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COMMUNICATION

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

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012Y. Sun,^a B. Y. Yoo^{a,b}

DOI: 10.1039/x0xx00000x

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A uniform four-petal flower structure was homogeneously synthesized through metalloporphyrin self-assembly and its growth pathway has been proposed. For the first time, we illustrated that it is possible to reversibly transform between the octahedron structure and the four-petal structure by controlling the Gibbs energy of the self-assembly system.

Self-assembly driven by non-covalent interactions, a bottom-up strategy, has attracted considerable attention not only because it provides practical and promising methods for the manufacture of a broad range of nano/micrometer-sized objects, but also because it is useful for exploring the growth mechanism of organic and/or inorganic crystals.¹ As one of the most promising building blocks for self-assembly, porphyrin, as well as its related compounds and metalloporphyrins, offers several attractive properties for molecular self-assembly and has been utilized in catalysis, fluorescence, sensing, optical imaging, electronics, photochemistry, and biology applications.^{2,3} The aggregation and dimerization of porphyrins and metalloporphyrins have been reported to influence their spectral and energetic characteristics as well as their efficacy in several applications. Thus, it is important to obtain the detailed information about the formation dynamics and the typology of aggregates.^{2,4} It has been well documented that the aggregation of (metallo-)porphyrins is promoted by various non-covalent interactions, such as π - π interactions, van der Waals interactions, intermolecular electrostatic interactions, hydrogen bonding, hydrophilic-hydrophobic interactions, and metal-ligand coordination.²⁻⁷ The (metallo-)porphyrin self-assembly process can proceed homogeneously⁵⁻⁷ in solution and heterogeneously at a solution-surface interface⁸ or upon vapour deposition of the constituents⁹. In many studies, the former process has been confirmed to produce various uniform structures with the aid of surfactants in either inorganic (mainly in water)^{4,5} or organic solvents^{6,7}.

In this work, we choose metalloporphyrin, zinc 5, 10, 15, 20-tetra(4-pyridyl)-21H, 23H-porphine (abbreviated to ZnTPyP), to investigate the self-assembly process and the evolution of various micro and/or nano structures. As ZnTPyP does not readily dissolve in water, a homogeneous solution of ZnTPyP was prepared by either acidifying its pyridyl groups to form soluble tetrapyrnidinium cations

or dissolving in organic solvent. The encapsulation and self-assembly processes were then initiated by adding the acidic ZnTPyP aqueous solution to a basic aqueous solution of surfactants^{4,5} or by adding the ZnTPyP organic solvent to the aqueous solution of surfactants,^{6,7} respectively. Here, we used the former process as the latter one usually requires a long time of aging during the self-assembly process. The acid-base neutralization reaction deprotonates the tetrapyrnidinium cations, producing insoluble ZnTPyPs, which is then, encapsulated within the micellar interiors of the surfactants. Therefore, micelle formation directly influenced the morphology of self-assembled ZnTPyP particles. Among all factors affecting micelle formation, the choice of solvent, in which the surfactant is dissolved, is considered as the most significant. It was also reported that irregular hexagonal nanorods were obtained instead of well-defined nanorods due to the fact that the surfactant used during self-assembly does not form stable micelles in alcohol media.^{5a} Thus, it is not possible to encapsulate hydrophobic ZnTPyPs for further molecular self-assembly. However, we believe that the use of alcohol as a co-solvent for ZnTPyP self-assembly actually changes the micellation and gelation processes to form different kinds of micelles depending on surfactants used and the interaction between surfactant and solvent.¹⁰

Therefore, based on the above-mentioned viewpoint towards how alcohol as a co-solvent influences the shape evolution of ZnTPyP self-assembly caused by diverse micelle formation, a series of experiments was first carried out by using ethanol as a co-solvent and Pluronic F-127 as the surfactant. Briefly, 250 μ L of a 0.01 M ZnTPyP stock solution was quickly injected into 5 mL of a basic stock solution, which was prepared by dissolving 4 g Pluronic F127 and 0.1 g NaOH in 200 mL solvent. (The basic stock solution was also referred to as the self-assembly solvent.), under vigorous stirring at room temperature. The solution turned cloudy immediately after the addition. After 2 h of reaction, the mixture was centrifuged and repeatedly washed with pure water in order to remove the surfactant. The detail experimental conditions are described in the supplementary data. A range of nano-/microscale structures was fabricated through the ZnTPyP self-assembly under different solvent conditions, as shown in Figure 1. When pure water

was used, uniform hexagonal ZnTPyP nanorods (Figure 1(A)) with a diameter of ~ 30 nm and a length of ~ 170 nm were synthesized. The self-assembly process of ZnTPyP in pure water with the same reaction time but under different concentrations of Pluronic F-127 was also investigated, revealing that uniform hexagonal nanorods with different lengths and widths were synthesized depending on the surfactant concentration. (See the supplementary data, Figure S1). In the case of self-assembly in pure water with a fixed concentration of Pluronic F-127, uniform nanorods with the same length and width were synthesized, independent of the chosen reaction time. (See the supplementary data, Figure S2). No other structure was fabricated if pure water was employed as the solvent. The same nanorod structure fabricated from ZnTPyP self-assembly was previously reported.^{5b} When ethanol was introduced into pure water (v/v, H₂O:C₂H₅OH = 8:2), an irregular structure formed in addition to the regular nanorod structure (Figure 1(B)). Interestingly, when the volume ratio of water to ethanol was adjusted to 6:4, a uniform four-petal flower structure (Figure 1(C)) was fabricated with an average diagonal line length of ~ 2.2 - 2.5 μm . Although a similar “four-leaf clover structure” has been synthesized heterogeneously^{8a} or from a mixture of two kinds of porphyrin,¹¹ detailed observation revealed that the four-petal flower structure produced in our study was different in that a rod-like structure was implanted in each “flower petal” and the “pistil” of this four-petal flower is a tiny tetrahedron. As the volume ratio of water to ethanol reduced to 4:6, a hollow micro-cross, and an octahedron structure were synthesized (Figure 1(D)). Nevertheless, the size and shape of the octahedron structures were quite variable, no single uniform structure existed. Furthermore, random and irregular octahedrons and belt-like structures (Figure 1(E)) were formed as the ratio decrease to 2:8. ZnTPyP self-assembly was not performed in a pure ethanol solution due to the insolubility of ZnTPyP in pure ethanol.

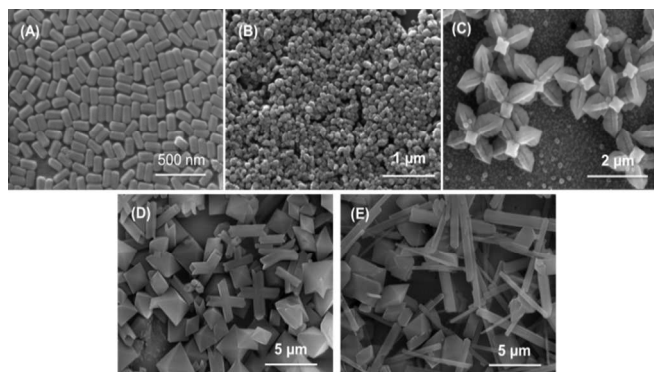


Figure 1. SEM images of self-assembled ZnTPyP particles synthesized in the water-ethanol solutions with the volumetric ratios of (A) 10:0, (B) 8:2, (C) 6:4, (D) 4:6, and (E) 2:8.

The intensity and color of porphyrins are derived from the highly conjugated π -electrons systems and the most fascinating feature of porphyrins is their characteristic UV-visible spectra.¹² In addition, porphyrin aggregation and its aggregation type can be detected through spectrum changes of the degenerated Soret band by comparing it with the one of porphyrin monomer.¹² Figure S3 compares the electronic absorption spectra of self-assembled ZnTPyP particles synthesized in water-ethanol solutions. As a reference, the electronic structure of ZnTPyP monomer which was

prepared by dissolving commercial ZnTPyP in a HCl solution was determined (Figure S3(A)), showing a single Soret band at 429 nm and two weak Q bands at 555 and 585 nm. In Figure S3(B), the single Soret band is split into two bands, with a weaker intensity peak appearing at 421 nm and a stronger intensity peak appearing at 460. The two Q bands are shifted to a lower energy at 571 nm and 610 nm. As shown in the SEM images, a uniform nanorod structure (Figure 1(A)) was fabricated in pure water. The same absorption bands including the split Soret band and two Q bands were found at the same positions for the four-petal flower structure (Figure S3(C)). These results suggest the formation of J-type aggregation with an edge-to-edge molecular arrangement in the ZnTPyP nanorod and four-petal flower structures. For the self-assembled ZnTPyP particles with an irregular structure (Figure 1(B)), the single Soret band also split into two bands but was not well-separated, suggesting that the particles are not fully aggregated (Figure S3(B)). However, we were not able to obtain the absorption spectra for the self-assembled ZnTPyP particles synthesized in the water-ethanol solvents with ratios of 4:6 (Figure 1(D)) and 2:8 (Figure 1(E)) (See Figure S3(D, E)) because large ZnTPyP particles cannot be dispersed uniformly in water solvent without any treatment and therefore cannot be detected by UV-Vis spectroscopy. As shown in Figure S3, the degrees to which the absorption spectra shifted for both the Soret and Q bands of the nanorods, irregular structure, four-petal flower structure, and other structures of the ZnTPyP monomer are different, indicating the effect of the various molecular interactions on the molecular packing conformation in the aggregates due to the introduction of ethanol and surfactant.

The variation of the microstructures with the different volumetric ratios of water to ethanol was analyzed by XRD measurements (See supplementary data, Figure S5). The observed peaks from all particles with different morphologies well matched with the simulated peaks calculated by another group,^[6b] which were obtained on the basis of the former study of the crystal structures of ZnTPyP compounds.¹³ The XRD patterns clearly indicate that ratios of water to ethanol of 4:6 and 2:8 produced strong relative peak intensities. Such intense peaks may be caused by facets of the microstructures. As shown in Figure 1, the hollow tubes ((D), vol.4:6) and hollow micro-crosses consisted of planar facets. On the other hand, the microstructures from the water-dominated solutions had rounded planes, which could decrease the intensity of the XRD peaks.

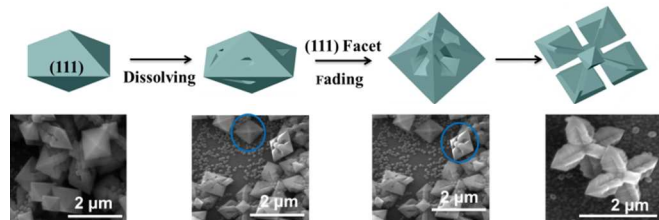
The SEM images and the analysis of the UV-Vis results indicate that the addition of ethanol to pure water as a co-solvent for ZnTPyP self-assembly with the aid of Pluronic F-127 as a surfactants triggered shape change resulting in the formation of various structures, such as octahedrons, hollow crosses, and belt-like structures and that J-type aggregation existed in all structures. However, the observation of the four-petal-flower structure prompted us to investigate its growth mechanism. At first, the four-petal flower structure was considered as the initial state of the previously reported octahedron structure.¹⁴ We conducted the experiment with a very short reaction time of 10 s and observed the octahedron structure and its sunken structure together with this four-petal flower structure, as shown in Figure S6. The (111) facet of the octahedron dissolved in the solvent, which may have contributed to the formation of small nanorods in addition to the main product, the four-petal flower structure (See supplementary data Figure S6). Here, we propose the most possible growth pathway based on the SEM observations as follows.

Step 0: The aggregation of ZnTPyP particles as nucleation sites in the micelles of the surfactant.

Step 1: The formation of octahedron structures with different sizes influenced by the surfactant micelles.

Step 2-3: The dissolution and fading of the (111) facet of the octahedrons.

Step 4: The formation and continuous growth of the four-petal-flower structure.



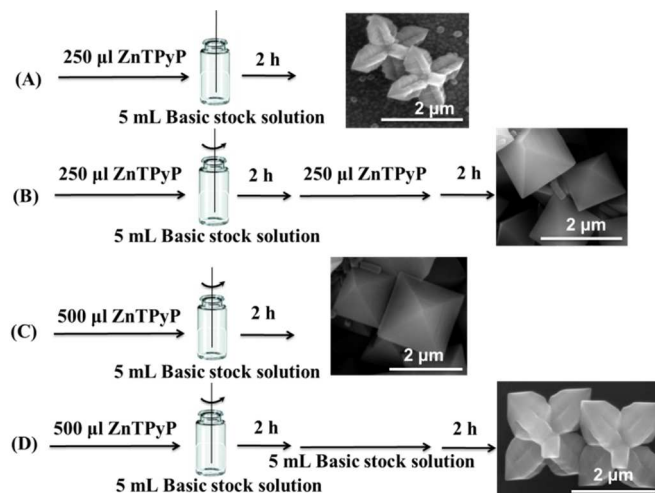
Scheme 1. Illustration of the most likely growth pathway of the ZnTPyP self-assembled four-petal-flower structure in a water-ethanol solution with a volumetric ratio of 6:4. The first three SEM images were obtained within 10 s. The blue circle shows the dissolution of the (111) facet.

These phenomena, in which octahedron structures were first fabricated and then converted into four-petal flower structures, can be explained thermodynamically. The nucleation and growth of nano/micro crystals in solution may be related to the Gibbs free energy, involving the atomic chemical potential and the surface tension of the crystals.¹⁵ The atomic chemical potential is related to the molar concentration of the solute, ZnTPyP here. At first, the molar concentration of ZnTPyP is high enough to form octahedron structures as the driving force to reduce the Gibbs free energy, which is governed by the chemical potential of the system. However, with increasing reaction time and decreasing concentration of ZnTPyP, the surface tension becomes the dominant factor to reduce the free energy of the whole system leading to formation of four-petal flower structures through dissolution of the (111) facet at a higher energy. Clearly, this four-petal flower structure is thermodynamically stable under the above-mentioned conditions, as is also illustrated in Scheme 2(A).

Another possible growth pathway is that the four-petal flower structure was formed by re-arrangement and connection of four small octahedrons accompanied by continuous growth at the connection point (See the supplementary data Scheme S1).

If the octahedron structure is the initial state of the four-petal flower structure (Scheme 1(A)) in bottom-up synthesis, we believe that the “top-down” transformation to synthesize octahedron structures is possible if the key parameter is the molar concentration of ZnTPyP. As shown in Scheme 2(B), we first carried out an experiment to synthesize the four-petal flower structure by injecting 250 μL ZnTPyP into 5 mL of the basic stock solution and reacting for 2 h. Then, we injected another 250 μL of ZnTPyP into this solution. After stirring for 2 h, the self-assembled particles were collected. The SEM images showed that the four-petal flower structure did not exist, and only octahedron structures were formed. This experiment confirmed our growth mechanism in which the formation of the four-petal flower structure from the octahedron structure is due to the lack of solute (ZnTPyP), also demonstrating the “top-down” synthesis from the four-petal flower structure to the octahedron structure.

Furthermore, we wanted to confirm the thermodynamic stability of the octahedron structure at high molar concentration of the solute. For this, 500 μL of ZnTPyP was injected into 5 mL of the basic stock solution and reacted for 2 h reaction (Scheme 2(C)). Again, the SEM images confirmed that only the octahedron structure was synthesized. To determine if the transformation from octahedron structure to four-petal flower structure was reversible, we injected 500 μL of the ZnTPyP stock solution into 5 mL of the basic stock solution and carried out the reaction for 2 h. Then, another 5 mL of the basic stock solution was injected into this solution in order to reduce the total molar concentration of ZnTPyP. After 2 h of reaction, the octahedrons were transformed back to the four-petal flower structure, as shown in Scheme 2(D).



Scheme 2. Illustration of the conditions used to form the four-petal flower structure (A), to confirm the top-down synthesis from four-petal flower structure to the octahedron structure (B), to form the octahedron structure as the stable product in one step (C), and to confirm the reversible transformation between the octahedron structure and four-petal flower structure (D).

Conclusions

In conclusion, we first showed that the addition of ethanol into water as a co-solvent allowed the diverse nano/microscale structure fabrication in a surfactant-assisted self-assembly method, depending on the volumetric ratio of water to ethanol. In particular, a four-petal flower structure was fabricated with an water:ethanol ratio (v/v) of 6:4. The UV-vis spectroscopy results confirmed J-type aggregation in all self-assembled ZnTPyP particles. The growth pathway of this four-petal flower structure was investigated, showing that the most likely one is the formation of an octahedron structure as the initial state and the subsequent dissolution and fading of the (111) facet, resulting in the four-petal flower structure. Thermodynamic explanation revealed that the initial formation of octahedron structure and the final conversion to the four-petal flower structure under ZnTPyP-deficient conditions are due to the reduced Gibbs free energy of the whole system governed firstly by the chemical potential and then by the surface tension of the crystals. For the first time, we demonstrated the feasibility of the “top-down” strategy to synthesize a stable octahedron structure from the four-petal flower structure, proposed the growth pathway, and achieved reversible transformation

between the four-pedal flower structure and octahedron structure.

Acknowledgements

This work was supported by the New & Renewable Energy of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant (No. 20123010010160) funded by the Korea government Ministry of Trade, Industry and Energy, and the Pioneer Research Center Program through the National Research Foundation of Korea (2010-0002231) funded by the Ministry of Education, Science and Technology (MEST).

Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

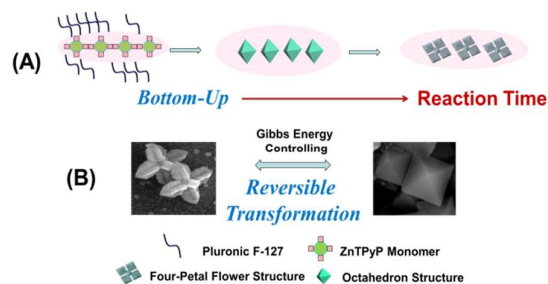
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Homogenous Four-Petal Flower Structure formation from Metalloporphyrin Self- assembly and its Reversible Transformation to an Octahedron Structure

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For the first time, uniform four-petal flower structure was fabricated and its reversible transformation to octahedron structure has been discovered.