Supplementary Information

Homogenous Four-Petal Flower Structure formation from metalloporphyrin Self-Assembly and its Reversible Transformation to an Octahedron Structure

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Experimental

1. Materials

Zinc 5, 10, 15, 20-tetra(4-pyridyl)-21H, 23H-porphyrin (ZnTPyP), Pluronic F-127, and ethanol from Aldrich Chemical Co. , Sodium hydroxide, hydrochloric acid from Wako Chemical was used without further purification.

2. **Preparation of stock solution**

2.1 ZnTPyP stock solution

The ZnTPyP stock solution was prepared by dissolving appropriate amount of ZnTPyP in 0.2 M HCl solution, resulting in the final ZnTPyP concentration as 0.01 M. This stock solution turns into brown immediately after the preparation. However, we do not use this brown solution until its colour changed into deep green.

2.2 Basic stock solution

The basic stock solution was prepared by dissolving 4 g Pluronic F127 and 0.1 g sodium hydroxide in 200 mL solvent. In this work, pure water and ethanol/water mixture was used as the solvent for self-assembly process.

2.3 Preparation of the self-assembled ZnTPyP particles

Typically, 250μl of ZnTPyP stock solution was quickly injected into 5 mL of a basic stock solution with vigorous stirring (1400 rmp) at room temperature. The solution turned cloudy immediately after the addition of ZnTPyP stock solution. After 2 h reaction, the mixture was centrifuged and washed with pure water repeatedly in order to remove the surfactant.

Besides, a series of experiment in order to understand how several parameters, including reaction time, concentration of ZnTPyP, and concentration of surfactant, influence the shape evolution have been carried out and the experimental condition are summarized as follows:

(1) The experiemnt condition to investigate the influence of reaction time, amount of surfactant on the shape evolution of nanorod. The SEM images are shown in Figure S1 and S2.

Condition	ZnTPyP Stock Solution μL	Basic Stock Solution			Reaction Time h
		Amount mL	Ethanol-Water Volume Ratio	Amount of Surfacatant g/200 mL	
Figure S1	250	5	0:10	4	0.5, 2, 3, 8, 15
Figure S2	250	5	0:10	0.1, 1, 4, 8	2

(2) The experiment condition to investigate the growth mechanism of the four-petal-flower structure

Condition	ZnTPyP Stock Solution μL	Basic Stock Solution			Reaction time h
		Amount mL	Ethanol-Water Volume Ratio	Amount of Surfacatant g/200 mL	

Scheme 1(A)	250	5	4:6	4	2
Scheme 1(C)	500	5	4:6	4	2
Scheme 1(B)	250 250	5 0	4:6	4	2 2
Scheme 1(D)	500 0	5 5	4:6 4:6	4 4	2 2

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 samples for field-emission scanning electron microscopy (FE-SEM, TESCAN, MIRA3) and the corresponding energy dispersive X-Ray (EDX) spectroscopy, the as-prepared ZnTPyP particles were re-dispersed in pure water, dropped onto silicon wafer substrate, and finally dried at 50 ^{0}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 re-dispersing particles in pure water.

Sumplementary experimental data

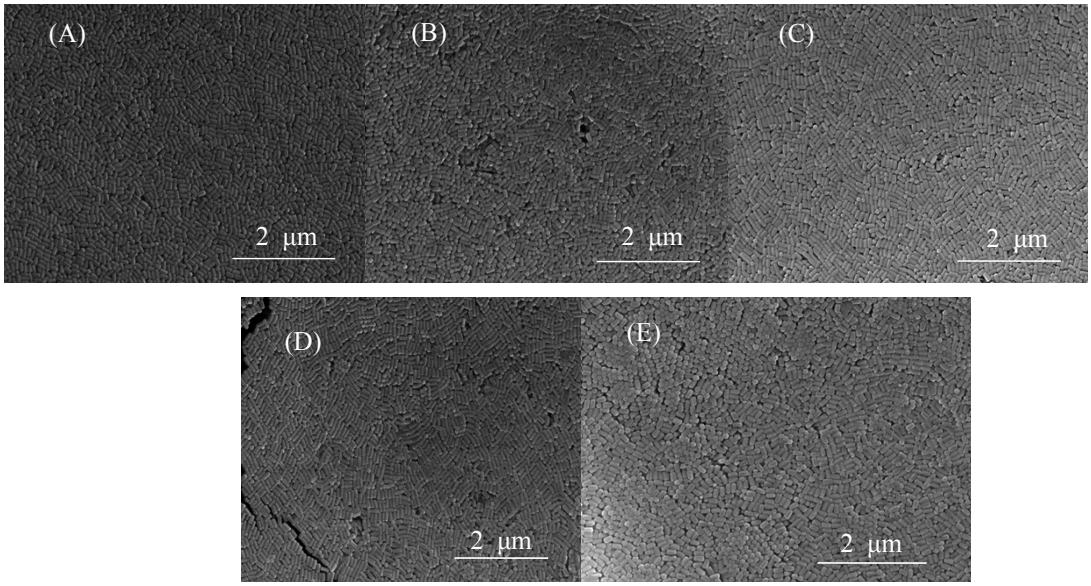


Figure S1: SEM images of ZnTPyP nanorod synthesized within different reaction time: 0.5 h (A), 2 h (B), 3 h (C), 8h (D), and 15 h (E).

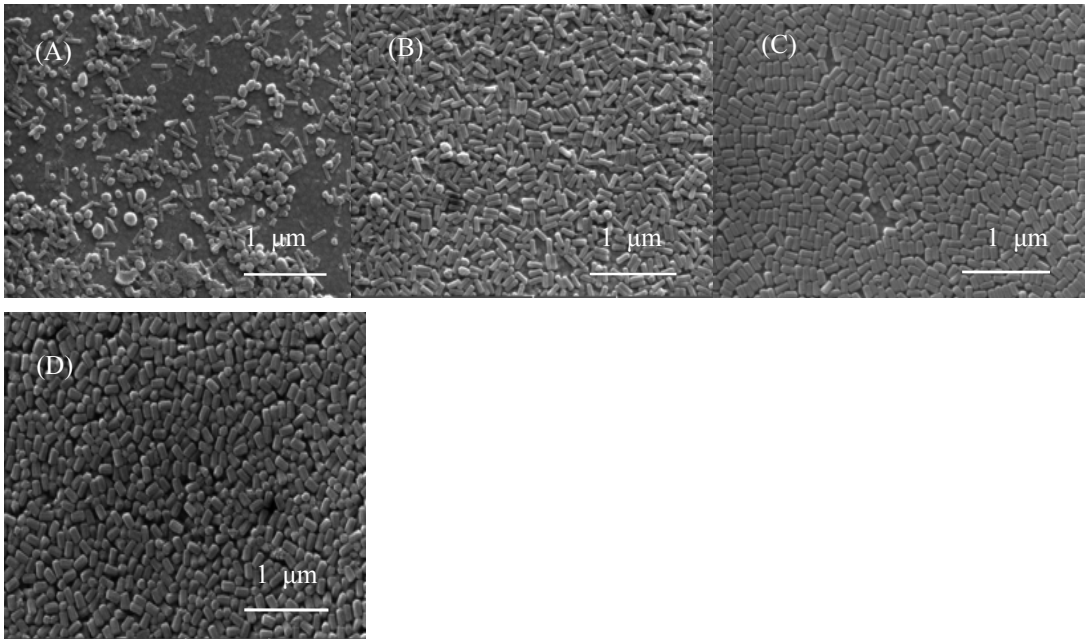


Figure S2: SEM images of ZnTPyP nanorod synthesized with different concentrations of Pluronic F-127: (A) 0.4 g, (B) 1 g, (C) 4 g, and (D) 8 g.

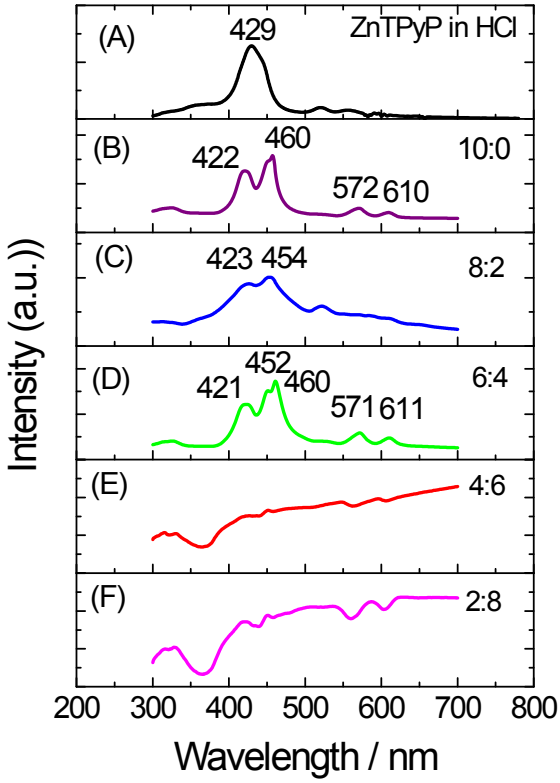


Figure S3: UV-vis spectroscopy of commercial ZnTPyP dissolving in a HCl solution (A) and the self-assembled ZnTPyP partilces synthesized in the water-ethanol solution with the volumetric ratio (B) 10:0, (C) 8:2, (D) 6:4, (E) 4:6, (F) 2:8.

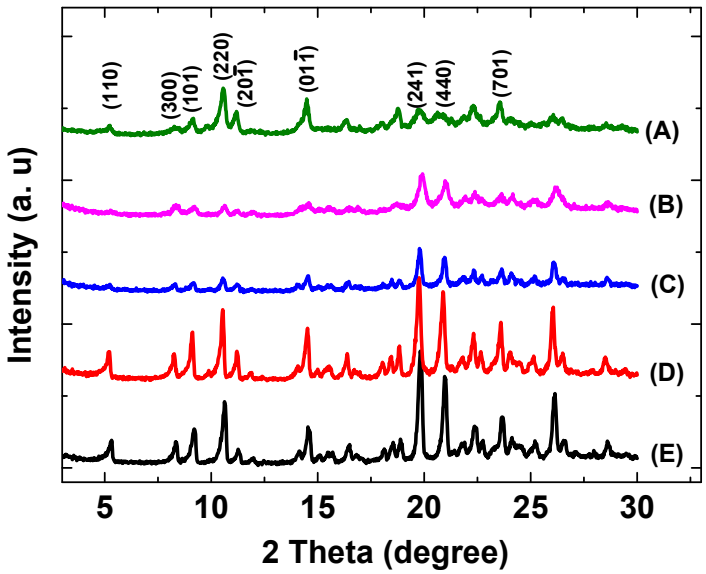
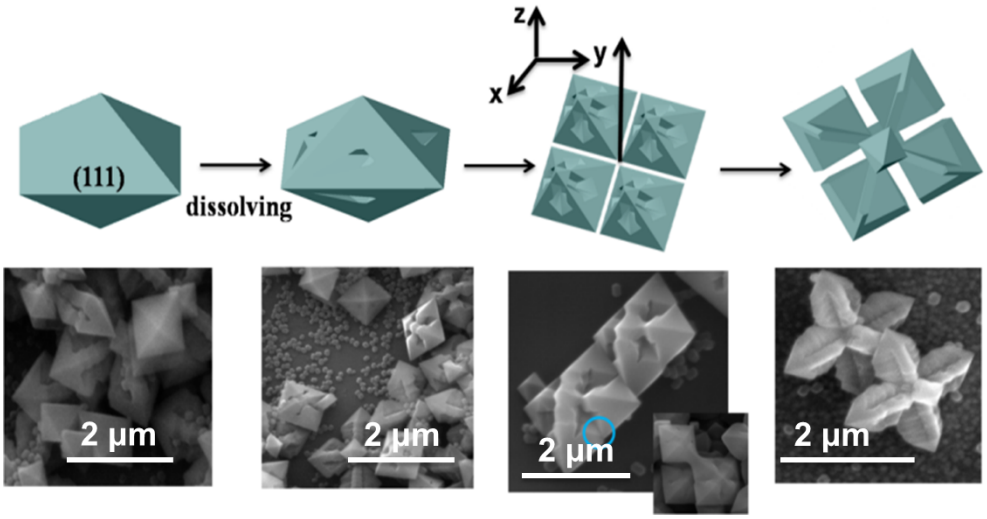


Figure S5: XRD patterns of the self-assembled ZnTPyP particles synthesized in the water-ethanol solution with the volumetric ratios of (A) 0:10, (B) 2:8, (C) 4:6, (D) 6:4, (E) 8:2.



Scheme S1: Illustration of another possible growth pathway of ZnTPyP four-petal flower structure

The reasons that lead us to this hypothesis are: (1) two octahedrons are found to be connected in the (100) direction; (2) unlike the sunken octahedron structure before forming the four-petal-flower structure, we found each edge of the sunken octahedron disconnected exactly at the center and the resultant two halves are not in direct line with each other; (3) although octahedrons and sunken octahedron structures were observed, still, we found that the length of the diagonal line of four-petal flower is almost two times larger than that of octahedron

or sunken octahedron. The third reason can be explained by the continuous growing, however, there is indeed another possibility that four small octahedrons were arranged together.

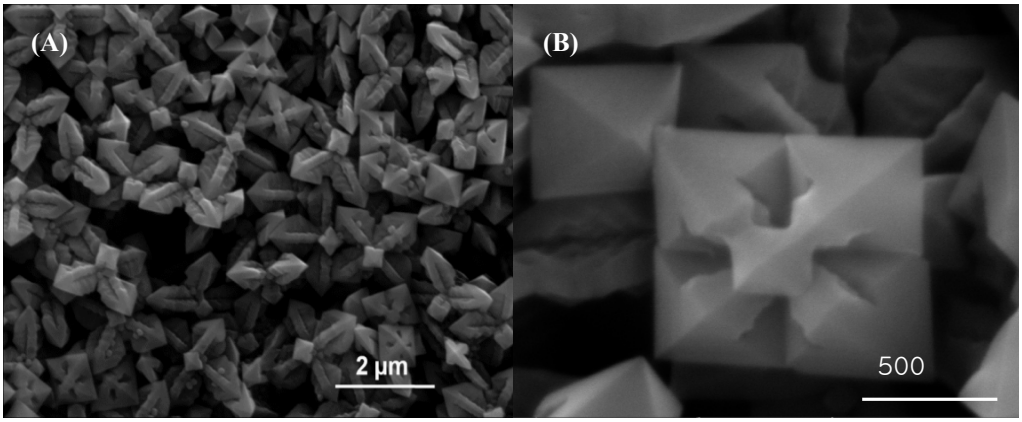


Figure S6: SEM images of ZnTPyP particles synthesized within 10 s. Except the reaction time, other synthesis conditions (the concentration of surfactant (4g), the amount of ZnTPyP 250 µl, etc) are as same as descrebied in experimental section. The solvent is water-ethanol mixture with the volumetric ratio as 6:4. (A) Lower magnifi cation and (B) higher magnification.