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Channel Structures from Self-Assembled Hexameric Macrocycles in Laterally Grafted Bent Rod Molecules

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Abstract: Internally grafted bent rod molecules consisting of a bent-shaped nona-*p*-phenylene and different lengths of oligoether chains at the bay position were synthesized and characterized. All of the bent-shaped molecules showed ordered bulk-state structures as characterized by differential scanning calorimetry, X-ray scatterings, and transmission electron microscopy. The bent rod based on a short oligo(propylene oxide) chain self-assembles into a 2-D channel-like columnar structure, whereas the molecules with an intermediate length of flexible chains self-assemble into discrete channels that self-organize into honeycomb layers. A further increase in the length of the flexible chain induces a layered structure. In contrast to the bent-shaped molecules based on a linear chain, the molecules based on a branched chain self-assemble into an inverted 2-D columnar structure with an aromatic core surrounded by branched chains. We proposed the model of the channel structure on the basis of experimental data obtained from X-ray results and density measurements. Within the channels, six bent rods self-assemble into hexameric macrocycles that stack on one another to form channel-like columns where the interiors are filled by the flexible oligoether chains. Remarkably, the elongated channels break up into discrete channels of a well-defined length with increasing length of the oligoether chain. The resulting discrete channels self-organize into a hexagonally ordered honeycomb layer. The defined length of a channel is believed to be responsible for the formation of unique honeycomb layers.

Introduction

A major challenging task in supramolecular chemistry is the design of simple molecular components that are capable of organizing into complex nanostructures, the essence of which is self-assembly through various types of intermolecular interactions.[1] Among their constituting units, aromatic rod building blocks have proven to be particularly interesting due to their great potentials as electrical and optical materials.[2] Self-assembled nanostructures of molecular rods can be manipulated by incorporation of flexible coils into the rod blocks.[3] The supramolecular structures are precisely controlled by systematic variation of the type and relative length of the respective blocks. Recently, the rigid−flexible combination in a molecular architecture has been extended to laterally grafted rod−coil molecules which organize into a unique solid-state structure such as scrolled layers and stepped strips.[4] Although this rod−coil concept has been widely exploited in the assembly of elongated rod segments, only a few examples of bent rod systems have been reported.[5,6] Lateral incorporation of a flexible coil into a bent rod is expected to lead to dramatic changes in self-assembly behavior, since the assembly of bent rods would, in effect, give rise to a curved assembly as opposed to flat local structures. In particular, we envisioned that, when the bent rods are internally grafted by a relatively short flexible coil, they may form self-assembled macrocyclic units with internal coil segments as a consequence of shape complementarity and phase separation of rigid and flexible blocks. Recently, internally grafted bent-core molecules have been reported to self-assemble into 2-D honeycomb structures which are the inverse of the columnar structures formed from conventional bent-core mesogens.[6] The aromatic cores containing hydroxyl groups of the molecules assemble to form channel walls through, predominantly, specific hydrogen bond interactions.

In this paper, we present the formation of 2-D and 3-D channel structures from self-assembly of internally grafted bent rod blocks with an oligoether flexible chain. Six bent rods self-assemble into hexameric macrocycles that stack on one another to form channel-like columns where the interiors are filled by the flexible oligoether chains. Notably, the long channels break up into discrete channels of a well-defined length with increasing

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Scheme 1. Molecular Structures of **1**−**6**

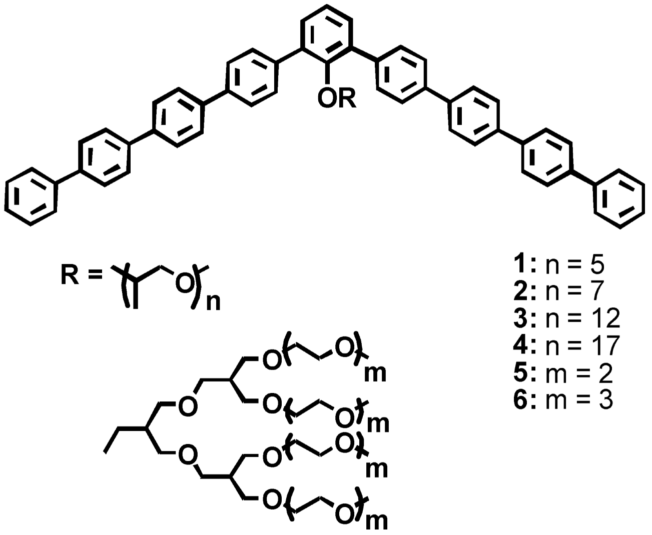

Table 1. Thermal Transitions and Corresponding Enthalpy Changes Determined from the Second Heating DSC Scans[a]

compd	f_{coil}	phase transitions (°C) and corresponding enthalpy changes (kJ/mol)
1	0.32	2-D-Ch$_{hex}$ 218.7 (31.1) i
2	0.39	3-D-Ch$_{hex}$ 88.0 (2.7) 2-D-Ch$_{hex}$ 216.2 (20.9) i
3	0.52	3-D-Ch$_{hex}$ 78.8 (4.3) 2-D-Ch$_{hex}$ 194.1 (13.5) i
4	0.59	Lam 183.6 (14.4) i
5	0.50	2-D-Col$_{ob}$ 159.2 (19.3) i
6	0.56	2-D-Col$_{ob}$ 110.5 (15.1) i

[a] Key: Ch$_{hex}$ = hexagonal, Lam = Lamellar, Col$_{ob}$ = oblique columnar, i = isotropic.

length of the oligoether chain. The resulting channels self-organize into a honeycomb layer. The internally grafted bent rod molecules that form these structures consist of a bent-shaped nona-*p*-phenylene and an oligo(propylene oxide) chain at the bay position.

Results and Discussion

The synthesis of the bent rod block molecules was performed with the preparation of a bent-shaped aromatic scaffold starting from a Suzuki coupling reaction with a 2,6-dibromophenol derivative and trimethylsilyl-substituted biphenylboronic acids.[7] The final block molecules were synthesized by an etherification reaction of an appropriate oligo(propylene oxide) chain and the phenolic intermediate and then a Suzuki coupling reaction with a biphenylboronic acid. See Scheme 1 for the structures of bent rod block molecules **1**−**6**.

The self-assembling behavior of the bent rod block molecules in the bulk was investigated by means of differential scanning calorimetry (DSC), X-ray scatterings, and transmission electron microscopy (TEM). All of the block molecules show an ordered structure, and the transition temperatures were determined from DSC scans (Table 1). As confirmed by small-angle X-ray scatterings, **1** based on a short penta(propylene oxide) chain self-assembles into a 2-D hexagonal structure with a lattice constant of 4.90 nm (Figure 1). The wide-angle X-ray diffraction pattern shows several sharp reflections that can be indexed as a monoclinic lattice with unit cell dimensions of $a = 0.51$ nm, $b = 0.76$ nm, and $c = 1.11$ nm together with a characteristic angle of 92.6° (Figure 2), indicating the rod building blocks within the columns are stacked with a $\pi-\pi$ stacking distance of 0.38 nm along the column axis. On the basis of these results and the measured density, the number of molecules in a single slice of the column could be calculated to be six. Therefore, we consider that the six bent rods in a single slice are packed in a hexameric macrocycle in which the flexible chains are filled inside the aromatic frameworks. Subsequently, the self-assembled macrocycles are stacked on top of each other to form channel-like columns that self-organize into a 2-D hexagonal structure (Figure 3).

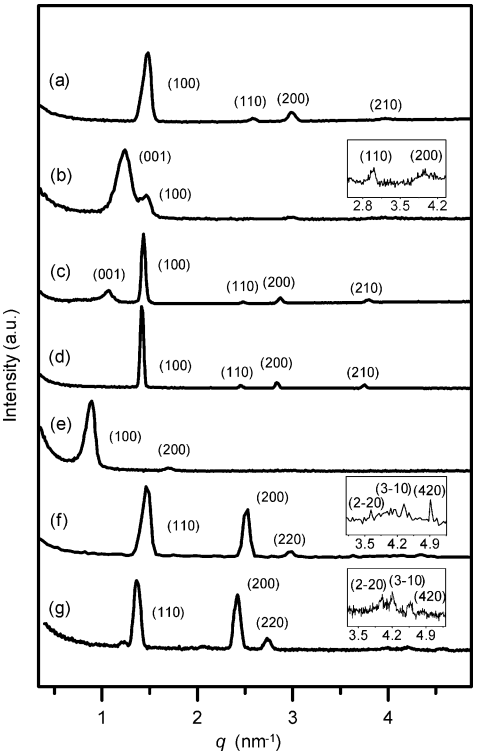

Figure 1. Small-angle X-ray diffraction patterns of (a) **1**, (b) **2**, (c) **3**, (d) **3** (at 180 °C), (e) **4**, (f) **5**, and (g) **6** [(a)−(c) and (e)−(g) at room temperature].

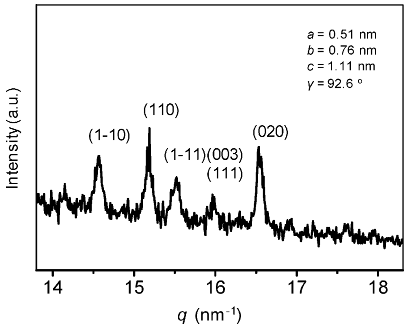

Figure 2. Wide-angle X-ray diffraction pattern of **1** at room temperature.

To explore the molecular origin of the intracolumn structure, molecular modeling was carried out using the COMPASS empirical force field calculation. Energy minimization of six molecules reveals that a cyclic arrangement of the molecules is energitically favorable, as shown in Figure 3. A side of the hexagon is made up of partial overlap between two adjacent bent rods. The outer and inner diameters of a hexameric cycle

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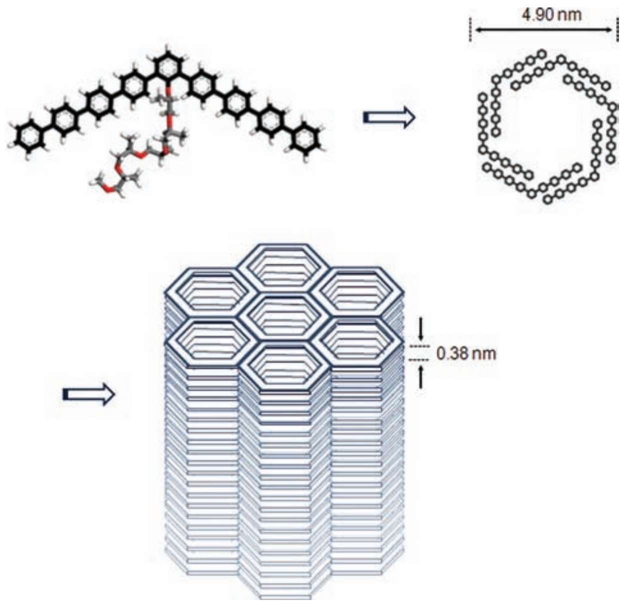

Figure 3. Schematic representation of a proposed mechanism for the formation of a 2-D hexagonal channel structure of **1**.

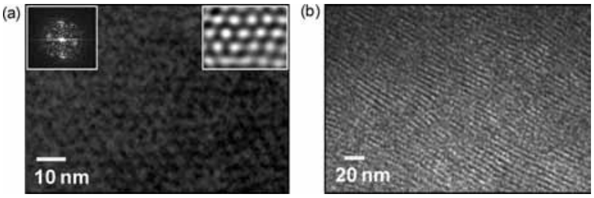

Figure 4. TEM images of ultramicrotomed films of **3** stained with RuO_4 revealing (a) the top view of a channel-like structure (inset image; 2-D Fourier transformation of 6-folded symmetry characteristic of a hexagonal structure) and (b) the side view of a columnar array of alternating light-colored aliphatic and dark aromatic layers.

are calculated to be 4.9 and 4.2 nm, respectively, consistent with the experimental results.

In contrast to **1**, both **2** and **3** based on a longer oligo(propylene oxide) chain show two phase transitions, as confirmed by DSC scans (Table 1). For both molecules at higher temperatures, small-angle X-ray patterns show several sharp reflections corresponding to a 2-D hexagonal lattice (Figures 1d and S3, Supporting Inforamtion). The lattice constants are 4.94 and 5.05 nm for **2** and **3**, respectively, which are values very similar to that of **1** (4.90 nm). Similarly to **1**, **3** reveals a number of sharp wide-angle X-ray reflections that can be indexed as a monoclinic unit cell with nearly the same dimensions as those of **1**. Upon cooling to the lower temperature structure for both molecules, however, an additional strong reflection next to the primary peak of the columnar lattice appears without any discernible change in the peak positions associated with the hexagonal lattice (Figure 1b,c). On the other hand, the wide-angle X-ray diffraction patterns remain identical upon cooling, indicating that the local packing of the aromatic segments within the column does not change at the phase transition (see the Supporting Information). Therefore, this additional peak can be considered to arise from long-range order along the columnar axis with values of 5.1 and 6.2 nm for **2** and **3**, respectively (Figure S6 and Table S4, Supporting Information). To further confirm this structure, we cryomicrotomed **3** to a thickness of ca. 50−70 nm; we then stained it with RuO_4 vapor and observed it by TEM. As shown in Figure 4, the image shows in-plane order of a hexagonal symmetry in which light flexible chain domains are regularly arrayed in a dark aromatic framework. The interdomain distance is approximately 5 nm, consistent with that obtained from X-ray scattering. The inset shows a 2-D Fourier transform of the image that has a 6-fold symmetry characteristic of a hexagonal structure.

On the basis of these results and density measurements, both **2** and **3** self-assemble into discrete channels that self-organize into a 3-D lattice based on a hexagonal order (Figure 5). Within the channels, the six bent rods in a single slice are arranged in a hexameric macrocycle in which the flexible chains are filled inside the aromatic frameworks. Considering the $\pi-\pi$ stacking distance of 0.38 nm determined from wide-angle X-ray diffraction, a column long axis for both molecules consists of 12 slices with a length of 4.56 nm, and thus, the coil layer thicknesses are estimated to be 0.47 and 1.66 nm for **2** and **3**, respectively (Figure S6 and Table S4, Supporting Information). Upon heating, the discrete channels hexagonally arranged in a layer plane are slipped with each other along their long axes, while the in-plane hexagonal order remains essentially unaltered. Consequently, the 3-D structure transforms into a 2-D structure in which the discrete channels are located in a random way along the *c*-axis without affecting the in-plane order (Figure 6), similar to a transition from a smectic B phase to a hexagonal columnar phase in liquid crystalline polymers.[8]

It has been reported that the 2-D columnar liquid crystals formed from bent-shaped mesogens and bolaamphiphilic systems transform into 3-D discrete columns on cooling.[9,10] The core parts of these columns, however, consist of aromatic segments, as opposed to the discrete channels. The hexagonally ordered channel structure has also been observed in other internally grafted bent-core molecules.[6] However, it is only 2-D, in contrast to our 3-D structure. In addition, the 2-D channel walls consist of short aromatic segments and hydrogen bonds which provide strong cohesive forces. On the other hand, the walls of our discrete channels consist of only aromatic stackings formed through weak nonspecific aromatic interactions, indicating that there is strong demixing of the rigid aromatic and flexible aliphatic segments in the laterally grafted bent rods.

In contrast to the molecules containing short chains, **4** based on a long flexible chain forms a layered structure, as confirmed by X-ray diffraction (Figure 1). The layer thickness is 5.59 nm, that is, smaller than the calculated molecular length (6.5 nm by CPK models), and suggests that the molecules are packed with an interdigitation. The formation of the layers is further supported by TEM experiments, as shown in Figure S4, Supporting Information. The layered structure implies that the bent rods assemble into an unfolded zigzag arrangement instead of a macrocyclic arrangement to maintain homogeneous density without sacrificing π-stacking interactions (Figure 6b).

The results described here demonstrate that, as the chain length of the oligo(propylene oxide) increases, the self-assembled structure of the hexameric macrocycle formed through self-assembly of the bent rods changes from long channels to discrete channels to layered structures. This structural evolution can be explained by considering the microphase separation

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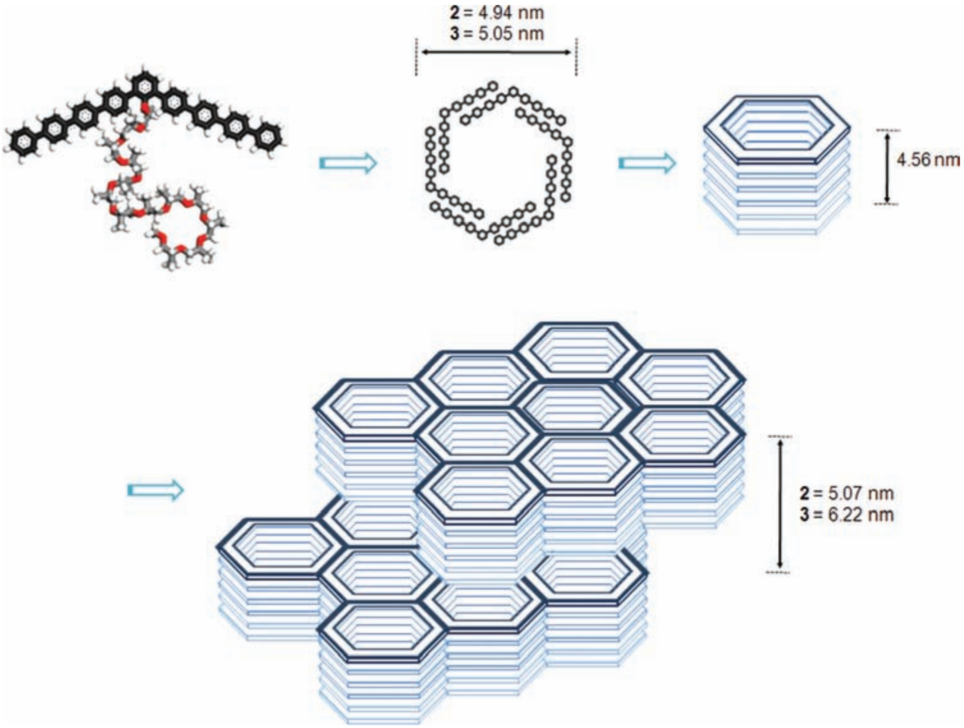

Figure 5. Schematic representation of a proposed mechanism for the formation of a honeycomb layer structure of **2** and **3**.

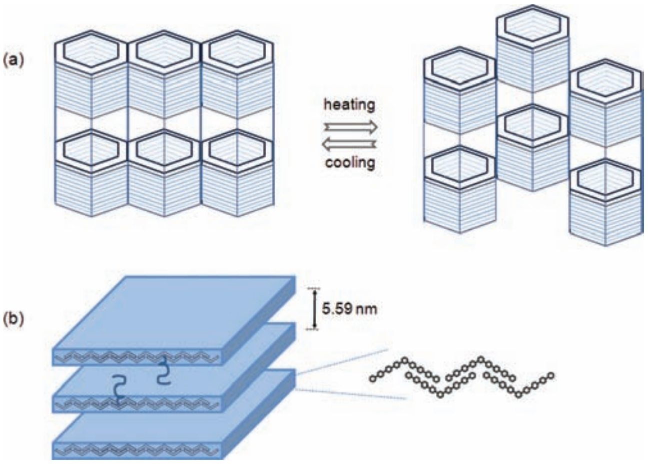

Figure 6. Schematic representation of (a) the transformation of 3-D honeycomb layers into a 2-D columnar structure of **2** and **3** and (b) the lamellar structure of **4**.

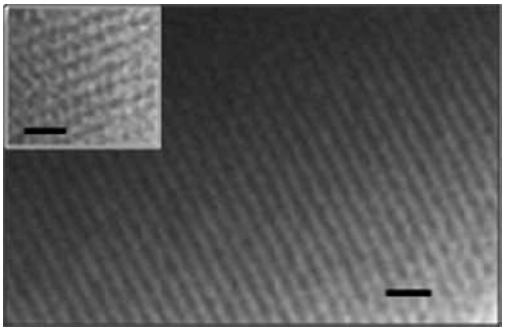

Figure 7. TEM image of ultramicrotomed films of **6** stained with RuO_4 revealing a columnar array of alternating light-colored dendritic and dark aromatic layers. The inset image at perpendicular beam incidence shows an oblique columnar array of aromatic segments. The scale bars indicate 10 nm.

between the dissimilar parts of the molecule and the resulting space-filling requirements.[11] The molecule based on a short flexible chain can be arranged with a hexameric cycles that stack on top of each other to form long channel-like columns in which the interiors are filled by the flexible chains. On increasing the coil length, however, the internal cores require more space to efficiently fill the flexible chains. To allow more volume for coils to be less confined without sacrificing intercycle $\pi-\pi$ stacking interactions, the long channels will break up into discrete channels that self-organize into a honeycomb layer. Further increasing the coil length, the macrocyclic arrangement of the bent rods eventually transforms into an unfolded zigzag arrangement to produce a flat interface which allows a greater volume for the flexible chains to explore compared to that of the channels, and thus leading to a layered organization.

To investigate the role of the cross section of the flexible chain in the channel-like molecular organization, we have prepared **5** (f_{coil} = 0.50) and **6** (f_{coil} = 0.56) based on tetrabranched oligoether chains. The melting temperature is shown to be 159.2 and 110.5 °C for **5** and **6**, respectively. Small-angle X-ray scattering of **5** shows several reflections that can be indexed as a 2-D oblique columnar structure with a lattice constant of 5.2 nm and a characteristic angle of 72° (Figure 1). Similar to **5**, **6** also organizes into a 2-D oblique columnar structure with a lattice dimension of 5.6 nm and an angle of 68.4°. This result indicates that the 2-D lattice dimension increases with increasing volume fraction of the coil segment, as opposed to the relationship of **2** and **3**. When cryomicrotomed films of **5** stained with RuO_4 were characterized by TEM, dark, more stained 1-D aromatic domains could be observed (Figure 7). In great contrast to **3** shown in Figure 4a, the top view image in the inset shows a 2-D array of dark rod domains in a light coil matrix. This result together with the X-ray scatterings demonstrates that the columns of **5** and **6** consist of aromatic

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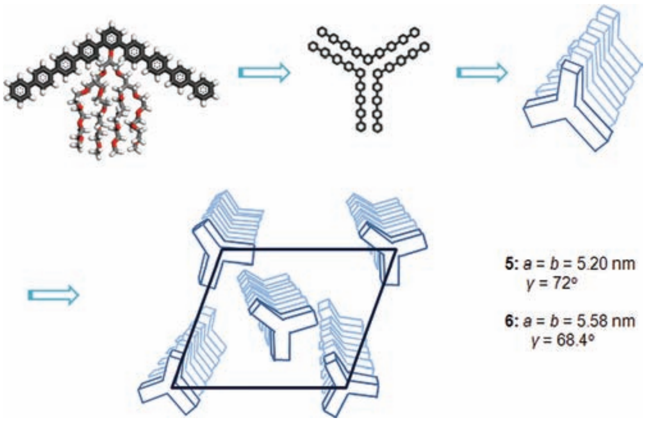

Figure 8. Schematic representation of a proposed mechanism for the formation of an oblique columnar structure of **5** and **6**.

domains surrounded by flexible chains. On the basis of these results and the measured density, the number of molecules in a single slice of the column could be calculated to be three. Therefore, we propose that the three bent rods in a single slice are arranged to form a triangle-shaped aromatic core surrounded by bulky dendritic chains. Subsequently, the self-assembled cores are stacked on top of each other to form long columns that self-organize into a 2-D oblique lattice (Figure 8).

Compared to the molecular organization of **3** with a similar volume fraction of flexible chains, this result indicates that, as the cross sectional area of the flexible chain increases, the channel structures transform into columnar structures through phase inversion. This structural inversion could be attributed to larger steric repulsion between branched chains than that between linear chains. To reduce the repulsive force, the channel structure changes into a columnar structure that allows more space for the branched chains to adopt a less strained conformation. This result implies that the steric hindrance at the aromatic/aliphatic interface plays a crucial role in the self-assembled structure of laterally grafted bent rods.

Conclusions

We have demonstrated that internally grafted bent rod blocks with a linear oligoether flexible chain self-assemble into unique supramolecular structures in the bulk. Six bent rods self-assemble into hexameric macrocycles that stack on one another to form 2-D channel-like columns where the interior is filled by the flexible oligoether chains. As the chain length of the oligo(propylene oxide) increases, the long channels break up into discrete channels and finally transform into a layered structure. In contrast, the bent rods based on a branched chain self-assemble into an inverted 2-D columnar structure consisting of an aromatic core surrounded by flexible chains. The most notable feature of the bent rod building blocks investigated here is their ability to self-assemble into a 3-D structure based on supramolecular macrocycles, through the combination of shape complementarity and phase separation of aliphatic and aromatic segments as an organizing force. This mechanism of macrocyclic assembly contrasts that of previous supramolecular macrocycles, which is dominated by attractive specific interactions.[12] Furthermore, all of these macrocycles stack to form only 2-D columnar structures. Although various honeycomb structures with rigid frameworks have been reported in polyphilic mesogens and bent core liquid crystals, they appear to be only 2-D.[6,13,14] Several examples of 3-D honeycomb structures have been reported in rigid-rod-like molecules.[15] However, all the cases are based on rod layers. Thus, it is remarkable that a 3-D honeycomb structure forms from self-assembly of discrete channels based on a self-assembled macrocycle. Another interesting point to be noted is that the hexameric macrocycles self-assembled from the bent rods are stacked to form discrete structures with a well-defined length. This is in significant contrast to conventional columnar structures from dendrimers,[16] amphiphilic rods,[13] discotic liquid crystals,[17] and rigid cycles[18] in which the lengths of the columns are not defined. Although a few examples of 3-D columnar structures have been reported in liquid crystalline molecules,[9,10] these columns consist of aromatic cores, which are opposed to the channel structure. We anticipate that the discrete channels with a hydrophilic cavity will provide a novel strategy to construct transmembrane ion transport channels,[19] which will be the subject of further investigation.

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Supporting Information Available: Synthetic and other experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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