1D4b

Chiral induction of helical supramolecular porphyrin polymers cross-linked by bispyridines

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Supramolecular polymers are a class of molecular assemblies, which are held together by non-covalent interactions. Reversible nature of supramolecular polymers results in unique properties such as self-healing and stimuli-responsivity. Therefore, supramolecular polymers have attracted a great deal of interest in material science. We reported a supramolecular polymer, formed by the self-assembly of tetrakisporphyrin through molecular recognition[1]. In this presentation, we will report the development of the supramolecular porphyrin polymer networks cross-linked by bispyridines **2** and **3**.

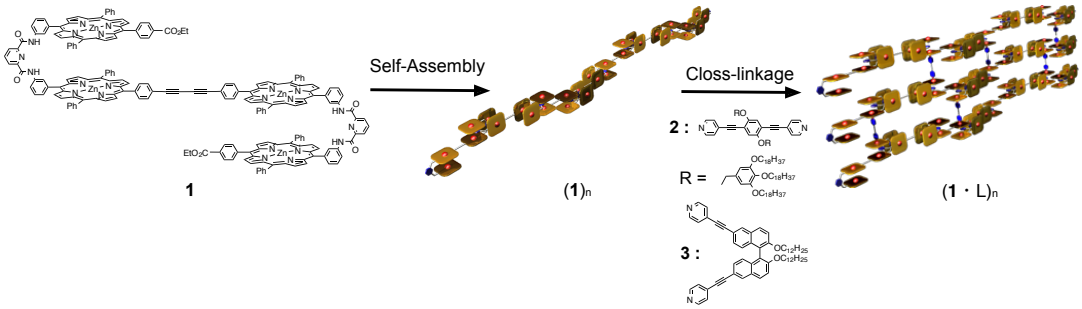

Figure 1 Schematic representation of supramolecular polymerization of monomer **1** with bispyridine ligands (L = **2** or **3**).

The formation of supramolecular polymers $(\mathbf{1})_n$ and their cross-linking were studied using DOSY experiments. Diffusion coefficients (D) of **1** were decreased as increasing its concentrations. The addition of 0.5 equivalent of **2** reduced the D values of **1**. These results suggested supramolecular polymers $(\mathbf{1})_n$ were cross-linked by **2**.

Well-organized helical morphologies were observed on AFM images of cross-linked supramolecular polymer networks (Figure2a), whereas random supramolecular polymers were observed at without **2**.

Dispersion CD signals were observed at the soret band of the porphyrin units when chiral cross-linker **3** was added to a solution of **1** (Figure 2b). Accordingly, cross-linking of $(\mathbf{1})_n$ with **3** induced the helical organization both in the solid state and in solution.

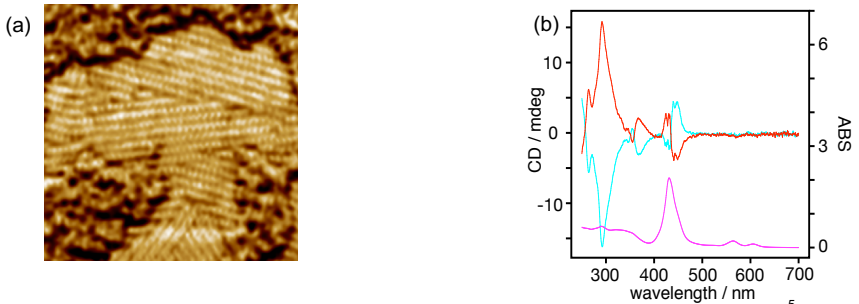

Figure 2 (a) The AFM image of **1** with 0.5 eq of **2** on HOPG. (b) CD Spectra of **1** (2.5×10^{-5} mol L^{-1}) in the presence of *R*-**3** (red) and *S*-**3** (blue), and UV Spectrum of **1** in the presence of *R*-**3** (pink) at 298 K in 1,2-dichloroethane. The concentrations of *R*-**3** and *S*-**3** were 5.0×10^{-4} mol L^{-1}.

[1] Haino T.; Fujii, T.; Watanabe, A.; Takayanagi, U., *Proc. Natl. Acad. Sci. USA*., **2009**, 106, 10477- 10481