Schizophyllan Acts as a One-dimensional Host to Accommodate 5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrinatozinc Acetate to Produce Its Fibrous Superstructure

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We established a novel strategy to construct porphyrin-nanofibers which may mimic a fibrous porphyrin-assembly observed in a natural light harvesting system in green bacterium. Our strategy utilizes alignment of 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinatozinc acetate in schizophyllan having one dimensional cavity along its helical superstructure. The resultant schizophyllan/porphyrin complex generates fibrous superstructures, in which porphyrins are aligned in a chirally-twisted packing mode.

Porphyrins and the related macrocycles are ubiquitously seen in nature as critical components of oxygen binding and light harvesting systems, in which each porphyrin is spatially aligned within protein scaffolds to accomplish effective and specific functions.[1] Various synthetic/supramolecular porphyrin-arrays have been developed to construct artificial light harvesting systems,[2] however, little artificial porphyrin-array so far reported can be a match for the natural ones from a viewpoint of electron/energy transfer efficiency. The most critical obstacles include highly complexed porphyrin-arrangements in the natural systems that can be hardly mimicked through the synthetic/supermolecular approaches.

Recently, a unique light harvesting system was found in green bacterium *Chlorobium tepidum*. It contains several tens of thousand of bacteriochlorophylls (magnesium-containing porphyrin-analogues) assembled in a parallely-slided packing (J-aggregation) to construct a fibrous superstructure without any protein scaffold.[3] Owing to its simple porphyrin-arrangement as well as its unique fibrous morphology, an increasing research effort has been launched to develop artificial light harvesting systems to mimic this unique porphyrin-nanofiber.[4] Quick and general methodologies to construct such porphyrin-nanofibers are now highly desired.

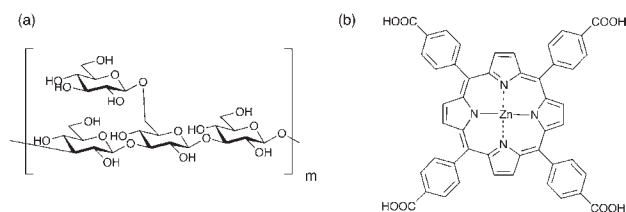Natural β-1,3-glucan, schizophyllan (SPG, Chart 1a), exists as a right-handed triple-stranded helix (t-SPG) in neutral water, whereas it is dissociated into random coiled single-strands (s-SPG) in NaOH aqueous solution (>ca. pH 12).[5] This structural transition is entirely reversible and can be controlled by changing pH values of the media. Recently, we reported that t-SPG has a one-dimensional (1D) cavity inside its helical superstructure and accommodate various hydrophobic polymers (single-walled carbon nanotubes, polyanilines, etc.) through the structural transition from s-SPG to t-SPG.[6] More recently, we found that various small monomers (e.g. diphenylbutadiynes) can be also accommodated in the 1D cavity to produce fibrous polymer-assemblies after their template-polymerization.[7] Furthermore, Au-nanoparticles can be also accommodated in the 1D cavity to produce a novel 1D Au-nanoarray.[8] These results clearly indicate that SPG can act as a unique 1D host to accommodate various guest molecules and to produce their fibrous superstructures. Herein, we report another example of SPG as a 1D host, that is, SPG can interact with 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinatozinc acetate[9] (TCPP-Zn, Chart 1b) to produce the corresponding porphyrin-nanofibers (Figure 1).
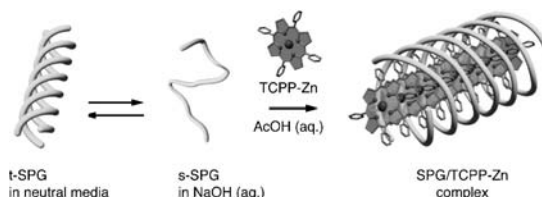

Figure 1. Schematic illustration of our concept to construct porphyrin-nanofibers.[10]

SPG/TCPP-Zn complex was prepared by mixing s-SPG and TCPP-Zn in 1.0 M aqueous sodium hydroxide followed by neutralization of the resultant basic solution by 1.0 M aqueous acetic acid. The resultant neutral solution (pH 6.0) showed one clear absorption band at 428 nm. Since free TCPP-Zn gives its Soret-band peak at 422 nm, the observed peak is assignable to a red-shifted Soret-band of TCPP-Zn. Along with its slightly weakened peak intensity, this red-shifted Soret-band of TCPP-Zn is assignable to their SPG-induced J-aggregation.

We carried out some referential experiments using other polysaccharides to clarify the detailed mechanism of the interactions (Figure 2a). The red-shift of the Soret-band was most clearly observed for s-SPG (ca. 6 nm), and no (dextran) or much smaller (pullulan and amylose, ca. 4 and ca. 3.5 nm, respectively) shifts were observed for other polysaccharides. These data indicate that some interactions (hydrophobicity, higher-order conformation, etc.), other than the specific hydrogen-bonding
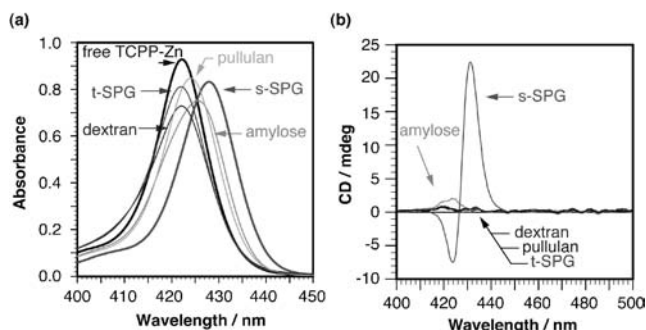

Chart 1. Structures of (a) SPG and (b) 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinatozinc acetate (TCPP-Zn).

Figure 2. (a) UV–vis and (b) CD spectra of free TCPP-Zn and those with s-SPG, amylose, pullulan, dextran, and t-SPG: [TCPP-Zn] = 28 nM, [polysaccharide] = 0.5 mg/mL, 25 °C, $d = 1$ and 2 mm for UV–vis and CD spectra, respectively. See ESI for the colored version.

interactions, should play substantial roles in the complex formation. Furthermore, it should be emphasized that no red-shift was observed for t-SPG, indicating that the *renature process* of SPG is indispensable for the interactions. The last finding is quite interest, since it suggests that TCPP-Zn is not adsorbed onto the surface of the t-SPG triple strands but encapsulated within the 1D cavity of SPG, as already reported for the other guest molecules.[6,7]

The interaction between SPG and TCPP-Zn is more clearly demonstrated by using circular dichroism (CD) spectra. As shown in Figure 2b, SPG/TCPP-Zn complex shows CD spectra having a clear positive Cotton signal at its Soret-band region, indicating that TCPP-Zn molecules are packed in a right-handed manner within the right-handed helical superstructure of SPG. This polysaccharide-induced CD spectral change is specific for SPG and no or only negligibly weak CD spectrum can be induced by other polysaccharides. It should be again emphasized that t-SPG does not induce any CD spectral change, clearly indicating that TCPP-Zn is accommodated within the 1D cavity of SPG.

Transmission electron microscopic (TEM) observations revealed that SPG/TCPP-Zn complex has fibrous morphologies (Figure 3a), although free TCPP-Zn shows amorphous aggregates (See ESI). An advantage of SPG to construct the nanofibers is clearly demonstrated by the fact that no other polysaccharide can give such fibrous porphyrin assemblies (Figure 3b for amylose; see ESI for other polysaccharides). Again, t-SPG cannot give any fibrous assemblies (see ESI), supporting the porphyrin-nanofibers within the 1D cavity of SPG. Energy dispersive X-ray (EDX) spectroscopic analysis of the nanofibers indicated co-existence of Zn atoms and excess oxygen atoms, confirming
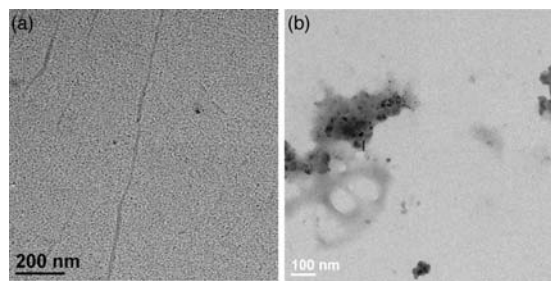

Figure 3. TEM image of (a) SPG/TCPP-Zn complexes and (b) amylose/TCPP-Zn complexes.

that they are composed of TCPP-Zn and SPG. Although the minimum diameter of the nanofibers is ca. 4 nm, many fibers have much larger diameters (10–20 nm) than the molecular size of TCPP-Zn (2 nm). These data suggest that SPG mainly accommodates TCPP-Zn *bundles*, although we showed a simplified image in Figure 1 to explain our beginning motivation of this research.

In conclusions, SPG can interact with TCPP-Zn to induce their chiral J-aggregation. This interaction is specific for SPG and the resultant SPG/TCPP-Zn complex can afford a fibrous superstructure. In our preliminary experiments, we found that not only TCPP-Zn but also TCPP-Cu (the copper analogue) as well as TCPP (the free-base analogue) are accommodated within the 1D cavity to form the corresponding porphyrin-nanofibers. Furthermore, fluorescence intensities of these encapsulated porphyrins are highly enhanced, presumably owing to their restricted molecular motion in the 1D cavity. We expect that this unique strategy should be useful to design artificial light harvesting systems to mimic the photosynthetic antenna complex in the green bacterium. Our research efforts are now focused on to produce narrow and well-structured nanofibers as well as to construct the light harvesting systems based on the fibrous SPG/porphyrin complex.

References and Notes
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9   See ESI for the synthesis of TCPP-Zn.
10   The detailed complex structure related to the number of SPG chains, the number of porphyrin arrays, etc. is not yet specified.