

The Trouble with 1-Octadecene; Polymerization During Nanocrystal Synthesis

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The trouble with 1-octadecene: polymerization during nanocrystal synthesis

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Abstract

1-octadecene is a widely used solvent for high temperature nanocrystal synthesis (120 – 320 °C). Here, we show that 1-octadecene spontaneously polymerizes under these conditions and the resulting poly(1-octadecene) has a comparable solubility and size to nanocrystals stabilized by hydrophobic ligands. Typical purification procedures (precipitation/redispersion cycles or size exclusion chromatography) fail to separate the poly(1-octadecene) impurity from the nanocrystal product. To avoid formation of poly(1-octadecene), we replaced 1-octadecene with saturated, aliphatic solvents. Alternatively, the native ligands are exchanged for polar ligands, leading to significant solubility differences between nanocrystals and poly(1-octadecene), therefore allowing isolation of pure nanocrystals, free from polymer impurities. These results will help design superior syntheses and improve nanocrystal purity, an important factor in many applications.

Main text

In the last 25 years, colloidal nanocrystals (NCs) have matured from an interesting physical phenomenon to a rich multidisciplinary field.¹⁻⁶ While the chemical identity of the core determines most of the NC properties, the large surface-to-volume ratio makes surface chemistry a key enabler for applications.⁷⁻¹⁰ There are many synthetic techniques available for NCs but solution phase synthesis stands out since it allows for crystallization at relatively low temperatures (< 400 °C) with high yield and versatility.¹¹

Tri-*n*-octylphosphine oxide (TOPO) is a commonly used solvent for nanocrystal synthesis due to its high boiling point and coordinating properties. However, commercial TOPO contains many impurities that bind to the NC surface and direct the crystal growth, yielding anisotropic structures.¹²⁻¹³ Even purified TOPO (obtained by recrystallization),¹⁴ can still decompose into by-products with high affinity for the surface.¹⁵ The resulting heterogeneous surface chemistry is disadvantageous as it complicates ligand exchange reactions.¹⁵

Non-coordinating 1-octadecene (ODE) is another frequently used solvent and seems to be plagued less by impurities.¹⁶⁻⁴⁶ Apart from its role as solvent, ODE has often been used as reagent in NC synthesis since ODE's terminal alkene (vinyl) has inherent reactivity. For example, its redox properties have been harnessed to reduce elemental sulfur or selenium to its –II oxidation state, prior to incorporation in metal sulphide or selenide NCs.^{34, 40, 47-49} Cao *et al.* reported a facile reduction of selenium dioxide by ODE (resulting in monodisperse NCs) but a more sluggish reaction with *n*-octadecane or diphenylether (resulting in polydisperse samples and low yield).⁵⁰ Furthermore, vinyl moieties can be polymerized by metallocene⁵¹⁻⁵⁴ or inorganic⁵⁵ catalysts. For this reason, Talapin *et al.* opted for saturated solvents and saturated ligands to avoid the gallium catalysed polymerization of ODE in the synthesis of GaAs NCs.⁵⁶

Here, we study ODE's propensity to polymerize in the *absence* of catalysts, at temperatures relevant for NC synthesis. We find that ODE auto-polymerizes above 120 °C with a temperature dependant molecular weight. Poly(ODE) is detected in the reaction product of five different NC syntheses; ZnS:Mn/ZnS¹⁶, CuInS₂¹⁷, CdS^{11, 18}, TiO₂¹⁹, and Fe₃O₄²⁰. We thus conclude that poly(ODE) is routinely contaminating NC production. To avoid the formation of poly(ODE), saturated solvents are used in those cases where ODE does not participate in the reaction. When ODE is necessary as reagent (and cannot be avoided), we show that a surface functionalization can provide a pathway to easily separate NCs from poly(ODE).

We heated ODE under argon to temperatures ranging from 100 °C to 320 °C. Whereas there is no reaction at 100 °C, a colourless oil can be separated after 24 hours at 120 °C (or higher) by the addition of acetone and subsequent centrifugation, a process not unlike the isolation of NCs from a crude reaction mixture. The ¹H NMR (nuclear magnetic resonance) spectrum of the oil confirms that an alkene resonance is absent (Figure S1), and the compound only consists of -CH₂- and -CH₃ moieties, with a relative intensity of 33:3, consistent with the polymerization of ODE into poly(ODE) (Figure 1A). To study the kinetics of the reaction, aliquots are taken at regular time intervals and analysed by quantitative ¹H NMR. The conversion of ODE to poly(ODE) is determined from the disappearance of the alkene resonance with respect to the methyl groups (Figure 1B). While the conversion becomes appreciable at 240 °C, the conversion rate is dramatically high at 320 °C (the boiling point of ODE). After 24 hours, conversions of 0.64%, 6.58%, 24.01%, and 88.51% are reached at 120, 160, 240, and 320 °C respectively. After isolation and purification, a yield by mass of respectively 0.07%, 3.38%, 14.79%, and 66.32% is obtained.

Poly(ODE), synthesized at various temperatures, is subsequently analysed by size exclusion chromatography (SEC), revealing that the molecular weight is inversely related to the reaction temperature (Figure 1C). This indicates that the reaction is thermodynamically controlled.⁵⁷

At higher reaction temperatures, the entropic factor dominates the free energy, thus favouring polymer chains with a lower molecular weight. Note that similar molecular weights are obtained using ODE which was either vacuum distilled or simply degassed (Figure S2). In addition to SEC, 2D diffusion ordered spectroscopy (DOSY) NMR has also been established as a technique to determine the molecular weight of polymers.⁵⁸ DOSY organizes NMR resonances according to their diffusion coefficient, which is related to their solvodynamic size. Indeed, 2D DOSY NMR of the poly(ODE), synthesized at 240 °C, yields a lower diffusion coefficient (265 $\mu\text{m}^2/\text{s}$) compared to the parent ODE (Figure 1D). Using the Stokes-Einstein relation, we calculate a corresponding solvodynamic diameter of about 3.0 nm.

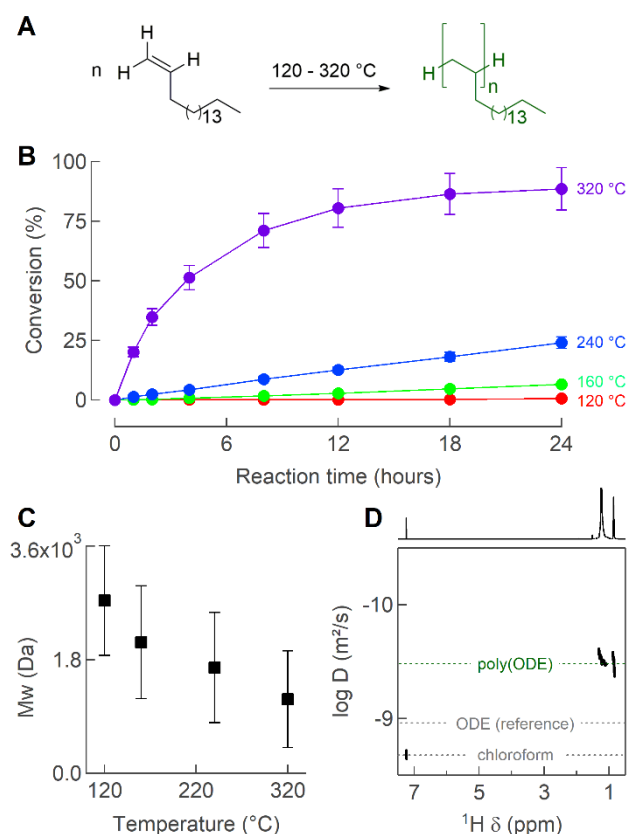


Figure 1. (A) Poly(ODE) is obtained at temperatures between 120 and 320°C. (B) The conversion kinetics were determined from the disappearance of the alkene resonance in quantitative ^1H NMR spectra of 10 μL aliquots in CDCl_3 . (C) The molecular weight of poly(ODE), measured by SEC in tetrahydrofuran, with their standard deviation calculated from the average molecular weight and dispersity ($\mathcal{D} = 1 + \frac{\sigma^2}{\mu^2}$), is inversely correlated to the reaction temperature. (D) 2D DOSY NMR in CDCl_3 of poly(ODE) formed at 240 °C after 24 hours. The diffusion coefficient of 1-octadecene is added as a reference point (Figure S3).

Since the polymerization of ODE proceeds without catalyst and is controlled by temperature and time, poly(ODE) is most likely formed in many NC syntheses. To demonstrate this, we analysed the reaction products of five different NC syntheses, including core, core-shell and doped NCs: ZnS:Mn/ZnS¹⁶, CuInS₂¹⁷, CdS^{11, 18}, TiO₂¹⁹, and Fe₃O₄²⁰. These NC syntheses are well-established and the synthetic protocols are widely used. TEM analysis confirmed the successful synthesis of the NCs (Figure 2). However, the ¹H NMR spectra of the purified nanocrystals reveal that the integrals of the resonances are not consistent with the expected ligand. Consistently, the integrals for the -CH₂- and -CH₃ resonances were too high, indicating an aliphatic impurity.

It is challenging to unambiguously confirm the presence of the polymer because of (i) the difficulty in physically separating the hydrophobic NCs from the hydrophobic polymer, and (ii) the spectral overlap between the aliphatic NMR resonances of the ligands and the polymer. Again, we use DOSY NMR to virtually separate the resonances according to their diffusion constant (Figure 2). In every nanocrystal sample we retrieved two sets of resonances, each diffusing with a different speed, one corresponding to the colloidal NCs and one to the poly(ODE). The ligand-capped NCs are larger in size than poly(ODE), and therefore have a lower diffusion coefficient. Note that the case of Fe₃O₄ NCs is special since the NCs are magnetic, thus prohibiting direct NMR analysis. To circumvent this limitation, we exchanged the native oleate ligand for trifluoroacetic acid, causing the Fe₃O₄ NCs to precipitate. The supernatant contains the free, unbound oleic acid (with a high diffusion coefficient) and the poly(ODE) (Figure 2). In the case of TiO₂ NCs, the production of poly(ODE) is most noticeable compared to the other syntheses. This is most likely due to the catalytic properties of titanium halide precursors with respect to the polymerization of olefins.⁵⁵ Overall, we conclude that poly(ODE) is present in all studied NC samples.

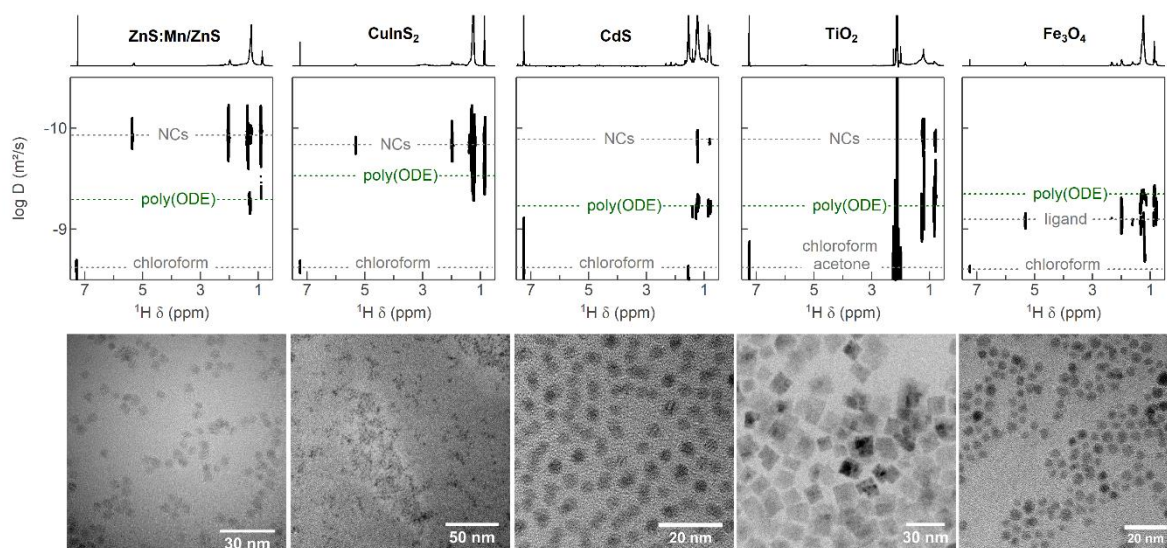


Figure 2. 2D DOSY NMR spectra and TEM images of NCs synthesized in ODE; ZnS:Mn/ZnS (oleate and oleylamine capped), CuInS₂ (oleate capped), CdS (oleate capped), TiO₂ (oleylamine capped), and Fe₃O₄ (oleate capped). The presence of acetone in the TiO₂ NCs sample is due to the NMR sample procedure (see experimental section). Since the Fe₃O₄ NCs are magnetic, the DOSY measurement is performed after a ligand stripping.

To simply avoid the polymerization of ODE, we explored the substitution of ODE by alternative, saturated solvents. The most obvious candidate is *n*-octadecane, which has a similar boiling point (317°C). However, *n*-octadecane is a solid at room temperature ($T_m = 26\text{-}29^\circ\text{C}$), which is inconvenient and especially problematic in procedures involving syringe pump addition of stock solutions. More convenient (i.e., liquid at room temperature) solvents are *n*-hexadecane ($T_b = 287^\circ\text{C}$) or 2,6,10,15,19,23-hexamethyltetracosane (also known as squalane, $T_b = 350^\circ\text{C}$). If the solvent is merely a heat transfer medium and does not partake in the reaction, it should be straightforward to substitute ODE. Indeed, for the CuInS₂, CdS, and TiO₂ NC syntheses in *n*-hexadecane and for the Fe₃O₄ NC synthesis in *n*-octadecane we observe no obvious differences in NC morphology, size and dispersity (Figure 3). DOSY NMR of those four cases confirms that poly(ODE) is absent (Figure 3) and the nanocrystal dispersion is thus pure. Unfortunately, the synthesis of ZnS:Mn/ZnS core/shell NCs is not controlled in *n*-hexadecane and results in highly polydisperse NCs (Figure 3 left). In this type of synthesis, the terminal alkene group of ODE is responsible for the controlled reduction of

elemental sulfur.⁴⁷ Therefore, ODE is a necessary component of the synthesis and the formation of poly(ODE) cannot be avoided without compromising the NC quality.

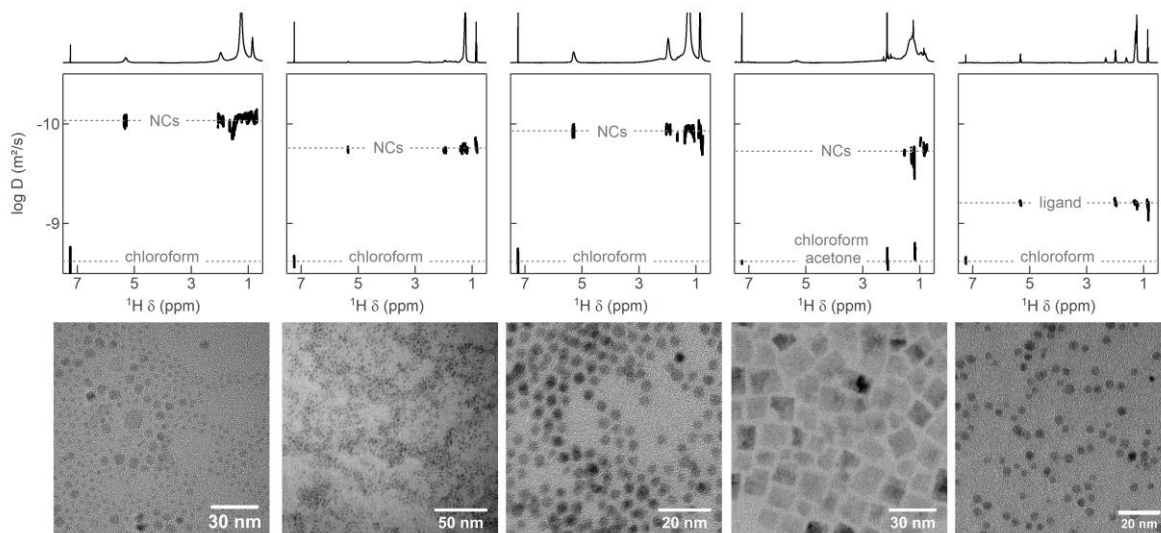


Figure 3. 2D DOSY NMR spectra and TEM images of NCs synthesized in saturated solvents, evidencing the absence of poly(ODE).

Nanocrystal syntheses are complex and it is clear that changing the solvent can have significant effects on the NC product. On the other hand, poly(ODE) hampers charge transfer in solid films of NCs⁵⁹, distorts NMR spectra (thus hampering surface chemistry studies), and generally decreases sample purity. Since poly(ODE) was observed in samples that were purified via the classical precipitation-redispersion cycles (Figure 2), it is desirable to develop alternative purification procedures. In literature, subtle ‘tricks’ and delicate procedures are reported, giving nanocrystal purification the aura of art instead of science.^{18-19, 60} While size exclusion chromatography has been proposed as an interesting new purification technique,⁶⁰⁻⁶¹ we did not succeed in separating the poly(ODE) from ligand capped nanocrystals (Figure S4).

The difficulty in obtaining pure NCs lies with the comparable size and polarity of poly(ODE) and ligand-capped-NCs. While the size cannot be changed, the polarity can be adjusted by modification of the surface. We thus exchange the native hydrophobic oleate ligands for the slightly more polar ligand **1**: (6-[2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy]hexyl) phosphonic

acid (Figure 4A). Ligands with multiple ethylene glycol moieties are highly versatile since they provide colloidal stability in a variety of solvents with different polarity, excluding hexanes.^{14, 62-64} Since poly(ODE) is highly soluble in hexanes, this provides a pathway to separate poly(ODE) from the NCs.

To illustrate the procedure, we functionalize the surface of CdS NCs, synthesized in ODE, with **1** (Figure 4A). The as-synthesized CdS NCs are capped with oleate ligands, as evidenced by ¹H NMR (Figure 4B). We infer from the high intensity in the aliphatic region of the NMR spectrum (0.5 – 1.5 ppm) that a substantial amount of poly(ODE) is present. To exchange the oleates for **1**, we only added a slight excess of **1** because phosphonates have a stronger binding affinity to the NC surface.^{63, 65-66} Subsequently, the NCs are precipitated by hexanes and redispersed in chloroform. The supernatant containing poly(ODE) is discarded. The ¹H NMR spectrum of the NCs confirms a successful purification since only the bound (broadened) resonances of **1** are observed and the aliphatic signals of poly(ODE) are absent (Figure 4B). The purity of the sample is further confirmed by 2D DOSY NMR which shows only 1 set of resonances with a low diffusion coefficient, corresponding to bound **1** (Figure 4C). This is also reflected in the single exponential fit of the DOSY decay curve for the region from 1.7 to 1.2 ppm (Figure 4D).

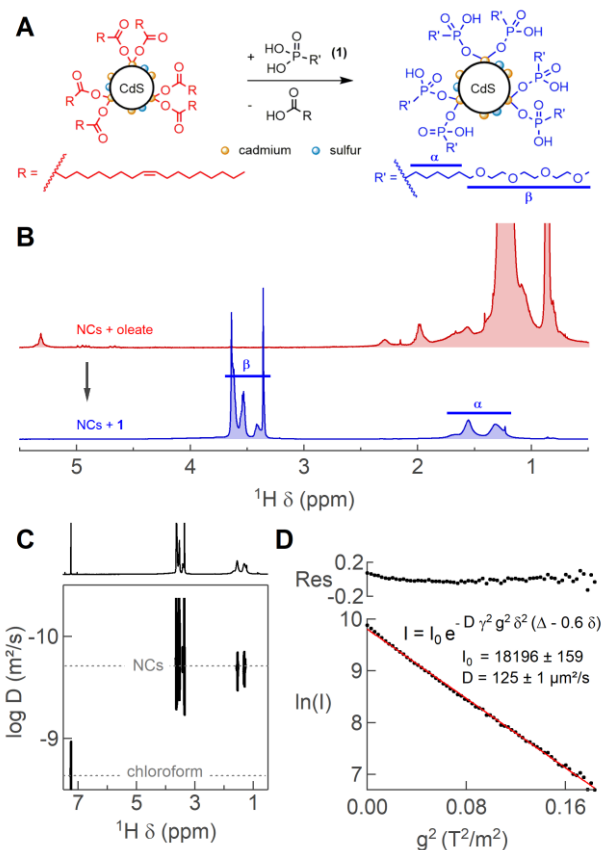


Figure 4. (A) Ligand exchange of oleate for **1** on CdS NCs. (B) The corresponding ^1H NMR spectra of CdS NCs capped with oleate and with poly(ODE) present, purified CdS NCs after ligand exchange with **1** and a reference spectrum of **1**, all in CDCl_3 . (C) 2D DOSY NMR spectrum shows only the presence of the purified CdS NCs functionalized with ligand **1**. (D) The analysis of the DOSY decay curve of the region from 1.7 to 1.2 ppm confirms the presence of only one component, i.e., the purified NCs.

The same procedure can be applied to ZnS:Mn/ZnS NCs but the surface chemistry of the as-synthesized NCs is more complex (Figure S6). By stripping the surface ligands with a strong acid, we determined a relative surface composition of 81% oleate and 19% oleylamine. We infer that oleate binds as an X-type ligand while oleylamine binds as an L-type ligand.⁷ This complicates ligand exchange because upon addition of **1**, both an X-for-X ligand exchange with oleate occurs and an ion pair is formed with oleylamine. Nevertheless, the functionalized NCs can be precipitated with hexanes and redispersed in chloroform. In the ^{31}P NMR spectrum, a broadened resonance at 30 ppm (FWHM = 1113.51 Hz) is observed, which is assigned to bound X-type phosphonate. The smaller and sharper resonance at 35 ppm (FWHM = 366.45 Hz) is assigned to the ion pair of **1** and oleylamine. It is not surprising that

ion pairs are still present given their low solubility in hexanes and their reasonably high affinity for the nanocrystal surface.⁶⁷⁻⁶⁸ Finally, the ¹H NMR spectrum confirms these conclusions as the spectrum is dominated by the resonances of **1**, but the resonances of oleylamine remain present. As hypothesized, this procedure allowed for the purification of the NCs from the poly(ODE) produced during the synthesis.

In conclusion, ODE spontaneously polymerizes at temperatures above 120°C and we have identified its presence in established syntheses of five types of nanocrystals, i.e., ZnS:Mn/ZnS, CuInS₂, CdS, TiO₂, and Fe₃O₄ NCs. Standard purification procedures were unable to separate the poly(ODE) impurity from the NC product. While the use of saturated solvents can prevent poly(ODE) from forming, we also developed a surface modification strategy to increase the polarity of the NCs. As such, the nonpolar poly(ODE) could be readily separated from the polar NCs based on solubility differences. In general, the contamination of NC products by poly(ODE) is a problem for NC-based applications. Here we have provided the tools to design improved synthetic protocols towards pure nanocrystals.

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Associated Content

Supporting information

Experimental procedures, techniques used to characterize, additional ^1H NMR and SEC spectra of poly(ODE), surface chemistry characterization, and rational ligand exchange of ZnS:Mn/ZnS core/shell NCs.

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Notes

The authors declare no competing financial interest.

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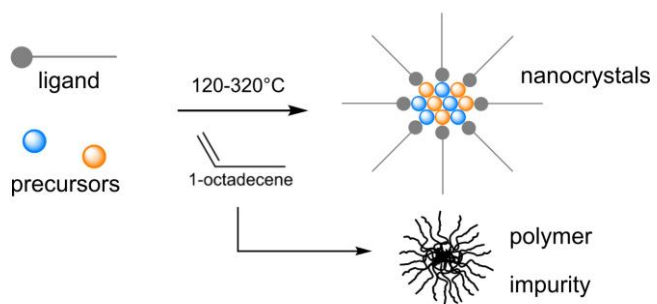
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TOC Graphic



The trouble with 1-octadecene polymerization during nano... (1.00 MiB)

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Supplementary Information

for

The trouble with 1-octadecene: 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 centrifuged, 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 FeCl₃.6H₂O (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.

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 ¹H 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 (CuInS₂) NCs are synthesized according to Chen *et al.*⁴

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

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 ¹H 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 (TiO₂) NCs are synthesized according to Gordon *et al.*, making use of the combination of TiF₄ with oleylamine.⁶

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

The TiO₂ NCs dispersions NMR samples are prepared by a solvent exchange procedure. Here, the dispersion is evaporated to a minimal amount of solvent, followed by the addition of deuterated solvent, and repeated 3 times. This procedure is used because once the TiO₂ NCs are pump dry, the redispersion is not stable anymore.

Iron oxide (Fe₃O₄) 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

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 ¹H frequency of 500.13 MHz and featuring a BBI probe. The sample temperature was set to 298.15 K. For the quantitative 1D ¹H 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.

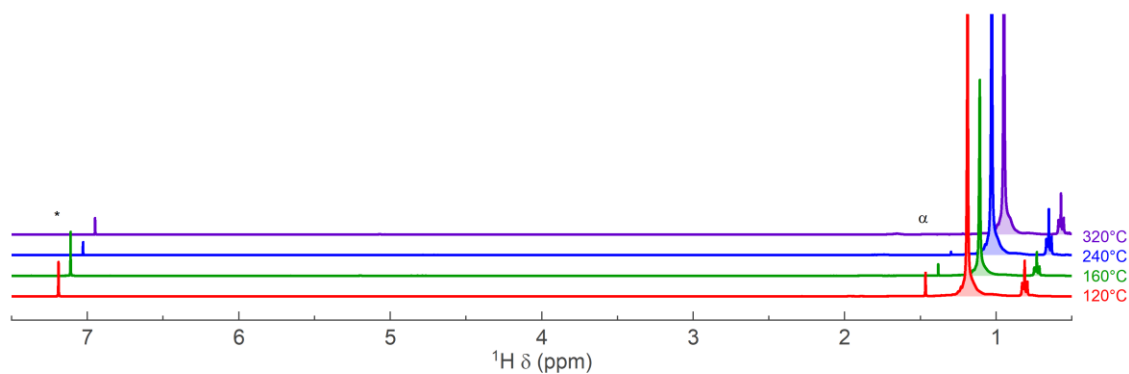


Figure S1. Pure poly(ODE) is obtained by heating at temperatures between 120 and 320°C for 24 hours and standard purification. ¹H NMR analysis in CDCl₃ (*) indicates the removal of the terminal alkene group of ODE. Residual solvent peaks may occur of water (α) at 1.5 ppm.⁸

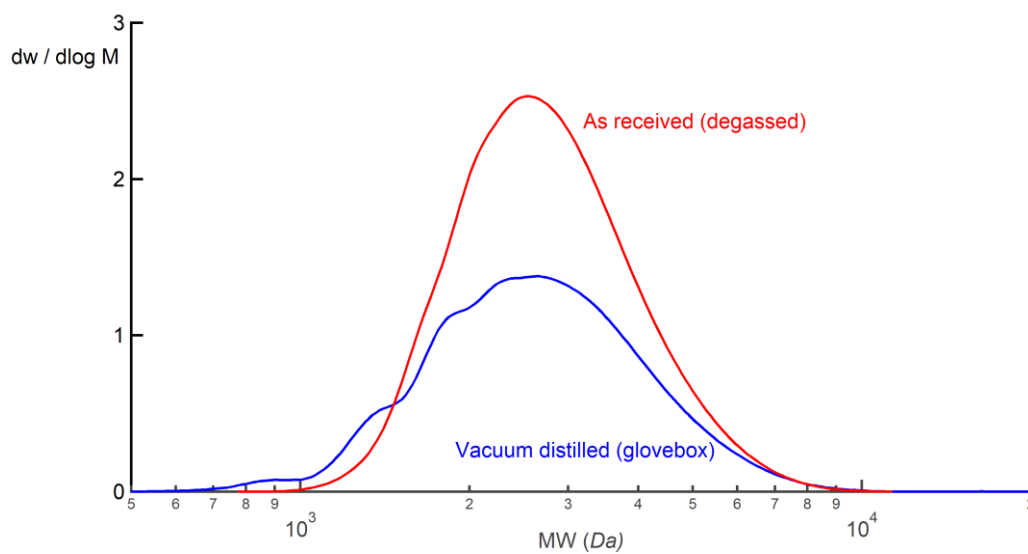


Figure S2. Size exclusion chromatography of poly(ODE) formed at 240 °C for 24 hours from 1-octadecene which is used after vacuum distillation and as-received after degassing (for 1 hour at 40 °C, repeated 3 times).

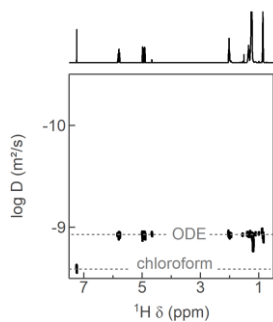


Figure S3. 2D DOSY NMR in CDCl_3 of ODE as received with a diffusion coefficient of $1118.5 \pm 0.8 \mu\text{m}^2/\text{s}$, used as a reference measurement in figure 1.

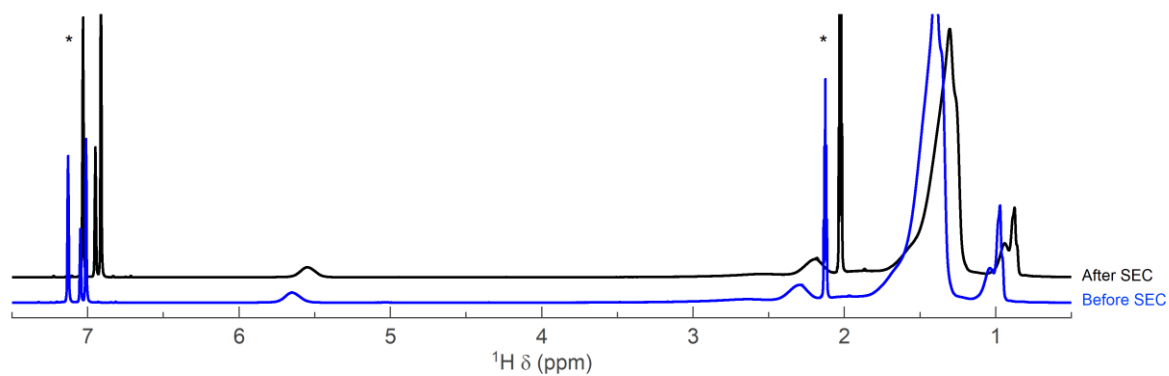


Figure S4. Purification of oleate stabilized NCs from poly(ODE) in a mixture by means of size exclusion chromatography (SEC) is unsuccessful. After SEC, ^1H NMR still shows a double peak at the methyl region (1 ppm) comparable to before.

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

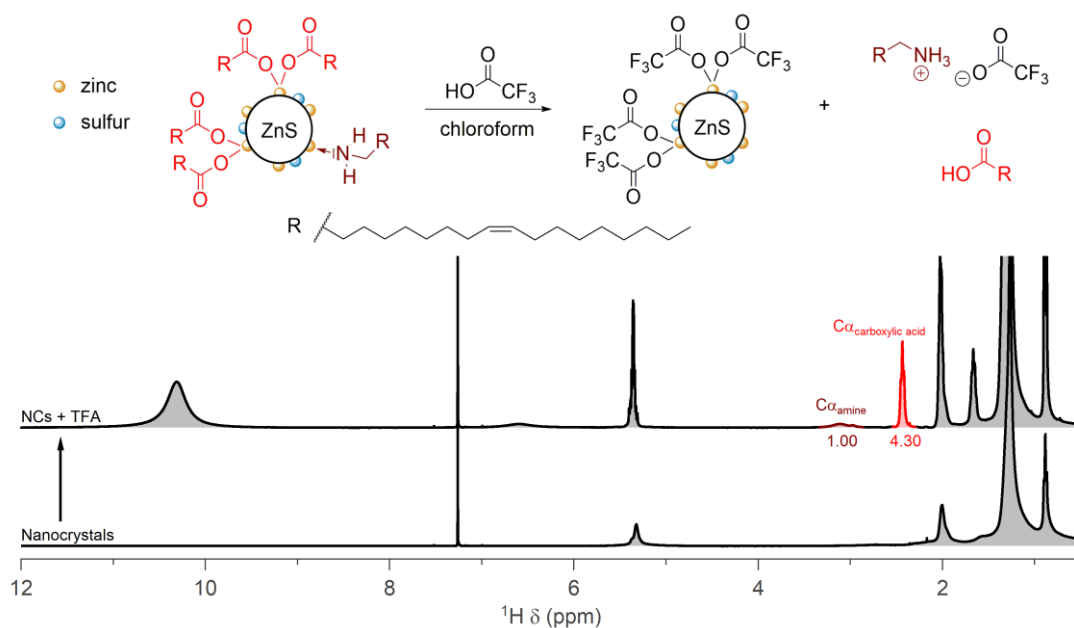


Figure S5. Surface chemistry analysis by means of ligand stripping by making use of a strong acid, i.e., trifluoroacetic acid (TFA), characterized by quantitative ^1H NMR (ERETIC). The purified NCs surface is identified with an 81%/19% mixture of oleate/oleylamine respectively.

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

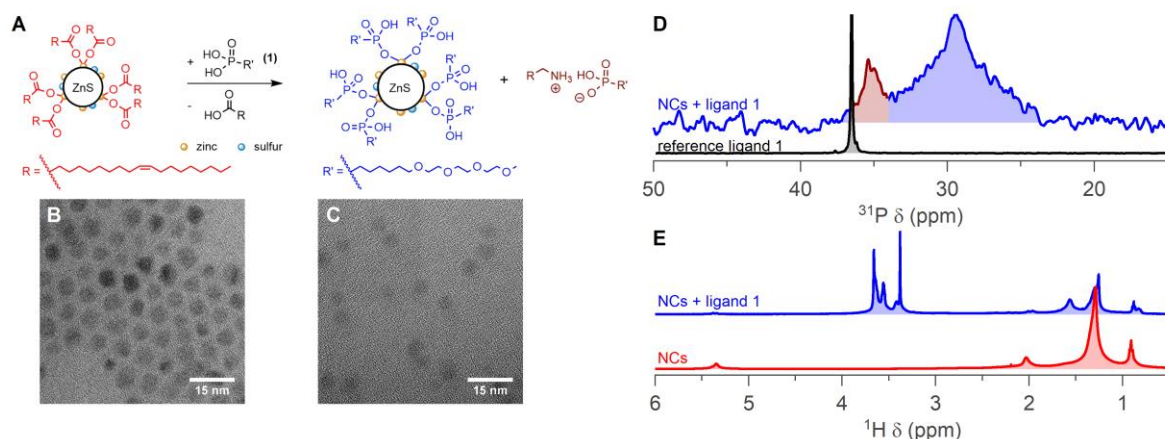


Figure S6. (A) Scheme of rational ligand exchange reaction of 81% oleate and 19% oleylamine capped surface of ZnS:Mn/ZnS NCs with ligand **1**. (B) TEM image of ZnS:Mn/ZnS NCs, stabilized with oleate and oleylamine, deposited from chloroform. (C) TEM image of

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

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