Supplementary Information

for

The trouble with ODE: polymerization during nanocrystal synthesis

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Experimental Section

General considerations. All manipulations were performed in air unless otherwise indicated. All chemicals are used as received unless otherwise mentioned. 1-Octadecene (90%), cadmium oxide (99.99%), chloroform-d1 (99.6%), manganese(II) chloride anhydrous (99.999%), methanol anhydrous (99.8%), oleic acid (90% and 99%), oleylamine (70%), sulfur (99.998%), tetraethylene glycol dimethyl ether (tetraglyme, 99%), tetramethyl thiourea (98%), triethylamine (99%), trifluoroacetic acid (99%), trifluoroacetic anhydride (99%), and zinc oxide (99.99%) were obtained from Sigma-Aldrich and used without further purification. Acetonitrile (99.9%), chloroform (99%), hexanes (mixture of isomers, 95%), sodium hydroxide (99%) were obtained from Carl-Roth. Copper(I) iodide (99.995%) was obtained from Acros Organics. Calcium hydride (82%), 1-dodecanethiol (98%), indium(III) acetate (99.99%), *n*-hexadecane (95%), *n*-octadecane (98%), and selenium (99.999%) were obtained from Alfa Aesar. Acetone (99.5%), 2-propanol (99.7%), methanol (99.8%), and toluene (99%) were obtained from Fiers. (6-[2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethoxy]hexyl) phosphonic acid was obtained from Sikémia.

Oleylamine, tetraglyme, 1-octadecene, *n*-hexadecane, and *n*-octadecane were vacuum distilled by following described procedure. Calcium hydride is added to the solvent and vacuum dried overnight. Afterwards, the solvent is vacuum distilled and collected in a Straus flask to introduce it in the glovebox where it is stored over molecular sieves.

Zinc(II) oleate is synthesized according to the procedure used to synthesize lead oleate of Hendricks *et al*. with some slight modifications.[1] On a 45 mmol scale, a yield of 98% is obtained. The ZnO is allowed to warm to room temperature and results in a clear and colourless solution overnight.

Cadmium(II) oleate is synthesized according to the procedure used to synthesize lead oleate of Hendricks *et al.* with some slight modifications.[1] Performed on a scale of 20 mmol, a yield of 91% is obtained. The CdO is allowed to warm to room temperature and results in a clear and colourless solution overnight in a volume of 12 mL of acetonitrile.[2]

Manganese(II) oleate. Manganese(II) chloride anhydride (617.9 mg, 5 mmol, 1 eq.) is dissolved in anhydrous methanol (5 mL) by sonification, is dropwise added to a solution of oleic acid (2966.1 mg, 10.5 mmol, 2.1 eq.) and triethylamine (1138.4 mg, 11.25 mmol, 2.25 eq.) in anhydrous methanol (20 mL). After 30 minutes, the mixture is centrifugated, redissolved in dichloromethane and washed with cold methanol. The washing step is repeated three times. The resulting light pink fine powder is vacuum dried overnight. A yield of 30% is obtained.

Iron(III) oleate. A $FeCl_3.6H_2O$ (1351.5 mg, 5 mmol, 1 eq.) in methanol (25 mL) solution is dropwise added to an oleic acid (4237.4 mg, 15 mmol, 3 eq.) and NaOH (600.0 mg, 15 mmol, 3 eq.) in methanol (50 mL) solution. During addition, a brown precipitation is formed which. After 30 minutes of stirring, the precipitate is filtered and 5 times washed with an excess of methanol. The resulting brown precipitate is vacuum dried. A yield of 52% is obtained.

Manganese doped zinc sulfide/zinc sulfide (ZnS:Mn/ZnS) core/shell NCs are synthesized according to the procedure of Srivastava *et al.* with some slight modifications.[3] Zinc stearate, manganese stearate, steric acid and octadecylamine are substituted by zinc oleate, manganese oleate, oleic acid and oleylamine respectively. After the first purification step with acetone, the precipitate is redispersed in toluene and pushed through a syringe filter to remove the unreacted, not soluble zinc oleate. Afterwards, the reaction mixture is purified another 2 times with acetone as non-solvent and redispersed in toluene after centrifugation.

When using *n*-hexadecane (7730.0 mg, 10 mL and 3092.0 mg, 4 mL) as substituted reaction solvent for 1-octadecene, all other parameters remained identical.

Rational ligand exchange for (6-[2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethoxy]hexyl) phosphonic acid (1) on ZnS:Mn/ZnS core/shell NCs. Quantitative ^{1}H NMR is used to determine the amount of surface ligands, i.e., oleate and oleylamine, based on the alkene resonance located at around 5.3 ppm in deuterated chloroform. A 1.5 equivalent of **1** is added, using a 100 mM stock solution in chloroform, and subjected to ultrasound for 10 minutes. Hexanes are added until the NCs precipitate and after centrifugation, a minimal volume of chloroform is used to redisperse the NCs again. This purification step is repeated three times. The NC dispersion could be dried and redispersed in various polar environments.

Copper indium sulfide ($CuInS_2$) NCs are synthesized according to Chen *et al.*[4] After synthesis, the NCs are purified 3 times by precipitating the NCs with acetone and redispersing in toluene after centrifugation.

When using *n*-hexadecane (12936.6 mg, 10 mL) as substituted reaction solvent for 1-octadecene, all other parameters remained identical.

Cadmium sulfide (CdS) NCs are synthesized according to Hamachi *et al.*, making use of N,N,N’,N’-tetramethyl thiourea as the sulfur precursor and a 2.4 equivalent (to the thiourea) of oleic acid.[5] After synthesis, the NCs are purified 3 times by precipitating the NCs with acetone and redispersing in toluene after centrifugation.

When using *n*-hexadecane (11015.3 mg, 14.25 mL) as substituted reaction solvent for 1-octadecene, all other parameters remained identical.

Rational ligand exchange for (6-[2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethoxy]hexyl) phosphonic acid (1) on CdS NCs. ERETIC ^{1}H NMR is used to determine the amount of oleate surface ligand, based on the alkene resonance located at around 5.3 ppm in deuterated chloroform. A 1.5 equivalent of **1** is added, using a 100 mM stock solution in chloroform, and subjected to ultrasound for 10 minutes. Hexanes are added until the NCs precipitate and after centrifugation, a minimal volume of chloroform is used to redisperse the NCs again. This purification step is repeated three times. The NC dispersion could be dried and redispersed in various polar environments.

Titanium dioxide (TiO_2) NCs are synthesized according to Gordon *et al.*, making use of the combination of TiF_4 with oleylamine.[6] After synthesis, the NCs are purified 3 times by precipitating the NCs with acetone and redispersing in toluene after centrifugation.

When using *n*-hexadecane as substituted reaction solvent for 1-octadecene, all other parameters remained identical.

The TiO_2 NCs dispersions NMR samples are prepared by a solvent exchange procedure. Here, the NC dispersion is evaporated to a minimal amount of solvent, followed by the addition of deuterated chloroform, and repeated 3 times. Due to this solvent exchange procedure, it is unavoidable to have a remaining acetone peak in the recorded NMR spectra, since acetone is used in big quantities as a non-solvent. This procedure is used because once the TiO_2 NCs are pumped dry, redispersion is possible anymore.

Iron oxide (Fe_3O_4) NCs are synthesized according to Jana *et al.* making use of iron oleate (900.2 mg, 1 mmol) and an extra 0.1 equivalent oleic acid (28.2 mg, 0.3 mmol) in 1-octadecene (5000.0 mg, 6.34 mL, 19.8 mmol) at 300 °C for 15 minutes.[7] After synthesis, the NCs are purified 3 times by precipitating the NCs with acetone and redispersing in toluene after centrifugation.

When using *n*-octadecane (5040.0 mg, 19.8 mmol) as substituted reaction solvent for 1-octadecene, all other parameters remained identical.

Characterization. Transmission Electron Microscopy (TEM) and High-Resolution Transmission Electron Microscopy (HRTEM) were performed on a JEOL JEM-2200FS TEM with Cs corrector operated at 200 kV. Nuclear Magnetic Resonance (NMR) measurements were recorded on a Bruker Avance III Spectrometer operating at a ^{1}H frequency of 500.13 MHz and featuring a BBI probe. The sample temperature was set to 298.15 K. For the quantitative 1D ^{1}H measurements, 64k data points were sampled with the spectral width set to 16 ppm and a relaxation delay of 30s. DOSY measurements were performed with a double stimulated echo pulses (dstegp3s). The gradient strength was varied quadratically from 2-95% of the probe's maximum value in 64 steps, with the pulse length gradient (D20) and diffusion time (P30) optimized to ensure a final attenuation of the signal in the final increment of less than 1% relative to the first increment. Size Exclusion Chromatography (SEC) was performed using a Varian PLGPC50plus instrument, using a refractive index detector, equipped with two Plgel 5 µm MIXED-D columns 40 °C. Polystyrene standards were used for calibration and THF as eluent at a flow rate of 1 mL/min. Samples were injected using a PL AS RT autosampler.

Reactions with pure 1-octadecene and molecular weight.

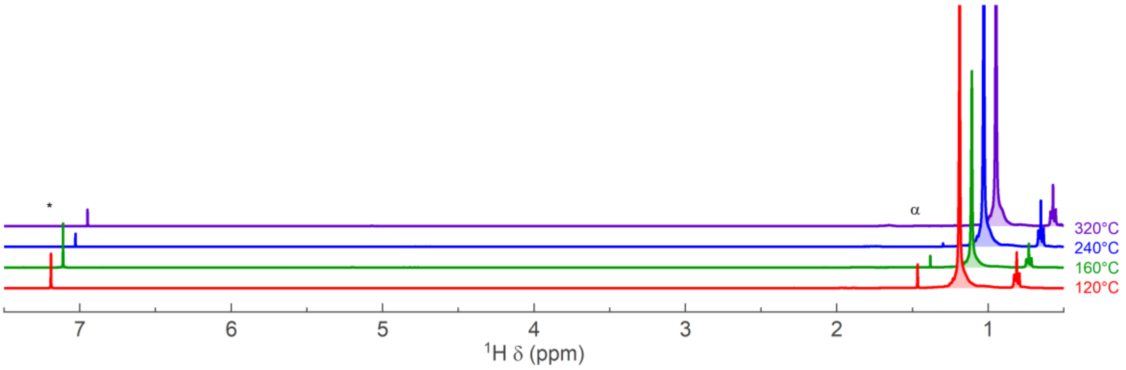

Figure S1. Pure poly(ODE) is obtained by heating at temperatures between 120 and 320°C for 24 hours and standard purification. ^{1}H NMR analysis in $CDCl_3$ (*) indicates the removal of the terminal alkene group of ODE at 5.80 an 4.94 ppm. Residual solvent peaks may occur of water (α) at 1.5 ppm.[8]

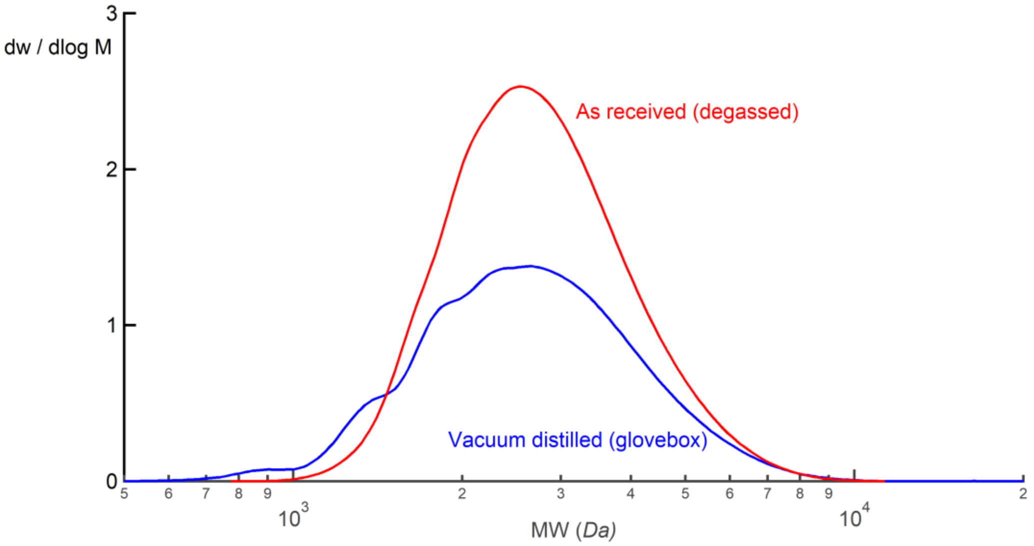

Figure S2. Size exclusion chromatography of poly(ODE) formed at 240 °C for 24 hours from 1-octadecene which is used after vacuum distillation and as-received after degassing (for 1 hour at 40 °C, repeated 3 times).

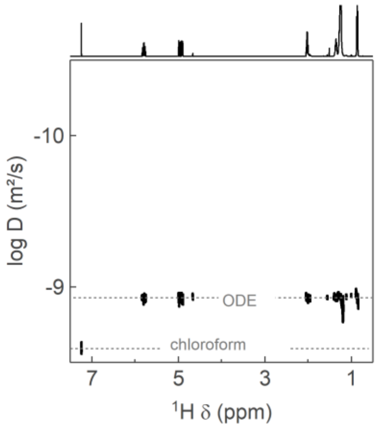

Figure S3. 2D DOSY NMR in $CDCl_3$ of ODE as received with a diffusion coefficient of 1118.5 ± 0.8 µm²/s, used as a reference measurement in figure 1.

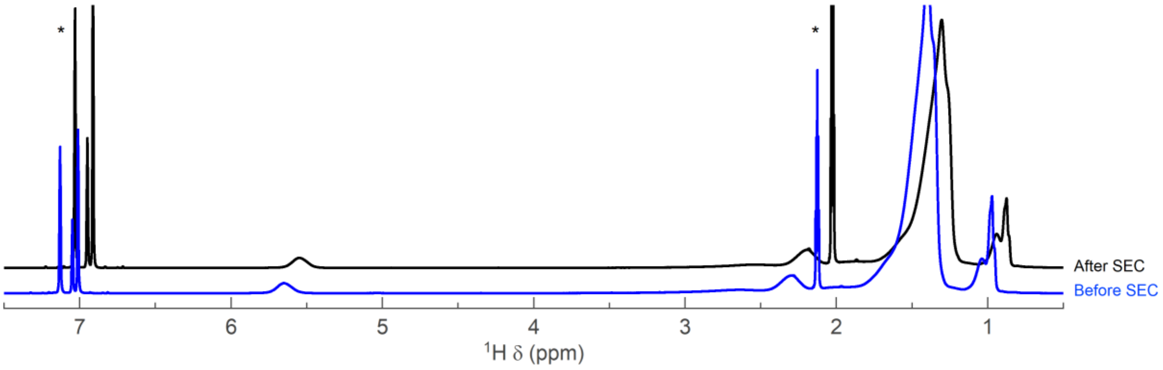

Figure S4. Purification of oleate stabilized NCs from poly(ODE) in a mixture by means of size exclusion chromatography (SEC) is unsuccessful. After SEC, ^{1}H NMR still shows a double peak at the methyl region (1 ppm) comparable to before.

Surface chemistry characterization of ZnS:Mn/ZnS NCs synthesized in ODE.

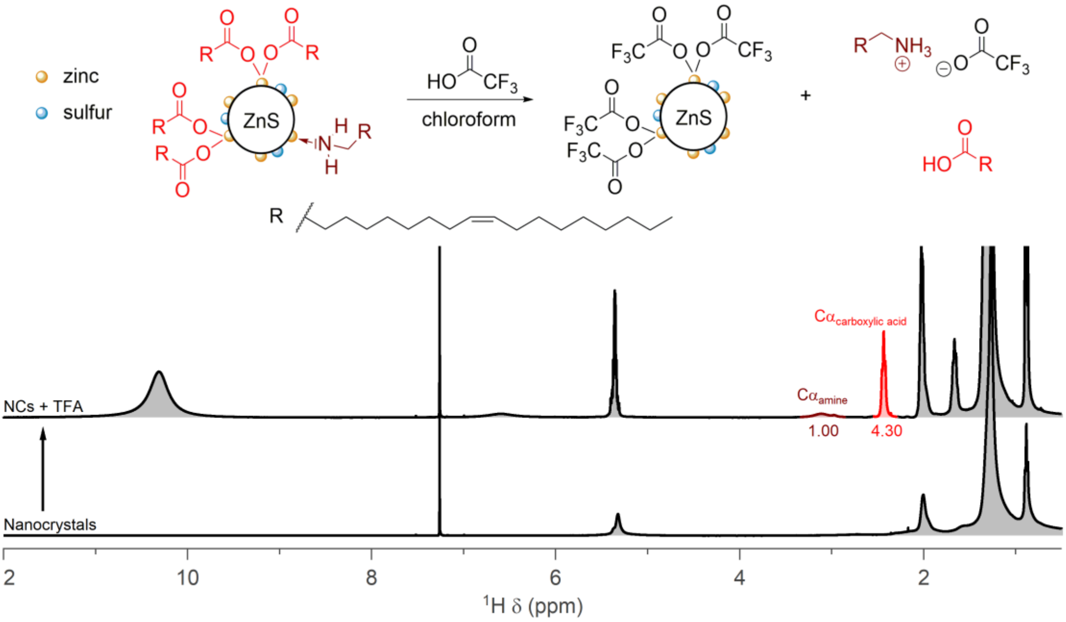

Figure S5. Surface chemistry analysis by means of ligand stripping by making use of a strong acid, i.e., trifluoroacetic acid (TFA), characterized by quantitative ^{1}H NMR (ERETIC). The purified NCs surface is identified with an 81%/19% mixture of oleate/oleylamine respectively.

Rational ligand exchange of ZnS:Mn/ZnS NCs synthesized in ODE.

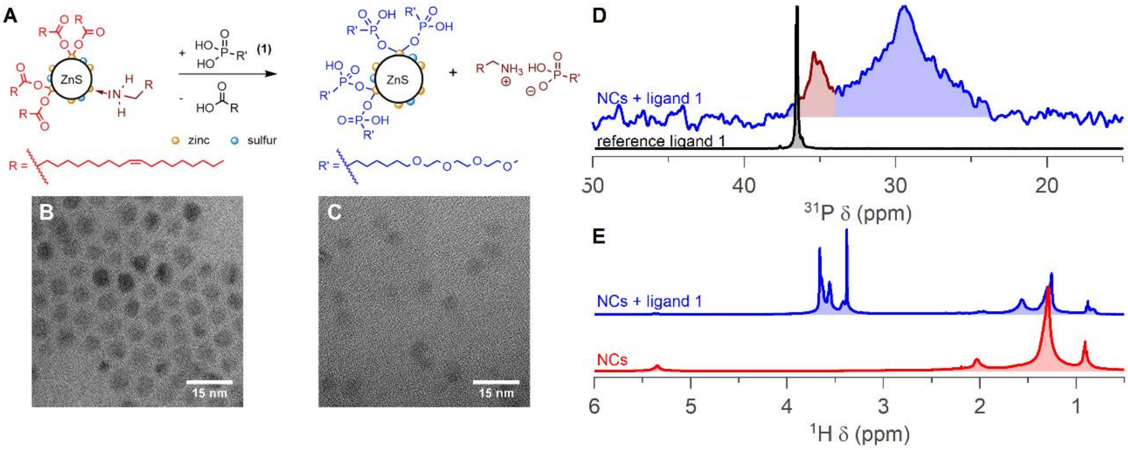

Figure S6. (A) Scheme of rational ligand exchange reaction of 81% oleate and 19% oleylamine capped surface of ZnS:Mn/ZnS NCs with ligand **1**. (B) TEM image of ZnS:Mn/ZnS NCs, stabilized with oleate and oleylamine, deposited from chloroform. (C) TEM image of

ZnS:Mn/ZnS NCs, stabilized with ligand **1**, deposited from chloroform. (D) ^{31}P NMR and (E) ^{1}H NMR of pure ligand **1** (blue) and ZnS:Mn/ZnS NCs before (red), and after exchange (black).

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