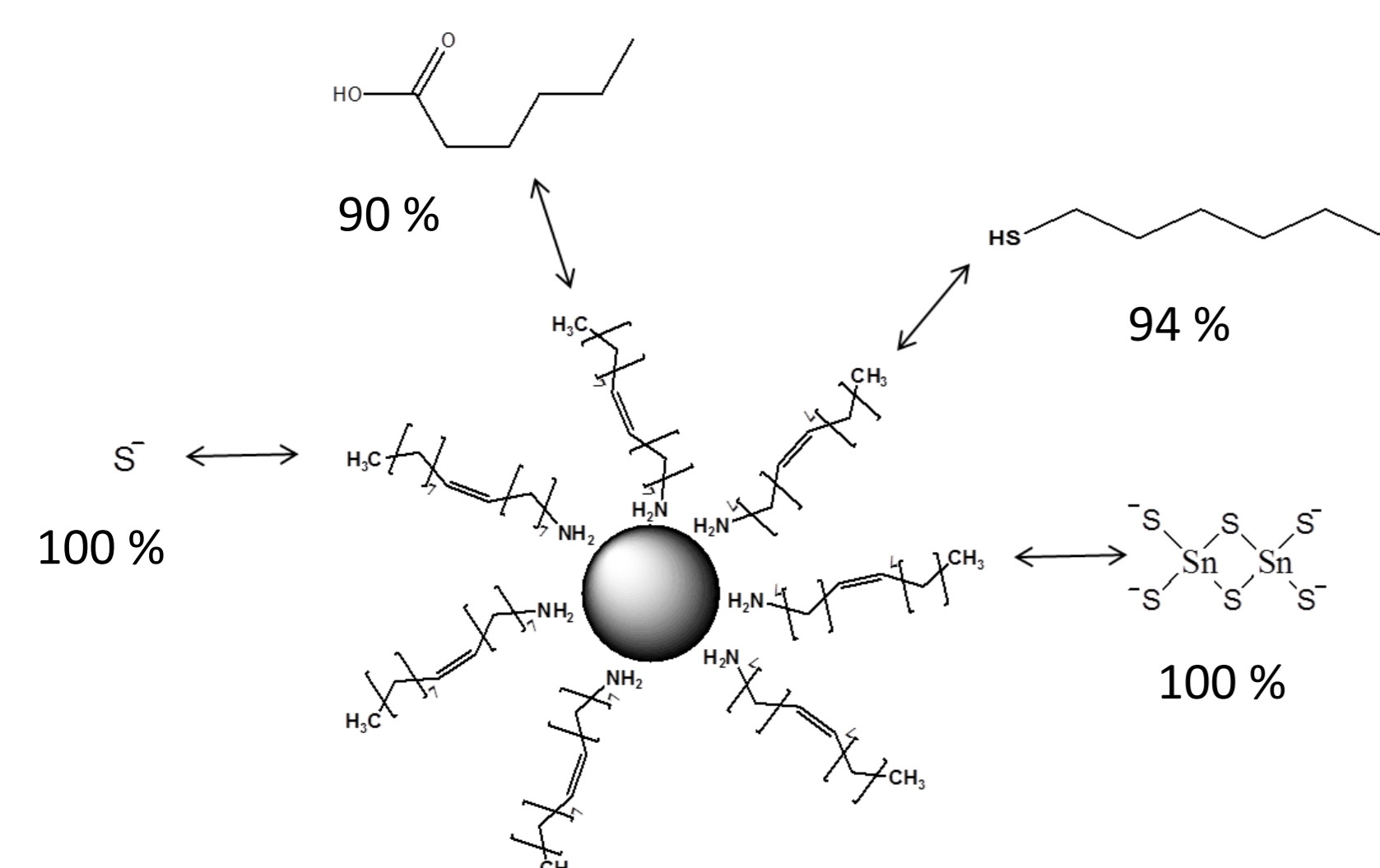


2D DOSY spectrum of colloidal CIS NPs with oleylamine ligands, recorded in CDCl₃ at 500 MHz, 25°C, with diffusion coefficients depicted in μm²/s.



1D proton NMR, quantitative, of CIS NP with oleylamine ligands (black) and the same solution after excessive exchange with hexanethiol, recorded in CDCl₃ at 500 MHz, 25°C.

Oleylamine is not a good ligand for the use of these colloidal CIS NPs in solar cell devices, because these should not contain that much organics. Therefore, an exchange towards other ligands is necessary. These other ligands are shorter organic chains or inorganic ligands. With NMR we can quantify this exchange.



CIS NP with oleylamine and possible exchanging ligands with the maximum percentage of oleylamine stripping so far.

NMR has shown to be a very reliable technique when studying colloidal NPs. Not only can we identify the ligand on the surface, we can also determine the surface chemistry and kinetics. With this knowledge, exchange to other ligands can be tested and the manufacturing of suitable colloidal NPs for solar cells becomes possible. Other parameters that will be tested are the influence of the solvent on the surface dynamics. Some preliminary tests have already shown that changing the solvent from toluene to chloroform induces changes in the line width of the signals and thus possibly influences the rigidity of the ligands on the surface.

[1] Y. Ying, A.P. Alivisatos, Nature (2005), **437**, 664-670

[2] I. Moreels, J.C. Martins, Z. Hens, ChemPhysChem (2006), **7**, 1028-1031

[3] B. Fritzing, *et al.*, JACS (2010), **132**, 10195-10201

[4] I. Moreels, *et al.*, JACS (2008), **130**, 15081-15086

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