Synthesis and Supramolecular Assembly of Amphiphilic β-Alkylporphyrin

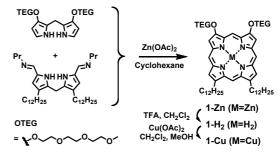
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 β -Alkylporphyrin is a π -conjugated macrocycle without any bulky substituents at the periphery, and in contrast to *meso*-arylporphyrin, it can be assembled into densely-packed and well-ordered supramolecules. Herein, we have developed a novel procedure to enable versatile molecular designs of β -alkylporphyrins, and with this procedure, we have succeeded in the first synthesis of a highly planar amphiphilic porphyrin **1** (Scheme 1). In a polar solvent, **1-H**₂ and **1-Cu** show unique self-assembling behaviors due to the amphiphilic properties, and when precipitated from THF/water mixed solvent, **1-Cu** exhibits H-aggregation (Fig. 1). With FE-SEM or TEM observations, supramolecular structures of **1-H**₂ and **1-Cu** depend on the

self-assembling conditions (Fig. 2). In the one-dimensional metal chain of **1-Cu**, each metal centers are closely packed with a short inter-metal distance, and the magnetic susceptibility measurements of **1-Cu** reflect the unique intermolecular interaction of the self-assembled structure.





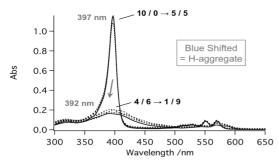


Fig. 1. UV-Vis absorption spectral changes of 1-Cu in THF/water mixed solvent. $[1-Cu] = 0.494 \times 10^{-4}$ M.

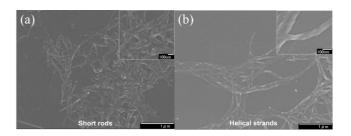


Fig. 2. FE-SEM images of **1-Cu** precipitated from (a) THF/Water, and (b) hot MeOH.