# Supporting Information to

# Morphogenesis of anisotropic nanoparticles: selftemplating via non-classical, fibrillar Cd<sub>2</sub>Se intermediates

Daniel Wurmbrand, Jörg Fischer, Rose Rosenberg, and Klaus Boldt\*

University of Konstanz, Department of Chemistry, Box 710, 78457 Konstanz, Germany

# **Experimental Details**

### Chemicals

CdO ( $\geq$  99.99%), tri-*n*-butylphosphine (TBP,  $\geq$  93.5%), tri-*n*-octylphosphine (TOP, 97%), tri-*n*-octylphosphine oxide (TOPO, 99%), 1-octadecene (ODE, 90%), 1-pentanethiol (98%) were purchased from Sigma-Aldrich. *n*-Octadecylphosphonic acid (ODPA, > 99%) was purchased from PCI Synthesis. Analytical grade solvents (hexane, toluene, acetone, acetonitrile, *o*-xylene) were purchased from VWR chemicals. 1-Aminohexane (99%) and toluene-*d*<sub>8</sub> (99.5% D) were purchased from ABCR. All chemicals were used as received without further purification.

### Preparation of the Se precursor (TBP-Se)

In a nitrogen glove box 0.63 g of Se shot and 2.3 mL of TBP (1.9 g) were mixed with 17.3 mL ODE (13.6 g) and heated to 150 °C until dissolved. After that the solution was diluted with 3.56 mL of toluene (3.0 g).

### Synthesis of [Cd<sub>2</sub>Se(ODPA)<sub>n</sub>]<sub>m</sub> coordination polymer

0.2054 g (1.6 mmol) CdO, 2.930 g TOPO, and 1.070 g (3.2 mmol) ODPA were loaded into a 50 mL three-neck round bottom flask equipped with septum and thermocouple. The mixture was heated to 130 °C under vacuum and kept at that temperature for 1 h to remove traces of water and oxygen. The flask was then flooded with argon and heated to 310-350 °C to form a Cd phosphonate complex (~ 30 min). After a clear solution was ob- tained the vessel was cooled to 100 °C and kept under vacuum for at least 1 h to remove water produced in the complexation reaction. The mixture was then heated to 340 °C under argon atmosphere. 2.32 mL of the TBPSe precursor was the loaded in a 5 mL syringe and rapidly injected into the reaction flask using a 2 gauge needle. Following injection, the reaction temperature dropped to about 300 °C. The temperature was then brought back up to and kept at 310 °C for the reaction. A colour change of the reaction mixture from colourless to red after selenium injection indicated the formation of CdSe nanocrystals. 2 minutes after injection the reaction was quenched by quick addition of 5 mL of toluene and removing the heating mantle. At 75 °C the solution was transferred to a centrifuge tube and centrifuged at 3260 × g (4500 rpm) for 5 min. The supernatant was removed and the waxy, white precipitate was carefully rinsed with 2 mL hexane to remove impurities like CdSe nanocrystals. The precipitate was then dissolved by addition of 20 mL hexane and heating the mixture to 50 °C. Finally the solution was centrifuged at  $13528 \times g$  (10000 rpm) for 5 min. The supernatant containing the CdSe coordination polymer was stored under argon atmosphere and protected from moisture. After ageing the gelled product in hexane for several days a white pellet precipitated, which was composed of excess Cd-ODPA.

#### **Preparation of CdSe aerogels**

After gelation for several days in hexane at ambient temperature the coordination polymer was transferred to an autoclave sample holder using a spatula. After exchange of the solvent from hexane to  $CO_2$  at 40 °C and 90 bar the sample was supercritically dried using a SPI-DRY critical point dryer-Jumbo. The product is a white, waxy, and extremely light solid. The pure white colour differed from that of coordination polymer dried under vacuum, which appeared slightly yellowish due to inclusions of small amounts of nanocrystals that occur as a reaction by-product. The aerogel was crushed for XRD analysis.

#### **Decomposition at high temperatures**

20 mL of a hexane solution of the CdSe coordination polymer with an OD = 0.868 at 348 nm was mixed with 5 mL TOP, after which the hexane was removed in vacuum. The resulting gel could be carefully melted using a heat gun. 3 g TOPO were then loaded into a 50 mL three-neck flask and degassed at 130 °C for 1 h. The mixture was then heated to 15 °C above the growth temperature (between 250 and 340 °C). 1 mL of the CdSe coordination polymer in TOP was rapidly injected, corresponding to the precursor amounts used in the nanocrystal synthesis by Carbone *et al.*<sup>[1]</sup> The temperature equilibrated at the growth temperature within 1 minute. 0.3 mL of toluene were loaded into 1 mL syringes, which were used to draw samples at regular intervals after injection. The syringes were weighed before and after the sample was drawn, and the measured OD at 348 nm was normalised to the sample weight.

#### Conversion to compounds with red-shifted absorption at 414 nm

4 ml of the hexane solution of the coordination polymer was mixed with 2 ml of 1-aminohexane and stirred for 3 h at 60 °C in the dark. The product was flocculated with acetonitrile and centrifuged at  $3260 \times g$  (4500 rpm) for 5 min. The pellet was dispersed in 4 ml of toluene and centrifuged at  $3461 \times g$  (6000 rpm) for 2 min to remove undissolved solids. The supernatant containing the reaction product was stored under argon.

#### Characterisation

UV/vis absorption spectra were acquired using an Agilent Cary 60 absorption spectrometer. Quartz cuvettes with a 1 cm path length were used and hexane or toluene were employed as solvent. All samples were diluted to yield a maximal OD below 1.0. To determine the temperature-dependent change in absorption the gel was dissolved in *o*-xylene and spectra were measured *in-situ* using an immersion fibre optics probe, which allowed measurement up to 140 °C. Fluorescence spectroscopy was performed using a PicoQuant FluoTime 300 spectrometer. All spectra were acquired at ambient temperature unless otherwise noted.

Powder XRD was performed on a Bruker AXS D8 diffractometer using Lynxeye and Vantec detectors and Cu-K $\alpha$  radiation. SAXS was performed on a Bruker AXS Nanostar diffractometer.

Solution NMR spectra were acquired on a Bruker Avance III 400 and 600 spectrometer in toluene- $d_8$ . <sup>31</sup>P spectra were acquired using power-gated CPD/BB decoupling and 30° pulses. 1H DOSY spectra (stebpgp1s pulse program) were analysed using the algorithms from Bruker TopSpin 3.5pl7, MestreNova 12.0 using Bayesian fits, and DOSYToolbox 2.7.<sup>[2]</sup>

Solid state <sup>31</sup>P-MAS- NMR spectra were acquired using a Bruker Avance III 400 solid state NMR spectrometer (161.976 MHz for <sup>31</sup>P) with a MAS spinning rate of 5, 10, and 12 kHz. A pulse strength of 125.0 kHz was used for the 90° hard pulse. The experiment was run with 16 scans and a  $T_1$  relaxation rate of 5.0 s. Peaks were fit with Lorentzians and spinning sidebands were assigned by their offset of multiples of 5 kHz from the centre band (isotropic shift). NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> was employed as an external reference, which has a shift of 0.80 ppm relative to 85% H<sub>3</sub>PO<sub>4</sub>.<sup>[3]</sup>

Infrared spectra were acquired using a PerkinElmer Spectrum 100 FT-IR spectrometer with ATR detection. Raman spectra were acquired on a PerkinElmer RamanStation 400 spectrometer with 785 nm excitation. A fluorescence background that occurred in all samples was reduced by photo-bleaching for 30 minutes.

TEM micrographs were taken using a Jeol JEM-2200FS transmission electron microscope using a FEG with 200 kV acceleration voltage. SEM and EDX data was acquired on a Hitachi TM3000 microscope equipped with a Quantax 70 EDX detector.

Analytical ultracentrifugation (AUC) measurements were performed on a Beckmann Coulter Optima XL-I ultracentrifuge with UV/vis detection at 350 nm. The ls-g\*(s) and diffusion-corrected c(s) distributions were performed using the SEDFIT software version 15.01b by Peter Schuck. The 2DSA analysis and simulations were done using the UltraScan III software version 4.0, release 2449 by Borries Demeler.<sup>[4]</sup> The density of the coordination polymer was determined from the sedimentation coefficients in toluene ( $\rho = 0.86427 \text{ g/cm}^3$ ,  $\eta = 5.52 \text{ mPa s}$ ) and toluene- $d_8$  ( $\rho = 0.94300 \text{ g/cm}^3$ ,  $\eta = 5.80 \text{ mPa s}$ ) and amounts to  $1.3 \pm 0.04 \text{ g/cm}^3$ .<sup>[5]</sup>

## **Reaction Kinetics**

The synthesis was usually stopped after 2 minutes (injection at 340 °C, growth at 310 °C), before the yield of the coordination polymer reached its maximum. This lies in the fact that the separation from the CdSe nanocrystals that form as a by-product was not possible to the same extent when the reaction progressed further.



**Figure S1:** The absorption of quantitative samples drawn from the reaction solution at 348 nm plotted against reaction time. A maximum of the yield occurs after approximately 4 minutes. The absorption of CdSe nanocrystals that form as a by-product contributes to 0.5% or less at 348 nm and was neglected. The red, dotted line is a guide to the eye.

### **Elemental Analysis**

	Area 1 (%)	Area 2 (%)	Area 3 (%)	Area 4 (%)	Area 5 (%)	Mean (%)
Cd	39.5	34.8	39.1	35.6	39.0	$37.6 \pm 2.0$
Se	16.3	18.5	18.2	16.1	15.1	$16.8 \pm 1.3$
Р	44.2	46.8	42.7	48.3	46.0	$45.6 \pm 2.0$
Cd/Se	2.43	1.88	2.15	2.21	2.58	$2.25 \pm 0.24$

EDX analysis was performed on 5  $\mu$ m-sized areas of dried CdSe coordination polymer using an SEM. The percentages of Cd, Se and P were determined and the sum set to 100 %.





Figure S2: SEM image (left) and EDX spectrum (right) of a CdSe coordination polymer sample. The elemental composition for five areas is summarised in the table above.

ICP-OES data was acquired on a Thermo Fisher iCAP 7600 ICP-OES. Three independent dilutions of three separately synthesized samples of  $[Cd_2Se(ODPA)_n]_m$  were analysed after digestion in HNO<sub>3</sub>/HCl (4:1) an a microwave oven. A quantitatively worked-up sample 1 was used to determine the extinction coefficient and a yield of 9.8 %, both based on Cd-content.

Sample	Se (wt-%)	P (wt-%)	Cd (wt-%)	Se (%)	<b>P</b> (%)	Cd(%)
1 (product)	$2.243 \pm 0.019$	$3.120 \pm 0.001$	$6.59 \pm 0.05$	15.2	53.8	31.0
1 (supernatant)	$0.903 \pm 0.008$	$5.76 \pm 0.05$	$2.5 \pm 0.02$	5.2	84.7	10.0
2 (aerogel)	$8.51 \pm 0.06$	$8.01 \pm 0.03$	$26.13 \pm 0.19$	18.1	43.3	38.6
3 (product)	$2.05 \pm 0.06$	$3.65 \pm 0.03$	$5.68 \pm 0.06$	13.4	60.8	25.8

#### Thermogravimetric Analysis



**Figure S3:** TGA traces of the dried CdSe coordination polymer under nitrogen (top left) and oxygen (top right). XRD patterns of the residue after heating to 370 °C (bottom left) and 1000 °C (bottom right) under O<sub>2</sub>.

Under N<sub>2</sub> atmosphere the dried compound loses 74% of its weight in three steps at 500 °C, with further loss around 1000 °C. Under O<sub>2</sub> atmosphere 80% of the weight is lost, also in three steps, with several violent reactions between 315 and 325 °C. At 370 °C powder XRD shows hexagonal CdSe with anisotropic shape; Scherrer analysis yields crystallites with a size of 100 nm along the [002] axis and 58 nm along the [100] axis. Above 650 °C the compound has completely turned into monoclinic cadmium pyrophosphate Cd<sub>2</sub>P<sub>4</sub>O<sub>7</sub>. This corresponds to a reaction

 $Cd_2SeP_5O_{15}C_{90}H_{183} + 136.5 O_2 \rightarrow Cd_2P_2O_7 + SeO_2 + 1.5 P_2O_5 + 90 CO_2 + 91.5 H_2O$ and thus a gel composition of  $[Cd_2Se(ODPA)_5]_n$ , ignoring possible anhydrides. All oxidation products except  $Cd_2P_2O_7$  are gases or sublimate below 1000 °C. The amount of phosphorous is larger than that determined by ICP-OES and EDX analysis (3.5 and 2.7 equiv, respectively, with respect to Se), which corresponds to an oxidation reaction

 $Cd_2SeP_3O_9C_{54}H_{111} + 83 O_2 \rightarrow Cd_2P_2O_7 + SeO_2 + 0.5 P_2O_5 + 54 CO_2 + 55.5 H_2O_2$ 

The discrepancy is explained by an excess of free ODPA in the dried sample used for TGA analysis.

# **IR Spectroscopy**

The IR spectrum of ODPA clearly shows the CH<sub>2</sub> and CH<sub>3</sub> stretching vibrations between 2956 and 2850 cm<sup>-1</sup>. Additionally, a broad band from 3250 to 2000 cm<sup>-1</sup> indicates the hydrogen bond stretches. In the fingerprint area the CH<sub>2</sub> deformation vibrations (1472 cm<sup>-1</sup>) and the P=O (1211 cm<sup>-1</sup>), P-O-(H) (1076-932 cm<sup>-1</sup>), and P-C stretching vibrations (783-715 cm<sup>-1</sup>) can be identified.<sup>[6,7]</sup>

After Cd complex formation the hydrogen bond vibrations between 3250 and 2000 cm<sup>-1</sup> disappear, indicating complete deprotonation. The bands for P=O and P-O vibrations in the fingerprint area broaden and merge, which indicates coordination to Cd as well as formation of octadecylpyrophosphonic acids (ODPPA).

In the coordination polymer  $Cd_2Se(ODPA)_n$  the P-O bonds shift to larger wave numbers by approximately 100 cm<sup>-1</sup> with respect to free ODPA, while the P-C vibration remains static at 923 cm<sup>-1</sup>. We attribute this to formation of the Cd-Se bond and to pyrophosphonates (P-O-P) that are a side product of the Cd-Se bond formation.<sup>[8]</sup>



Fig. S4: FTIR spectra of ODPA, Cd-ODPA, and Cd<sub>2</sub>Se(ODPA)<sub>n</sub> (from bottom to top)

**ODPA**  $\tilde{\nu}$  (cm<sup>-1</sup>): 2956 (w) v<sub>as</sub>(CH<sub>3</sub>), 2915 (s) v<sub>as</sub>(CH<sub>2</sub>), 2850 (s) v<sub>s</sub>(CH<sub>2</sub>), 2270 (w, br) v<sub>as</sub>(H···OH), 1472 (m)  $\delta$ (CH<sub>2</sub>), 1401 (w)  $\delta$ (CH<sub>3</sub>), 1211 (s) v(P=O), 1076 (s) v<sub>as</sub>(P-OH), 1004 (s) v<sub>s</sub>(P-OH), 932 (s) v(P-C), 783 (m)  $\delta$ (P-C), 715 (s)  $\delta$ (P-O).

**Cd-ODPA**  $\tilde{\nu}$  (cm<sup>-1</sup>): 2956 (w) v<sub>as</sub>(CH<sub>3</sub>), 2917 (s) v<sub>as</sub>(CH<sub>2</sub>), 2850 (s) v<sub>s</sub>(CH<sub>2</sub>), 1468 (m)  $\delta$ (CH<sub>2</sub>), 1160 (s, br) v(P=O), 1091 (s, br) v<sub>as</sub>(P-O), 941 (s, br) v<sub>s</sub>(P-O), 782 (m)  $\delta$ (P-C), 719 (s)  $\delta$ (P-O).

Cd<sub>2</sub>Se(ODPA)<sub>*n*</sub>  $\tilde{\nu}$  (cm<sup>-1</sup>): 2952 (w) v<sub>as</sub>(CH<sub>3</sub>), 2917 (s) v<sub>as</sub>(CH<sub>2</sub>), 2850 (s) v<sub>s</sub>(CH<sub>2</sub>), 1467 (m)  $\delta$ (CH<sub>2</sub>), 1377 (w)  $\delta$ (CH<sub>3</sub>), 1179 (s) v(P-O), 1108 (s) v<sub>as</sub>(P-O), 1055 (m) v<sub>s</sub>(P-O), 923 (s) v(P-C), 782 (m)  $\delta$ (P-C), 719 (s)  $\delta$  (P-O).

#### NMR Spectroscopy

<sup>1</sup>H NMR (600 MHz, Tol-*d*<sub>8</sub>) δ 2.03 (m, TBP-Se), 1.66–1.54 (m, TOPO and TBP-Se), 1.50–1.40 (m, TOPO and TBP-Se), 1.39–1.31 (m, *n*-hexane), 1.29 (s,TOPO), 0.96 (t, TOPO), 0.85 (t, TBP-Se).

<sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, Tol- $d_8$ )  $\delta$  47.01 (impurity), 46.70 (impurity), 41.61 (free TOPO), 35.16 (TBPSe, <sup>1</sup>*J*<sub>P-Se</sub> = 718 Hz), 26.90 (br, bound ODPA).

<sup>31</sup>P CP-MAS NMR (162 MHz) δ 48.2 (impurity), 47.7 (impurity), 43.2 (free TOPO), 36.9 (TBPSe), 27.1 (ODPPA), 24.5 (ODPA).



**Figure S5:** <sup>31</sup>P NMR spectra of the crude product (left and centre, magnified) with sharp peaks for unreacted TBP-Se (35.16 ppm with <sup>77</sup>Se satellites), free TOPO (41.61 ppm) and an unidentified impurity (46.70 and 47.01 ppm). A broad peak of bound ODPA is observed at 26.90 ppm. The chemical shifts were identified by comparison to spectra of the pure compounds. The graph on the right shows the broad peak in a purified sample, which was enhanced by apodisation using an exponential window.



**Fig. S6:** Solid state <sup>31</sup>P-NMR CP-MAS spectrum of the dried gel acquired with a MAS rate of 5 kHz. Spinning sidebands are indicated with \*.



**Fig. S7:** The full range of the <sup>31</sup>P-NMR CP-MAS spectrum shown in Fig. 2 of the main text, with MAS rates of 10 (red) and 12 kHz (black). Spinning sidebands are indicated with \*.



Chemical shift /ppm

**Figure S8:** <sup>1</sup>H DOSY spectrum of the coordination polymer in toluene-d8. Four components with different diffusion coefficients can be identified: toluene  $(3.7 \cdot 10^{-10} \text{ m}^2/\text{s})$ , unreacted TBP-Se  $(1.6 \cdot 10^{-10} \text{ m}^2/\text{s})$ , free TOPO  $(1.4 \cdot 10^{-10} \text{ m}^2/\text{s})$ , and bound ODPA  $(0.5 \cdot 10^{-10} \text{ m}^2/\text{s})$ . The aliphatic chains of the ligands overlap, which causes a V-shaped pattern round the peaks between 0.9 and 2 ppm, in which the centre corresponds to the quickly diffusing, free species and the tails to the slowly diffusing, bound ODPA. As expected from linear molecules bound to a large particle the  $\alpha$ - and  $\beta$ -CH<sub>2</sub> groups have the smallest diffusion coefficient.

Additional Transmission Electron Micrographs of the Gel



**Figure S9:** Additional TEM micrographs of the CdSe coordination polymer dried on an amorphous carbon film. Clearly visible are parallel stripes that originate from 1D nanowires, which attach along one edge to form a gel composed of lamellar sheets. The dark stripes are  $2.1 \pm 0.3$  nm thick, which is 2/3 the lamellar periodicity from SAXS analysis (3.24 nm), as discussed in the manuscript.

## **Analytical Ultracentrifugation**



**Figure S10:** Distribution of sedimentation coefficients for the  $Cd_2Se(ODPA)_n$  fibrils in hexane (top left), toluene (top right), toluene- $d_8$  (bottom left) and after reaction with hexylamine in toluene (bottom right). The green line is the distribution after normalisation to water at 20 °C, the blue dotted line is the same data after correction for diffusion broadening using the diffusion-corrected c(s) model in SEDFIT. It can be clearly seen that the distribution broadens and apparently splits into several populations after amine addition. Note the different scales of the abscissa in the left and right graph.



**Figure S11:** 2D Plot of the 2DSA-Monte Carlo for of the melted  $Cd_2Se(ODPA)_n$  fibrils in hexane against frictional ratio  $f/f_0$  (left) and calculated molecular weight (right)



**Figure S12:** (Left) 2D Plot of the 2DSA-Monte Carlo for of the melted  $Cd_2Se(ODPA)_n$  fibrils in toluene as a function of frictional ratio  $f/f_0$  and sedimentation coefficient rescaled for water at 20 °C. (Right) the same plot for the fibrils after reaction with hexylamine, again with toluene as solvent. The calculation has a bias to turn a broad distribution into several sharp peaks, which needs to be considered in the interpretation of the data. It can be clearly seen that  $f/f_0$  (and with that the aspect ratio) drops and broadens after addition of the amine. Note the different scaling for the *x* and *y* axes.



**Figure S13:** Same data as in Figure S7.3, but plotted against calculated molecular weight in Da instead of frictional ratio  $f/f_0$ . (Left) Cd<sub>2</sub>Se(ODPA)<sub>n</sub> fibrils in toluene. (Right) after reaction with hexylamine at 60 °C in toluene.

**Additional Transmission Electron Micrographs after Heating** 



**Figure S14:** (Left) TEM micrographs of CdSe nanorods extracted from the residue of the coordination polymer after heating to 250 °C under air, mixed with CdSe coordination polymer. During the reaction the solvent (toluene) evaporated and the solid residue turned red. It was then extracted with toluene. The data shows that nanorods form at high concentration with reaction-limited kinetics. The image shows the same sample as Figure 3C of the main text. (Right) When injecting the coordination polymer into hot TOPO monomer concentration is low and the coordination polymer is not stable. Under these diffusion-limited reaction conditions the resulting nanocrystals are spherical.



**Figure S15:** Absorption spectra of the pristine coordination polymer (black) and the reaction products after addition of butylamine with absorption at 380 nm (blue) and 414 nm (green). We were able to isolate the latter species, which can be seen in Figures S8.1 and S8.2.

Structural Analysis after Reaction of the Fibrils with Alkylamines



**Figure S16:** Before (left) and after (right) beam damage of the amine-treated fibrils after irradiation with the electron beam for approximately 10 minutes. Fragmentation into discrete particles can be observed. The figure shows representative regions and not the same area before and after extended exposure.



**Figure S17:** (Left) SAXS region of the powder XRD of the reaction product of the coordination polymer with hexylamin with an absorption peak at 414 nm in red, with the data from the aerogel in Figure 1B shown in black as a comparison. Vertical lines indicate the lamellar structure of the original coordination polymer, which is lost after reaction with hexylamine. (Right) Radial average of the FFT in Figure 4C of the main text. It shows a broad distribution of periodicities centred around 4.5 nm (gray line), about 1.8 nm larger than that of the original gel.

#### **Discussion of the Possible Molecular Structure**

Due to the lack of reliable structural data (e.g. x-ray structure or solution NMR) assignment of a molecular structure in the scope of this work must be regarded as conjecture. Nonetheless one can make some reasonable assumptions: (a) the stoichiometry is known. In this paragraph we assume the likely formula of  $[Cd_2Se(ODPA)_4]_m$ , which corresponds to the amounts of Cd, Se, and ODPA used in the reaction. (b) From the Cd-Se bond formation<sup>[8]</sup> as well as from the high temperature it is expected that the phosphonic acid reacts to pyrophosphonic acid (ODPPA) *in situ*. This is corroborated by IR data.



Figure S18: Reaction between the precursors to form CdSe, an anhydride, and TOPO, adapted from [8].

For simplicity's sake we will argue with the dimeric form, but longer chains are likely and a possible reason for the large error in the phosphorous content on elemental analysis. Since no coordination polymer is formed if water is not removed prior to TBPSe injection the pyrophosphonates are likely crucial in the formation of the intermediate. (c) The Cd(ODPA)<sub>2</sub> precursor shown in the scheme above is actually not known in literature. Due to the bi- or tridentate nature of the ligand it forms small clusters and 2D sheets, which are a likely starting point of the reaction.<sup>[9,10]</sup> The smallest cadmium phosphonate for which a crystal structure is known contains 4 Cd atoms. From this we conclude that the coordination polymer may have a structure similar to the following scheme (2 subunits are shown):



Figure S19: Proposition for the structure of [Cd<sub>2</sub>Se(ODPA)<sub>4</sub>]<sub>m</sub> based on the arguments given in the text.

This structure replicates the anisotropic nature of the coordination polymer (polymerisation in x direction, aggregation of fibrils in z, stacking of lamella in y). Additionally, the thickness of a single repetition unit (2.59 nm) is in good agreement with TEM data (2.69  $\pm$  0.35 nm), assuming intercalation of the C<sub>18</sub> chains of ODPA in z direction.

We would like to stress that we provide no proof that this is the actual crystal structure beyond the logical arguments and MMFF molecular mechanics-based energy minimisation of the 3D structure.



**Figure S20:** Ball and spoke model of a single  $Cd_4Se_2(ODPPA)_4$  unit minimised with the MMFF algorithm. The thickness of a fibril was calculated as the distance from the end of one  $C_{18}$  chain to the Se atom at the opposite end of the inorganic layer. Colour codes: Cd green, Se orange, P brown, O red, C grey, H white.

We also performed DFT calculations on the structure fragment  $Cd_4Se_2(ODPPA)_4$  shown in Figure S9.1, using the TURBOMOLE 7.2 package and employing a B3LYP potentials and a def2-TZVP basis set. It yielded a HOMO-LUMO gap of 3.7-3.9 eV (331-318 nm), which is in reasonable agreement with the values from reference [18] of the main text for  $Cd_2Se_2$  clusters (3.5-3.7 eV, 354-335 nm), and our experimental results (3.56 eV, 348 nm).

# **Mass Spectrometry**

MALDI-TOF MS was performed on a Bruker Microflex MALDI-TOF spectrometer using DCTB as a matrix. ESI-MS was performed on a Bruker micrOTOF II spectrometer on both positive and negative mode. No signals was obtained that could be assigned to the coordination polymer. This is not unexpected when considering the large size and high stability of the material.

# Analysis of the Hydrodynamic Diameter

The hydrodynamic diameter  $D_H$  of the coordination polymer after melting at 50 °C was determined independently by three methods: DLS ( $D_H = 8.4$  nm), AUC ( $D_H = 9.9 \pm 1.3$  nm), and <sup>1</sup>H DOSY NMR for  $\alpha$ - and  $\beta$ -CH<sub>2</sub> groups of ODPA ( $D_H = 9.4$  nm) yielded values that are all in agreement within the experimental error. However, all three methods assume a spherical shape, which is inconsistent with TEM and SAXS data.

AUC data was used to determine the shape anisotropy from the relative coefficient of friction  $f/f_0$  after normalising the sedimentation coefficients to that in water at 20 °C, as discussed in the main text.

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