## **Supporting information**

### for

# Probing solvent-ligand interactions in colloidal nanocrystals by the NMR line broadening.

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#### Homogeneous line broadening.

The  $T_2$  relaxation time constant is related to the full width at half maximum (FWHM) of the NMR resonance by

$$FWHM (Hz) = \frac{1}{\pi T_2}$$

The  $T_2$  relaxation time constant decreases with increasing the rotational correlation time (average time necessary to rotate 1 radian) which is expressed for a *rigid* object by the Stokes-Einstein equation:

$$\tau_c = \frac{4\pi\eta r^3}{3k_h T}$$

 $\eta$  is the viscosity of the solvent, r is the radius of the object,  $k_b$  is Boltzmann's constant and T is the temperature.

### Additional figures.



Figure S1. UV-VIS spectrum of cadmium oleate capped CdSe NCs (3.3 nm in diameter)



**Figure S2.** DOSY decay fitting and residuals of the methyl resonance of oleate capped CdSe NCs (see Figure 1). The same fitting function as in Figure 2D is used.



Figure S3. DOSY decay fitting and residuals of the alkene resonance of oleate capped CdSe NCs (see Figure 1).



**Figure S4.** T<sub>2</sub> decay fitting of the methyl resonance of oleate capped CdSe NCs (see Figure 1). The fitting function is  $I = M \exp(-\frac{t}{T_2})$ 



Figure S5. T<sub>2</sub> decay fitting of the alkene resonance of oleate capped CdSe NCs (see Figure 1).



Figure S6. <sup>1</sup>H NMR spectrum of oleic acid processed with different singlet line broadening.



**Figure S7.** <sup>1</sup>H NMR spectrum of oleate capped CdSe NCs (see Figure 1), green. Hole burning experiments at the alkene resonance (red) or at the methyl resonance (blue).



**Figure S8.** <sup>1</sup>H NMR spectrum of oleate capped  $HfO_2 NCs$  (d = 5 nm).



**Figure S9.** <sup>1</sup>H NMR spectrum of oleate capped PbS NCs (d = 3.6 nm).



Figure S10. Diffusion filtered spectra of hafnia nanocrystals capped with MEEAA in methanol, a methanol/water mixture (80-20 v%) or a methanol/toluene mixture (40-60v%).



Figure S11. DOSY decay fitting of the methyl resonance of MEEAA capped HfO<sub>2</sub> NCs in methanol.



Figure S12. DOSY decay fitting of the methyl resonance of MEEAA capped HfO<sub>2</sub> NCs in ethanol.



Figure S13. DOSY decay fitting of the methyl resonance of MEEAA capped HfO<sub>2</sub> NCs in acetone.



Figure S14. DOSY decay fitting of the methyl resonance of MEEAA capped HfO<sub>2</sub> NCs in toluene.



Figure S15. Diffusion filtered spectra of MEEAA capped CdSe NCs in methanol, ethanol, acetone and toluene.



**Figure S16.** Fitting of the diffusion filtered spectrum of MEEAA capped  $HfO_2$  NCs in acetone (left) and toluene (right), cf. Figure 3A. Peak 0 belongs to the CH<sub>3</sub> resonance **f** while peak 1 is a convolution of the CH<sub>2</sub> resonances **b-e**.



Figure S17. Reference <sup>1</sup>H NMR spectra of MEEAA in water, methanol, ethanol, acetone and toluene.



**Figure S18.** Correlation of the FWHM of the methyl resonance of bound MEEAA molecules on  $HfO_2$  and CdSe NCs with the Hanssen polarity solubility parameter.



**Figure S19.** Single exponential DOSY decay fitting of the alkene resonance of oleate capped CdSe NCs in chloroform, showing that cadmium oleate remains tightly bound.



Figure S20. <sup>1</sup>H NMR spectrum of oleate capped CdSe NCs in different solvents.



**Figure S21.** <sup>1</sup>H NMR spectrum (alkene region, resonance **5**) of oleate capped HfO<sub>2</sub> (4 nm) or CdSe (3.3 nm) nanocrystals in dichlorobenzene- $d_4$  (DCB- $d_4$ ) or benzene (C<sub>6</sub>D<sub>6</sub>) and calibrated at 6.93 and 7.16 ppm, respectively. The measurements in DCB are conducted at 60 °C because the NCs are not dispersible in DCB at room temperature.



**Figure S22**. <sup>1</sup>H NMR spectrum of oleate capped CdSe (3.3 nm), PbS (3.6 nm) and HfO<sub>2</sub> (4 nm) nanocrystals in toluene- $d_8$  (tol- $d_8$ ) and CDCl<sub>3</sub> and calibrated at 6.98 and 7.24 ppm, respectively. The spectrum of free oleic acid is also displayed to highlight the difference in chemical shift between free and bound ligands.



Figure S23. The homogeneous broadening is plotted either against the radius or the cubed radius. The figure seems to suggest that the homogeneous broadening scales linearly with  $r^3$  rather than with r. This follows the dependency of the rotational correlation time with  $r^3$  (see above). However, one should be careful from drawing too drastic conclusions since the T<sub>2</sub> relaxation time is not simply linearly dependent on the rotational correlation time.