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[1] and self-assembled nanostructures[2-6] has recently attracted much attention.[4d] 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, rod, fibers, tubes, disks, and spheres. Notably, these nanostructures can be constructed with high efficiency and accuracy, and yet with minimum energy.[7]

Organic amphiphiles typically possess a chiral moiety as well as functional groups with potential to form multiple hydrogen bonds, such as sugars,[8] peptides,[9] or nucleotide bases.[4c-d,8] However, only a few examples for self-assembled supramolecular structures of organic amphiphiles consisting of achiral moieties have been described.[10] 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 guest 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.[3a] 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
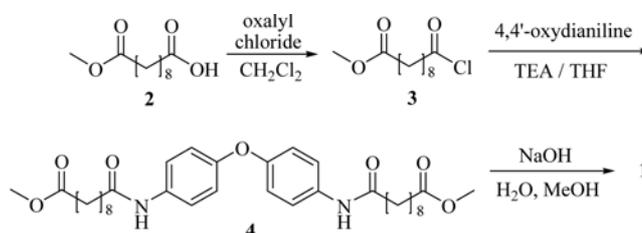

Scheme 1. Synthetic route for achiral bolaamphiphilic diacid **1**.

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 **2** was chlorinated with oxalyl chloride to give methyl-10-chloro-10-oxadecanoate **2**. 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.[11] 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**] (0.50 mM) obtained at pH = 4 show a film-like structure (Figure 1a) whereas at pH = 7, the structures are comprised of bundles
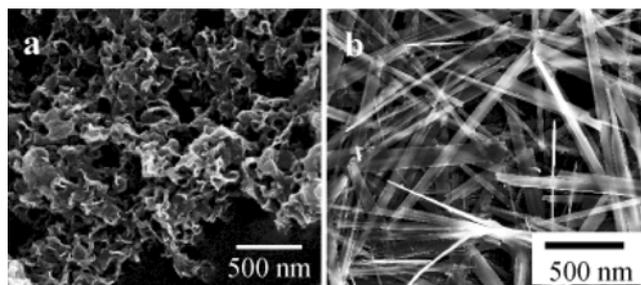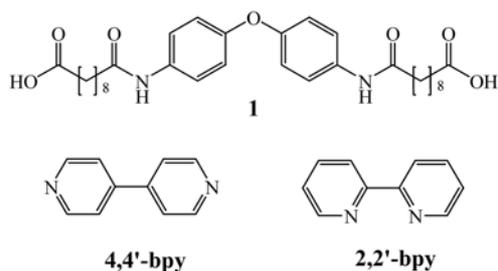
Figure 1. SEM pictures for [**1**] obtained at (a) pH = 4 and (b) pH = 7, respectively.
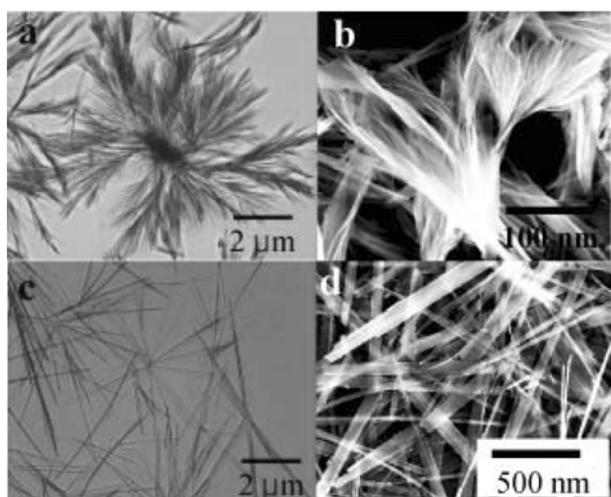
Figure 2. Optical microscopic (a and c) and SEM (b and d) pictures of [**1**+4,4'-bpy] (a and b) and product obtained from the reaction of **1** with 2,2'-bpy (c and d) obtained at pH = 7.

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.* $COO^- \cdots PyH^+$) 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
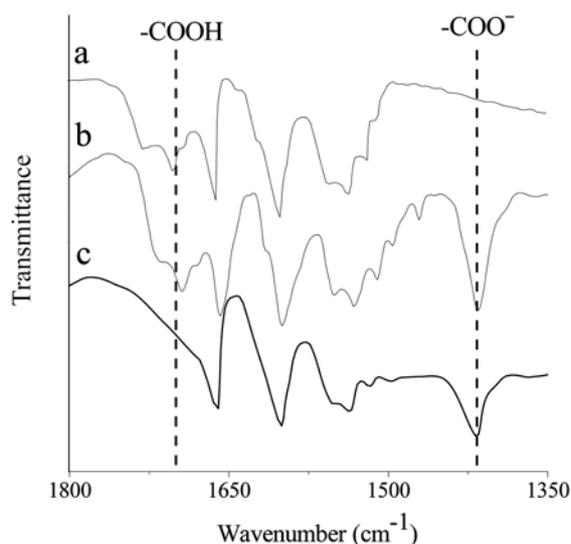
Figure 3. FT-IR spectra for [**1**] obtained at (a) pH = 4, (b) pH = 7, and (c) pH = 10.

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.
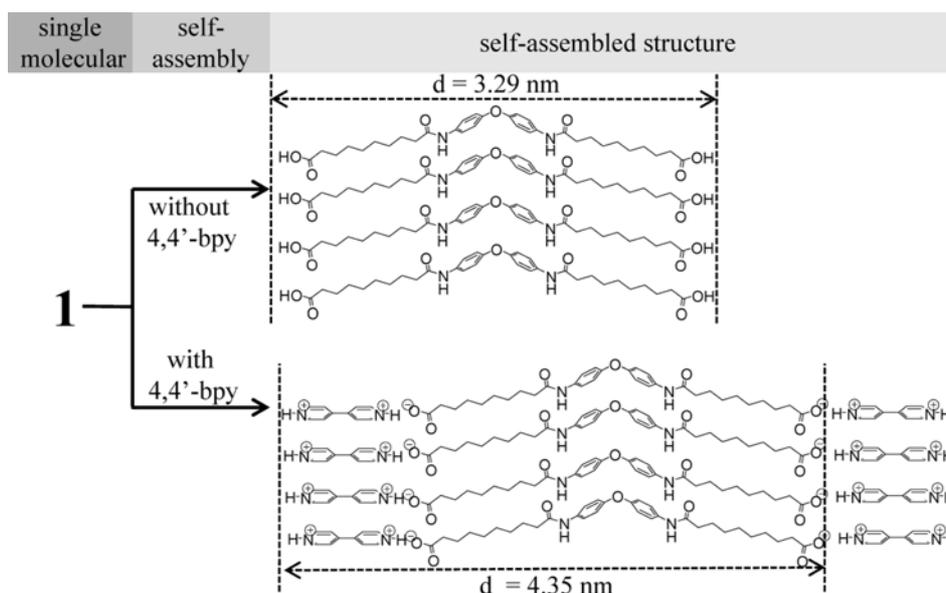
The intermolecular ionic hydrogen-bonding for [**1**+4,4'-bpy] was also confirmed by Fermi resonance (v_{OH}) by FT-IR analysis as depicted in Figure 4.[12] For example, we observed the respective v_{OH} and its Fermi resonance at 2450 and 1930 cm^{-1} (Supporting Information: Figure S1). Additionally, 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-

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

cular 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 μA.

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 Kα 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 °Cmin^{-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 temper-

ature 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_2Cl_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 $C_{34}H_{48}N_2O_7$: 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_2O and dried **1** (0.180 g, 91%). No further purification was done. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ 7.59 (d, 4H, J = 9 Hz), 6.99 (d, 4H, J = 9 Hz), 2.48-2.45 (m, 8H), 1.49-1.24 (m, 24); MS (FAB) m/z 569 (M+H)$^+$; Anal. Calcd for $C_{32}H_{44}N_2O_7$: C: 67.58, H: 7.80, N: 4.93, found C: 68.02, H: 7.65, N: 4.90.

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