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COMMUNICATION

Designed Two-step morphological transformations: A new strategy to synthesize uniform metalloporphyrin-containing coordination polymer particles[†]

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Inspired by the shape evolution of metalloporphyrin-containing coordination polymer particles (CPPs), morphological transformation reactions were carried out, and for the first time we achieved facile two-step shape transformations, illustrating a new strategy to synthesize CPPs in a controlled manner.

Nano/micro-scale coordination polymer particles (CPPs) in which metal ions or metal clusters are connected by molecular building blocks have attracted exceptional attentions during recent decades because of their useful applications in electronics, gas storage, optics, sensing, catalysis, and so on.¹⁻⁵ In 1989, top-down and bottom-up strategies were introduced into the field of nanotechnology for manufacturing various structures. The top-down method often uses external tools to shape materials into the desired shapes or orders, which is quite difficult to apply to fragile organic materials. In contrast, the bottom-up method uses the physical or chemical properties of single molecules to synthesize various structures through self-assembly or self-organization processes. Porphyrins offer several attractive properties for molecular self-assembly and have been used in catalysis, fluorescence, optical imaging, sensing, photochemistry, electronics, and biology applications.^{6,7} Also, the aggregation and dimerization of porphyrins have been documented to affect their spectral and energetic characteristics as well as their efficacy in several applications.⁶ It is of fundamental interest in the field of coordination polymer materials to investigate their structural variations. Therefore, various pathways have been developed for the synthesis of metalloporphyrin-containing CPPs, including precipitation, solvothermal synthesis and reverse micro-emulsion methods.^{6,7} In our previous work, reversible transformation between four-petal flower structures and octahedron structures was achieved

by controlling the metalloporphyrin concentration in the reaction solvent.^{7(f)} This phenomenon suggests that different structures are possibly related to each other and one structure can be transferred to another depending on the synthesis conditions. It was documented that the nucleation and growth of nano/micro crystals in solution are related to the Gibbs 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 Here, we first investigated the shape evolution of zinc 5, 10, 15, 20-tetra(4-pyridyl)-21*H*,23*H*-porphine (ZnTPyP)-CPPs influenced by surfactants, reaction temperature, pH in the reaction solvent by the traditional bottom-up method. Based on the synthesized CPPs, a new strategy was developed, aiming at manufacturing CPPs through the morphological transformation reactions in a designable and controllable manner. As ZnTPyP does not readily dissolve in water, a homogeneous solution of ZnTPyP can be prepared by acidifying its pyridyl groups to form soluble tetrapyrroline cations that will be deprotonated via an acid-base neutralization reaction when the ZnTPyP acid solution is injected into a basic aqueous solution of surfactants, producing ZnTPyP aggregates within the micelle interiors.⁹ The details of the experimental conditions are shown in the Electronic Supplementary Information (ESI) [†].

The shape evolution of ZnTPyP-CPPs depends on the choice of surfactant and its related micelles; a series of experiments using two kinds of surfactants in varying amounts was first carried out. Fig. S1[†] shows the SEM images of ZnTPyP-CPPs fabricated using

Pluronic F-127 as a surfactant in pure water solvent. Uniform hexagonal nanorod structures were synthesized. The average length of the nanorods varied with the surfactant concentration, showing a length decrease from ~190 nm to ~145 nm with increasing Pluronic F-127 concentration. No other structure was fabricated if pure water was used as the solvent. Fig. S2† shows the SEM images of the ZnTPyP-CPPs fabricated by using β -cyclodextrin as a surfactant in pure water solvent. In contrast to the experiments using Pluronic F-127 as a surfactant, only octahedron-like structures were formed, not rod-like structures. Under higher β -cyclodextrin concentrations, both large- and small-sized octahedrons were formed; uniform octahedron structures were fabricated under lower β -cyclodextrin concentrations. These experiments indicated that the shape evolution of ZnTPyP-CPPs relies on the choice of surfactants: rod-like structures are preferentially formed in the presence of Pluronic F-127 in pure water solvent at room temperature, whereas octahedron-like structures were fabricated with β -cyclodextrin as a surfactant.

We then investigated how NaOH concentration in the basic stock solution affects the shape evolution of ZnTPyP-CPPs. The SEM images obtained by using Pluronic F-127 as a surfactant and with different NaOH concentrations are shown in Fig. S3†. When the NaOH concentration was 0.006 M (Fig. S3(A)†), octahedron structures with terraces were formed. With the concentration increase, oval structures, also with terraces, were fabricated instead of octahedron structures. When NaOH concentration was increased to 0.01 M, nanorod structures and disordered structures were synthesized. Uniform nanorod structures were finally fabricated when the concentration was increased to 0.0125 M. Fig. S4† shows the SEM images obtained using β -cyclodextrin as a surfactant with different NaOH concentrations. When the NaOH concentration was 0.006 M, octahedron structures together with irregular structures were fabricated. Interestingly, uniform octahedron structures and four-leaf clover structures were formed at 0.008 M and 0.0125 M, respectively. These experiments indicated that lower NaOH concentration facilitated the formation of octahedron structures and rod-like structures were preferred under higher NaOH concentration when using Pluronic F-127 as a surfactant; when using β -cyclodextrin as a surfactant, octahedron structures formed under lower NaOH concentration and four-leaf clover structure formed under higher NaOH concentration.

Finally, we investigated the shape evolution of ZnTPyP-CPPs by reaction temperature. Fig. S5† shows SEM images obtained at different reaction temperature when using Pluronic F-127 as a surfactant. Nanorod structures together with spherical ones were synthesized at 30 and 40 °C and the average length of nanorods decreased as the temperature increased. At 50 °C, small octahedron structures together with rod-like structures were synthesized. At 60, 70, and 80 °C, rod-like structures and disordered structure were formed and the yield of rod-like structures decreased as the temperature increased. At 100 °C, octahedron structures were fabricated. Disordered structures together with a small number of nanorod structures were synthesized at 90 and 110 °C. When using β -cyclodextrin as a surfactant (Fig. S6†), octahedron structures were fabricated as the main product in the whole temperature range. The temperature change did not affect the formation of octahedron structures, but rod-like structures emerged at high temperature (100 and 110 °C). This temperature-dependence

experiment revealed that, in the presence of Pluronic F-127, the main product changed with temperature, leading to the formation of rod-like structures (nanorod and nanotube) and octahedron structures. In contrast, the main product was unaffected by temperature when β -cyclodextrin was used as a surfactant.

As just described, we investigated how the choice of surfactants, NaOH concentration in the basic stock solution, and reaction temperature influenced the shape evolution of ZnTPyP-CPPs. We found that NaOH concentration in the basic stock solution, not reaction temperature, affected the final shapes of ZnTPyP-CPPs when β -cyclodextrin was used as a surfactant, and both reaction temperature and NaOH concentration in the basic stock solution played important roles in the shape evolution of ZnTPyP-CPPs in the presence of Pluronic F-127 as a surfactant. Furthermore, we realized from these results that morphological transformation between different structures could be made by adjusting the experimental conditions. We thus designed and carried out a series of experiments according to these results to achieve shape transformations.

We injected 250 μ L of the ZnTPyP stock solution into 5 mL of basic stock solution (A) prepared by dissolving 0.1 g NaOH and 3 g Pluronic F-127 in 200 mL of pure water solvent with vigorous stirring for 1 h at room temperature. This solution was taken as a seed solution (Seed-A). We also injected 250 μ L of the ZnTPyP stock solution into 5 mL of basic stock solution (B), which composed of 0.125 M NaOH and 0.01 M β -cyclodextrin, with vigorous stirring at room temperature for 1 h. This solution was also taken as a seed solution (Seed-B). As shown in Fig. 1(A), hexagonal nanorods with an average length of ~170 nm and average width of ~60 nm were synthesized in the Seed-A solution. Four-petal flower structures at the micrometer scale were fabricated in the Seed-B solution (Fig. 1(C)). As mentioned in the previous report, (metallo)porphyrin aggregation and aggregation type can be detected through spectrum changes in the degenerated Soret band by comparison with a porphyrin monomer.^{9(c)} Fig. S7(B)† and S7(C)† show the electronic absorption spectra of ZnTPyP-CPPs synthesized in Seed-A and Seed-B solutions, respectively. As a reference, the electronic structure of the ZnTPyP monomer, which was prepared by dissolving commercial ZnTPyP in a HCl solution, was determined and shown in Fig. S7(A)†. The single Soret band (429 nm, Fig. S7(A)†) is split into two bands with a weaker intensity peak at 422 nm and a stronger intensity peak at 462 nm for nanorod structures. The two Q bands of nanorod structures are shifted to lower energy. Therefore, nanorod structures synthesized in the Seed-A solution are aggregated by J-type aggregation. Different from our previous report,^{9(c)} the adsorption spectra of four-petal flower structures did not appear, probably due to the inhomogeneous formation of both large-sized and small-sized four-petal flower particles. The particles were further characterized by fluorescent microscopy (FM, Figure 1(B), 1(D)), showing the fluorescent property in the red region of the spectrum. The fluorescent spectroscopy measurement matched well with the FM images, showing intense emission bands in the wavelength region from ~600 to ~700 nm (See the ESI,† Fig. S8).

Variation in the microstructures of the nanorod structures and four-petal flower structures was analysed by XRD measurement (See the ESI,† Fig. S9). All structures showed similar XRD patterns, which indicated that the internal structure of the one-dimensional nanorod structures was similar to that of the three dimensional four-

petal flower structures. Also, the observed peaks of the nanorods and four-petal flower structures are well-matched with the simulated peaks calculated by another group^{10(a)} on the basis of a study of the crystal structures of ZnTPyP compounds.^{10(b-d)}

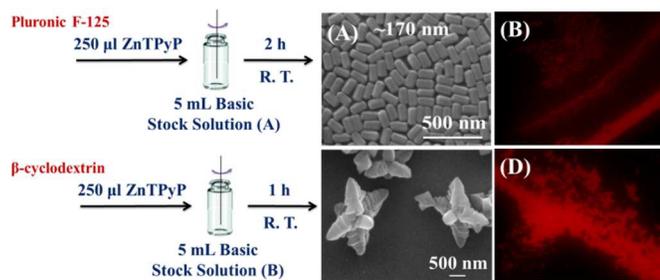


Fig. 1 Illustration of the preparation of seed structures: SEM images of ZnTPyP-CPPs synthesized in the Seed-A solution (A) and in the Seed-B solution (C); FM images of ZnTPyP-CPPs synthesized in the Seed-A solution (B) and in the Seed-B solution (D).

For the morphological transformation of nanorod structures synthesized in the Seed-A solution, we added 7.5 mL Pluronic F-127 solution to the Seed-A solution with vigorous stirring for 1 h, aiming at a shape transformation from nanorod structures to octahedron structures as they were fabricated under low NaOH concentration. The Pluronic F-127 solution was prepared by dissolving Pluronic F-127 in aqueous solution without adding sodium hydroxide, which is different from basic stock solution (A). However, the nanorod structures did not become octahedron structures, but partially changed into disordered structures (See the ESI,† Fig. S10.). This experiment indicated that even though we adjusted the NaOH concentration to conditions suitable for the micelle formation of octahedron structures, the nanorod structures could not be transformed into octahedron structures by pH adjustment alone. However, from a volume viewpoint, we noticed that it would probably be feasible to transform nanorod structures to octahedron structures by adjusting the NaOH concentration and supplying enough ZnTPyP at the same time. Therefore, we carried out a series of experiments by injecting different amounts of the ZnTPyP stock solution and 7.5 mL of the Pluronic F-127 solution into the Seed-A solution. We found that the octahedron structure was fabricated when 550 µL of ZnTPyP stock solution and 7.5 mL of Pluronic F-127 solution were injected simultaneously (Fig. 2(A)). If the ZnTPyP supply was less than 550 µL, octahedron structures with terraces formed, indicating the regrowth of ZnTPyP monomers on nanorod structures (See the ESI,† Fig. S11.). Different from the shape transformation of nanorod structures to octahedron structures, which rely on ZnTPyP re-growth, the morphological transformation from octahedrons to nanorods requires ZnTPyP re-dissolution. The temperature-dependence experiment showed that octahedron structures were formed at 105 °C, which reveals that the micelle formation at this temperature is also suitable for the formation of octahedron structures. In the previous report, we achieved a reversible shape transformation between four-petal flower structures and octahedron structures by adjusting only the ZnTPyP concentration in the reaction solvent. Here, we assume that octahedron structures could be transformed into nanorod

structures at high temperature by diluting the reaction solvent. Therefore, octahedron structures were transferred into an oil bath at 105 °C, and 5 mL of basic stock solution (A) was injected into the reaction solution with vigorous stirring for 6 h. As shown in Fig. 2(B), nanorod structures, as the main products, were finally fabricated from octahedron structures. However, the average length of the nanorod structures transferred from the octahedron structures is longer than that of nanorod structures synthesized in the Seed-A solution, with an average length of ~395 nm. Disordered structures were also formed as side products.

The morphological transformation of four-petal flower structures was carried out by injecting 250 µL of the ZnTPyP stock solution into the Seed-B solution. After 1 h, the mixture was centrifuged and washed with pure water repeatedly to remove the surfactants. A similar method had been used in our previous report to transform four-petal flower structures into octahedron structures using Pluronic F-127 as a surfactant in an ethanol-water solvent. As shown in Fig. 2(C), micro-octahedron structures were synthesized from the four-leaf clover structure. However, the reversible transformation from octahedron structures to four-petal flower structures was not achieved by diluting the reaction solvent with 5 mL of basic stock solution (B), which is quite different from what we obtained before.^{7(f)} The SEM images obtained by injecting different amounts of the basic stock solution into the solution containing octahedron structures are shown in Fig. S12,†, revealing that no morphological transformation could be triggered by simply diluting the reaction solvent. Because we confirmed that rod-shaped ZnTPyP-CPPs were preferentially synthesized when using Pluronic F-127 as a surfactant, we tried to dilute the reaction solvent by injecting 5 mL of basic stock solution (B) together with 50 µL of Pluronic F-127 basic stock solution (C), which was prepared by dissolving 4 g Pluronic F-127 and 1.6 g NaOH in 200 mL of pure water solvent. After 1 h of vigorous stirring, the mixture was centrifuged and repeatedly washed with pure water to remove the surfactant. We found that micro-octahedron structures were transformed into hexagonal nanorod structures with an average length of ~400 nm and an average width of ~80 nm. The FM images indicated that nano-octahedron structures (Fig. 2(A)) transformed from nanorod structures (Fig. 1(A)), long nanorod structures (Fig. 2(B)) transformed from nano-octahedron structures, micro-octahedron structures (Fig. 2(C)) transformed from four-petal flower structures (Fig. 1(C)), and hexagonal nanorod structures (Fig. 2(D)) transformed from micro-octahedron structures are also fluorescent in the red region of the spectrum, which is quite reasonable as all these structures are transformed from seed structures step by step. The detail description of designed two-step shape transformations is shown in the ESI by Scheme S1, S2, S3, and S4.†

In conclusion, we have investigated the shape evolution of ZnTPyP-CPPs synthesized by traditional self-assembly method assisted by surfactants and have synthesized various ZnTPyP-CPPs with different structures. It was found that the NaOH concentration in the basic stock solution affected the shape evolution of ZnTPyP-CPPs when using β-cyclodextrin as a surfactant, and that both NaOH concentration in the basic stock solution and temperature influenced shape evolution of ZnTPyP-CPPs when using Pluronic F-127 as a

surfactant. For the first time, we achieved a two-step shape transformation from short nanorod structures to nano-octahedron structures and then to long nanorod structures in the presence of Pluronic F-127 as a surfactant and from four-petal flower structures to micro-octahedron structures and then to nanorod structures in the presence of β -cyclodextrin as a surfactants. All particles are fluorescent in the red region of the spectrum. We illustrated a new strategy to synthesize uniform CPPs through shape transformation reactions in a designable and controllable manner. As a member of the porphyrin family, ZnTPyP shares a similar molecular structure to its photoactive counterparts such as chlorophyll and heme, the further application of synthesized ZnTPyP-CPPs as photocatalysts is under investigation.

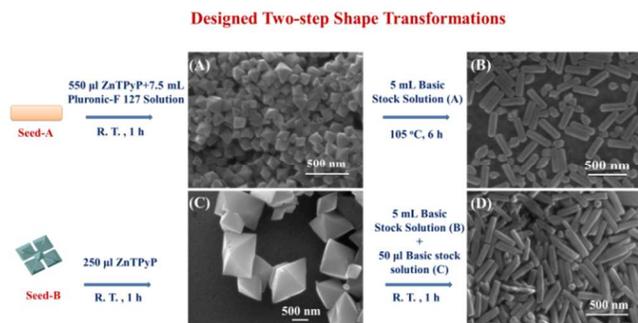


Fig. 2 Illustration of designed two-step shape transformations from nanorod structures in the Seed-A solution and four-petal flower structures in the Seed-B solution to other structures: (A) nano-octahedron structures, (B) long nanorod structures, (C) micro-octahedron structures, and (D) hexagonal nanorod structures.

Experimental

Typically, 250 μ L of a ZnTPyP stock solution was injected into 5 mL of a basic stock solution with vigorous stirring. The solution turned cloudy immediately after the addition of ZnTPyP stock solution. After 1 h reaction, the mixture was centrifuged and washed with pure water repeatedly in order to remove the surfactants.

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Notes and references

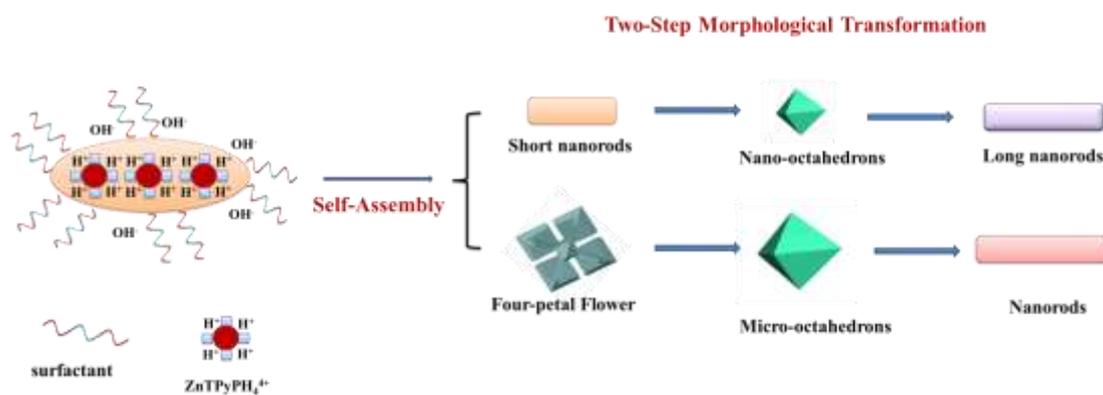
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Designed Two-step Morphological Transformations: A New Strategy to Synthesize Uniform Metalloporphyrin-containing Coordination Polymer Particles

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Uniform metalloporphyrin-containing coordination polymer particles were synthesized from seed structures by designed two-step morphological transformation.