Supporting information

Unravelling the Surface Chemistry of Metal Oxide Nanocrystals, the Role of Acids and Bases

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1. Comments on synthesis

During the workup, two phases are retrieved. The organic phase is the top phase (diethyl ether, benzyl ether and benzyl alcohol) and the bottom phase is a stable dispersion of HfO_2 (or ZrO_2) nanoparticles in only 400 µL of water. The concentration of particles in the water phase is considerable (900 mM of hafnium). Without the water phase at this point, no colloidal stabilization nor subsequent surface functionalization is possible. This demonstrates the influence of the precursor ($HfCl_4$) concentration. When the concentration of $HfCl_4$ is low, the amount of released catalyst (HCl) is minute. The amount of water thus produced is too low and a precipitate is the final result.

In the experimental section, the amount of fatty acid (0.2 mmol) is an excess, as is the amount of amine (0.15 mmol). As suggested by the chloride density density, only 0.05 mmol of both would actually be needed. 0.15 mmol oleylamine corresponds to 50 µL and this works very well in all cases. It allows a standard procedure irrespective of slight variations in yield or the higher metal concentration in case of zirconia. If higher concentrations of one or both surfactants are used, the outcome remains identical.

2. ZrO_2

Stable dispersion of ZrO_2 NCs can only be obtained via the above described method if the $ZrCl_4$ concentration is 130 ± 10 mM. The particles can directly be dispersed in water, ethanol or methanol after synthesis. Via our regular post-synthetic modification with dodecanoic acid (DDAc) and oleylamine (OAm), transfer to non-polar solvents is attained. Figure 1A shows the particle distribution by DLS in ethanol and in chloroform. In ethanol the distribution is centered at 43.8 nm and in chloroform the average hydrodynamic diameter is 10 nm. The

TEM pictures in the inset clarifies, similar to the HfO_2 NCs, that the particles are agglomerated in ethanol and not in chloroform. XRD analysis confirms the monoclinic nature of the particles (fig 1B). The reactions that occur during this particular microwave assisted solvothermal synthesis are similar to the synthesis of HfO_2 NCs. The clustered particles in ethanol are charge stabilized by a positive charge (ξ = + 30.5 mV).

In order to confirm the role of the DDAc and OAm during post-modification, figure S2 depicts representative ^1H spectra of ZrO_2 NCs stabilized with DDAc and OAm. Sample 1 (grey spectrum) was purified only once, sample 2 (black spectrum) was purified 5 times. The lack of signals from OAm in the black spectrum (sample 2) proves that OAm is completely removed by purification. OAm has the same basic function as in the case of HfO_2 NCs and dodecanoic acid is tightly bound to the ZrO_2 NCs.

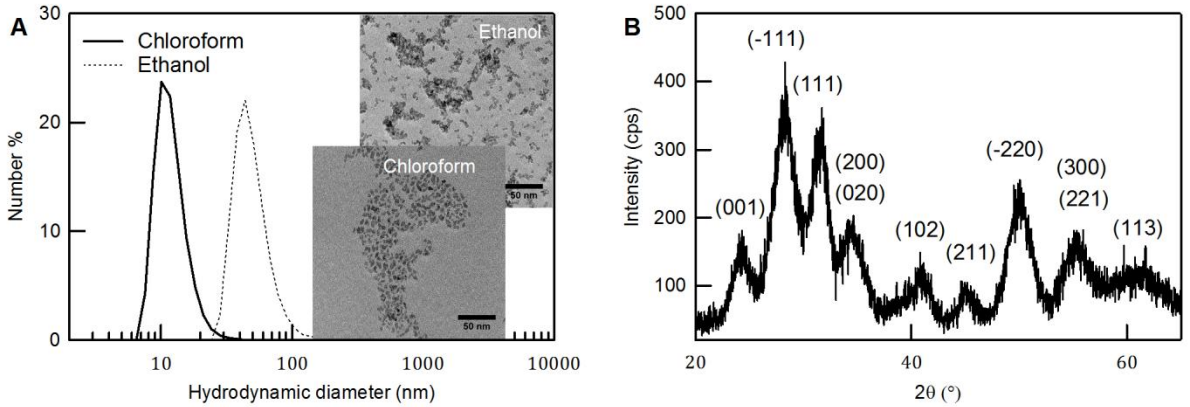

Figure S1. (A) Size distribution by DLS of ZrO_2 nanoparticles dispersed in either ethanol or chloroform. The insets show the corresponding TEM pictures (scale bar is 50 nm). (B) XRD diffractogram of one batch of ZrO_2 nanoparticles.

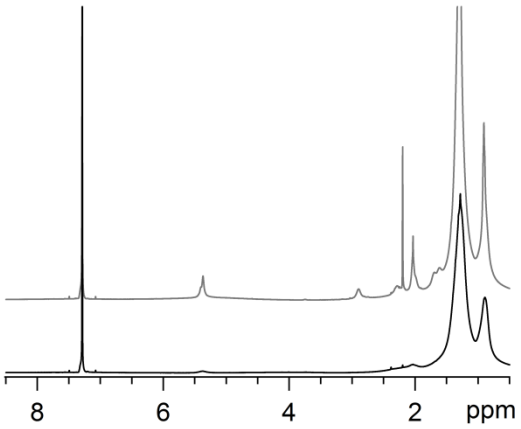

Figure S2. ^1H NMR spectra of ZrO_2 NCs in $CDCl_3$ stabilized with DDAc and OAm after (grey spectrum) 1 and (black spectrum) 5 purification steps.

3. Photometric chloride determination and chloride density

One batch of hafnia NCs was suspended in 2 mL of ethanol and the concentration was gravimetrically determined: 33 mg HfO_2/mL.

To 0.4 mL of that suspension diethyl ether was added to precipitate the NCs and after centrifugation, the NCs were washed once with diethyl ether and redispersed in 4 mL of ethanol with the aid of an ultrasonic bath (10x dilution). 1 mL of that resulting suspension was diluted with 10 mL deionized water. To measure the amount of chloride in the aqueous suspension the VWR chloride test 1.14897.0001 was used. 5 mL of sample was brought in a 20 mL vial. 2.5 mL of Cl-1 reagent was added and subsequently 0.5 mL of Cl-2 reagent was added. The samples were shaken and measured almost instantly with UV-VIS at a wavelength of 445 nm. The absorbance at 445 nm (0.283 on average) was multiplied with the factor 28.2 to obtain the concentration of chloride in mg/L (8 mg/L on average). This number was then transformed to the amount of chloride in mmol in the one batch of hafnia NCs.

$$\frac{8\ mg/L}{35.45\ g/mol} \times 0.011\ L \times 4 \times \frac{2\ mL}{0.4\ mL} = 49.7\ \mu mol\ chloride$$

Two measurements were executed with the 11 mL of sample. In addition, to check the reproducibility of the procedure, another 0.4 mL of original suspension was treated in the same fashion. The number was averaged and the error was calculated: 49.7 $\pm$ 2 µmol.

The same procedure was performed but the NCs were washed zero times or washed twice with diethyl ether and is graphically shown in Figure S3. In conclusion, additional washing doesn't change the chloride concentration.

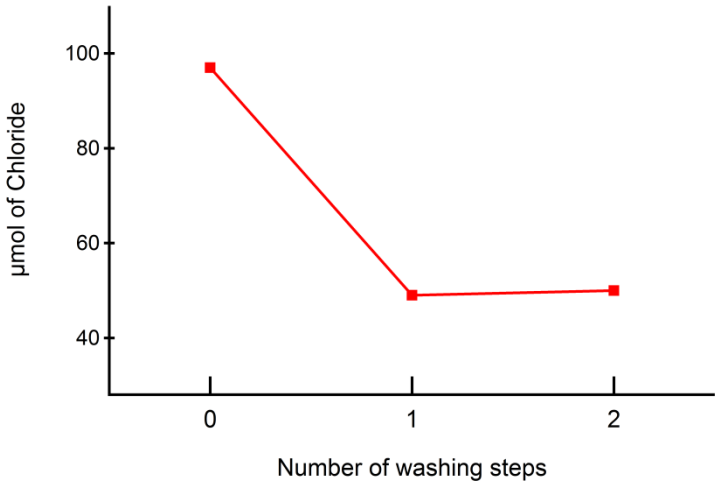

Figure S3: The dependence of the amount of chloride in one batch of hafnia on the number of washing steps with diethyl ether.

The chloride density was calculated: in one batch 66 mg of HfO_2 is present. This corresponds to 0.314 mmol of hafnium. With an average diameter from TEM of 5 nm, a volume of 65.45 nm^3 per NC was calculated. The molar volume of hafnia is the molecular weight (210 g/mol)

divided by the density (9.68 g/cm³): 21.7 cm³/mol. Consequently, the amount of HfO_2 per NC expressed as mol HfO_2 per NC is

$$\frac{65.45\ nm^3/NC}{21.7\ cm^3/mol} \times 10^{-21} = 3.017\ \times 10^{-21}\ mol\ HfO_2/NC$$

The number of particles in one batch will be:

$$\frac{0.314\ \times 10^{-3}\ mol\ HfO_2}{3.017\ \times 10^{-21}\ mol\ HfO_2/NC} = 1.04\ \times 10^{17}$$

There is 49.7 µmol chloride in one batch so this corresponds to $2.99\ \times 10^{19}$ chloride ions, so there are 287.3 chloride ions per NC. Also the surface area of one NC can be calculated as the surface of a sphere of 2.5 nm radius: 78.53 nm² and finally the chloride density is

$$\frac{297.3\ Cl^-/NC}{78.53\ nm^2/NC} = 3.7\ Cl^-/nm^2$$

In case of zirconia nanocrytals, the same procedure and calculations apply and the result is 69.1 ± 2 µmol, in one synthesis batch of zirconia. This higher than the case of hafnia but also the amount of zirconia is higher so everything taken into account, this corresponds to a ligand density of 3.35 ± 0.2 Cl^-/nm², which is very comparable to the chloride density of hafnia NCs.

The similar chloride densities are no surprise since both hafnia and zirconia are monoclinic and have almost the same lattic parameters. (see Table S1). The density of hafnium atoms on unreconstructed lattice planes, was calculated to be 3.75/nm² (010), 7.5/nm² (001) and 10/nm² (1-11). On average, the surface density of chloride is about 50 % of the surface density of hafnium. Our numbers are therefore realistic values.

Table S1: Overview of the lattice constants of monoclinic zirconia (Wang, D. *et. al.* Sci. China Ser. A-Math. **1999**, 42, 80) and hafnia (Zhao, X. Y. *et al.,* Phys. Rev. B **2002**, 65, 233106).

	a (nm)	b (nm)	c (nm)	β (°)
HfO_2	0.512	0.518	0.529	99
ZrO_2	0.514	0.520	0.531	99

4. Confirmation of chemical exchange

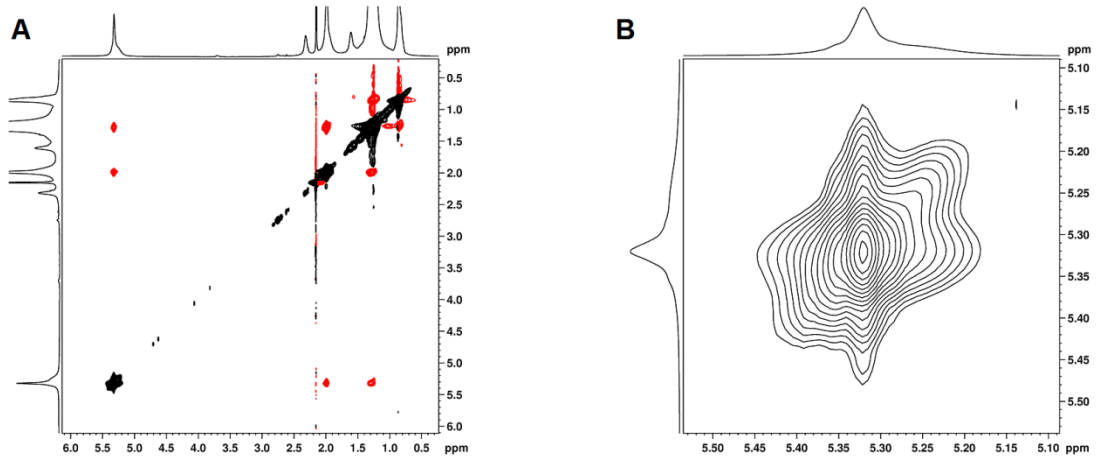

Figure S4. (A) 2D ROESY experiment of a HfO_2 NC suspension in $CDCl_3$ with excess OAc (B) zoom of the ROESY spectrum on the alkene resonance.

With an off-resonance ROESY (Rotating-frame Nuclear Overhauser effect Spectroscopy) measurement, a distinction can be made between close-contact and chemical exchange cross peaks. Since the cross peaks between the sharp and broad resonances of OAc in figure S4B are negative, these are resulting from the chemical exchange between the two types of oleic acid present in the sample.

5. Titration with d_1-OAc

Preparation of d_1-OAc. Oleic acid with a deuterated carboxylic acid d_1-OAc was prepared by dissolving sodium oleate (100 mg, 99% pure) in a DCl/D_2O mixture (50 µL DCl (99 atom % D) in 2.0 mL D_2O (99.97 atom% D)), followed by a phase transfer of the formed d_1-OAc to cyclohexane-d_{12} (500 µL – 99.6% atom% D). The organic phase was separated from the aqueous phase in an O_2 and H_2O free glove box. This was considered the d_1-OAc stock solution.

NMR sample preparation. Extreme care was taken to prevent contamination of NMR tubes and HfO_2 NCs samples by residual H_2O. This involved loading and drying of NMR tubes and a (5 times) purified oleic acid capped HfO_2 suspension in the glove box 48 h prior to the NMR sample preparation. The required oleylamine for post-modification was removed during the purification. Finally, in the glovebox, $CHCl_3$ of the purified suspension was evaporated and dry $CDCl_3$ was added. This procedure was repeated and this was called the NC stock solution. No water resonance was observed in the spectra of the stock solution and after addition of d_1-OAc to the nanocrystal suspension, the carboxylic acid resonance was observed at 12 ppm so that we can conclude that the samples are water-free.

Experiments, observations and calculations.

30 µL of d_1-OAc hexane solution was added to 490 µL $CDCl_3$. The concentration of OAc was determined via the ERETIC method to be 12.14 mM in the NMR sample which means the real concentration in the d_1-OAc stock solution was

$$c_{OAc} = \frac{12.14\ mM\ \times 520\ \mu L}{30\ \mu L} = 210\ mM$$

The degree of deuteration was determined from the residual carboxylic acid signal. When the integration of the alkene signal was set to 2, the integral of the carboxylic acid was 0.0766. So 7.66 % of oleic acid molecules still have a proton. As a results 92.34 % is deuterated. This gives an overall concentration of d_1-OAc in the d_1-OAc stock solution of 210 x 0.9234 = 194 mM.

600 µL of the NC stock solution was measured in NMR and the concentration of bound OAc was determined to be 12.87 mM.

In the final experiment, 450µL of NC stock solution was combined with 150 µL of the d_1-OAc stock solution. Solution useful number were calculated:

$$450\ \mu L\ \times 12.87\ mM = 5.79\ \mu mol\ bound\ OAc$$

$$150\ \mu L\ \times 210\ mM = 31.5\ \mu mol\ excess\ OAc$$

$$5.79 + 31.5 = 37.29\ \mu mol\ totaal\ OAc\ in\ the\ sample$$

$$31.5\ \mu mol\ \times 0.9234 = 29.09\ \mu mol\ d_1\text{-}OAc$$

$$31.5\ \mu mol - 29.09\ \mu mol = 2.41\ \mu mol\ H_1\text{-}OAc$$

The experimentally observed proton concentration (derived from the carboxylic acid signal at 12 ppm) relative to the total concentration of oleic acid molecules (from the alkene resonance) was [H]/[OAc] = 18.6 %. We can also calculate the expected ratio for the situation when either there are or there aren't protons on the surface.

$$HfO_2.R_1COO + R_2COOD \rightleftharpoons HfO_2.R_2COO + R_1COOD \quad (1)$$
$$HfO_2.R_1COOH + R_2COOD \rightleftharpoons HfO_2.R_2COOD + R_1COOH \quad (2)$$

If there are no protons on the surface, the only protons that will be visible are the ones from the incomplete deuteration: 2.41 µmol. So the ratio would be

$$\frac{[H]}{[OAc]} = \frac{2.41\ \mu mol\ H}{37.29\ \mu mol\ totaal\ OAc} = 6.5\ \%$$

If there are as many protons on the surface as there are bound OAc then the total amount of protons would be: 5.79 + 2.41 = 8.2 µmol. However, not all these protons will be present in solution, they will be stochastically distributed among all the OAc molecules, bound (i.e. invisible proton) and unbound (i.e. visible protons). Thus the amount of visible protons will be $8.2\ \times \frac{31.5}{37.29} = 6.93$. this results in a ratio:

$$\frac{[H]}{[OAc]} = \frac{6.93\ \mu mol\ H}{37.29\ \mu mol\ totaal\ OAc} = 18.57\ \%$$

Which is exactly the experimental number so there are as many protons near the surface as there are bound OAc.

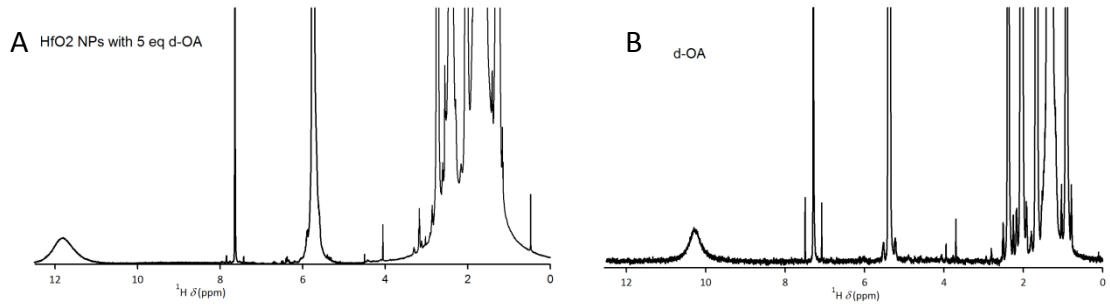

Figure S5. (A) HfO_2 NC suspension with 5 equivalents of d_1-OAc added. (B) d_1-OAc

6. XRF results (chlorine)

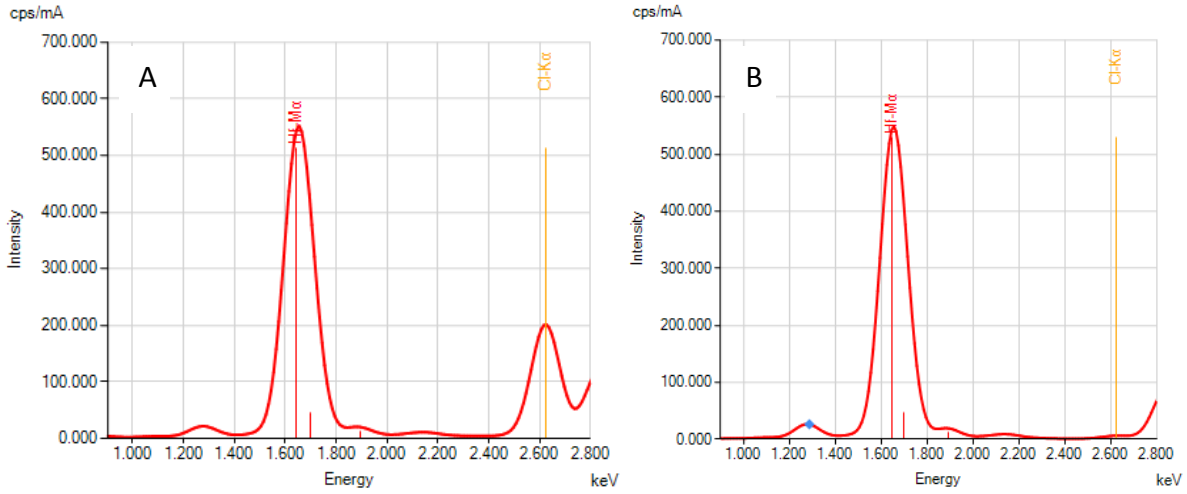

Figure S6: (A) XRF measurement of once purified HfO_2 NC suspensions, stabilized by dodecanoic acid and oleylamine. (B) XRF measurement on the same sample after 5 purifications cycles.

7. DOSY measurements

As referred to in the experimental section, the diffusion coefficients were obtained by fitting the appropriate Stejskal-Tanner equation (Sinnaeve, D. *Concepts Magn. Reson. Part A* **2012**, *40A*, 39) to the signal intensity decay using an in-house MATLAB script.

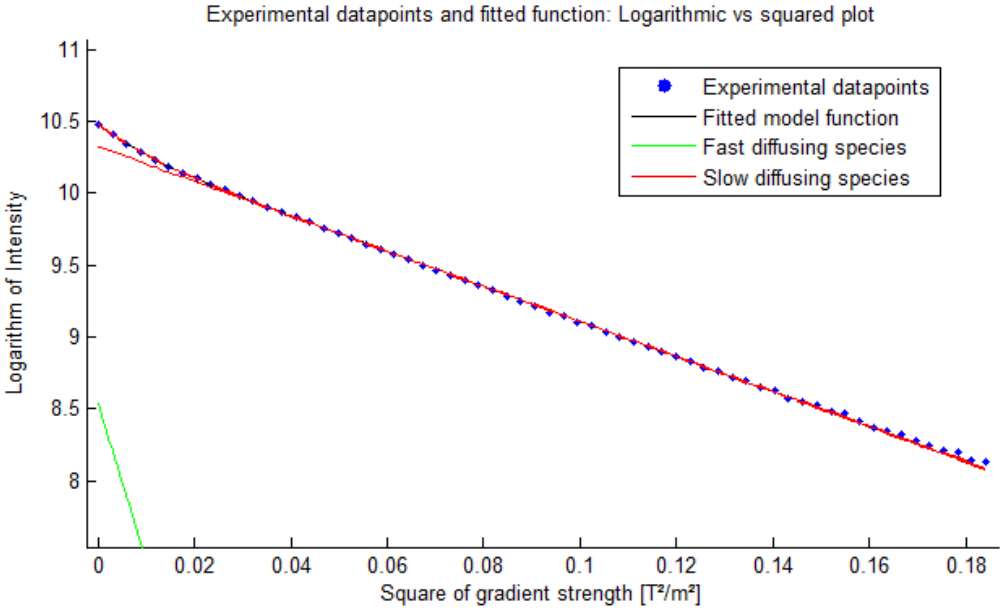

Figure S7: Fitting curve of the DDAc signal intensity decay during DOSY measurement of HfO_2 NCs in $CDCl_3$ stabilized with DDAc and OAm after 5 purification steps.

A small fraction of free DDAc is still present, resulting in a biexponential intensity decay curve. The two diffusion coefficients are 691 ± 46 and 77.1 ± 0.4 µm²/s. The slowly diffusing species is assigned to bound DDAc and can be converted to a hydrodynamic radius using the Stokes-Einstein equation with a temperature of 298.2 K and a viscosity of 0.54 mPa s.

$$r_H = \frac{k_B T}{6\,\pi\eta D}$$

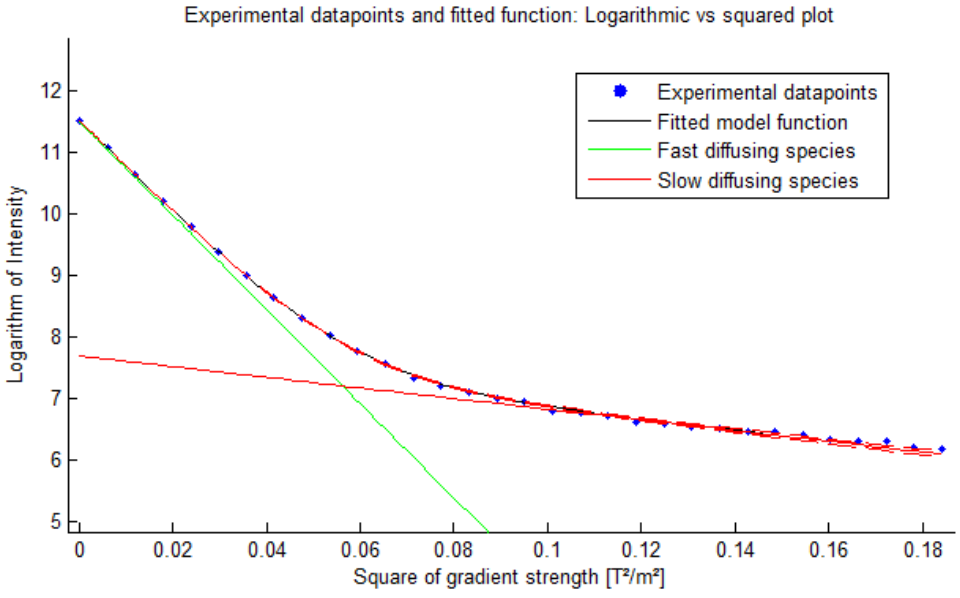

Figure S8: Fitting curve of the 10-undecenoic acid signal intensity decay during DOSY measurement of HfO_2 NCs in $CDCl_3$ stabilized with 10-undecenoic acid and OAm.

The signal intensity decay of 10-undecenoic acid follows a biexponential curve. The two fitted diffusion coefficients are 842 ± 2 µm²/s and 96 ± 6 µm²/s, which were assigned to respectively free and bound 10-undecenoic acid.

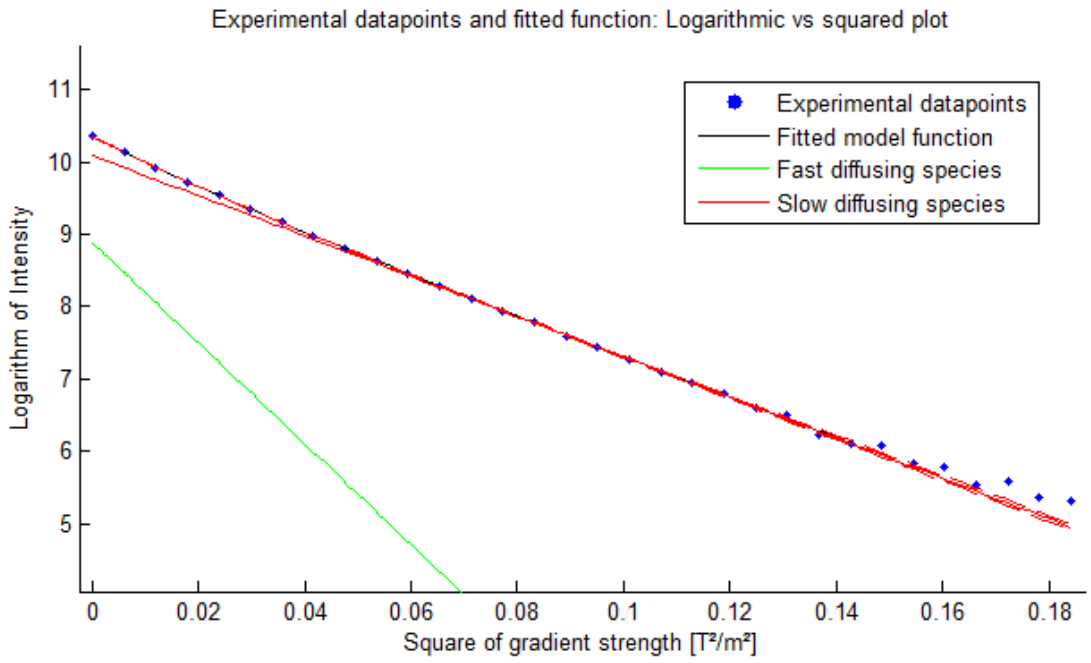

Figure S9: Fitting curve of the OAm signal intensity decay during DOSY measurement of HfO_2 NCs in $CDCl_3$ stabilized with 10-undecenoic acid and OAm.

The signal intensity decay of OAm displays a biexponential behavior, with fitted diffusion coefficients 767 ± 61 µm²/s and 307 ± 5 µm²/s. Only a very small fraction of the fast diffusing species is present and as a consequence its fitted value is less accurate. Slight deviation between data points and fitted curve seen at higher gradient strength can be attributed to a very small contribution of the tail of the neighboring slow diffusing signal of 10-undecenoic acid. However this will have no significant effect on the fitting. The slowly diffusing species is assigned to OAm in fast exchange between a bound and a free state.