Supporting Information

Spherical Self-aggregates Formed with an Alanine-functionalized Porphyrin Derivative in Organic Solvent

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Experimental Section

Apparatus for spectroscopy measurement: ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 300 apparatus. IR spectra were obtained in KBr pellets using a Shimadzu FT-IR 8100 spectrometer. CLSM (Confocal Laser Scanning Microscope) was obtained by LSM 510. 2D-XRD (X-ray Diffractometer with Area Detector) was obtained by Bruker D8 Discover with GADDS.

TEM and SEM observations: For transmission electron microscopy (TEM) a piece of the gel was placed on a carbon-coating copper grid (400 mesh) and removed after one min, leaving some small patches of the gel on the grid. After specimens had been dried at low pressure, they were shadowed with 10 mg of OsO_4 (2.0 wt% aqueous solution). Then, they were dried for 1 h at low pressure. The specimens were examined with Hitachi H-7100, using accelerating voltage of 100 kV and a 16 mm working distance. Scanning electron microscope (SEM) was taken on Hitachi S-4500. The thin gel was prepared in a 1-2 mL bottle and frozen in liquid nitrogen or dry ice-acetone. The frozen specimen was evaporated by a vacuum pump for 24 h. The dry sample was coated with palladium-platinum. The accelerating voltage of SEM was 5-15 kV and the emission current was 10 μA.

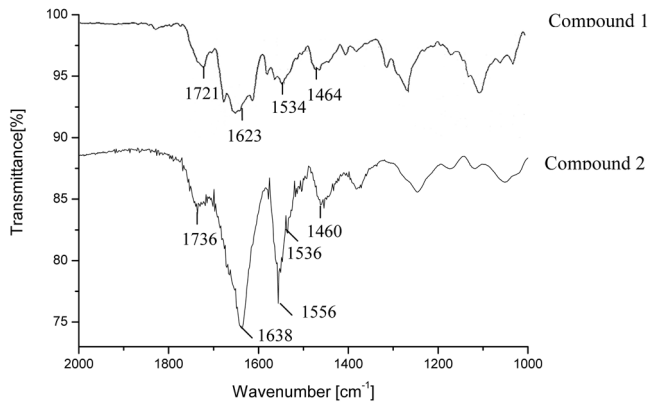


Figure S1. FT-IR spectra of the self-assembled **1** and **2**.

Calculation Results

The optimized structures of the three different dimer units of uuuu, uudd, and udud structures were shown in Figure S2. It is clearly shown that the hydrogen bonding between amide groups play an important role in growing by self-assembly. In particular, all the four chains seem to be involved in the intermolecular hydrogen bonding in the self-assembly. The thermodynamic stability of uuuu, uudd, and udud structures is virtually equivalent (within 0.12 kcal/mol) at the AM1 calculations. In our experiment, the globular self-assembled structure was observed, thus, the building block is expected to be "udud" type structure because "udud" is the only structure that can result a 3-dimensional network in self-assembly. Considering that there are two possibilities, up or down, for the chain orientation attached at the porphyrin, the molecule can have total 16 different structures because it have four chains. Of them, for the self-assembly growth, we selected three possible dimer units (we denote them, uuuu, uudd, and udud), and we expanded them as shown in Scheme S1. It should be noted that the uuuu structure cannot make a 3-dimensional network because all the chains are up, thus, the neighboring unit should have the chains with all down, etc. For uuuu, in Scheme S1, we depicted the case when the number of nearest neighbor is 2, where the molecule grows to be a 1-dimensional network. Of course, uuuu can also have four nearest neighbors, then it grows to be a 2-dimensional network. Similarly, uudd grows to be a 1-dimensional frame. More interestingly, udud has four nearest neighbors, and grows to be a 3-dimensional frame like a diamond structure with sp^3 hybridization.

With this picture in mind, we have carried out the semiempirical AM1 calculations for the simplified system. The optimized structures of the three different dimer units of

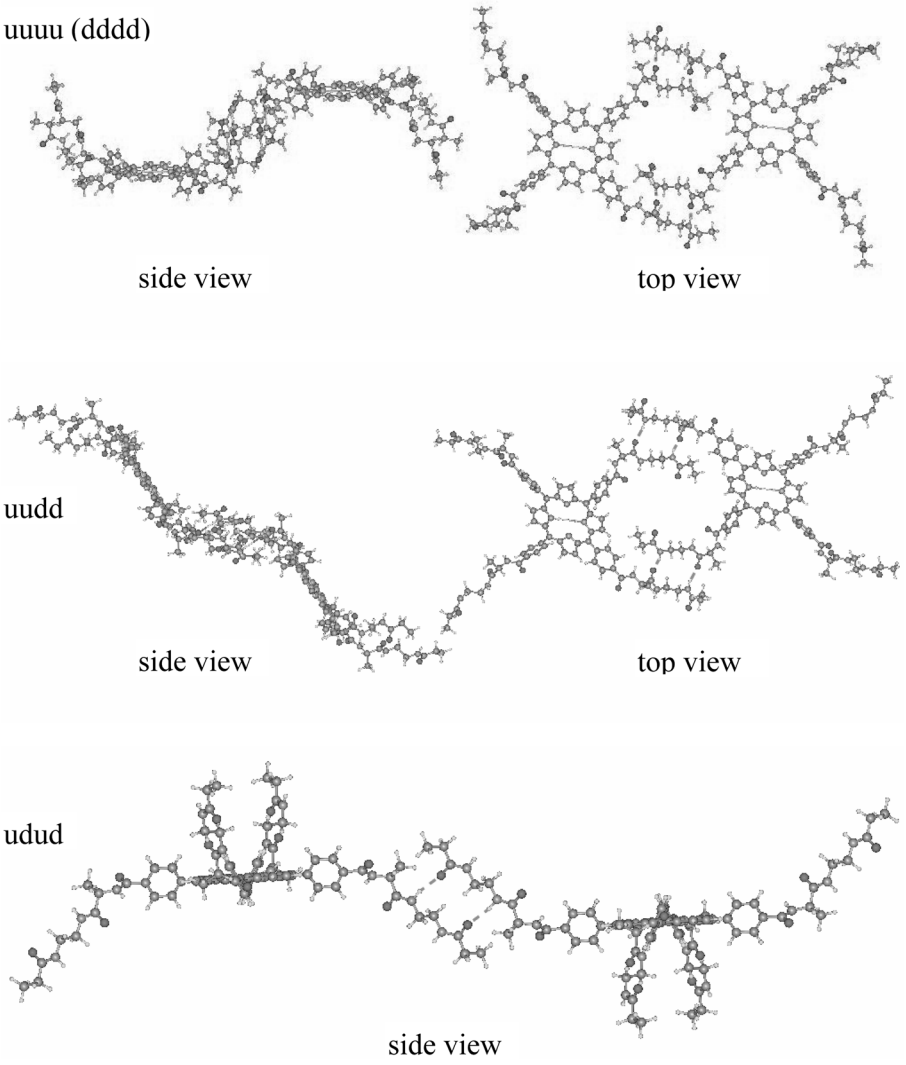
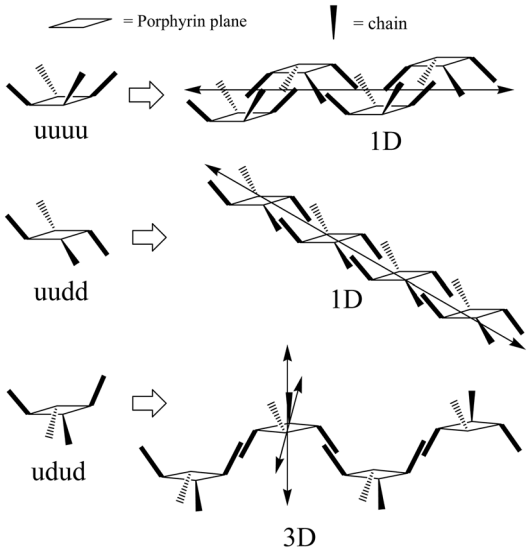


Figure S2. Semiempirical AM1 optimized structures for the possible three different dimmer units for the self-assembly growth. u/d represents the chain shape to be up/down.



Scheme S1. Schematic representation for the possible growing by self-assembly of different building blocks (uuuu, uudd, and udud).

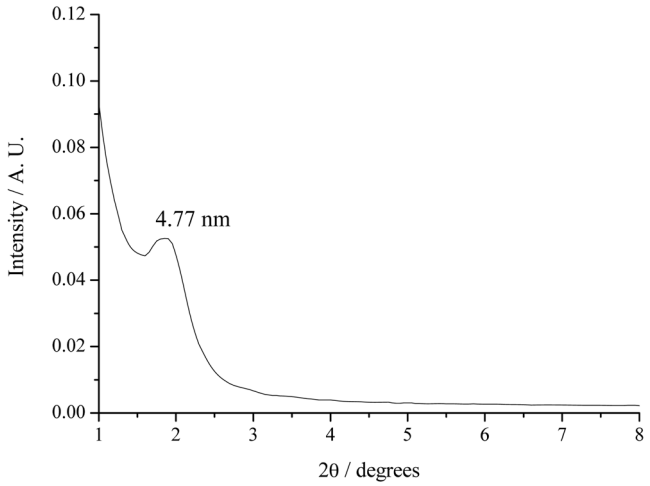


Figure S3. XRD profile of the self-assembled **1**.

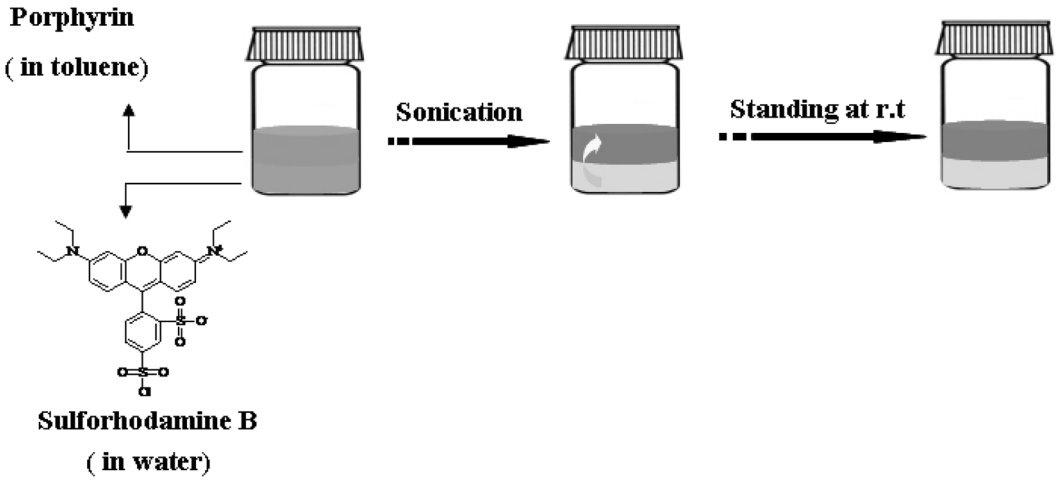


Figure S4. Representation for Rhodamine B loading method into the self-assembled **1**.

uuuu, uudd, and udud structures were shown in Figure S2. It is clearly shown that the hydrogen bonding between amide groups play an important role in growing by self-assembly. In particular, all the four chains seem to be involved in the intermolecular hydrogen bonding in the self-assembly. The thermodynamic stability of uuuu, uudd, and udud structures is virtually equivalent (within 0.12 kcal/mol) at the AM1 calculations. In our experiment, the globular self-assembled structure was observed, thus, the building block is expected to be "udud" type structure because "udud" is the only structure that can result a 3-dimensional network in self-assembly.