

SUPPORTING INFORMATION

Self-Assembly of Colloidal Hexagonal Bipyramid- and Bifrustum-shaped ZnS Nanocrystals into Two-Dimensional Superstructures

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Methods

Synthesis.

Colloidal hexagonal bipyramid-shaped Cu_{2-x}S NCs were synthesized based on a modification of the method described by Kuzuya *et al.*¹ Typically, 1.0 mmol CuCl and 0.5 mmol SnBr₄ were mixed in 8 mL 1-dodecanethiol (DDT) and 2 mL oleylamine (OLAM) and gradually heated to 225 °C. At first, a turbid white suspension was obtained at RT. The solution turned turbid yellow around 80 °C, and clear yellow at 130 °C. When the temperature reached 225 °C, the solution turned brown/black, indicating the formation and growth of Cu_{2-x}S NCs. The solution was maintained at this temperature for one hour. Finally, the nanoparticles were washed by adding methanol/butanol solution as anti-solvent, followed by centrifugation and redispersion in toluene. This cycle was repeated 3 times.

Colloidal hexagonal bipyramid-shaped Cu_{2-x}S NCs were synthesized according to Li *et al.*² In a typical synthesis, 8 mmol of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 12 g OLAM were heated to 200 °C under nitrogen flow. After one hour the clear dark brown solution was cooled to 180 °C and 2 mL tert-butyl disulfide (10 mmol) was swiftly injected. The solution was re-heated to 200 °C and after 40 minutes of growth the reaction mixture was cooled. Subsequently, the NCs were washed three times with a methanol/butanol solution as anti-solvent, and redispersed in toluene.

Cation exchange reactions of Cu^+ for Zn^{2+} were performed as described by Li *et al.*³ First, 1 mmol ZnCl_2 was dissolved in 3 mL 1-octadecene and 2 mL OLAM (both previously degassed) at 250 °C. Subsequently, Cu_{2-x}S NCs dispersed in trioctylphosphine (TOP) were injected at that temperature. The mixture was allowed to react for 5 min. under heating and stirring, after which the temperature was lowered to 70 °C, followed by the addition of several mL's toluene. The final sample was precipitated by adding a methanol/butanol solution. The NCs were isolated by centrifugation and redispersed in toluene. This cycle was repeated twice.

Self-assembled NC superlattices were obtained by the liquid-air interface method, described by Chen *et al.*⁴ In this method, a concentrated NC solution is brought onto a very dense liquid surface (di-ethylene glycol). The toluene is allowed to slowly evaporate at room temperature, resulting in the formation of a continuous membrane at the liquid-air interface. These membranes were transferred to a TEM-grid by dipping it in the liquid substrate and subsequently the grid was dried overnight prior to further investigation.

Ligand exchange reactions were performed by dispersing the NCs with the native capping ligands in an excess of the new ligand at ~100 °C for several hours. The NCs were subsequently precipitated by the addition of methanol/butanol solution, isolated by centrifugation, and redispersed in toluene.

Characterization

X-Ray Diffraction (XRD) patterns were obtained by using a PW 1729 Philips diffractometer, equipped with a Cu K α X-ray source ($\lambda=1.5418 \text{ \AA}$). Samples for XRD analysis were prepared by depositing purified NCs on a Si wafer substrate under inert atmosphere. The purification procedure consisted of precipitating the NCs from a solution of NCs in toluene by adding anhydrous methanol (1:1 volume ratio). The sediment was isolated by centrifugation (3000 rpm, 15 min) and redispersed in chloroform. The concentrated solution of NCs was dropcasted on the Si wafer and the chloroform was allowed to evaporate at RT, resulting in a concentrated NC solid.

Transmission Electron Microscopy (TEM) and Energy Dispersive X-Ray Spectroscopy (EDS). TEM and EDS measurements were performed on a Tecnai20F (FEI) microscope equipped with a Field Emission Gun, a Gatan 694 CCD camera and an EDAX spectrometer. The microscope was operated at 200 kV. Acquisition time for EDS measurements was 30 s. Samples for TEM imaging were prepared by dipping a carbon coated polymer film copper grid (300 mesh) into a self-assembled thin film on a dense diethylene glycol surface after evaporation of the solvent (toluene). The TEM-grids were dried overnight prior to imaging.

Table S1. Elemental composition of the hexagonal bipyramid- and bifrustum-shaped ZnS NCs obtained by Cu^+ for Zn^{2+} cation exchange in $\text{Cu}_{1.96}\text{S}$ NCs. The elements were quantified by Energy Dispersive X-Ray Spectroscopy (EDS). To ensure that the elemental concentrations were statistically valid and representative of the whole NC ensemble, EDS analyses were performed on wide areas ($\sim 10^4$ - 10^5 nm², ~ 1000 to 5000 NCs), and averaged over several observation spots.

Sample ID	Zn:S:Cu
Bipyramids	0.99:1.00:0.05
Bifrustums	1.11:1.00:0.01

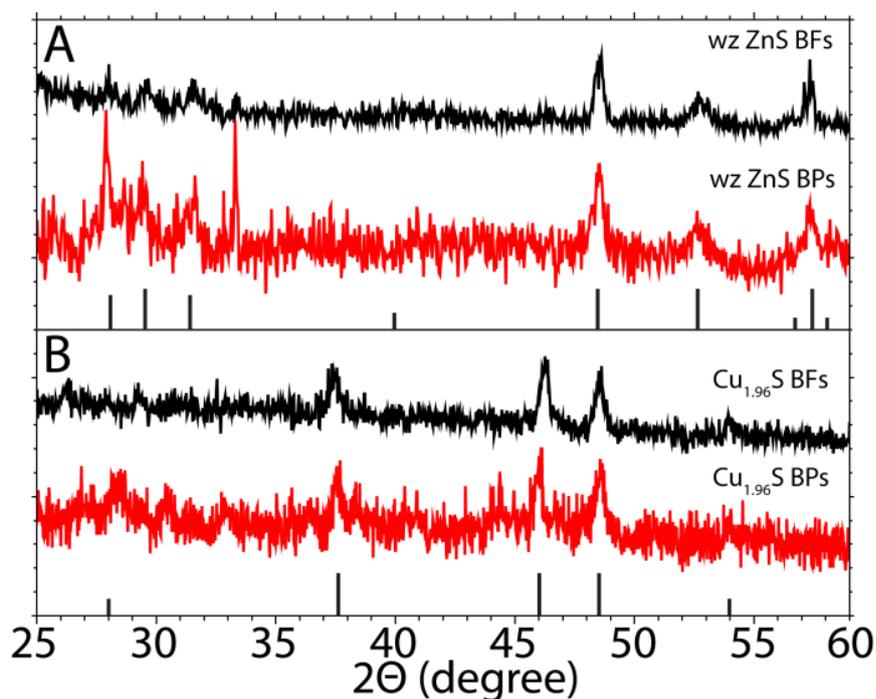


Figure S1. X-ray Diffraction patterns, indicating that (A) wurtzite ZnS hexagonal bipyramids (BPs) and bifrustums (BFs) were successfully synthesized from (B) djurleite $\text{Cu}_{1.96}\text{S}$ hexagonal BPs and BFs by Cu^+ for Zn^{2+} cation exchange. Reference bars are from JCPDS card no. [05-0492] and [20-0365] for wurtzite ZnS and djurleite $\text{Cu}_{1.96}\text{S}$, respectively.

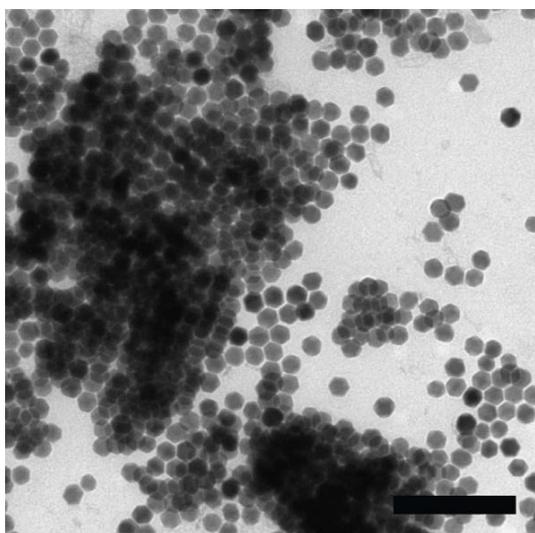


Figure S2. Self-assembled superstructures obtained from hexagonal bifrustum-shaped $\text{Cu}_{1.96}\text{S}$ NCs, capped with alkythiols. Scale bar corresponds to 200 nm.

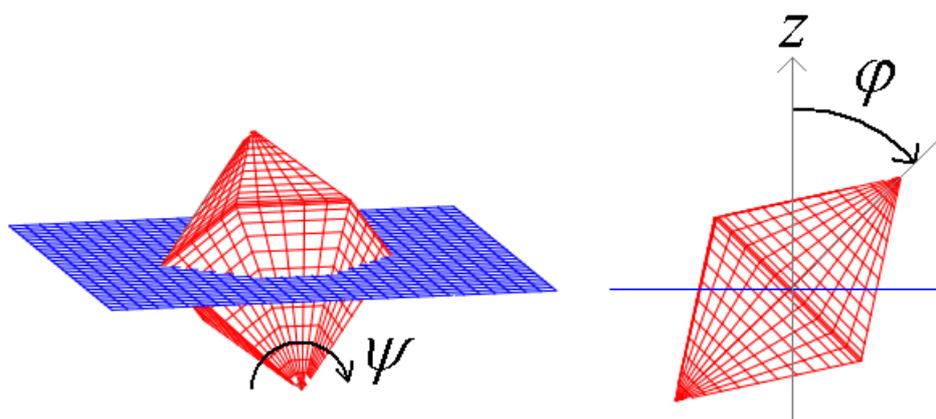


Figure S3. Definition of different orientational angles of the hard particles with respect to the interface (Equation 1 of the main text).

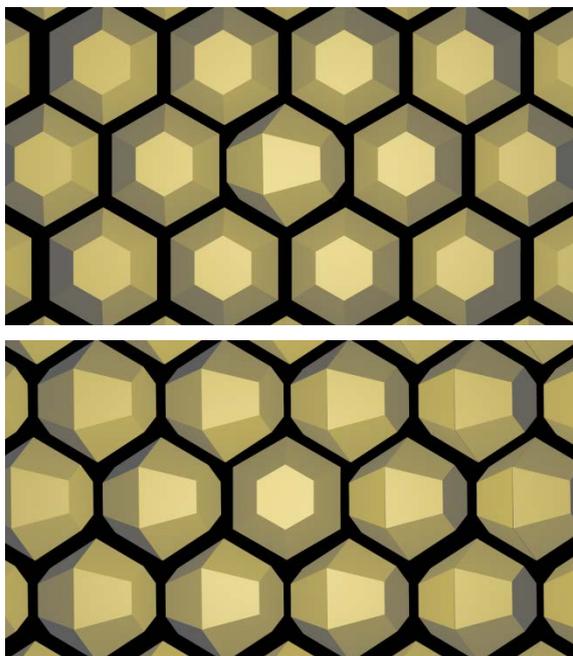


Figure S4. Schematic showing the different orientations of the hexagonal bifrustums at the interface, indicating that the NC can occupy a hexagonal site in the array regardless of whether a trapezoidal or hexagonal facet is adsorbed to the interface. Therefore, solely adsorption with the hexagonal facet is considered for simplicity in the FBMC simulations.

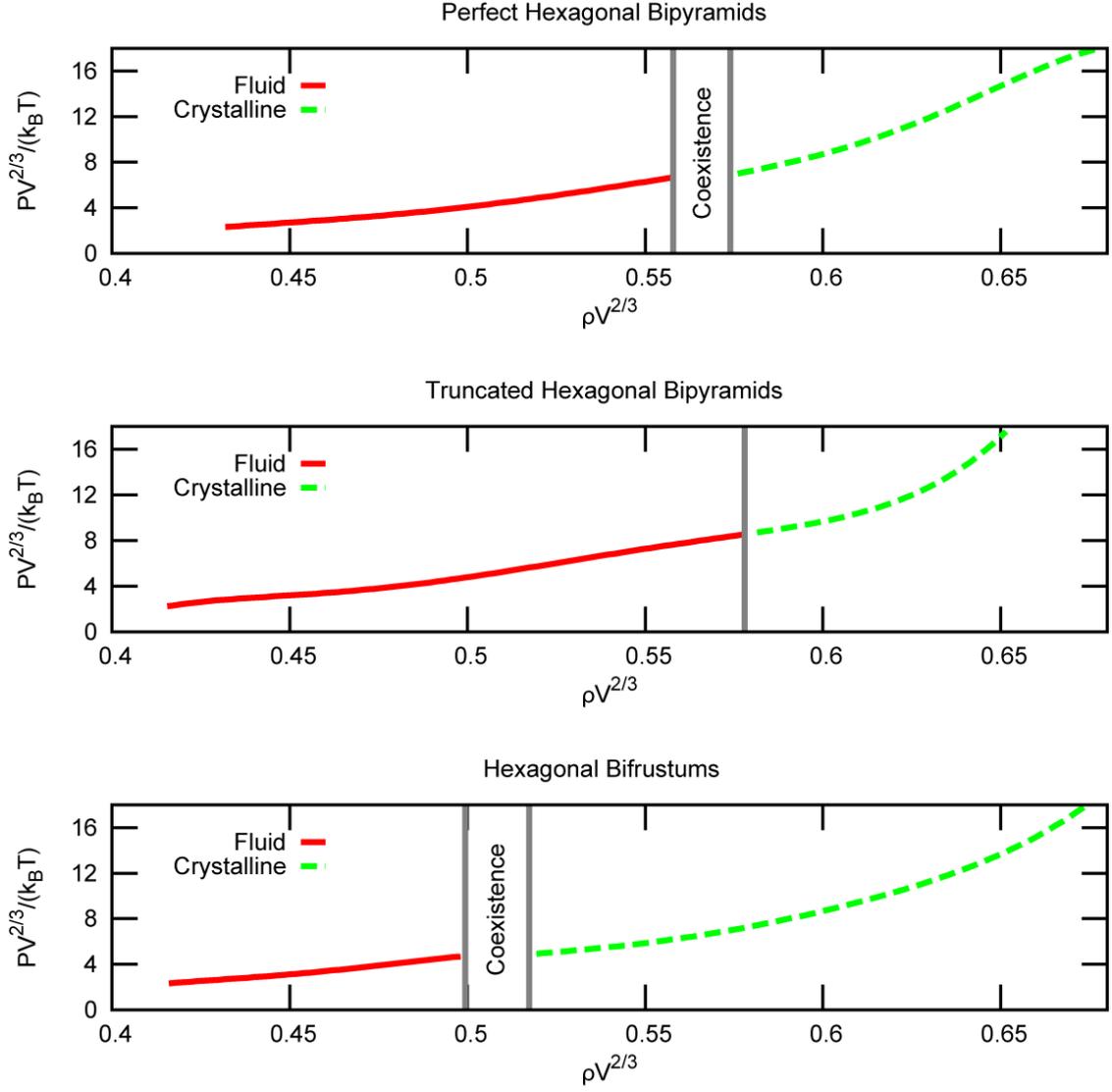


Figure S5. Equations of State (EOS), reduced pressure $P^* = \beta P v^{2/3}$ versus number density $\rho^* = \rho v^{2/3}$, obtained using floppy-box Monte Carlo (FBMC) simulations with $\beta = 1/k_B T$ as the inverse temperature. Perfect hexagonal bipyramids (BPs) undergo a first-order transition with coexisting densities $\rho^* \approx 0.56$ and 0.57 from the isotropic fluid phase to a hexagonal lattice, while slightly truncated hexagonal BPs show a weak first-order transition around $\rho^* \approx 0.58$ from an isotropic phase to a tetragonal lattice. Hexagonal bifrustums (BFs) crystallize *via* a first-order phase transition from the isotropic fluid into a hexagonal lattice with coexisting densities $\rho^* \approx 0.50$ and 0.52 .

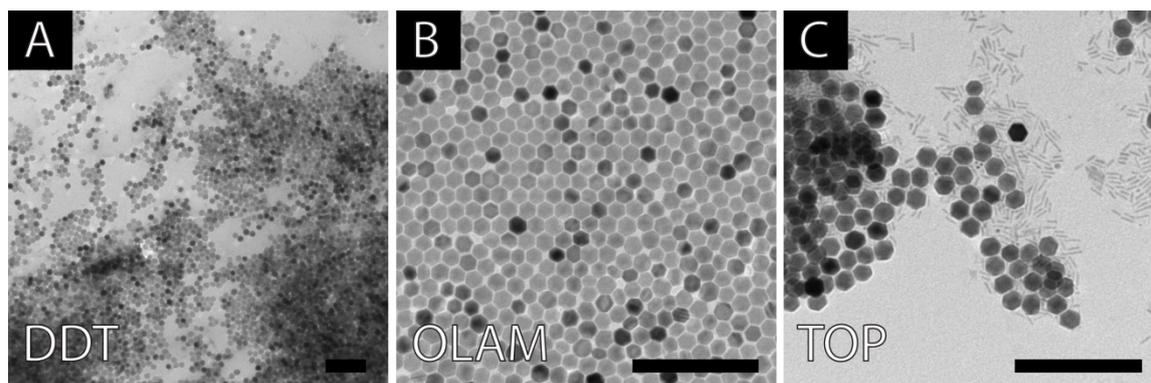


Figure S6. TEM images of the NC solids obtained from self-assembly experiments using hexagonal bipyramid ZnS NCs with different capping ligands: 1-dodecanethiol (DDT, A), additional oleylamine (OLAM, B), and trioctyl phosphine (TOP, C). These experiments show that self-assembled superlattices of ZnS NCs were only obtained when OLAM is used as the capping ligand. Scale bars correspond to 200 nm.

SUPPORTING REFERENCES

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