Construction and Applications of Self-Assembled Gigantic Multiporphyrin Arrays

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Well-ordered architectures of self-assembling porphyrins have attracted considerable interest in light of potential applications to material sciences, template-directed syntheses, catalyses, and bioinspired molecular design of artificial photosynthetic systems. For the construction of such organized supramolecular architectures in both infinite and discrete forms, coordination interactions between metalloporphyrins and

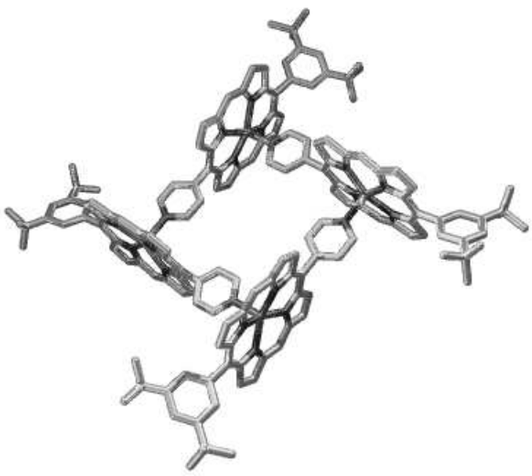
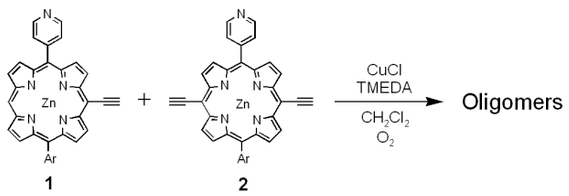
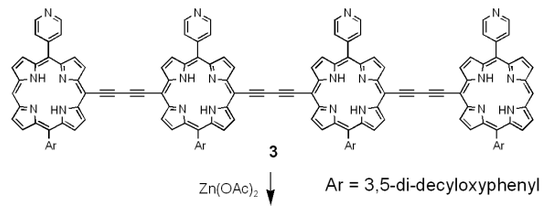


Figure 1. X-ray crystal structure of self-assembled cyclic tetramer of 5-*p*-pyridyl-15-(3,5-di-*tert*-butylphenyl) Zn-porphyrin

pyridine groups have often been used [1, 2]. For example, one of the authors has reported that a zinc complex of 5-*p*-pyridyl-15-(3,5-di-*tert*-butylphenyl) forms a self-assembled cyclic tetramer with a square conformation (Figure 1) [3]. In the present work, we investigated the self-assembling behaviors of novel discrete π-conjugated zinc porphyrin arrays having multiple pyridyl moieties, and wish to highlight a new supramolecular approach to gigantic multiporphyrin arrays. Thus, the Glaser-Hay



coupling reaction of **1** and **2** at a ratio of 1:2 gave a mixture of porphyrin oligomers, and subsequent separation by size exclusion chromatography (SEC) allowed isolation of discrete oligomers up to tetramer. We found that all the multiporphyrin arrays thus synthesized are self-assembled, upon incorporation of zinc ions, to form discrete cyclic tetramers in a highly selective manner, as observed by ^{1}H NMR and electronic absorption spectroscopies, SEC-HPLC analysis, and CSI-MS spectrometry. Figure 2 shows a molecular model of self-assembled tetrameric zinc porphyrin array **3**, which adopts a tubular structure. We will present details of this interesting self-assembling event.



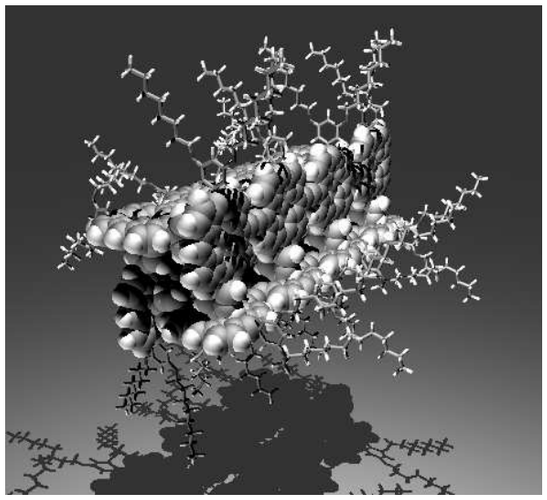


Figure 2. A molecular model of self-assembled cyclic tetramer of **3**

Acknowledgments

We thank Dr. H. Hu and R. Tanaka for their active collaboration, and also acknowledge Professor K. Yamaguchi and Dr. S. Sakamoto (Chiba Univ.) for CSI-MS spectrometry.

References

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