

Supporting Information for

Self-Assembly of One-Dimensional Nanocrystal Superlattice Chains Mediated by Molecular Clusters

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METHODS

Materials. Oleic acid (OA, 90%), oleylamine (OAm, 70%), trioctylphosphine (TOP, 97%), and 1-octadecene (ODE, 90%) were purchased from Aldrich. Lead oxide (PbO, 99.999%), lead chloride (PbCl₂, 99.999%), sulfur (99.999%), tetrabutylammonium hydrogen sulfate (TBAHS, 98%), iron chloride hexahydrate (FeCl₃ 6H₂O, 99%), silver nitrate (AgNO₃, 99.999%), cadmium acetate dehydrate (Cd(OAc)₂ 2H₂O, 99.99%), and selenourea (99.9%) were purchased from Aladdin. Sodium oleate (>97.0%) and tetrabutylammonium bromide (TBAB, >99.0%) were obtained from TCI. Trichlorogold hydrate hydrochloride (HAuCl₄ 4H₂O) was purchased from Sinopharm. All chemicals were used as received without further purification.

Synthesis of PbSO₄ clusters. The OAm-ligated PbSO₄ clusters were synthesized by reaction of lead chloride (PbCl₂) or lead oleate with a number of alkyl-ammonium sulfate compounds such as TBAHS and oleylammonium sulfate (OAm H₂SO₄) at room temperature. A stock solution of PbCl₂ was prepared by mixing 139 mg of PbCl₂ (0.5 mmol) in OAm (8 mL) at room temperature, followed by heating of the mixture at 150 °C under N₂ for 1 h to form a clear solution (0.0625 M). A stock solution of TBAHS was prepared by dissolving 424.4 mg of TBAHS (1.25 mmol) in 10 mL of acetone (0.125 M). A stock solution of oleylammonium sulfate was prepared by the direct reaction of OAm with H₂SO₄ with vigorous stirring and the resulting white precipitate was dissolved in acetone to form a clear solution. In a typical procedure to synthesize PbSO₄ clusters from PbCl₂ and TBAHS, 0.4 mL of PbCl₂ stock solution, 0.2 mL of TBAHS stock solution, and 0.4 mL of OA were mixed in 10 mL of chloroform in a vial, and the resulting mixture was stirred at room temperature for 10 min, yielding a clear colorless solution. The subsequent addition of 30 mL of ethanol led to a white cloudy suspension, suggesting the formation of PbSO₄ clusters. The as-synthesized PbSO₄ clusters were separated by centrifugation (5000 rpm, 3 min) and the resulting white precipitate was redispersed in 2.5 mL of chloroform to form a clear colorless solution with a concentration of ~ 0.01 M. A photograph of PbSO₄ clusters dispersed in chloroform was shown on the right. It should be noted that although the precise symmetry and structure of PbSO₄ clusters could not be determined due to the difficulty to prepare single crystals, the empirical formula of PbSO₄ clusters was determined to be [(PbSO₄)₆ (OAm)₆] by various characterization techniques (see Figure S1 for characterization details).



Synthesis of (CdSe)₁₃ clusters. The OAm-ligated (CdSe)₁₃ clusters were synthesized by a method developed by Buhro and coworkers (Ref. S1). In a typical synthesis, 65 mg of Cd(OAc)₂ 2H₂O (0.24 mmol) was dissolved in 1.5 g of OAm (5.6 mmol) at 70 °C for 1 h and cooled to room temperature. After that, 65 mg of selenourea (0.24 mmol) dissolved in 6.8 g of OAm (0.025 mol) was injected into the Cd(OAc)₂ solution. The mixture was kept still for 2 days and TOP (65 mg) was added to remove the excess

selenium. The precipitate was separated by centrifugation and washed 3 times with an OAm solution (20% w/w in toluene).

Synthesis of colloidal NCs. All preparative procedures were conducted using standard Schlenk-line techniques under nitrogen atmosphere.

Fe₃O₄ NCs with a diameter of ~ 15 nm were synthesized according to a modified literature method (Ref. S2). In a typical synthesis, iron oleate (0.8 mol, 72 g) and OA (11.4 g) were dissolved in ODE (400 g) in a three-neck flask and heated at 320 °C for 1 h. After cooling down to room temperature, ethanol and isopropanol were added to precipitate Fe₃O₄ NCs. The precipitated NCs were redispersed in hexane to form a stable colloidal solution with a concentration of ~ 10 mg mL⁻¹.

Au NCs with a diameter of ~ 7 nm were synthesized by a literature method (Ref. S3). In a typical synthesis, 103 mg of HAuCl₄ 4H₂O (0.25 mmol) and 11 mL of OAm were added into 11 mL of toluene, and the resulting solution was stirred at 15 °C for 10 min. After that, a solution containing 22 mg of TBAB (0.25 mmol), 1 mL of OAm, and 1 mL of hexane was injected and the reaction was allowed to proceed for 1 h. Ethanol was added to precipitate Au NCs, and the precipitated NCs were redispersed in hexane to form a stable colloidal solution with a concentration of ~ 8 mg mL⁻¹.

Ag NCs with a diameter of ~ 14 nm were synthesized according to a modified literature method (Ref. S4). In a typical synthesis, 169.9 mg of AgNO₃ (1 mmol) and 20 mL of OAm were first heated at 60 °C for 1 h and then quickly heated up to 240 °C and maintained at this temperature for 1 h. Acetone was added to precipitate Ag NCs. A size-selective precipitation procedure was used to improve the size uniformity, and the resulting relatively monodisperse Ag NCs were redispersed in hexane to form a stable colloidal solution with a concentration of ~ 8 mg mL⁻¹.

PbS nanocubes with an average side length of ~ 13 nm were synthesized according to a modified literature method (Ref. S5). In a typical synthesis, 0.28 g of PbCl₂ (1 mmol) and 5 mL of OAm were heated in a three-neck flask at 90 °C under vacuum, yielding a clear solution. After that, 27 mg of element sulfur (0.83 mmol) dissolved in 2.5 mL of OAm was injected into the flask at 90 °C. The resulting mixture was then heated at 220 °C for 1 h. After cooling down to room temperature, ethanol was added to precipitate PbS nanocubes, which were redispersed in hexane to form a stable colloidal solution with a concentration of ~ 10 mg mL⁻¹.

CsPbBr₃ nanocubes with an average side length of ~ 11 nm were synthesized according to a literature method (Ref. S6). In a typical procedure, Cs₂CO₃ (0.814 g) was degassed in ODE (40 mL) and OA (2.5 mL) at 120 °C for 1 h to obtain the Cs-oleate solution (0.125 mM). Then ODE (5 mL) and PbBr₂ (0.188 mmol, 69 mg) were loaded into a 3-neck flask and dried under vacuum at 120 °C for 1 h. After that, dried OAm (0.5 mL) and OA (0.5 mL) were injected into the flask at 120 °C. When the PbBr₂

salt was completely dissolved, the temperature was raised to 170 °C and 0.4 mL of the Cs-oleate solution was quickly injected. The reaction mixture was cooled by an ice-water bath. The crude solution was purified via centrifugation (12000 rpm, 3 min), and the precipitated nanocubes were redispersed in hexane to form a stable colloidal solution with a concentration $\sim 10 \text{ mg mL}^{-1}$.

Self-assembly of 1D NC superlattice chains. In general, the linear assembly of colloidal NCs was realized by introducing PbSO_4 clusters into a hexane solution containing NCs followed by incubation under ambient conditions. In a typical procedure to assemble Fe_3O_4 NC chains, PbSO_4 clusters ($\sim 0.025 \text{ mmol}$) were added into 2 mL of Fe_3O_4 NC solution in hexane, and the resulting mixture was incubated without stirring for a certain period of time. The chain growth process could be completed within 30 min upon the addition of a small amount of OAm ($\sim 0.5 \text{ mL}$). The as-assembled NC chains isolated by centrifugation were re-dispersed in hexane for further characterization. Linear assembly of other types of NCs was conducted similarly to Fe_3O_4 NCs.

Instrument. TEM and HRTEM images were obtained using a Tecnai G2 F20 S-TWIN microscope operated at 200 kV, while HAADF-STEM images and EDS spectra were obtained using a JEOL JEM-ARM200F microscope operated at 300 kV. Fourier-transform infrared (FTIR) spectra were collected on a Perkin-Elmer Spectrum Two spectrometer. UV-visible absorption spectra were recorded on a Shimadzu UV-3600 UV-vis-NIR spectrophotometer. Photoluminescence (PL) spectra of PbSO_4 clusters were collected on a Shimadzu RF-5301PC spectrofluorophotometer with an excited wavelength of 300 nm. Small-angle XRD was carried out on a Bruker D4 X-ray diffractometer ($\text{Cu K}\alpha$ irradiation, $\lambda = 1.541 \text{ \AA}$). X-ray photoelectron spectrum (XPS) was acquired using a PHI 5000C ESCA system, and the C 1s peak at 284.6 eV was used as the reference line. Thermogravimetric analysis (TGA) was carried out in air on a Perkin-Elmer Pyris 1 thermogravimetric analyzer with a heating rate of 10 °C/min. Laser desorption/ionization (LDI) mass spectra were recorded without matrix on an AB SCIEX 5800 MALDI-TOF mass spectrometer. The samples were prepared by drop-casting PbSO_4 cluster solutions in chloroform onto a 384-position stainless-steel LDI plate followed by drying.

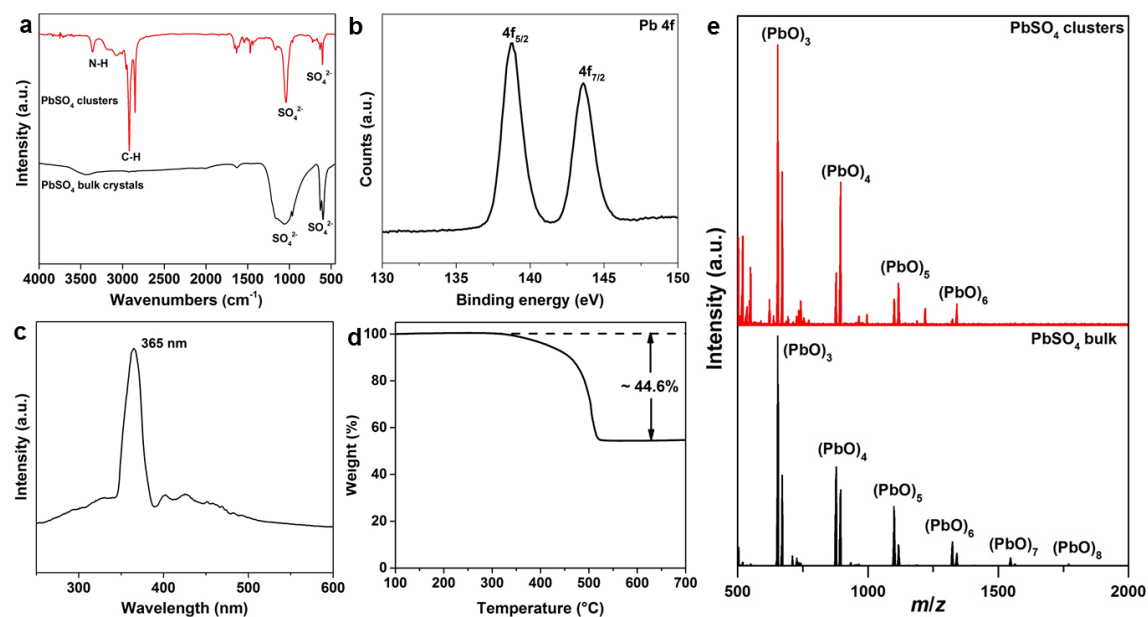


Figure S1. (a) FTIR spectra of PbSO₄ clusters and bulk crystals. (b) XPS scan of the Pb 4f signal from PbSO₄ clusters. (c) Room-temperature PL spectrum of PbSO₄ clusters dispersed in chloroform. (d) TGA curve of PbSO₄ clusters. (e) LDI mass spectra of PbSO₄ clusters and bulk crystals.

Figure S1a presents the FTIR spectrum of PbSO₄ clusters. The intense C-H stretching bands at $\sim 2800\text{--}3000\text{ cm}^{-1}$ and N-H stretching bands at $\sim 3068\text{--}3360\text{ cm}^{-1}$ were ascribed to the OAm ligands stabilizing PbSO₄ clusters, while the intense bands at ~ 1050 and 600 cm^{-1} were ascribed to the vibrations of SO₄²⁻ (Ref. S7), consistent with PbSO₄ bulk crystals. The FTIR results confirmed the existence of OAm and SO₄²⁻ in PbSO₄ clusters. Figure S1b shows the XPS scan of PbSO₄ clusters, in which the Pb 4f signal at 138.8 eV could be attributed to PbSO₄, consistent with previous reports (Ref. S8). Figure S1c presents the PL spectrum of PbSO₄ clusters, showing that PbSO₄ clusters were optically active, exhibiting a PL peak at $\sim 365\text{ nm}$, which is in agreement with the previous results based on PbSO₄ nanostructures (Ref. S7). Figure S1d shows the TGA profile, which was acquired by heating PbSO₄ clusters up to 700 °C in air. The weight percentage of OAm in clusters was determined to be $\sim 44.6\text{ wt}\%$, suggesting that the stoichiometric ratio between PbSO₄ and OAm was close to 1:1. Figure S1e shows the LDI mass spectrum of PbSO₄ clusters, in which (PbO)_x was found to be the dominant species as in the bulk. Presumably, (PbO)_x species were generated by the fragmentation of PbSO₄ clusters under laser excitation. The observed (PbO)₆ species coupled with FTIR, XPS, PL, and TGA results strongly suggested that PbSO₄ clusters possessed a molecular formula of [(PbSO₄)₆ (OAm)₆].

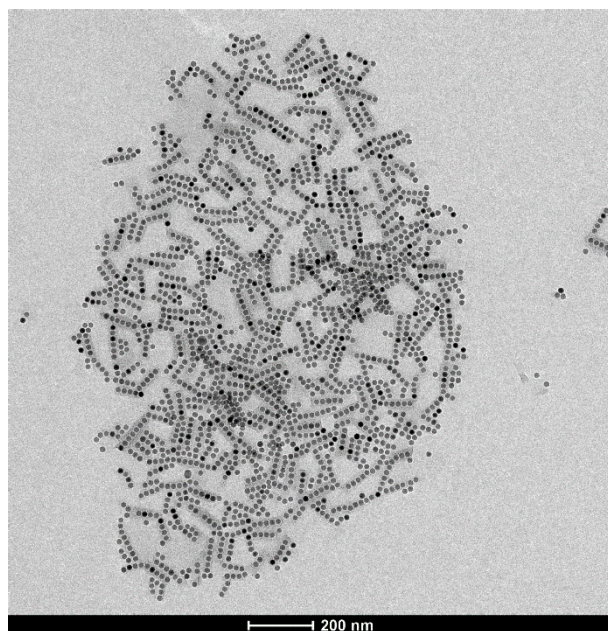


Figure S2. Representative TEM image of short NC chains observed within the first 5 min of incubation.

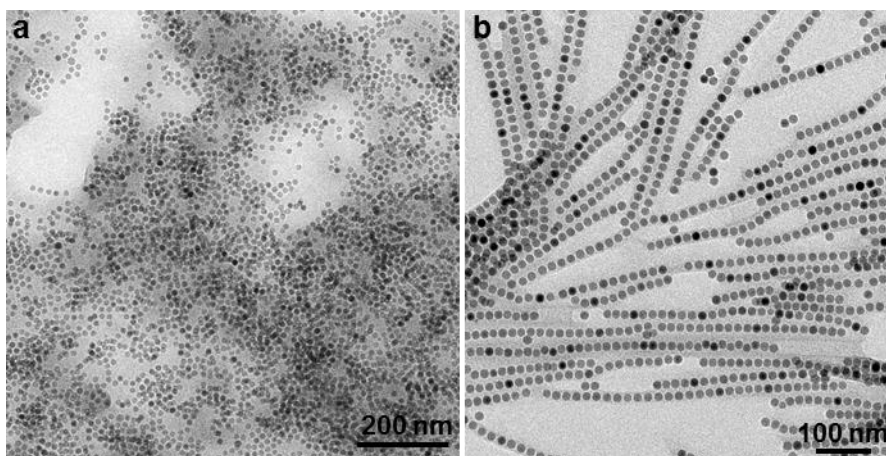


Figure S3. (a) TEM image of Fe_3O_4 NC and cluster mixtures, which were obtained by dispersing the preformed NC chains in chloroform. (b) TEM image of NC chains re-assembled from Fe_3O_4 NC and cluster mixtures shown in (a) when the incubation solvent was switched back to hexane.

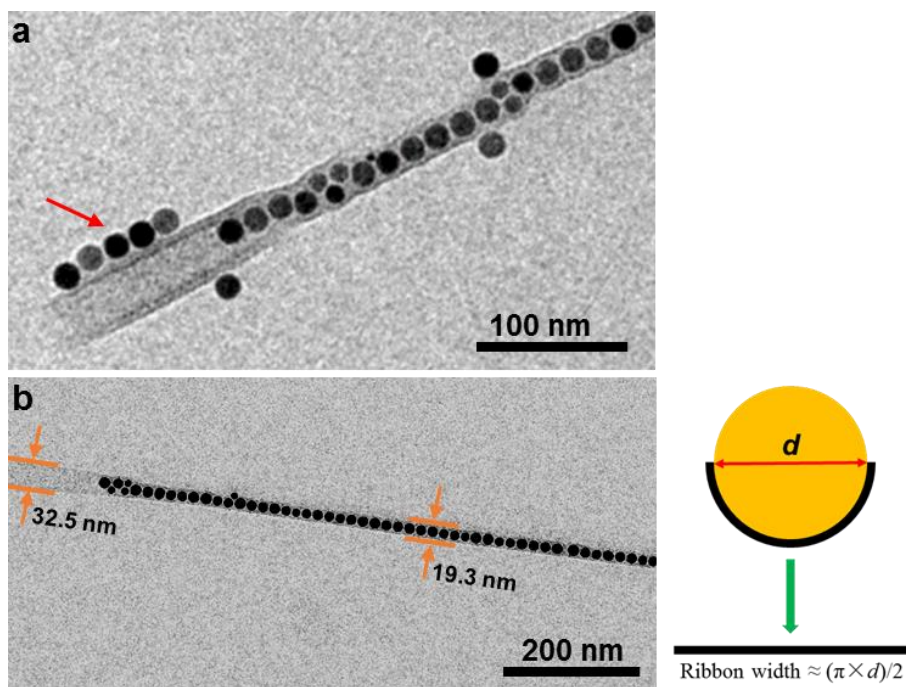


Figure S4. (a) TEM image of Fe_3O_4 NC chains upon vigorous sonication for 10 min. The dislocation of NCs (indicated by the red arrow) shows that the cluster shell possesses a tubular morphology. (b) TEM image of a single Fe_3O_4 NC chain, in which the empty cluster shell completely unrolled to form a flat ribbon with a width of ~ 32.5 nm. Considering that the diameter (d) of Fe_3O_4 NCs with two monolayers of OA is ~ 19.3 nm, complete encapsulation of NC arrays requires a ribbon having a width of ~ 60.6 nm (ribbon width $\approx \pi \times d$), which is about two times of the ribbon width (~ 32.5 nm) observed. Therefore, the original cluster shell should resemble a half cylinder, with approximately half of NC surfaces exposed, as schematically illustrated on the right.

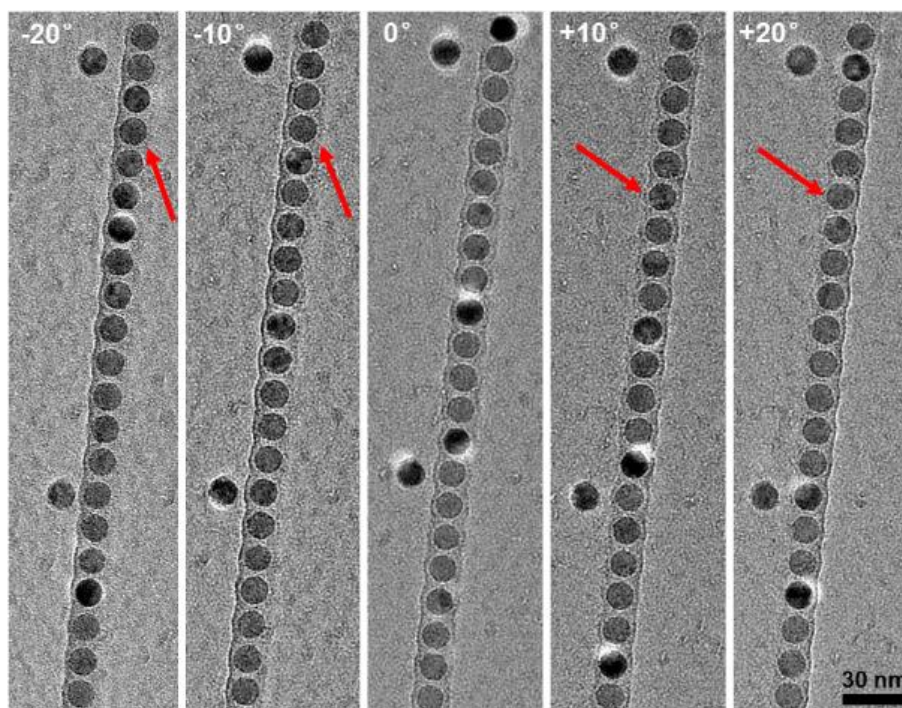


Figure S5. TEM images of a single Fe₃O₄ NC chain acquired at different tilting angles. As indicated by the red arrows, the right (or left) side wall of the cluster shell gradually disappeared as the TEM grid was tilted from 0° to -10° and -20° (or 10° and 20°), suggesting that NC chains exhibit structural anisotropy across the chain width.

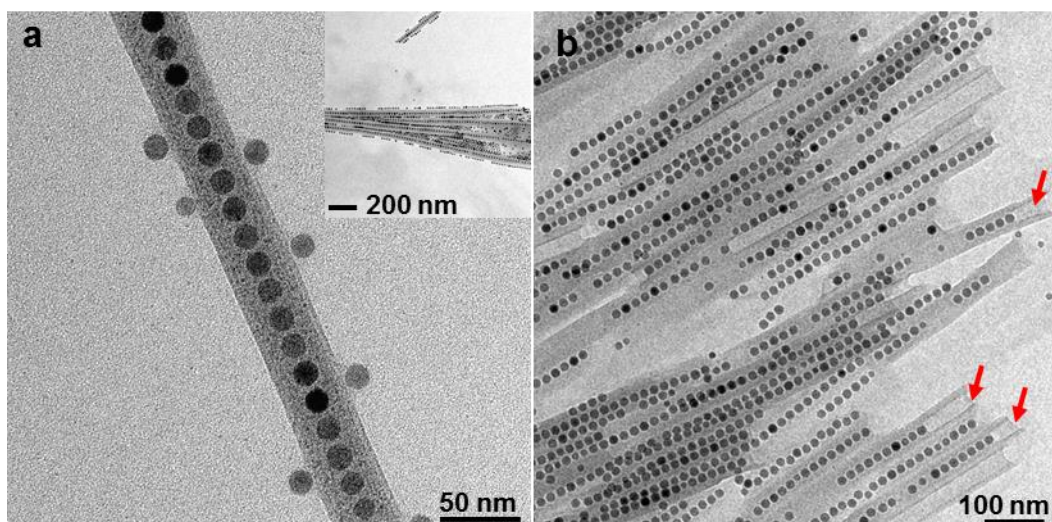


Figure S6. (a) TEM image of a single Fe_3O_4 NC chain with a thicker cluster shell, which was obtained by doubling the cluster concentration under otherwise identical conditions. The inset shows a low-magnification TEM image. (b) TEM image of the same sample after sonication (~ 10 min). The dislocation of the encapsulated Fe_3O_4 NCs revealed that the thicker cluster shells were partially opened (indicated by red arrows), suggesting that increasing the cluster concentration did not change the half-cylindrical morphology of cluster shells.

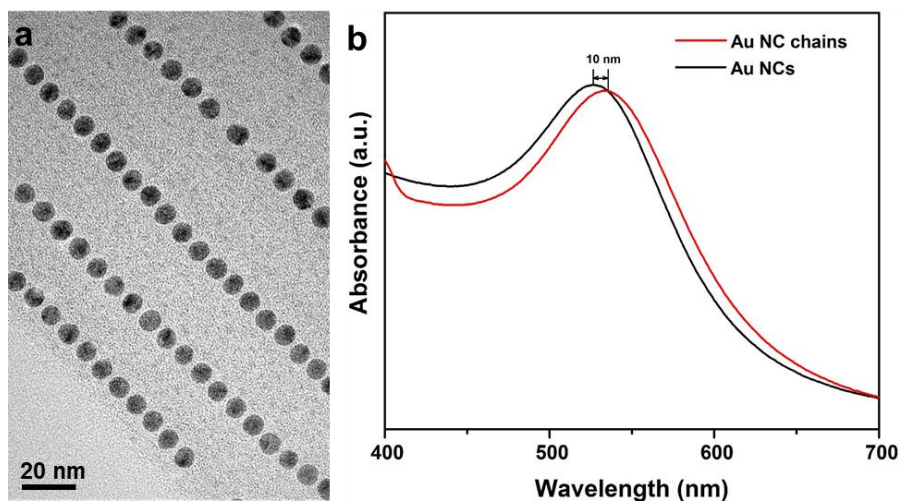


Figure S7. (a) Low-magnification TEM image of Au NC chains. (b) Absorption spectra of Au NCs and Au NC chains. Both samples were dispersed in hexane for measurements. The plasmonic peak of Au NC chains was red-shifted by ~ 10 nm relative to that of Au NCs, primarily attributed to the enhanced interparticle interactions.

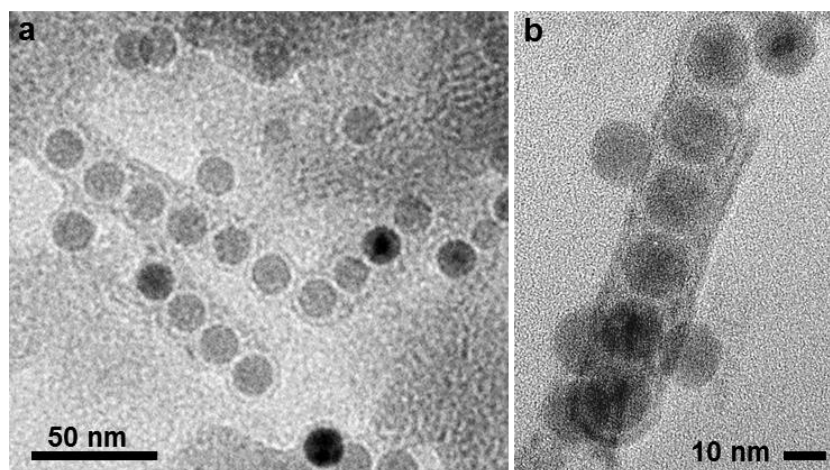


Figure S8. (a, b) Representative TEM images of Fe_3O_4 NC chains self-assembled with the aid of $(\text{CdSe})_{13}$ clusters.

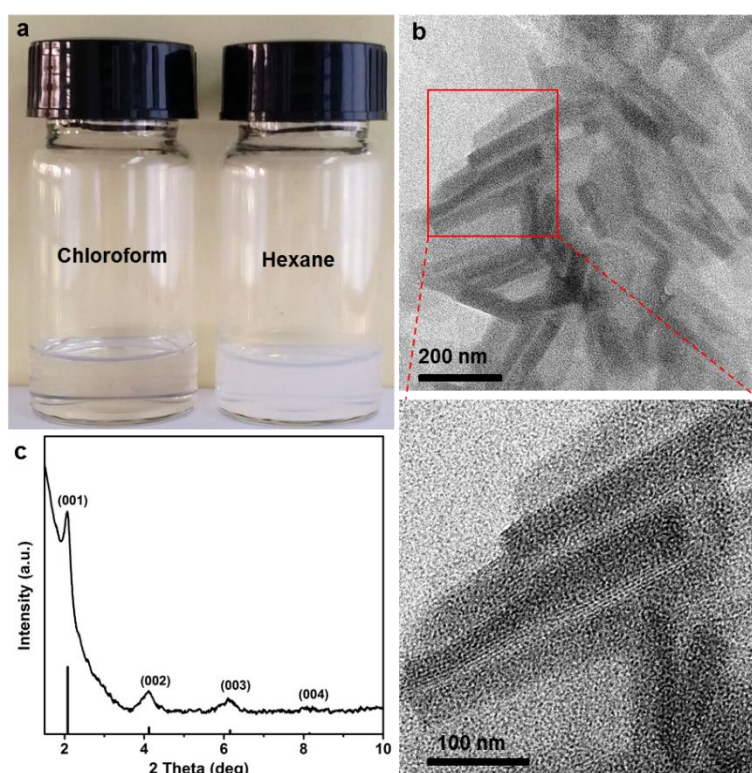


Figure S9. (a) Photographs of PbSO_4 clusters dispersed in chloroform (left) and hexane (right). Dispersing PbSO_4 clusters in chloroform yielded a clear colorless solution, suggesting that chloroform is a good solvent for PbSO_4 clusters. In contrast, dispersing PbSO_4 clusters in hexane led to a cloudy suspension with white precipitates, suggesting that hexane is a poor solvent for PbSO_4 clusters. (b) TEM images of the precipitate, showing the formation of lamellar ribbons with a dimension of $\sim 400 \times 60$ nm. (c) Low-angle XRD pattern of PbSO_4 cluster ribbons. The interlayer spacing was determined to be ~ 4.2 nm, consistent with the two stacking layers of OAm ligands stabilizing PbSO_4 clusters (Ref. S1).

References

- S1. Wang, Y.; Liu, Y.; Zhang, Y.; Kowalski, P. J.; Rohrs, H. W.; Buhro, W. E. *Inorg. Chem.* **2013**, *52*, 2933-2938.
- S2. Park, J.; An, K. J.; Hwang, Y. S.; Park, J. G.; Noh, H. J.; Kim, J. Y.; Park, J. H.; Hwang, N. M.; Hyeon, T. *Nat. Mater.* **2004**, *3*, 891-895.
- S3. Wu, B.; Yang, H.; Huang, H.; Chen, G.; Zheng, N. *Chin. Chem. Lett.* **2013**, *24*, 457-462.
- S4. Peng, S.; McMahon, J. M.; Schatz, G. C.; Gray, S. K.; Sun, Y. *Proc. Natl. Acad. Sci.* **2010**, *107*, 14530-14534.
- S5. Joo, J.; Na, H. B.; Yu, T.; Yu, J. H.; Kim, Y. W.; Wu, F. X.; Zhang, J. Z.; Hyeon, T. *J. Am. Chem. Soc.* **2003**, *125*, 11100-11105.
- S6. Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. *Nano Lett.* **2015**, *15*, 3692-3696.
- S7. Deng, B.; Wang, C.; Li, Q.; Xu, A. *J. Phys. Chem. C* **2009**, *113*, 18473-18479.
- S8. Konstantatos, G.; Levina, L.; Fischer, A.; Sargent, E. H., *Nano Lett.* **2008**, *8*, 1446-1450.