doi:10.1246/cl.2011.1278

Self-assembly of Compact Molecules Possessing Two Carboxy and One Amide Groups into Tubular Nanostructures in Liquid Crystal Phases

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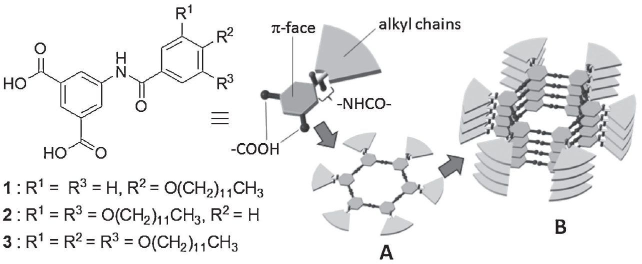
Compact molecules **1**–**3** possessing two carboxy and one amide groups were synthesized, and their self-organization into tubular nanostructures in liquid crystal phases was studied. The tubular structures were confirmed by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and one- and two-dimensional X-ray diffractions (1D- and 2D-XRDs).

Tubular nanostructures are biologically important as basic structures of channels and receptors, while they are also important in chemical fields to realize reversible encapsulation or stochastic sensing.[1] To construct tubular nanostructures artificially, self-assembly of low-molecular-weight molecules using intermolecular hydrogen bonds is a highly effective methodology. Those tubular superstructures reported are categorized into two types, coiled supramolecular polymers[2] and columnar molecular aggregates composed of cyclic supramolecular oligomers (tetramers[3] and hexamers[4]). However, the construction is still difficult and only a few examples are known. It is especially difficult to synthesize a tubular structure with a large inside diameter (>12 Å). In this paper we describe a methodology for construction of a tubular superstructure with a large inside diameter by assembling simple and compact molecules.

We designed molecules **1**–**3** (Scheme 1) consisting of five components; 1) two carboxy groups with an angle of 120°, 2) one benzene ring for π stacking, 3) one amide group, and 4) alkyl chains. We expected self-assembly of the molecules into cyclic hexamers (A) by using intermolecular hydrogen bonding between the carboxy groups, stacking of the hexamers into a tubular structures (B) by π–π interactions and linear intermolecular hydrogen-bonding network of the amides, and generation of tubular structures in a columnar liquid-crystal phase. The internal diameter of the tubular structure is estimated to be about 14 Å by an analogy between the holes of this hexamer and the trimesic acid network in crystal.[5]

The phase behaviors were investigated by POM and DSC, and the results are shown in Table 1. Compounds **1** and **2** exhibited a hexagonal columnar ($\mathrm{Col_h}$) liquid-crystal phase, and **1** decomposed before the transition from the $\mathrm{Col_h}$ to isotropic liquid phase on heating. These compounds did not show the typical textures of $\mathrm{Col_h}$ phases because of their high viscosities (Figure 1). Compound **3** showed $\mathrm{Col_h}$ and cubic (Cub) phases. Though the textures were not typical for these phases, in the transition from the $\mathrm{Col_h}$ to Cub phase the texture became dark on heating because Cub phases are optically isotropic (Figures 2a and 2b).



1 : $R^1 = R^3 = H, R^2 = O(CH_2)_{11}CH_3$
2 : $R^1 = R^3 = O(CH_2)_{11}CH_3, R^2 = H$
3 : $R^1 = R^2 = R^3 = O(CH_2)_{11}CH_3$

Scheme 1. Molecular structures **1**–**3** and concept for generation of the tubular superstructures.

Figure 3 shows the XRD profiles of **1** and **2**. Compound **1** has *d*(100), *d*(110), and *d*(200) peaks at 37.3, 21.8, and 18.8 Å, respectively. Compound **2** has *d*(100), *d*(110), *d*(200), and *d*(210) peaks at 40.9, 23.7, 20.5, and 15.6 Å, respectively. The column diameters *a* of **1** and **2** are 43.1 ($Z = 5.3$) and 47.2 Å ($Z = 6.1$), respectively.[6] In these profiles, the intensity of each *d*(110) peak is larger than that of the *d*(200) peak. This feature is quite different

Table 1. Phase behaviors of **1**, **2**, and **3**

Compound	Phase behavior[a]
1	Cr 220 (1.7) $\mathrm{Col_h}$ 300 (—) dec.
2	Cr 150 (0.2) $\mathrm{Col_h}$ 245 (6.3) Iso
3	Cr1 43 (9.9) Cr2 196 (2.8) $\mathrm{Col_h}$ 240 (—) Cub 259 (11.2) Iso

[a]The transition temperatures (°C) and transition enthalpies ($\mathrm{kcal\,mol^{-1}}$) were determined by DSC ($5\,^{\circ}\mathrm{C\,min^{-1}}$) on heating and are given in the parentheses. Cr, Cr1, and Cr2 indicate crystal phases, and $\mathrm{Col_h}$, Cub, and Iso indicate hexagonal columnar, cubic, and isotropic liquid phases, respectively.

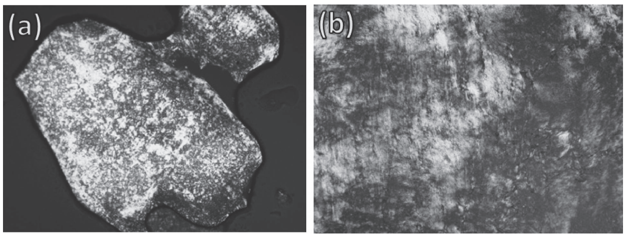


Figure 1. Polarized microphotographs of (a) **1** at 280 °C ($\mathrm{Col_h}$ phase) on heating (×200) and (b) **2** at 220 °C ($\mathrm{Col_h}$ phase) on heating (×200).

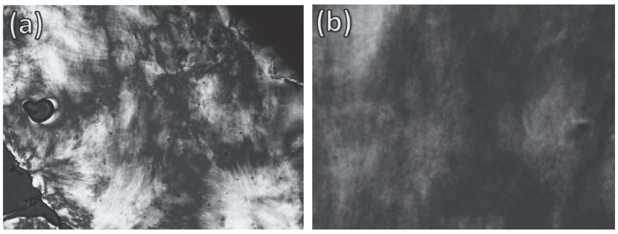


Figure 2. Polarized microphotographs of **3** (a) at 220 °C ($\mathrm{Col_h}$ phase) on heating (×200) and (b) at 245 °C (Cub phase) on heating (×200).

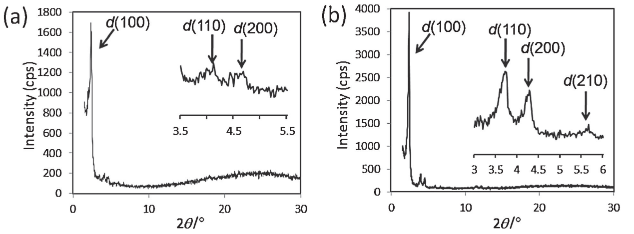


Figure 3. XRD profiles of (a) **1** and (b) **2** at 230 and 220 °C (Col$_h$ phases) on heating, respectively.

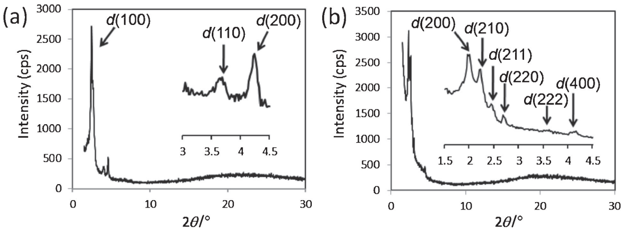


Figure 4. XRD profile of **3** at (a) 220 (Col$_h$ phase) and (b) 240 °C (Cub phase) on heating.

from those in general Col$_h$ phases. Usually, intensity of *d*(200) peak is larger than that of *d*(110) peak. Percec et al. explained that the large intensity of *d*(110) in Col$_h$ phases originated in the tubular structure of each column.[1,7] We also simulated the peak intensities of *d*(100), *d*(110), and *d*(200) and could confirm that this intensity balance was obtained when the central part of each column has a low electronic density area. It is difficult to know the reason why the maximum of the halo of **1** in Figure 3a is not located at around $2\theta = 20°$ (ca. 4.5 Å). One of the reasons is that the intensity of the halo of the alkyl chains is much weaker than that of the disordered columnar packing.

In the Col$_h$ phase of **3** (Figure 4a), the XRD profile shows $d(100) = 41.8$ Å, $d(110) = 24.3$ Å, and $d(200) = 20.9$ Å in the small-angle region. From the intensity ratio ($d(110) < d(200)$), the column may not have the large low-density space at its center. The column diameter *a* is 51.5 Å ($Z = 5.6$).[6] In the Cub phase of **3** (Figure 4b), the XRD profile showed *d*(200), *d*(210), *d*(211), *d*(220), *d*(222), and *d*(400) peaks at 44.6, 39.8, 36.2, 32.7, 25.0, and 21.8 Å, and the Cub phase was classified as *Pm*3*n* with the lattice parameter $a = 89.0$ Å. Further, it is obtained that the diameter of the spherical micelle is 55.2 Å (the average number of molecules per micelle: $\mu = 63.3$) and that each micelle consists of about 10 hexamers. It is rare for disc-shaped molecules to exhibit a cubic phase.[3]

To investigate the superstructure of **2** which gave the Col$_h$ phase with a wide temperature range and the typical XRD profile for a tubular structure, 2D-XRD was performed.[8] The sample in the Col$_h$ phase was sheared at 220 °C and cooled to room temperature quickly to give the supercooled Col$_h$ phase. The 2D-XRD profile of the supercooled sample was obtained by using an imaging plate. The *d*(100), *d*(110), and *d*(200) peaks are observed on the meridian (Figures 5a and 5b). Figure 5c shows two lines corresponding to the π–π stacking distances. These observations strongly suggest the following self-assembly (Figure 6). The molecules generate cyclic hexamers using intermolecular hydrogen bonds of the carboxy groups, and then the hexamers stack using π–π interaction and intermolecular hydrogen bonds of the amide groups. The two aromatic stacking distances *d* (=3.4 Å) and *d*′ (=3.3 Å) shown in Figure 5c originate in the stacking of the cyclic hexamers and the peripheral phenyl groups and are indicated with arrows in Figure 6C, respectively. The *Z* value (=6.1) of compound **2** is fully consistent with that the one-disk unit consists of the six molecules. Even though the *Z* values of **1** and **3** (5.3 and 5.6) are 12% and 6.6% smaller than the ideal *Z* value (=6.0), it is reasonable to consider that these values are close to the ideal one because of the fluidity of these materials.

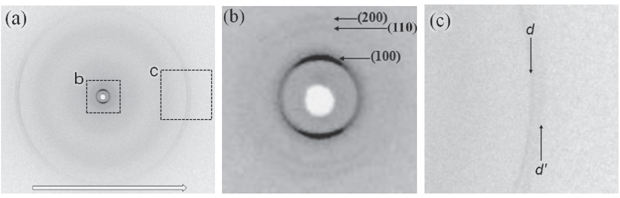


Figure 5. (a) 2D-XRD profile of **2** in the Col$_h$ phase supercooled (25 °C) and (b) (c) its magnified figures of the central and outer parts. The sheared direction is indicated by a white arrow.

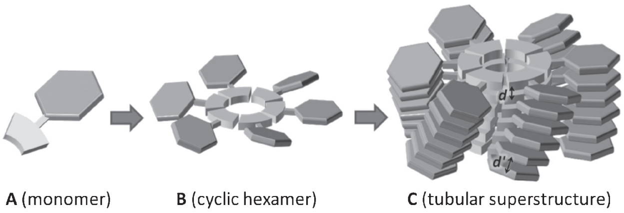


Figure 6. Schematic representation of the tubular structure. The repeat distances of aromatic rings (*d* and *d*′) are indicated.

We demonstrated that the small molecules consisting of five components self-assemble effectively into a tubular superstructure in a liquid crystal phase.

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6 The *Z* value was calculated based on $\rho = 1.0\,\mathrm{g\,cm^{-3}}$ and $c = 3.4$ Å.

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8 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.