Electronic Supporting Information (ESI)

Solution structure of cadmium carboxylate and its implication to the synthesis of cadmium chalcogenide nanocrystals

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Table of Contents

MATERIALS AND GENERAL METHODS
EXPERIMENTAL PROCEDURES AND CHARACTERIZATION DATA
Procedures for NMR Experiments
Synthesis of cadmium oleate complex, Cd(OA) ₂
Synthesis of SePMe ₃
SOLUTION NMR STUDY OF CADMIUM ACETATE IN OCTYLAMINE
Copies of NMR spectra for cadmium acetate in octylamine
Figure S1. ¹¹³ Cd NMR spectrum of Cd(OAc) ₂ •2H ₂ O dissolved in neat octylamine
Figure S2. ¹ H NMR spectrum of Cd(OAc) ₂ •2H ₂ O dissolved in neat octylamine

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Figure S3. ¹³ C NMR spectrum of Cd(OAc) ₂ •2H ₂ O dissolved in neat octylamine	S8
Figure S4. ¹ H- ¹³ C HMQC and ¹ H- ¹³ C HMBC spectra of Cd(OAc) ₂ •2H ₂ O dissolved in neat octylamine	S9
¹ H and ¹¹³ Cd DOSY experiments	S10
Figure S5. Signal attenuation curve for ¹¹³ Cd DOSY and ¹ H DOSY for Cd(OAc) ₂ 2H ₂ O in octylamine	S10
¹ H DOSY NMR: Formula weight determination for Cadmium acetate complexes in octylamine	S11
Table S1. Diffusion coefficients of Cd(OAc) ₂ 2H ₂ O in the presence of internal references	S11

Figure S6. Calibration curves for the determination of FW	of Cd(OAc) ₂ 2H ₂ O in octylamineS	12

Copies of NMR spectra for cadmium oleate	S13
Figure S7. ¹ H NMR quantitative spectrum of cadmium oleate and 1 eqv of OP(C ₆ H ₅) ₃	S13
Figure S8. ¹ H NMR spectrum of cadmium oleate in toluene-d _{8.}	S14
Figure S9. ¹³ C{ ¹ H} NMR spectrum of cadmium oleate in toluene-d ₈	S15
Figure S10. ¹¹³ Cd NMR spectrum of cadmium oleate in toluene-d ₈	S16
Figure S11. ¹ H- ¹ H NOESY spectra of cadmium oleate in toluene-d ₈	S17
¹ H DOSY NMR: Formula weight determination of Cadmium oleate in toluene	S18
Table S2. Diffusion coefficients for Cd(OA) ₂ with and without internal references	S18
Table S3. Diffusion coefficients obtained from the ¹ H DOSY NMR experiment shown in Figure 2 of the manuscript.	18
Figure S12. Calibration curves for the determination of FW of Cd(OA) ₂ in toluene	S19
¹ H DOSY NMR studies in the presence of other internal references: polystyrene standards	S20
Table S4. Diffusion values for Cd(OA) ₂ in the presence of 3 different Polystyrene standards	S20

Figure S13. Stacked ¹ H- DOSY spectra of Cd(OA) ₂ before and after the addition of 1.5 eqv of octylamine	S22
Figure S14. Stacked ¹ H- DOSY spectra of Cd(OA) ₂ before and after the addition of 3.3 eqv of OPMe ₃	S23
Figure S15. Stacked ¹ H- DOSY spectra of the $Cd(OA)_2$ s before and after the addition of 4.3 eqv of SePMe ₃	S24
Table S5. Diffusion coefficients and estimated FW for Cd(OA) ₂ in the presence of different ligands	S25

Electronic Supplementary Material (ESI) for Chemical Communications This journal is C The Royal Society of Chemistry 2013

¹ H and ¹¹³ Cd DOSY NMR experiments of Cd(OA) ₂ in the presence of octylamine in toluene-d ₈	S26
Figure S16. Signal attenuation curve for ¹¹³ Cd DOSY and ¹ H DOSY	S26
Table S6. Diffusion coefficients and estimated FW for Cd(OA) ₂ in the presence of 4 equivalents of octylamine	S27
NMR Study of a mixture of Cd(OA) ₂ and 2 equivalents of octylamine in toluene-d ₈	S28
Figure S17. ¹ H NMR spectrum acquired under quantitative conditions	S28
Figure S18. ¹ H- ¹³ C HMBC and ¹ H- ¹ H COSY spectra	S28
Figure S19. ¹ H- ¹ H NOESY spectrum	S29
Figure S20. ¹ H- ¹ H ROESY spectrum	S30
Figure S21. Schematic representation of a plausible species formed in solution	S31

Scheme S1.	S32
REFERENCES	

Materials and general methods

Cd(OAc)₂ 2H₂O (\geq 98.0%, Aldrich), CdO (99.5 %, Aldrich), trimethylphosphine (99%, Strem), oleic acid (HOA; Aldrich, 99%), 1-octadecene (ODE, 90% Aldrich), selenium powder (Aldrich, \geq 99.5%), 4,4'-di-tert-butylbiphenyl (Aldrich, 99%) were used as received. NMR samples were prepared in toluene-d₈ (dried with 4 Å molecular sieves) or CDCl₃ (dried with 4 Å molecular sieves) All NMR solvents were stored in a glove box. All the NMR samples were prepared inside a glovebox flushed with N₂ and using J-Young NMR tubes unless otherwise stated. NMR experiments were measured on Bruker Avance III 400MHz, Bruker Avance III 500MHz, Bruker Avance III 600MHz and Bruker Avance III 700MHz spectrometers. A 5 mm TXI-Z (¹H, ¹³C, ¹⁵N) 3-channel probe was used in the case of the 700MHz instrument and a 5mm BBFO (¹H, X-BB) 2-channel probe was used for the other three instruments. The terms m, s, d, t, q, br. represent multiplet, singlet, doublet, triplet, quadruplet and broad, respectively. Chemical shift values are given in ppm. ¹H and ¹³C chemical shifts are referenced to TMS. Quantitative ¹H NMR spectra were recorded with 15 s relaxation delay and using a flip angle of 30 °. ³¹P NMR spectra were acquired with inverse gated decoupling and 85% H₃PO₄ was used as external reference.. Coupling constants (*J*) are given in Hertz (Hz).

The following polymers were used as standards: Polyisoprene 1,4- rich addition (Polymer Source Inc, sample #: P9410-Ip) MW=75500, $M_w/M_n = 1.08$; Polydimethylsiloxane (Polymer Source Inc, sample #: P7279-DMS) MW=28500 ($M_w/M_n = 1.15$); Poly(methyl methacrylate) Atactic Form, (Polymer Source Inc, sample #: P13206-MMA) MW=68500 ($M_w/M_n = 1.10$). Polystyrene standards: MW= 2400, (Fluka, Lot Number: MKBF6071V); MW= 4130, $M_w/M_n = 1.01$ (Fluka, Lot Number: MKBH9606V); MW =13200, $M_w/M_n = 1.06$, (Fluka, Lot Number: MKBG2015V); MW= 30740 , $M_w/M_n = 1.03$ (Pressure Chemical, Lot Number 80317).

Experimental procedures and characterization data

Procedures for NMR Experiments

¹¹³Cd NMR

¹¹³Cd NMR spectra were obtained on natural abundance samples and acquired without proton decoupling with a Bruker Avance III 500MHz and a Bruker Avance III 600MHz spectrometers operating at 111.00 and 133.35 MHz, respectively. The experiments were carried out at 300K, using a 9.5 microsecond 90 ° pulse and a recycle delay of 4.0 s, unless otherwise stated. Deuterated solvent (Toluene-d₈) or a (CD₃)₂SO capillary was used as the internal lock, and chemical shifts were given in ppm and referenced to a 0.1M solution of Cd(ClO₄)₂ in D₂O (0 ppm). Thus, negative chemical shifts are upfield from the 0.1M solution of Cd(ClO₄)₂ in D₂O and indicate increased shielding. We choose Cd(ClO₄)₂ in D₂O as reference because it is the most widely extended one^{S1} and because of its relative insensitivity to

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sample concentration as compared with other employed references such as $Cd(NO)_3$ or $CdCl_2$ in D_2O . ^{S2} Chemical shift values in this work can be referred to the Bruker default reference for ¹¹³Cd, $Cd(CH_3)_2$ (neat liquid), by subtracting 641.5 ppm.

DOSY NMR

All DOSY NMR measurements were carried out at 300K, unless otherwise stated, with variable temperature gas flow of 535 1 h⁻¹. All DOSY processing was performed using the TopSpin 3.1 software package and diffusion coefficients were extracted by analyzing the signal decays using the Stejskal–Tanner Equation.^{S3, S4} Individual rows of the psuedo-2-D diffusion spectrum were phased and baseline corrected. The measurements were carried out without sample spinning and were usually repeated at least twice. In the case of ¹H DOSY studies of Cd(OA)₂, a very useful resonance is that of the alkene protons at ~ 5.5 ppm since it is well resolved and is not overlapped with any resonance from the internal references. Therefore, the diffusion coefficient for Cd(OA)₂ is extracted from this resonance. Based on our experience, for a given sample the uncertainty in the diffusion coefficient determined by ¹H DOSY is less than 5% as estimated by measuring the same sample several times using the same pulse sequence under slightly different experimental conditions (*e.g.*, gradient pulse, diffusion delay, *etc*) and processing parameters. In the case of ¹¹³Cd DOSY the discrepancy can increase up to 10%.

Pulse programs. To correct for convection, the convection compensating double-stimulated echo pulse sequence dstebpgp3s was used for samples in a J-Young NMR tube, or in the case of the ¹¹³Cd DOSY experiments, the standard single-stimulated echo pulse sequence stebpgp1s was used with the sample in a 3 mm NMR tube.^{S4, S5, S6} When comparisons of diffusion coefficients obtained from ¹H and ¹¹³Cd DOSY were made from the same sample, the same conditions and the same pulse sequence were used. The pulsed-field gradients were incremented in 16 or 32 steps (¹H DOSY) or 8 or 16 steps (¹¹³Cd DOSY) from 2% to 95% of the maximum gradient strength (4.78 G/cm) in a linear ramp. A sinusoidal gradient shape was used. The diffusion parameters, gradient pulse and the diffusion delay were chosen such that a signal decay of around 95% was obtained at the highest gradient strength used. Usually for ¹H NMR experiments the gradient pulse and the diffusion delay were chosen between 1.5-3 ms and 0.05-0.2s respectively. For ¹¹³Cd DOSY experiments, larger values were chosen in order to obtain enough signal decay; the particular conditions and diffusion parameters are detailed for each ¹¹³Cd DOSY experiment (see below).

Method verification. To compare possible deviations in diffusion values obtained by the three pulse programs due to gradient or amplifier non-linearity, a "doped water" standard (1% H₂O in D₂O, with 0.1% GdCl₃ and 0.1% ¹³CH₃OH, purchased from Bruker BioSpin P/N Z100933) was used. A diffusion time of 100 ms and a total gradient pulse width of 2000 μ s were used for all pulse programs (a pair of bipolar 1000 μ s pulses). The temperature was controlled at 298K as calibrated with a solution of 80% ethylene glycol in DMSO-d₆. A total of 16 spectra were acquired for each of the pulse programs, with gradient strength varied linearly between 2% and 95%.

The diffusion coefficient for the water resonance was determined using TopSpin (Bruker BioSpin, Billerica, US). Diffusion coefficients of $1.740 \times 10^{-9} \text{ m}^2/\text{s}$ and $1.917 \times 10^{-9} \text{ m}^2/\text{s}$ were obtained with the stebpgp1s and dstebpgp3 pulse programs, respectively. Thus, to ensure the accuracy of comparison, the same pulse sequence, sample, and experimental conditions were used whenever ¹H and ¹¹³Cd DOSY data were compared.

Synthesis of cadmium oleate complex, Cd(OA)₂

Oleic acid (99%, 4.550 g, 16.1 mmol) and CdO (0.518 g, 4.03 mmol) were combined in a 3-neck flask. The mixture was degassed at 100 \C and then heated at 190 \C under flowing N₂. A colorless solution was obtained which was heated at 190 \C for an additional 20 min. After that, the solution was cooled to 110 \C and degassed for 20 min. The solution was cooled to room temperature and acetone was added to precipitate Cd(OA)₂ as a white solid, which was isolated by centrifugation in air, washed with acetone (5 x 10 ml) and dried in *vacuo* overnight. ¹H NMR (600.87 MHz, toluene-d₈, 300K.) δ = 5.58-5.48 [br, 4H, 2CH=CH], 3.08-2.37 [m(br), 4H, 2CH₂COO], 2.24-2.11 [br, 8H, 2CH₂CH=CHCH₂], 1.94-1.72 [br, 4H, 2CH₂CH₂COO], 1.57-1.24 [m(br), 40H, 2(CH₂)₅], 1.02-0.91 [br, 6H, 2CH₃]. ¹³C{¹H} (151.09 MHz, toluene-d₈, 300K.) δ = 185.66 [C=O], 184.38 [C=O], 130.27 [CH=], 130.17 [CH=], 35.34 [CH₂COO], 32.52 [CH₂], 30.67 [CH₂], 30.44 [CH₂], 30.24 [CH₂], 29.99 [CH₂], 28.02 [CH₂], 27.89 [CH₂CH=C], 26.84 [CH₂CH₂COO], 2.32.55 [CH₂], 14.45 [CH₃]. ¹¹³Cd NMR (133.35 MHz, toluene-d₈, 300K.) δ = -9.1ppm, fwhm = 95Hz.

Note: Two resonances in the carbonyl region suggest the presence of different chemical environments for COO, possibly a result of different coordination modes. This preliminary conclusion was also supported by the complex broad shape of the CH_2 COO resonance which suggests the presence of different environments for the alpha oleate protons. However, no free HOA was detected in the Cd(OA)₂ complex (see Figures S7 and S8). Further studies are being carried out to probe the origin of the observed line shape and its dependence on the synthesis and purification conditions.

Synthesis of SePMe₃

Trimethylphosphine (2.50 g, 32.86 mmol) was added to a vial and cooled to -30 °C. Se powder (2.725 g, 34.51 mmol) was then added slowly to the vial inside a glove box. The mixture was stirred for 24 hours at room temperature to give a white precipitate. CH₂Cl₂ (5 mL) was added to dissolve the white precipitate and unreacted Se was removed by filtration. Addition of hexane and slow evaporation at reduced pressure gave white microcrystals which were stored in a glove box.

¹H NMR (500.16 MHz, CDCl₃, r.t.) δ = 1.93 [d(13.3), 9H, CH₃]. ¹³C{¹H} NMR (125.77 MHz, CDCl₃, r.t.) δ = 23.08 [d(49.1), CH₃]. ³¹P {¹H} NMR (202.47 MHz, CDCl₃, r.t.) δ = 8.77 (¹J_{P-Se} = 682 Hz).

Solution NMR study of Cadmium acetate in octylamine





Figure S1. ¹¹³Cd NMR (300 K, 133.35 MHz) spectrum of $Cd(OAc)_2 \cdot 2H_2O$ dissolved in neat octylamine. DMSO-d₆ was used as the internal lock in a sealed capillary tube. The full width at half maximum (fwhm) of the resonance at 154.6 ppm was 15 Hz. Note that the ¹¹³Cd signal was more than 160 ppm downfield from the ¹¹³Cd signal of cadmium oleate dissolved in toluene (see Figure S10), suggesting coordination of octylamine to cadmium.



Figure S2. ¹H (300K, 700.05 MHz) NMR spectrum of $Cd(OAc)_2 \cdot 2H_2O$ dissolved in neat octylamine. DMSO-d₆ was used as the internal lock in a sealed capillary tube.



Figure S3.¹³C{1H} (300K, 176.03 MHz) NMR spectrum of Cd(OAc)₂•2H₂O dissolved in neat octylamine. DMSO-d₆ was used as the internal lock in a sealed capillary tube. The asterisk (*) represents signal from DMSO.



Figure S4. ¹H-¹³C HMQC (300K, 700.05 MHz) left and ¹H-¹³C HMBC (300K, 700.05 MHz MHz) spectra of $Cd(OAc)_2 \cdot 2H_2O$ dissolved in neat octylamine. DMSO-d₆ was used as the internal lock in a sealed capillary tube. The singlet resonance at 1.60 ppm in the ¹H NMR spectrum is attributed to the $Cd(OAc)_2$ complex since it is correlated with the resonances at 176.0 (COO group) and 22.42 (CH₃ group) ppm in the ¹³C NMR spectrum. No other resonance besides that attributed to octylamine was observed, suggesting a fast exchange on the NMR time scale between free octylamine and coordinated octylamine to cadmium (see also ¹¹³Cd NMR spectrum, Figure S1).

Note: No formation of N-Octylacetamide as a result of reaction between octylamine and acetate was observed in any experiment performed in this work.

¹H and ¹¹³Cd DOSY experiments

 $Cd(OAc)_2 2H_2O$ (69 mg, 0.26mmol) and 1mL of octylamine were combined in a J-Young NMR tube and the mixture was heated and stirred at 65 °C for 1h. After that a small precipitate still remained at the bottom of the NMR tube and 0.15mL of the supernatant was transferred in air to a 3-mm NMR tube. ¹¹³Cd DOSY and ¹H DOSY experiments were conducted in this sample. No precipitate was observed after all NMR experiments. No formation of N-Octylacetamide as a result of reaction between octylamine and acetate was observed in any experiment performed in this work (see Figures S2-S4).

In all these experiments the NMR samples were not diluted with deuterium solvent to preserve the original condition. Deuterium field lock was turned off during the whole measurement, and the static field was shimmed by ¹H gradient shimming on the most intense resonance of the ¹H spectrum, using the TopShim algorithm incorporated in the Bruker TopSpin software.



Figure S5. Signal attenuation curve for ¹¹³Cd DOSY (300 K, 133.35 MHz, left), and ¹H DOSY (300K, 600.87 MHz, right,) for Cd(OAc)₂ 2H₂O in octylamine. ¹¹³Cd DOSY parameters: stebpgp1s pulse sequence, P30 = $\delta/2$ = 5.0ms, d1 = relaxation delay = 7s, d20 = Δ = 0.5s. ¹H DOSY parameters: stebpgp1s pulse sequence, P30 = $\delta/2$ = 2.7ms, d1 = relaxation delay = 4s, d20 = Δ = 0.1s. As can be seen in Fig 1 of the manuscript, the ¹H DOSY spectrum showed two markedly different diffusion coefficients for octylamine (D= 6.00 x 10⁻¹⁰ m²s⁻¹) and cadmium acetate (1.78x10⁻¹⁰ m²s⁻¹).

Note: Since the experiments were carried without addition of deuterium solvent to preserve the original condition of the sample and in a 3mm-NMR tube to prevent convection, the chemical shifts of ¹H and ¹¹³Cd NMR spectra are slightly different in comparison to the ones using a DMSO capillary as an internal lock (*i.e.*, ¹¹³Cd δ = 155.1 ppm vs 154.6 ppm, see Figure S1).

¹H DOSY NMR: Formula weight determination for cadmium acetate complexes in octylamine.

All the experiments were carried out in air in a 3 mm NMR tube using the same sample prepared in the previous experiment. Polystyrene (MW = 2400) and 4,4'-di-tert-butylbiphenyl (MW = 266.42) were added as internal references; their amount was adjusted to give adequate signal for the DOSY experiment (integration ratio 1:1:3 for CH₃ group of Cd(OAc)₂, aromatic protons of 4,4'-Di-tert-butylbiphenyl and aromatic protons of polystyrene, respectively). In all these experiments the NMR samples were not diluted with deuterium solvent to preserve the original condition. Deuterium field lock was turned off during the whole measurement, and the static field was shimmed by ¹H gradient shimming on the most intense resonance of the ¹H spectrum, using the TopShim algorithm incorporated in the Bruker TopSpin software.

Table S1. Diffusion coefficients extracted from ¹H DOSY NMR experiment of $Cd(OAc)_2 2H_2O$ in the presence of polystyrene (MW = 2400) and 4.4'-Di-tert-butylbiphenyl(MW = 266.42) as internal reference.

Compound	MW	D/ 10 ⁻¹⁰ m ² /s
Polystyrene	2400	0.606
Di-tert-butylbiphenyl	266.42	2.53
Octylamine	129.24	4.57
Cd(OAc) ₂ •2H ₂ O	-	1.24



Figure S6. Calibration curves for the determination of FW of $Cd(OAc)_2 \cdot 2H_2O$. Left: Calibration curve obtained from the two internal references: 4,4'-Di-tert-butylbiphenyl (MW = 266.42) and polystyrene (MW = 2400). Right: calibration curve obtained from octylamine (Mw= 129.24) and the two internal references: 4,4'-Di-tert-butylbiphenyl (MW = 266.42) and polystyrene (MW = 2400).

Note: 1. A FW=799 was obtained for the cadmium complex using two internal references. If the solvent, octylamine, was introduced in the calibration curve, a similar value of FW = 825 was estimated for the cadmium acetate and a good correlation of the values of the three internal references is obtained with a high $r^2 = 0.9976$. We caution the use of octylamine carefully since a fraction of it is interacting with the cadmium complex and also because the solvent does not fit the criterion specified for application of the Stokes-Einstein equation, which is based upon the assumption that the solution is infinitely diluted and the solute molecule is much larger in size than the solvent molecule. Nevertheless, a good correlation was obtained and a similar FW was predicted for the cadmium complex when octylamine was used as an additional internal reference.

2. As the result of the addition of relative large amounts of polystyrene and 4,4'-Di-tert-butylbiphenyl, slight decreases in the diffusion coefficients for octylamine and Cd(OAc)₂ were observed due to the increase of viscosity. However, because the change of viscosity will impact diffusion constants of both sample and references, the estimated FW should not be affected to a significant degree.

3. We note that the FW obtained by DOSY are underestimated, due to the fact that the complexes contain a heavy cadmium atom, which is absent in the reference molecules. Nevertheless, these two measured FW are very close to the expected ones for a monomeric or dimeric cadmium complex

Solution NMR study of cadmium oleate in toluene-d₈.

Copies of NMR spectra for cadmium oleate



Figure S7. Quantitative ¹H NMR (300K, 600.87 MHz) spectrum of cadmium oleate in the presence of 1 eqv of $OP(C_6H_5)_3$ (used as a reference) in CDCl₃. A 1:1 stoichiometry is observed within the integration error (*ca.* 1.2%), suggesting a negligible amount, if any, of free HOA in the sample. The sample was prepared as following: 100 mg (0.148 mmol) of Cd(OA)₂ and 41.2 mg (0.148 mmol) of $OP(C_6H_5)_3$ were dissolved in CDCl₃ (2 mL) and 0.6 mL of the solution were taken for NMR study.

Note: Oleate resonances are sharp as a result of phosphine oxide coordination to the cadmium complex (see the discussion about the addition of ligands to $Cd(OA)_2$ in the manuscript and in the SI).



Figure S8. ¹H NMR (300K, 600.87 MHz) spectrum of cadmium oleate in toluene- d_8 . The line widths of the oleate ligand resonances are considerably broader than the residual toluene solvent signals, marked with an asterisk, (*). No acidic signal corresponding to free oleic acid (HOA) was observed at around 12 ppm.



Figure S9. ¹³C{¹H} NMR (300K, 151.09 MHz) spectrum of cadmium oleate in toluene-d₈. Two resonances in the carbonyl region suggest the presence of different environments for COO, possibly as a result of different coordination modes.



Figure S10. ¹¹³Cd NMR (300K, 133.35 MHz) spectrum of cadmium oleate in toluene- d_8 . The FWHM of the resonance at -9.1ppm (95 Hz) was broader than that observed for cadmium acetate in octylamine (fwhm =15Hz, see Figure S1). This sample was prepared by dissolving approximately 50 mg of Cd(OA)₂ in 1 mL of toluene- d_8 .

Note: A similar ¹¹³Cd resonance was observed at the same chemical shift (-9.1 ppm) for a more diluted samples in toluene (10 mg/mL and 3mg/mL).

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Figure S11. 1 H- 1 H NOESY (300K, 600.87 MHz) spectra of cadmium oleate in toluene-d₈. Above: a dilute sample, with mixing time 100 ms. Below: a more concentrated sample with a mixing time of 500 ms. Strong negative crosspeaks, characteristic of slowly tumbling molecules (large molecules) are observed in both cases.

¹H DOSY NMR: Formula weight determination of cadmium oleate in toluene

In a glove box $Cd(OA)_2$ (30 mg, 0.0444 mmol) was dissolved in 3 ml of toluene-d₈. This $Cd(OA)_2$ solution (0.6 mL) was transferred inside a glovebox into a J-Young NMR tube and studied by ¹H-DOSY. A second J-Young NMR tube containing 3 mg MMA and 3 mg of polystyrene (MW=13200) was introduced into the glovebox and 0.6 mL of the $Cd(OA)_2$ solution were added. The resulting solution was also studied by ¹H DOSY NMR. After that, a small drop of DMS (MW = 28500) was added as a third internal reference to the second J-Young NMR tube and the ¹H DOSY measurements were repeated.

Table S2. Diffusion coefficients obtained from ¹H DOSY NMR experiments in toluene: $Cd(OA)_2$ without the addition of any internal reference (experiment 1); in the presence of MMA and Polystyrene as internal references (experiment 2); in the presence of three internal references: MMA, DMS and Polystyrene (experiment 3). Note that the diffusion coefficients are the same within the experimental error suggesting that the polymers do not interact among themselves under the studied conditions.

Exp #	Compound	MW	$D(10^{-10} m^2/s)$
1	Cd(OA) ₂		1.128
2	$Cd(OA)_2$		1.102
	Polystyrene	13200	1.420
	MMA	68500	0.6451
3	$Cd(OA)_2$		1.094
	Polystyrene	13200	1.396
	DMS	28500	0.8742
	MMA	68500	0.6396

Table S3. Diffusion coefficients obtained from the ¹H DOSY NMR experiment shown in Figure 2 of the manuscript.

Compound	MW	$D (10^{-10} m^2/s)$
Cd(OA) ₂		1.094
Polystyrene	13200	1.396
DMS	28500	0.8742
MMA	68500	0.6396



Figure S12. Calibration curves for the determination of FW of Cd(OA)₂ in toluene. Three internal references: Polystyrene (MW = 13200) DMS (MW = 28500) and MMA (MW = 68500) were used (see table S3 for the self-diffusion coefficient values) and a reasonably good correlation of the FW and self-diffusion coefficient values of the three internal references was obtained, r^2 = 0.97702. A FW=20650 was calculated for Cd(OA)₂ in toluene. Note: A reasonably good estimation of FW=22428 was obtained just using two internal references (see table S2).

¹H DOSY NMR studies in the presence of other internal references: polystyrene standards

No evidence of interaction between oxygen-containing internal references (MMA or DMS) and $Cd(OA)_2$ was observed in our study; very similar diffusion coefficients for $Cd(OA)_2$ were obtained before and after the addition of those internal references (see table S2). Also, another sample was prepared in a similar manner as described above: 0.6 ml of $Cd(OA)_2$ solution was added inside a glove box to a J-Young NMR tube containing Polystyrene (MW= 13200), MMA (MW= 68500) and poly-isoprene (MW=75500) as internal references to give a FW = 19000 for $Cd(OA)_2$. Nevertheless, we also studied $Cd(OA)_2$ in toluene in the presence of only polystyrene as an internal reference as a precaution.

In a glove box $Cd(OA)_2$ (30 mg, 0.0444 mol) was dissolved in 3 mL of toluene-d₈. Three J-Young NMR tubes were each loaded with 3 mg of one of the polystyrene references (MW = 4130, MW = 13200, MW = 30740) and 0.6 mL of the $Cd(OA)_2$ solution inside the glovebox, and each of the three samples were studied by ¹H DOSY. $Cd(OA)_2$ was found to diffuse faster than polystyrene MW = 4130 and MW=13200 but slower than polystyrene MW=30740. The results show that $Cd(OA)_2$ in toluene behaves under these conditions as a polymer with a FW between 13200 and 30740, in agreement with the FW = 20650 previously calculated.

Table S4. Diffusion values for three ¹H DOSY experiments in toluene- d_8 in which the diffusion coefficient for Cd(OA)₂ was measured in the presence of one of the 3 different Polystyrene standards.

Exp #	Compound	$D(10^{-10} m^2/s)$
1	Cd(OA) ₂	1.017
	Polystyrene MW=4130	2.431
2	Cd(OA) ₂	0.961
	Polystyrene MW=13200	1.453
3	Cd(OA) ₂	1.020
	Polystyrene MW= 30740	0.925

Addition of ligands to Cd(OA)₂ dissolved in toluene.

In a glove box a stock solution was prepared by dissolving $Cd(OA)_2$ (40 mg, 0.059 mmol) in 4 ml of toluene-d₈. To this solution 60 µL of ODE and 20 mg of polystyrene (MW=2400) were added as internal references for the DOSY experiments and the resulting stock solution was kept in a glovebox for the following experiments.

Effect of octylamine. To a J-Young NMR tube was added 0.6 ml (6mg, 0.0089 mmol of $Cd(OA)_2$) of the stock solution. This sample was studied with DOSY without the addition of any ligand. After that, increasing amounts of octylamine were successively added to the same NMR tube in the glovebox: 2.2µL (0.013mmol, 1.5 eqv), 3.7µL (0.022 mmol, 2.5eqv,) and 7.3µL (0.044 mmol, 5 eqv). The exact amount of octylamine present in each experiment was determined by ¹H NMR.

*Effect of OPMe*₃. Two J-Young NMR tubes were loaded with 2.7mg (0.029 mmol, 3.3eqv) and 6.2mg (0.067mmol, 7.6 eqv) of OPMe₃, respectively and transferred to a glovebox where 0.6mL of the stock solution were added to each sample. The obtained solutions were studied by NMR.

*Effect of SePMe*₃. Two J-Young NMR tubes were loaded with 3.5mg (0.0225 mmol, 2.5 eqv) and 6.0mg (0.039 mmol, 4.3eqv) of SePMe₃, respectively and transferred to a glovebox where 0.6 mL of the stock solution were added to each sample. The obtained solutions were immediately studied by NMR. After each DOSY experiment was finished, ¹H and ³¹P NMR experiments were carried out to confirm that there was no reaction between SePMe₃ and Cd(OA)₂. No OPMe₃ or oleic anhydride was observed, showing that the reaction did not significantly progress during the time taken to carry out the DOSY experiments.



Figure S13. Stacked ¹H- DOSY spectra of the Cd(OA)₂ solution in toluene-d₈ in the presence of ODE (MW = 252.48) and polystyrene (FW = 2400) before (blue) and after (red) the addition of 1.5 eqv of octylamine. 1D ¹H NMR spectrum after the addition of 1.5 eqv of octylamine was shown as the 'external projection'. Only the aromatic/olefinic region of the spectra was shown for the sake of clarity. The ¹H NMR resonances for oleate, initially very broad, drastically sharpen after the addition octylamine as can be seen for the olefinic oleate resonance shown in the 'external projection'.



Figure S14. Stacked ¹H DOSY spectra of Cd(OA)₂ solution in toluene-d₈ in the presence of ODE (MW = 252.48) and polystyrene (FW = 2400) after (red) and before (blue) the addition of 3.3 eqv of OPMe₃. 1D ¹H NMR spectrum after the addition of 3.3 eqv of OPMe₃ was shown as the 'external projection'. Only the aromatic/olefinic region of the spectra was shown for the sake of clarity. The ¹H NMR resonances for oleate, initially very broad, drastically sharpen after the addition of OPMe₃ as can be seen for the olefinic oleate resonance shown in the 'external projection'.



Figure S15. Stacked ¹H DOSY spectra of Cd(OA)₂ solution in toluene-d₈ in the presence of ODE (MW = 252.48) and polystyrene (FW = 2400) after (red) and before (blue) the addition of 4.3 eqv of SePMe₃. 1D ¹H NMR spectrum after the addition of 4.3 eqv of SePMe₃ was shown as the 'external projection'. Only the aromatic/olefinic region of the spectra was shown for the sake of clarity. The ¹H NMR resonances for oleate, initially very broad, drastically sharpen after the addition of SePMe₃ as can be seen for the olefinic oleate resonance shown in the 'external projection'.

Table S5. Diffusion coefficients obtained from ¹ H DOSY experiments and estimated FW for Cd(OA) ₂ in the presence of different ligands.
Overlp indicates that the resonance for the CH_3 group of SePMe ₃ overlapped with the aliphatic resonances of $Cd(OA)_2$.

	D _{Cd(OA)2} /	D_{polyst}	D _{ODE} /	D_{ligand}	Cd(OA) ₂
Ligand added	$10^{-10} \text{m}^2/\text{s}$	$10^{-10} m^2 / s$	$10^{-10} m^2 / s$	$10^{-10} m^2 / s$	FW
-	0.9134	3.154	10.74	-	23500
C ₈ H ₁₇ NH ₂					
1.5 eqv	3.353	3.450	10.81	3.343	2499
4 eqv	3.596	3.466	10.81	10.99	2230
9 eqv	3.711	3.369	10.61	13.47	1985
OPMe ₃					
3.3 eqv	4.788	3.692	10.33	11.56	1359
7.6 eqv	5.014	3.552	10.68	13.94	1188
SePMe ₃					
2.5eqv	3.667	3.507	11.07	overlp	2200
4.3 eqv	4.040	3.572	10.62	overlp	1861

^{1}H and ^{113}Cd DOSY NMR experiments of Cd(OA)₂ in the presence of octylamine in toluene-d₈

The ligand added (octylamine, $OPMe_3$ or $SePMe_3$) is in fast exchange between a coordinated and uncoordinated state on the NMR time scale. As a result, averaged chemical shift and diffusion coefficients are obtained (and in general any NMR observable parameter), approaching values of the free ligand if they are in excess (see table S5). Naturally, if the coordination of the ligand to $Cd(OA)_2$ would involve the complete displacement of an oleate ligand, the observed diffusion coefficient for oleate would reflect an averaged diffusion coefficient between coordinated and free oleate, resulting in a larger diffusion coefficient and compromising the information extracted from ¹H DOSY regarding the cadmium complex.

To rule out this possibility, we carried out ¹¹³Cd DOSY experiment for a sample of 1:4 molar ratio of Cd(OA)₂ and octylamine, in which case the presence of octylamine sharpened the ¹¹³Cd resonance for Cd(OA)₂ to allow ¹¹³Cd DOSY be performed .The diffusion coefficients measured by ¹H DOSY ($3.53 \times 10^{-10} \text{ m}^2\text{s}^{-1}$) and ¹¹³Cd DOSY ($3.65 \times 10^{-10} \text{ m}^2\text{s}^{-1}$) are essentially the same within experimental error. This result shows that ¹H DOSY measurements are a good estimation of the real diffusion of the complex and suggests that the coordination of amine to Cd(OA)₂ does not involve the complete displacement of an oleate ligand rather than limit its tendency to form bridges to cadmium centers.

¹¹³Cd DOSY experiments were performed in a more concentrated sample. $Cd(OA)_2$ (60mg, 0.0888 mmol) was combined with 0.6mL of toluene-d₈ and octylamine (59µL, 0.355 mmol). The obtained solution was studied by ¹H and ¹¹³Cd DOSY. In order to estimate the FW of the Cd(OA)₂ complex under these conditions ODE (120 µL) and 20mg of polystyrene (MW=2400) were dissolved in the Cd(OA)₂ solution as internal references. A FW=2100 was calculated for Cd(OA)₂ (see Table S6). Note that under these more concentrated conditions higher concentrations of internal references are needed in order to have comparable intensity signals with respect to that of Cd(OA)₂.



Figure S16. Signal attenuation curve for ¹¹³Cd DOSY (305K, 133.35 MHz, left), and ¹H DOSY (305K, 500.16 MHz, right) for Cd(OA)₂ and 4 equivalents of octylamine in toluene-d₈. ¹¹³Cd DOSY parameters: stebpgp1s pulse sequence, P30 = $\delta/2$ = 5.0ms, d1 = relaxation delay = 7s, d20 = Δ = 0.2 s. ¹H DOSY parameters: stebpgp1s pulse sequence, P30 = $\delta/2$ = 1ms, d1 = relaxation delay = 4s, d20 = Δ = 0.2 s.

D _{Cd(OA)2} /	D_{polyst}	D _{ODE} /	$D_{\text{octylamine}}$	$Cd(OA)_2$
$10^{-10} \text{m}^2/\text{s}$	$10^{-10} m^2/s$	$10^{-10} m^2/s$	$10^{-10} m^2/s$	FW
2.423	2.226	8.961	8.529	2100

Table S6. Diffusion coefficients obtained from ¹H DOSY and estimated FW for Cd(OA)₂ in the presence of 4 equivalents of octylamine.

Note: As the result of the addition of relatively large amounts of polystyrene and 4,4'-Di-tert-butylbiphenyl (see above) slight decreases in the diffusion coefficients for Cd(OAc)₂ were observed as the result of the more concentrated media.



NMR Study of a mixture of Cd(OA)₂ and 2 equivalents of octylamine in toluene-d₈.

Figure S17. ¹H NMR (298 K, 700.05 MHz) spectrum acquired under quantitative conditions of cadmium oleate in the presence of 2.2 eqv of octylamine in toluene- d_8 . Signal assignment for oleate (labeled black) and octylamine (labeled red) were done with the help of additional 2D-NMR experiments (some of which are shown in Figure S18). Note: The resonance at 2.10 overlapped with the residual CH₃ resonance of toluene- d_8 .



Figure S18. ${}^{1}\text{H}{}^{13}\text{C}$ HMBC (left) and ${}^{1}\text{H}{}^{1}\text{H}$ COSY (298 K, 700.05 MHz) spectra of cadmium oleate in the presence of 2.2 eqv of octylamine in toluene-d₈. The region shown in the ${}^{1}\text{H}{}^{-13}\text{C}$ - HMBC spectrum allows the correlation of the oleate resonances at 2.57 and 1.89 ppm with the COO resonance at 182.0 ppm in the ${}^{13}\text{C}$ NMR spectrum, confirming the initial assignment.



Figure S19. ¹H-¹H NOESY (298 K, 700.05 MHz) spectrum of cadmium oleate in the presence of 2.2 eqv of octylamine in toluene- d_8 (mixing time of 800 ms).

Note: Figure S19 shows both positive (blue) and negative (green) crosspeaks for octylamine and oleate resonances. This is in contrast with the NOESY spectrum of Cd(OA)₂ in toluene (see Figure S11) where the oleate resonances are connected by strong negative cross-peaks, associated with slow tumbling and in agreement with a polymeric structure. The NOESY spectrum and the sharpness of the oleate signals after the addition of amine agrees with the breakdown of the Cd(OA)₂ polymer into smaller species. A cross-peak that deserves a closer look is the one between CH₂COO and NH₂-CH₂ (highlighted with a circle) since it connects protons on different molecular species (CH₂COO protons from the oleate and CH₂N form the amine). The cross-peak should originate from intramolecular cross-relaxation of protons that are close to other in space, strongly suggesting that both molecules at one point are simultaneously coordinated to cadmium (see Figure S21). Other, much weaker cross-peaks between oleate and amine resonances are observed: between CH₂-CO and NH₂-, and between CH₂CH₂COO and CH₂NH₂. Finally, it is worth mentioning that the negative cross-peak involves protons close to the coordination point of the metal centre (amine and carboxylic functionalities) in contrast with positive cross-peaks observed for protons of the chain far-

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ther away from the metal centre (see for instance the crosspeaks involving the olefinic protons of the oleate chain), suggesting restricted motion of the protons closer to the metal centre compared to a greater segmental mobility at the free end of the alkyl chain. Observations of positive and negative NOEs cross-peaks for different regions of the same molecule due to different segmental motion has already been reported in the literature.^{S7-S9} A ROESY experiment (see Figure S20) confirmed that the crosspeak observed between CH₂COO and NH₂-CH₂ arises from intramolecular cross-relaxation of protons that are close to each other in space.



Figure S20. 1 H- 1 H ROESY (298 K, 400.22 MHz) spectrum of cadmium oleate in the presence of 1.95 eqv of octylamine (as determined from the quantitative 1 H NMR spectrum), in toluene-d₈ (200 ms spin lock mixing time).

Note: 1. The spectrum only shows crosspeaks of oppositely signed intensity to the diagonal peaks. The ROESY experiment features all NOEs cross-peaks with oppositely signed intensity to the diagonal peaks, regardless of the molecular tumbling rate and in contrast to NOESY where NOEs cross-peaks can be positive or negative.^{S10, S11} The ROESY experiment confirms that the crosspeak observed between CH₂COO and NH₂-CH₂ arises from intramolecular cross-relaxation of protons that are close to each other in space, strongly suggesting that both molecules at one point are simultaneously coordinated to cadmium (see Figure S21).

2. The NH_2 resonance appears 0.3 ppm downfield with respect to the previous sample due to different experimental conditions (different sample concentration, amount of octylamine and spectrometer used).



Figure S21. Schematic representation of a plausible species formed in solution in which octylamine and oleate ligands are coordinated simultaneously to the cadmium metal center as the NOESY experiment suggested. Note that due to the fact that Cd^{2+} ion can take a wide range of coordination numbers, other monomeric complexes are also possible. All the complexes formed in solution are expected to be in fast exchange on the NMR time scale and as a result no individual species are observed.

 $Cd(OAc)_2$ (octylamine)_x

Small complexes (Observed in solution by DOSY)

 ${Cd(OAc)_2 (octylamine)_x}_n$

Lamellar mesophase (Observed by Buhro et al.by low-angle XRD ^{S12})

Scheme S1. While our results showed by ¹H and ¹¹³Cd NMR DOSY that cadmium acetate exists in octylamine forming discrete complexes no more highly aggregated than a dimer, Buhro and coworkers has recently shown by low-angle XRD that cadmium acetate in octylamine existed as a lamellar mesophase which was proposed to be responsible for templating the growth of flat CdSe nanocrystals.^{S12} One possible explanation to reconcile the two studies is that there is a dynamic equilibrium between the lamellar structure observed by low-angle XRD and small cadmium species observed by DOSY. In the presence of a fast equilibrium, DOSY measures an averaged diffusion constant. Therefore, DOSY may not detect the presence of large scale assemblies if their concentration is low. Low-angle XRD, on the other hand, will selectively detect the presence of ordered structures but will not detect the presence of small cadmium complexes. If the equilibrium is slow on the NMR time scale we would expect to be able to observe individual signals for the species involved in the equilibrium. Even though only a single sharp signal is observed in the ¹¹³Cd NMR spectrum (see Fig S1), we cannot completely rule out the possibility of having equilibrium because the lamellar mesophase could produce a signal broad enough to prevent its detection by NMR. The mechanism by which discrete complexes units assemble to form the lamellar mesophase (*i.e.* non-covalently or covalently) is unclear.

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