Preparation and Photophysical Properties of Photofunctional Supramolecular Architectures of Porphyrins

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Increased efforts to assemble dye molecules into desired structures have been recently made because of their extended π -electron conjugation. Such organization of molecular assembly of porphyrins is an interesting topic because of a variety of applications such as photocatalytic and electronic devices. Construction of organized assemblies makes it possible to show the new property and phenomenon in comparison with those of the corresponding monomeric forms.

In general, the driving force of self-assembly is mainly dependent on the single interaction such as π - π or van der waals interaction. However, by introducing new functional groups or bonds onto the peripheral positions, which induce additional intermolecular interactions, we can construct a variety of superstructures with different sizes and shapes.¹⁻³ Therefore, one of methods for the useful controlling the superstructures is to employ coordination and hydrogen bonds. Herein we demonstrate synthesis, structural and photophysical properties of supramolecular architectures of porphyrins from nanocubes to microfibers. Figure 1 shows the basic chemical structure of porphyrin (H₂TCPP) metal coordination-assisted and architectures of supramolecular porphyrins utilizing metal-organic frameworks (MOFs).⁴ Transmission electron microscopy (TEM) was employed to examine the sizes and shapes of these porphyrin self-assemblies as shown in Figure 1. In the case of low concentrated condition (52.5 μ M), H₂TCPP assembly shows cubic structures, whereas longer bar-shaped structures with high aspect ratios (i.e., rods) are observed with increasing the concentration of H₂TCPP. In this presentation, the detail synthesis and structural and photophysical properties including other systems will be discussed systematically.



Figure 1. (A) A chemical structure of H_2TCPP and TEM images of (B) nanocubes (52.5 μ M), (C) nanorods (105 μ M) and (D) microrods (420 μ M).

References

- (1) Hasobe, T.; Sandanayaka, A. S. D.; Wada, T.; Araki, Y. *Chem. Commun.* **2008**, 3372-3374.
- (2) Sandanayaka, A. S. D.; Araki, Y.; Wada, T.; Hasobe, T. J. Phys. Chem. C 2008, 112, 19209-19216.
- (3) Hasobe, T., Phys. Chem. Chem. Phys. 2012, 14, 15975-15987.
- (4) Sakuma, T.; Sakai, H.; Hasobe, T., Chem. Commun. 2012, 48, 4441-4443.