Supplementary Data for

Designed Two-step Morphological transformations: A new strategy to synthesize uniform metalloporphyrin-containing coordination polymer particles

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Experimental

1. Materials

Zinc 5, 10, 15, 20-tetra(4-pyridyl)-21*H*, 23*H*-porphine (ZnTPyP), Pluronic F-127, β-cyclodextrin from Aldrich Chemical Co., Sodium hydroxide, hydrochloric acid from Wako Chemical were used without further purification. All solvents were prepared by using Milli-Q water. All solvents are prepared in the pure water solvent.

2. Preparation of Stock Solution

2.1 ZnTPyP Stock Solution

The ZnTPyP stock solution (0.01 M) was prepared by dissolving an appropriate amount of ZnTPyP in 0.2 M HCl solution.

2.2 Basic Stock Solution

The basic stock solution was prepared by dissolving an appropriate amount of surfactants and sodium hydroxide in aqueous solution. The surfactants used in this work are Pluronic F-127 and β-cyclodextrin.

The basic stock solution (A) is prepared by dissolving 3 g of Pluronic F-127 and 0.1 g NaOH in pure water solvent.

The basic stock solution (B) composed of 0.1 M of β-cyclodextrin and 0.0125 M NaOH.

The basic stock solution (C) is prepared by dissolving 4 g of Pluronic F-127 and 0.16 g NaOH in pure water solvent.

The Pluronic F-127 solution is prepared by dissolving 3 g Pluronic F-127 in pure water solvent without adding sodium hydroxide.

3. Characterization

Powder X-ray diffraction data were collected on a Rigaku (D/MAX-2500/PC) diffractometer using Cu-Kα radiation (λ= 1.54056 Å) at room temperature. To prepare the samples for field-emission scanning electron microscopy (FE-SEM, TESCAN, MIRA3), the as-prepared ZnTPyP particles were re-dispersed in pure water, dropped onto silicon wafer substrate, and finally dried at 50 ^{o}C in the oven. UV-vis absorption spectroscopy (Lambda 750 UV-vis spectrometer, PerkinElmer), florescence spectroscopy (Nanolog-FluoroLog-3, HORIBA JOBIN YVON) were also measured by dispersing the particles in pure water. The florescence microscopy was measured by Olympus IX71 microscope.

Supplementary Experimental data

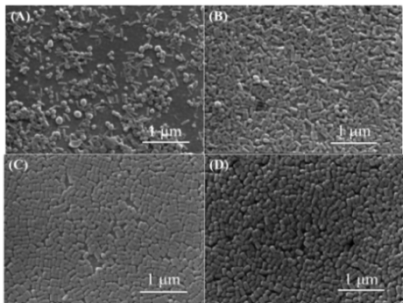


Fig. S1 SEM images of ZnTPyP-CPPS synthesized with different amounts of Pluronic F-127: (A) 0.4g, (B) 1g, (C) 4g, (D) 8g in the basic stock solution. The NaOH concentration is 0.0125 M.

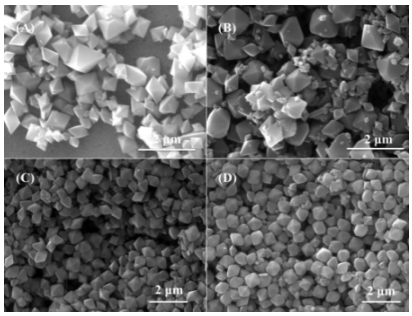


Fig. S2 SEM images of ZnTPyP-CPPs synthesized with different concentrations of β-cyclodextrin: (A) 0.02 M, (B) 0.015 M, (C) 0.01 M, and (D) 0.005 M in the basic stock solution. The NaOH concentration is 0.008 M

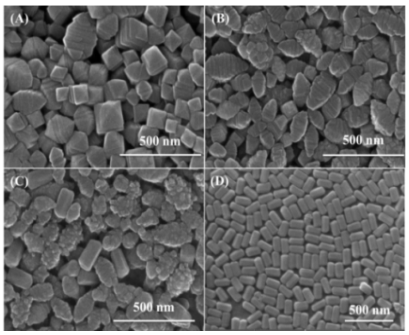


Fig. S3 SEM images of ZnTPyP-CPPs synthesized with different concentrations of NaOH: (A) 0.006 M, (B) 0.008 M, (C) 0.01 M, and (D) 0.0125 M in the basic stock solution. Pluronic F-127 was used as the surfactant and 4g was dissolved in 200 mL pure water solvent.

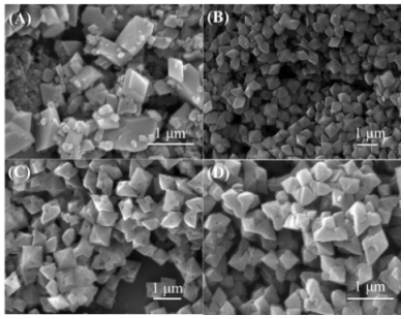


Fig. S4 SEM images of ZnTPyP-CPPs synthesized with different concentrations of NaOH: (A) 0.006 M, (B) 0.008 M, (C) 0.01

M, and (D) 0.0125 M in the basic stock solution. β-cyclodextrin was used as a surfactant, and its concentration was 0.01 M.

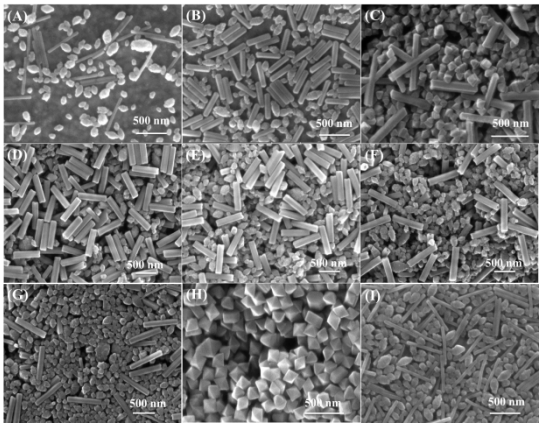


Fig. S5 SEM images of ZnTPyP-CPPs synthesized at different temperatures: (A) 30, (B) 40, (C) 50, (D) 60, (E) 70, (F) 80, (G) 90, (H) 100, and (G) 110 °C. The basic stock solution was prepared by dissolving 4 g Pluronic F-127 and 0.1 g NaOH (0.00125 M) in 200 mL water solvent.

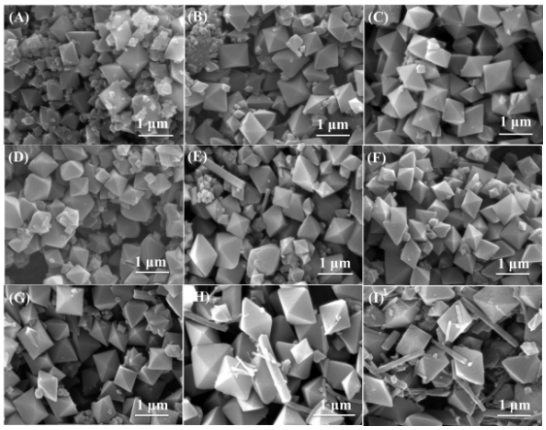


Fig. S6 SEM images of ZnTPyP-CPPs synthesized at different temperatures: (A) 30, (B) 40, (C) 50, (D) 60, (E) 70, (F) 80, (G) 90, (H) 100, and (G) 110 °C. The basic stock solution composed of 0.01 M β-cyclodextrin and 0.008 M NaOH in water solvent.

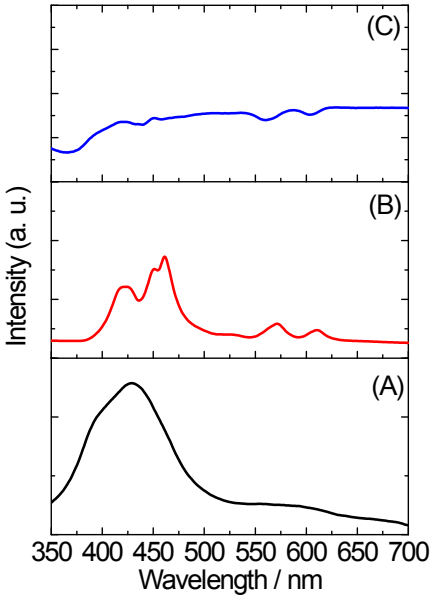


Fig. S7 The electronic adsorption spectra of (A) ZnTPyP monomer together with ZnTPyP-CPPs with (B) nanorod structures synthesized in the Seed-A solution, and (C) four-petal flower structures synthesized in the Seed-B solution.

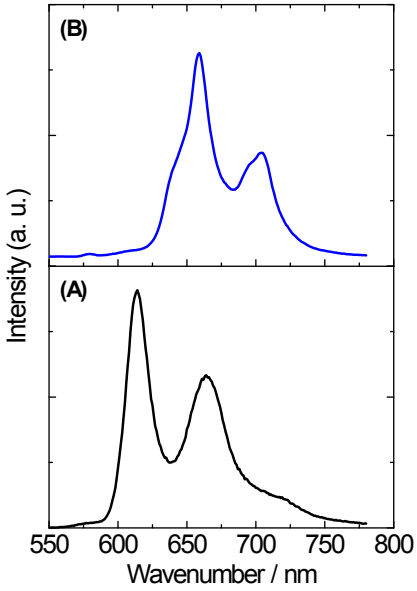


Fig. S8 The fluorescent spectroscopy of (A) ZnTPyP monomer together with ZnTPyP CPPs with (B) nanorod structures synthesized in the Seed-A solution, and (D) four-petal flower structures synthesized in the Seed-B solution.

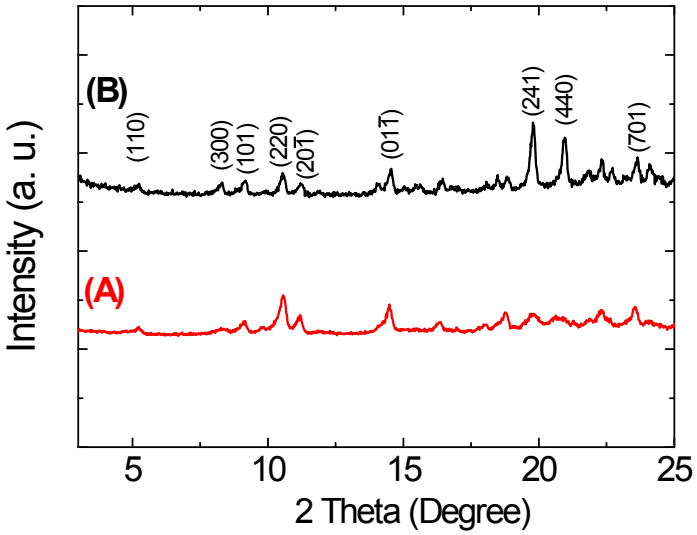


Fig. S9 XRD patterns of ZnTPyP CPPs with (A) nanorod structure synthesized in Seed-A and (B) four-leaf clover structure synthesized in Seed-B solution.

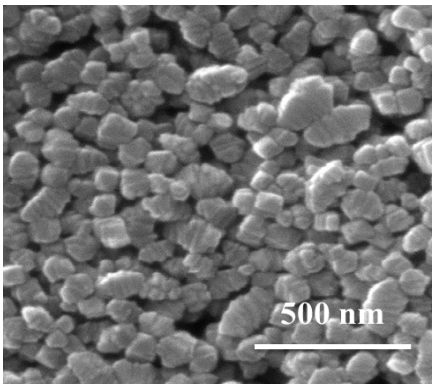


Fig. S10 SEM images of ZnTPyP-CPPs synthesized by diluting Seed-A solution with 7.5 mL of the Pluronic F-127 solution.

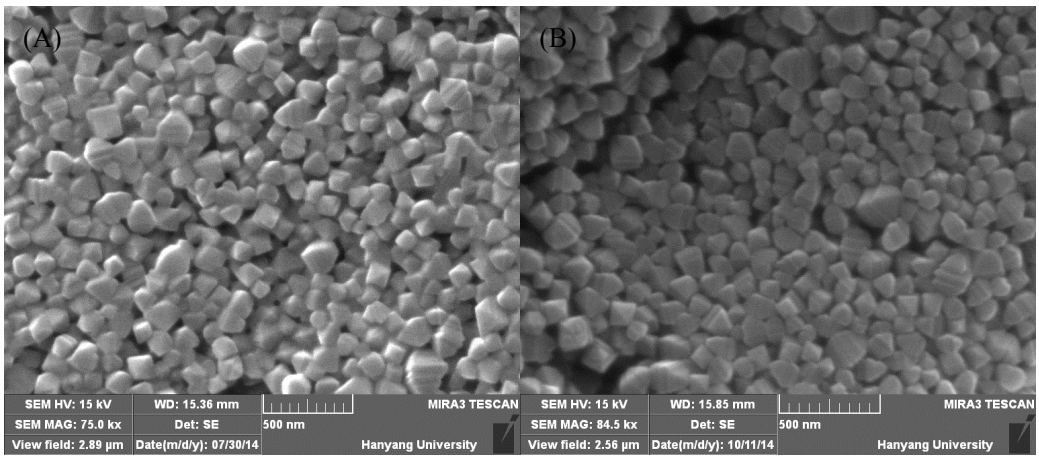


Fig. S11 SEM images of ZnTPyP-CPPs synthesized in the parallel experiments by injecting 7.5 mL of Pluronic F-127 solution and (A) 350 µL and (B) 450 µL of ZnTPyP stock solution.

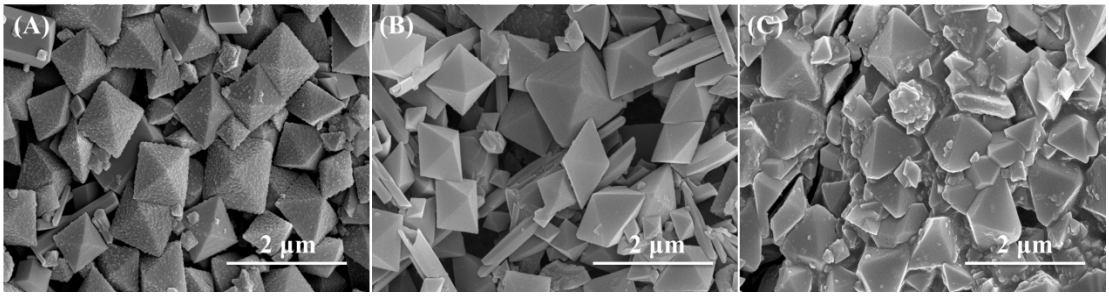
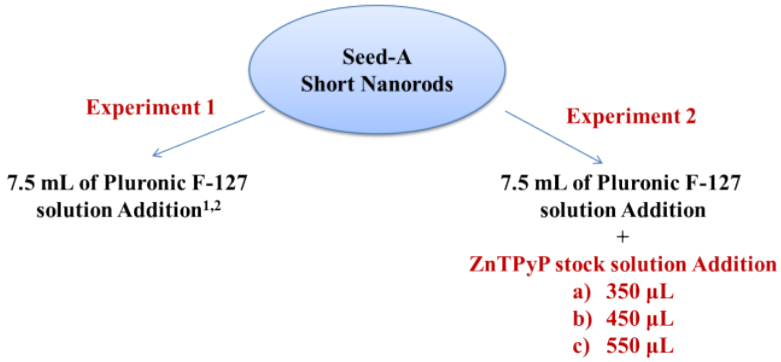


Fig. S12 SEM images of ZnTPyP-CPPs synthesized by injecting (A) 1 mL, (B) 3 mL, and (C) 5 mL of the basic stock solution (B) into the Seed-B solution.

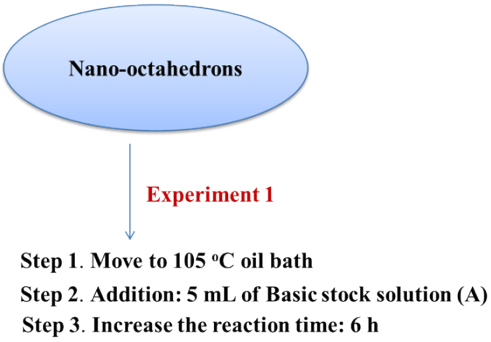
Summary of designed experiments for two-step shape transformation

1. Shape Transformation from Short Nanorod Structures to Nano-octahedron Structures



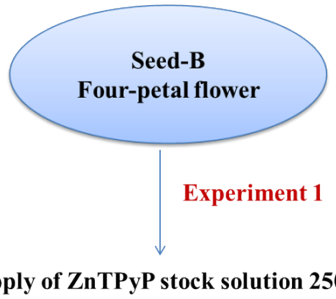
Scheme S1: Illustration of the experimental processes conducted for the shape transformation from short nanorod structures to nano-octahedron structures.

2. Shape Transformation from Nano-octahedron Structures to Long Nanorod Structures



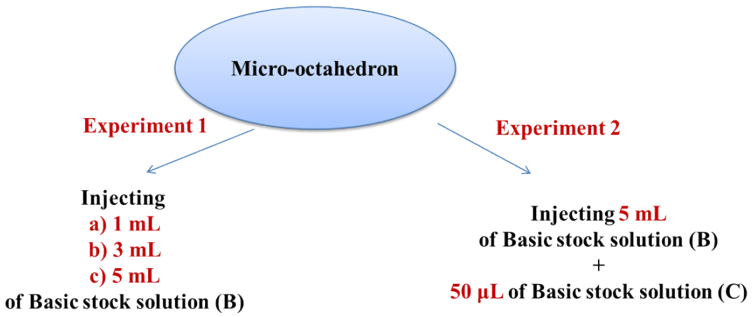
Scheme S2: Illustration of the experimental processes conducted for the shape transformation from nano-octahedron structures to long nanorod structures.

3. Shape Transformation from Micro-octahedron Structures to Nanorod structures



Scheme S3: Illustration of the experimental processes conducted for the shape transformation from four-petal flower structures to micro-octahedron structures.

4. Shape Transformation from Micro-octahedron Structures to Nanorod Structures



Scheme S4: Illustration of the experimental processes conducted for the shape transformation from micro-octahedron structures to nanorod structures.

a) Thermodynamics for shape transformation reactions

The nucleation and growth of nano/micro crystals in solution are related to the Gbbis free energy, which is governed by the atomic chemical potential and surface tension of the crystals. Therefore, the shape conversion

could be driven by reducing or changing the Gibbs free energy of the investigated system, in which the atomic chemical potential could be externally influenced by pressure, temperature, reactant concentration, the solvent used in the self-assembly system, the crystal surface tension influenced by the surfactant, pH, and so on.[8] (According to Wulff theorem (or Wulff Construction), the final morphology is determined by the surface Gibbs free energy. A droplet or crystal will arrange itself such that its surface Gibbs free energy is minimized. (Josiah Willard Gibbs, 1878))

b) Micelle formation

The micelle is defined as particle of colloidal dimensions that exists in equilibrium with the molecules or ions in solution from which it is formed. The shape and size of a micelle are a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength.

c) Inclusion complexes

Some surfactants, such as PF-127, can penetrate into the inner cavity of cyclodextrin, [1] forming an inclusion type of supramolecular complexes.

1. B. J. Ravoo, J. Jacquier and Gerhard Wenz, *Angew. Chem.*, 2003, **115**, 2112.