Supporting Information

for

Stabilization of colloidal Ti, Zr, and Hf oxide nanocrystals by protonated tri-*n*-octylphosphine oxide (TOPO) and its decomposition products.

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Calculation of the ligand density

Nanocrystal diameter = 3.5 nm (from TEM)

Nanocrystal concentration = 280 µmol/L (from TGA)

Alkyl chain concentration = 30.6 mmol/L (from NMR)

$$Nanocrystal\ surface\ =\ 4\pi r^2 = 38.5\ nm^2$$

$$alkyls\ per\ NC = \frac{30.6\ \text{mmol/L}}{280\ \mu\text{mol/L}} = 109.3\ alkyls\ per\ NC$$

$$ligand\ density = \frac{109.3}{38.5\ nm^2} = 2.84\ nm^{-2}$$

Figures

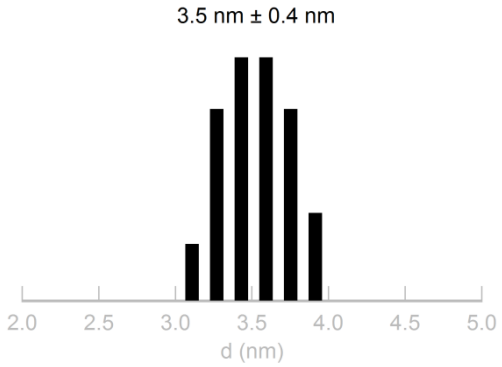

Figure S1. Histogram of the ZrO_2 NCs as determined from TEM.

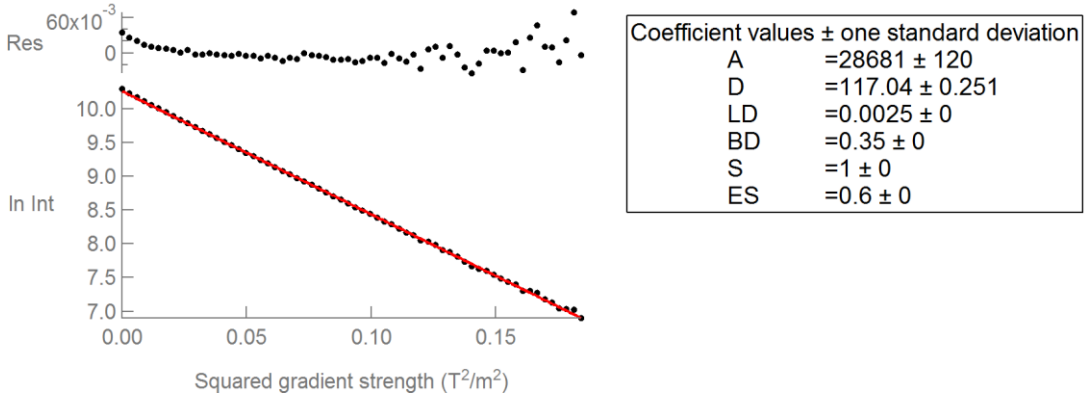

Figure S2. Monoexponential diffusion decay and fitting of the CH_3 resonance of ZrO_2 NCs that have been purified three times.

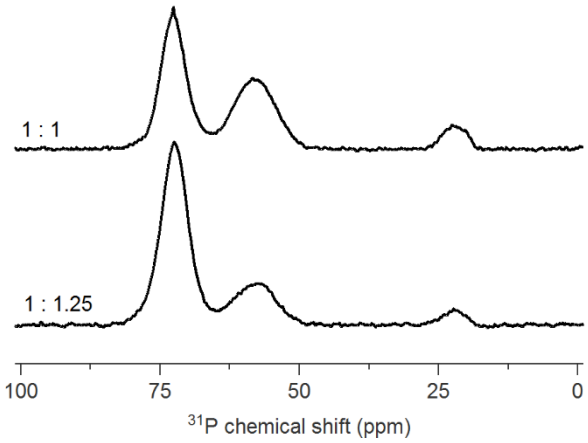

Figure S3. ^{31}P NMR spectrum of two ZrO_2 NC dispersions in toluene-d_8. In the optimized synthesis, either a 1:1 or a 1:1.25 mixture of $Zr(OiPr)_4$.*i*PrOH : $ZrCl_4$ was used. The fraction of protonated TOPO is larger for 1.25 equivalents of $ZrCl_4$.

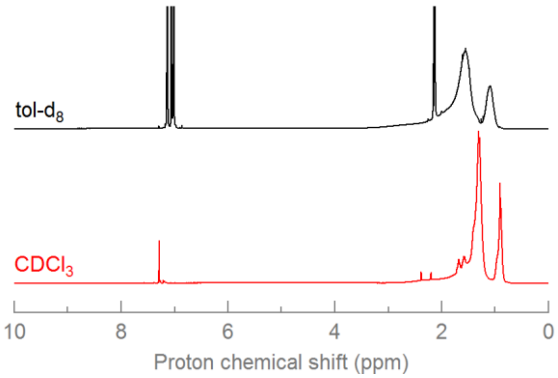

Figure S4. ^{1}H NMR spectrum of a ZrO_2 NC dispersion in either toluene-d_8 or deuterated chloroform.

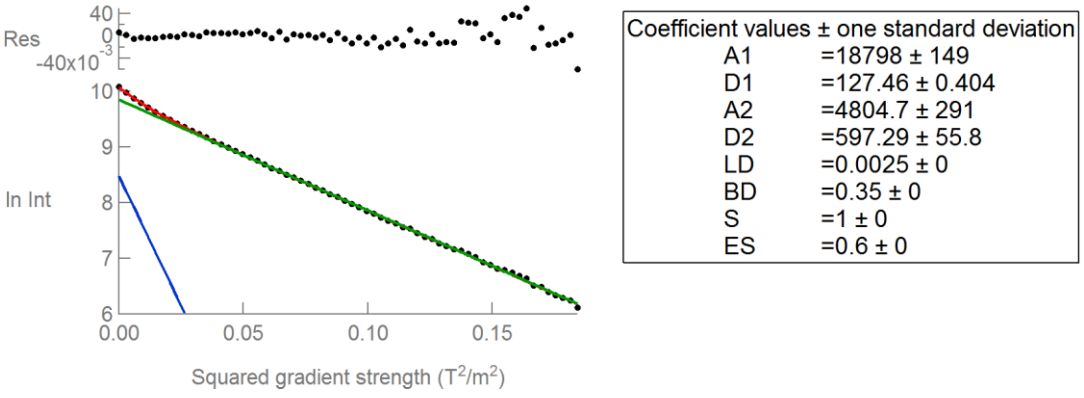

Figure S5. Bi-exponential fitting of the DOSY decay curve of a ZrO_2 NC dispersion in $CDCl_3$.

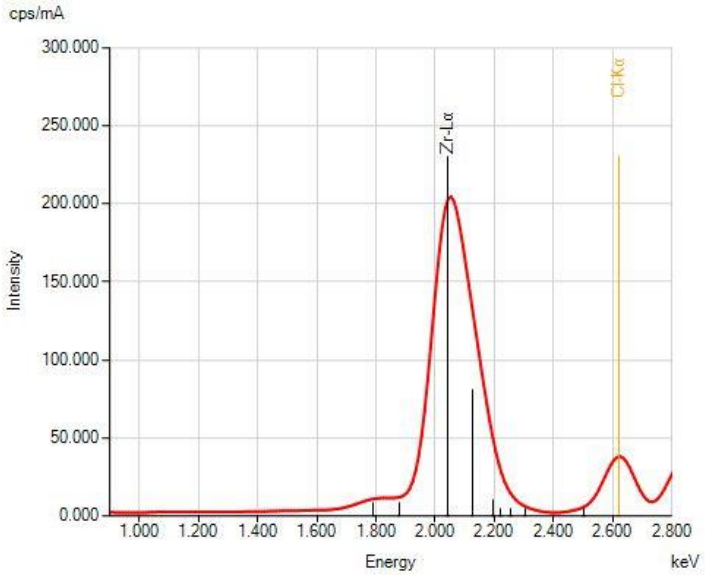

Figure S6. XRF measurements of a ZrO_2 NC dispersion in toluene, purified three times with acetone and synthesized by reacting 2 mmol $ZrCl_4$ and 2 mmol $Zr(OiPr)_4$.*i*PrOH in 10 g TOPO.

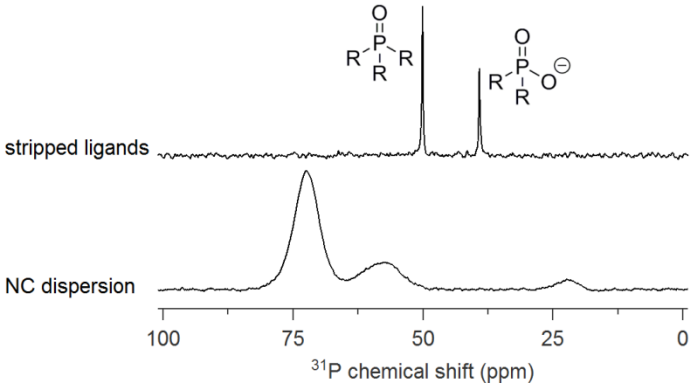

Figure S7. ^{31}P NMR spectrum of a ZrO_2 NC dispersion purified three times in toluene-d_8 (bottom) and the stripped ligands after treatment of the NCs with benzyltrimethylammonium propionate in THF and redissolution in $CDCl_3$, see experimental section for details (top).

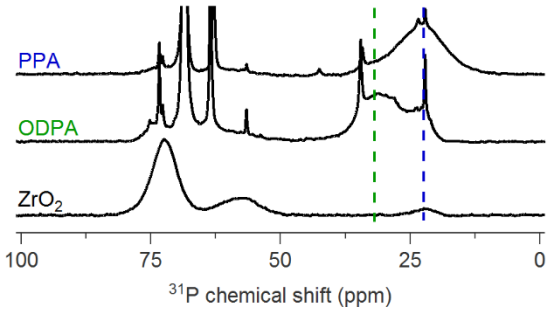

Figure S8. ^{31}P NMR spectrum of a ZrO_2 NC dispersion purified three times in toluene-d_8 (bottom) and the ^{31}P NMR spectra of these NCs with either an excess of octadecylphosphonic acid (ODPA) or P,P' (di-n-dodecyl) pyrophosphonic acid (PPA) added. Although both resonances are quite broad, it is clear that the bound PPA resonance has the same chemical shift as the broad peak at 20 ppm in the purified nanocrystals. Therefore, we assign the latter to bound pyrophosphonate. A little peak at the chemical shift of phosphonic acid is also observed upon addition of PPA and although this could be due to hydrolysis of the pyrophosphonate under acid conditions by adventitious water, it cannot be fully excluded that this originates from the surface of the nanocrystals.

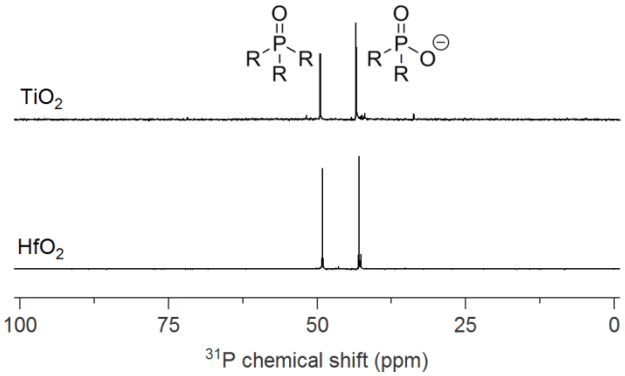

Figure S9. ^{31}P NMR spectrum of TiO_2 and HfO_2 NCs stripped with octylamine and oleic acid in $CDCl_3$.

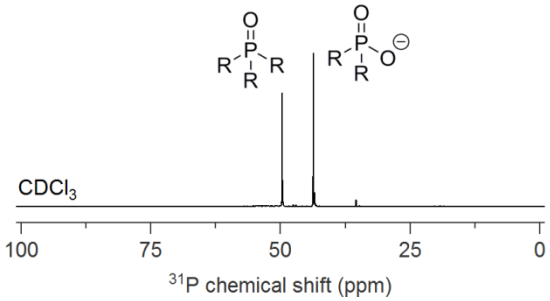

Figure S10. ^{31}P NMR spectrum of a ZrO_2 NC dispersion in $CDCl_3$ with octylamine and oleic acid added.

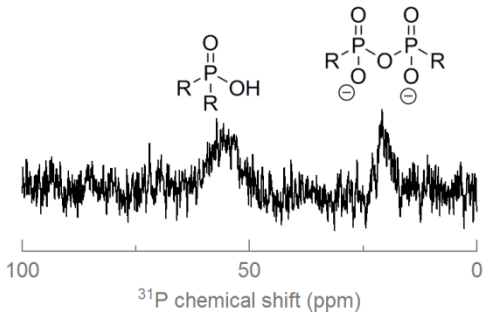

Figure S11. ^{31}P NMR spectrum of 500 µL ZrO_2 NC dispersion in chloroform, treated three times with 200 µL octylamine, 400 µL oleic acid and precipitated with 1 mL of acetone. Afterwards, the dispersion was purified three times with acetone and dispersed in toluene-d_8.

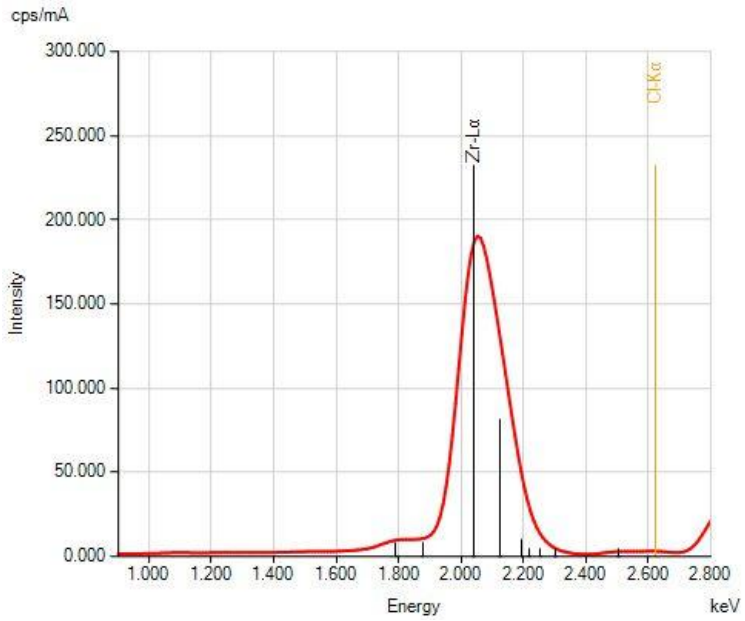

Figure S12. XRF measurements of 500 µL (25 mg) ZrO_2 NC dispersion in chloroform, treated three times with 50 µL oleic acid and 25 µL octylamine and purified with methanol.

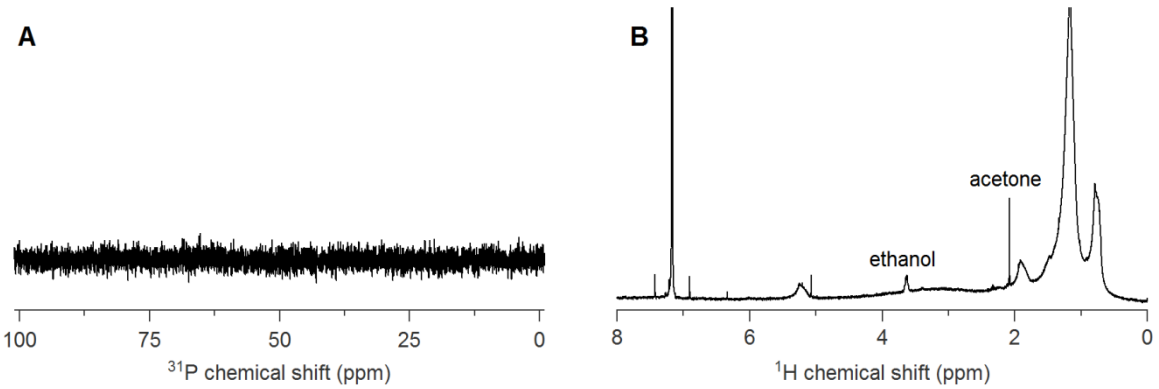

Figure S13. ^{31}P NMR spectrum (A) and ^{1}H NMR spectrum (B) of TiO_2 NCs capped with oleic acid, see experimental for details. The ^{31}P spectrum is recorded with the same number of scans as the other experiments.

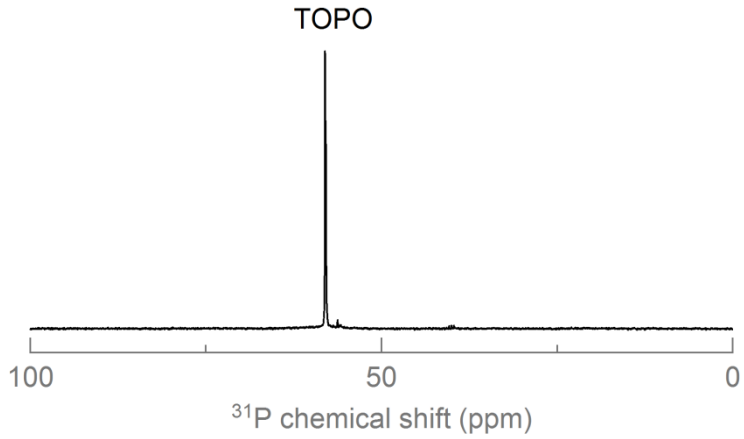

Figure S14. ^{31}P solution NMR spectrum of ZrO_2 NCs in MeOD-d_4, stabilized with citric acid.

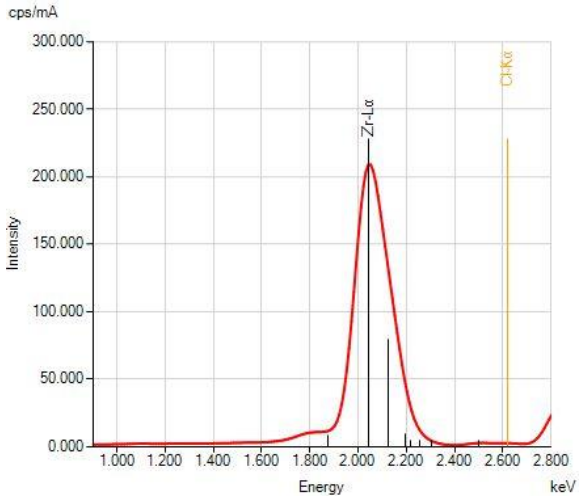

Figure S15. XRF measurement of ZrO_2 NCs capped with octadecylphosphonic acid and precipitated with methanol.

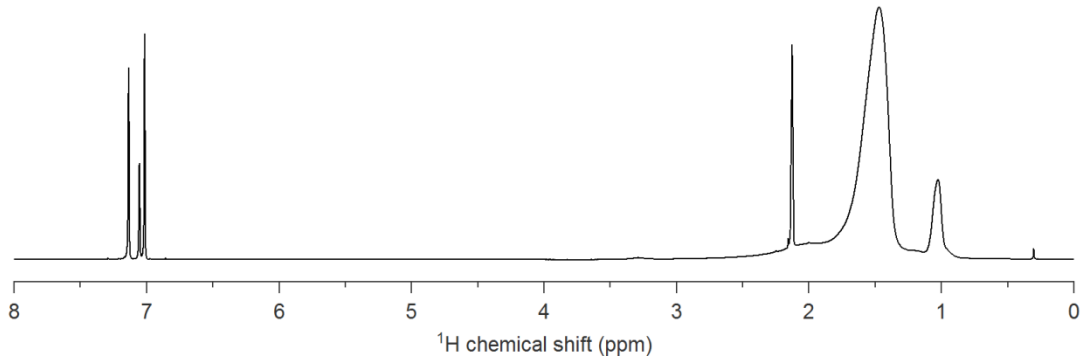

Figure S16. ^{1}H NMR spectrum of ZrO_2 NCs capped with octadecylphosphonic acid and precipitated with methanol.

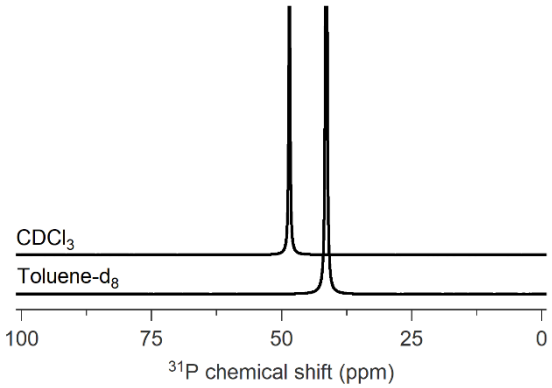

Figure S17. ^{31}P NMR spectra of recrystallized TOPO in chloroform and toluene.