Self-Assembled Supramolecular Architecture Based on an Achiral Bolaamphiphilic Diacid in Binary System

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A new family of polymers that includes topologically complex polymers and self-assembled nanostructures has recently attracted much attention. The non-covalent self-assembly technique, unlike chemical reaction or polymerization methods, has the advantage of directly producing well-defined two- and three-dimensional structures such as sheets, rods, fibers, tubes, disks, and spheres. Notably, these nanostructures can be constructed with high efficiency and accuracy, and yet with minimum energy.

Organic amphiphiles typically possess a chiral moiety as well as functional groups with potential to form multiple hydrogen bonds, such as sugars, peptides, or nucleotide bases. However, only a few examples for self-assembled supramolecular structures of organic amphiphiles consisting of achiral moieties have been described. Therefore, our initial motivation to prepare bolaamphiphilic diacids was to develop self-organized pseudo-linear polymers stabilized by intermolecular hydrogen bonds, and that incorporated suitable guest additives with achiral functional groups.

With this idea in mind, we employed a simple bola-form amphiphile (“bolaamphiphile”) 1, consisting of one diphenyl ether group as a hydrophobic moiety at the center, flanked by two carboxylic acids as the terminal hydrophilic groups. In 1, the linkage we introduce between the hydrophobic and the hydrophilic moieties is an amide group, known to form a linear hydrogen bond chain. We herein report the assembling behavior of 1 with and without dipyridyl additives. The additives such as 4,4'-dipyridyl (4,4'-bpy) and 2,2'-dipyridyl (2,2'-bpy) are so common that their interaction behaviors have been well-defined especially in the coordination polymer networks.

We have investigated the influence of the dipyridyl additives on the morphologies of self-assembled 1 and self-assembled 1 combined by bpy which are denoted with [1] and [1+bpy], respectively, by optical microscopy, SEM, FT-IR, powder-XRD and differential scanning calorimetry (DSC).

Achiral bolaamphiphile 1 was synthesized in three steps (Scheme 1). The monomethyl sebacate was chlorinated to give methyl-10-chloro-10-oxadecanoate. Reaction of 3 with 4,4'-oxydianiline afforded diamide derivative 4. Treatment of 4 with NaOH gave the desired product 1 as a brown powder.

The self-assembly reactions of 1 (3-5 mg) with and without dipyridyl additives (3 equiv) were accomplished by dissolving the reactants in acidic, neutral, and basic conditions in water/ethanol (4:1 v/v, 50 mL) at 80 °C, respectively. The pH of each solution was adjusted with 0.1 M NaOH or 0.1 M HCl aqueous solution. After the incubation of the solutions at room-temperature for several hours, the formation of stable supramolecular assemblies was confirmed. In the absence of additives, SEM pictures for [1] obtained at pH = 4 show a film-like structure (Figure 1a) whereas at pH = 7, the structures are comprised of bundles with [1+bpy], respectively, by optical microscopy, SEM, FT-IR, powder-XRD and differential scanning calorimetry (DSC).

Scheme 1. Synthetic route for achiral bolaamphiphilic diacid 1.
of 100 nm diameter submicro-fibers (Figure 1b). At pH = 10, however, the self-assembly of 1 did not occur. These results indicate that the morphologies of [1] are strongly dependent on the pH of the solutions.

The morphological changes of [1+4,4'-bpy] and [1+2,2'-bpy] were observed (Figure 2). The [1+4,4'-bpy] (1.50 mM) was revealed as a loosely twisted fiber at pH = 7 (Figures 2a and 2b), showing the influence of the ionic hydrogen-bonding between the carboxyl groups of 1 and the pyridyl nitrogen atoms of 4,4'-bpy (e.g. COO−…PyH+) on the morphology of the assembled product. However, no significant differences were noted in the visual morphology between [1] and [1+2,2'-bpy] (Figures 2c and 2d).

Since the microscopic structural views for [1] indicated the participation of the ionic intermolecular hydrogen-bonding, we compared the FT-IR spectra of [1] obtained at pH = 4 and 7 (Figure 3). At pH = 7, spectral bands of [1] appear at 1701 and 1410 cm⁻¹ for COOH and COO⁻ species, respectively. Meanwhile, at pH = 4, the spectrum of [1] contains only a band at 1701 cm⁻¹ for COOH. The solid sample 1 obtained at pH = 10 shows a band for the fully ionized COO⁻ species, and gave no specific morphology. Hence, the superstructure of [1] is provided mainly by intermolecular hydrogen bonding interactions between COOH and COO⁻ species at pH = 7.

The intermolecular ionic hydrogen-bonding for [1+4,4'-bpy] was also confirmed by Fermi resonance (vOH) by FT-IR analysis as depicted in Figure 4.12 For example, we observed the respective vOH and its Fermi resonance at 2450 and 1930 cm⁻¹ (Supporting Information: Figure S1). Additionally, by NMR analysis, we determined that 40-45 mole% of 4,4'-bpy existed within the same fiber. These multiple evidences strongly support the view that 4,4'-bpy was truly incorporated into the superstructure of [1] to form the pseudo-linear polymer. However, the product obtained from the self-assembly reaction of 1 with 2,2'-bpy shows no peak corresponding to the 2,2'-bpy, indicating that 1 does not interact with 2,2'-bpy.

The IR spectrum for [1] in solid state also shows a strong band at 1630 cm⁻¹ corresponding to C=O group whereas the spectrum for 1 in DMSO solution shows an absorbance band at 1680 cm⁻¹ for the same functional group (Figure S2). These findings suggest that the amide groups of [1] obtained from a mixture of water and ethanol play a critical role for the intermolecular hydrogen-bonds between C=O and NH.

To confirm the molecular packing structure, we measured the powder-X-ray diffraction pattern for [1] and [1+4,4'-bpy] (Figure S3). [1] shows a strong high-ordered reflection peak at 2.75°, indicating that it forms a well-organized layer structure by intermolecular hydrogen bonding interaction and π–π stacking (Figure 4). The d-spacing was calculated from the Bragg equation to be 3.29 nm (3.42 nm predicted by the CPK molecular modeling). In contrast, the small-angle diffraction pattern for [1+4,4'-bpy] appeared at 4.35 nm, less than twice the extended molecular length of 1, but larger than the length of one molecule. This result suggests that [1] was well-assembled and constructed in a layer structure through the ionic hydrogen bonds with 4,4'-bpy (Figure 4).

The self-assembled fibers were isolated from the aqueous dispersion by a nitrocellulose membrane with 0.22 μm of pore size, and the isolated samples were dried and used for DSC measurement. [1] showed a phase transition at 222.9 °C (Figure S4), while the [1+4,4'-bpy] exhibited an endothermic peak at 212.9 °C, indicating that 4,4'-bpy is incorporated into the organized systems in microscopic levels (Figure 3). However, the phase transition temperature for the assembled product obtained from 1 and 2,2'-bpy was same as that for [1], also indicating the absence of 2,2'-bpy in the product.

In conclusion, the bolaamphiphile 1 in the absence and presence of bpy additives can be self-assembled into supramolecular nanostructures. In particular, the self-assembly reaction of 1 and 4,4'-bpy forms the pseudo-linear polymer [1+4,4'-bpy] as a result of objective architectures via mole-
cicular assemblies based on effective intermolecular hydrogen-bonding interaction between these two components.

**Experimental Section**

**Apparatus for spectroscopy measurement:** $^1$H and $^{13}$C NMR spectra were measured by a Bruker ARX 300 apparatus. IR spectra (KBr pellets) were obtained using a Shimadzu FT-IR 8100 spectrometer.

**SEM observations:** Scanning electron micrographs (SEM) was taken on Hitachi S-4500. The dry sample was coated with palladium-platinum. The accelerating voltage of SEM was 5-15 kV and the emission current was 10 $\mu$A.

**XRD measurements:** The XRD of a freeze-dried sample was measured with a Rigaku diffractometer (Type 4037) using graded d-space elliptical side-by-side multilayer optics, monochromated Cu K$\alpha$ radiation (40 kV, 30 mA), and an imaging plate (R-Axis IV). The typical exposure time was 10 min with a 150-mm camera length. $[1]$ and $[1+4,4'-bpy]$ were vacuum-dried to constant weight and then put into capillary tubes, without being powdered.

**DSC measurement:** Differential scanning calorimetry (DSC) was performed on a Seiko DSC6100 high-sensitivity differential scanning calorimeter equipped with the nitrogen as cooling unit. The self-assembly was hermetically sealed in silver pan and measured against a pan containing alumina as the reference. The thermograms were recorded at a heating rate 1°C/min$^{-1}$.

**Preparation of the self-assembled samples and pH adjustment:** For self-assembly, a weighted powder (3.0-5.0 mg) of products was dispersed in acidic, neutral, or basic solution (water and ethanol: 4:1 v/v, 30 mL) at 80 °C for 30 min. The pH of solutions was then adjusted with 0.1 M NaOH or 0.1 M HCl aqueous solution. The transparent aqueous dispersion was gradually cooled to room temperature and kept standing without vibration. After several hours, the cotton-like product formed by self-assembly was obtained. The product was collected for further analysis.

3. To a suspension of 2 (0.40 g, 1.85 mmol) in dry CH$_2$Cl$_2$ (2 mL) containing a few drops of DMF was added oxalyl chloride (1.17 g, 9.2 mmol) carefully via syringe. After the effervescence has ceased, the reaction mixture was stirred for 1 h at room temperature. Removal of the solvent and the unreacted oxalyl chloride in vacuo afforded 3. No further purification was done.

4. To a solution of 4,4'-oxydianiline (0.138 g, 0.69 mmol) in dry THF (5 mL) at 66 °C under N$_2$ was added TEA (0.6 g, 5.2 mmol). The reaction mixture was stirred at 66 °C for 10 min. The reaction mixture was added 3 (0.4 g, 1.7 mmol). After 6 h, the precipitate was removed by filtration. Then, the solvent was removed by rotary evaporation to produce a yellow solid. This crude product was purified by column chromatography (silica-gel, ethyl acetate/n-hexane, 1:4) to give the product 4 (330 mg, 81%). $^1$H NMR (300 MHz, CDCl$_3$, 25 °C) δ 7.63 (d, 4H, $J = 9$ Hz), 6.89 (d, 4H, $J = 9$ Hz), 3.67 (s, 6H), 2.35-2.37 (m, 8H), 1.45-1.21 (m, 24); MS (EI) m/z 597 (M+H)$^+$; Anal. Calcd for C$_{34}$H$_{48}$N$_2$O$_7$: C: 68.43, H: 8.11, N: 4.69, found C: 67.50, H: 8.25, N: 4.72.

1. 4 (200 mg, 0.33 mL) was dissolved in MeOH (5 mL) and 1 N NaOH (1.5 mL, 1.5 mmol) was added. The mixture was stirred at room temperature for 4 h. The MeOH was removed under reduced pressure and the solution thus obtained cooled in an ice bath and acidified with 1 N HCl (10 mL) with vigorous stirring. The white solid precipitated was filtered off, washed with H$_2$O and dried 1 (0.180 g, 91%). No further purification was done. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C) δ7.75 (d, 4H, $J = 9$ Hz), 6.99 (d, 4H, $J = 9$ Hz), 2.48-2.45 (m, 8H), 1.49-1.21 (m, 24); MS (FAB) m/z 569 (M+H)$^+$; Anal. Calcd for C$_{32}$H$_{44}$N$_2$O$_7$: C: 67.58, H: 7.80, N: 4.93, found C: 67.50, H: 8.25, N: 4.72.

![Figure 4](image-url). Molecular packing modes for [1] (top) and [1+4,4'-bpy] (bottom).
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References


