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Self-organized spiral columns in laterally grafted rods†

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Attachment of a flexible coil on the mid-part of a rigid rod block generates T-shaped rod–coil block molecules that self-assemble into a stepped column. These layers, in turn, self-curve into a spiral column with tunable core structure in the solid state.

The organization of nanoscale self-assembled structures has attracted considerable attention in the fields of materials chemistry, supramolecular chemistry, and biological science.[1] To date, many types of molecular components have been designed for construction of complex structures, most of which have amphiphilic characteristics.[2] Block molecules based on a rigid rod segment, in this context, are useful building blocks, especially for confined aromatic nanostructures when both nanophase separation and anisotropic interactions are employed as driving forces for molecular assembly.[3] On increasing the volume fraction of flexible chains that are linearly attached to a rod segment, flat layers are separated into elongated columns that self-assemble into a 2D organized structure.[4] Within the columns, the rod blocks are aligned perpendicular to the column long axis. On the other hand, the rod segments, when they are grafted by flexible chains in a lateral way, are arranged approximately parallel to the column long axis.[5] However, most of the elongated columnar structures are based on linear domains without bending. Curved supramolecular structures based on rod building blocks can be constructed by frustration of the growth of rod segments in a two-dimensional way. This is achieved by macrocyclic attachment of a flexible chain into both ends of rods or lateral attachment of a linear chain into a mid-part of rod segments.[6]

Recently, we have shown that lateral attachment of a flexible chain into an oligo(*p*-phenylene) rod enforces planar layers to roll-up into scrolls that are highly curved structures.[7] This result stimulated us to envision whether the scrolls break up along the rod direction to form spiral columns with increasing cross-sectional area of a flexible chain (Fig. 1). Although curved 1D objects have been observed in block copolymer solutions and Langmuir–Blodgett films of an amphiphilic molecule,[8,9] they have not yet been realized in the bulk state without any template or solvents.

Here we report the formation of unusual spiral columns from the self-assembly of molecular rods with a laterally attached branched chain in the bulk. The spirally curved columns are self-organized into a 2D rectangular lattice. The laterally attached molecular rods described herein consist of a penta(*p*-phenylene) rod and an oligo(ethylene oxide) branched chain that are laterally grafted together at the mid part of the rod.[10,11] The synthesis of the laterally grafted rod–coil molecules was performed with preparation of intermediate rod scaffolds by coupling reaction of 3,6-dibromobenzene-1,2-diamine and 4-hydroxybenzaldehyde. The final block molecules were synthesized by an etherification reaction of appropriate dendritic chain segments and the phenolic intermediates, and then a Suzuki coupling reaction with biphenylboronic acid. All of the resulting rod–coil molecules based on a laterally grafted branched chain were purified by silica gel column chromatography and then prep-HPLC to yield waxy solids. All molecules were characterized by ^{1}H and ^{13}C-NMR spectroscopy, elemental analysis and MALDI-TOF mass spectroscopy, and shown to be in full agreement with the expected chemical structures. All of the laterally grafted rods have an ordered bulk-state structure that melts into isotropic liquid at 134 °C, 105 °C, and 98 °C for **1**, **2**, and **3**, respectively.

The small-angle X-ray scattering (SAXS) pattern of **1** in the solid state shows several sharp reflections that correspond to a 2D primitive rectangular structure with lattice constants a = 2.94 nm and b = 1.54 nm (Fig. 2a). **2** and **3** also show similar SAXS patterns to those of **1**, indicative of a 2D rectangular ordering. The lattice constants are a = 3.45 nm and b = 1.54 nm for **2**, and a = 3.78 nm and b = 1.56 nm for **3**, respectively. These results indicate that the lattice parameter a increases with increasing the coil volume fraction, while b remains nearly unaltered irrespective of the coil volume fraction. The wide angle X-ray scatterings (WAXS) of all the molecules show a reflection centered at a q-spacing of 12.1 nm^{-1}, which is due to crystal packing of the rod

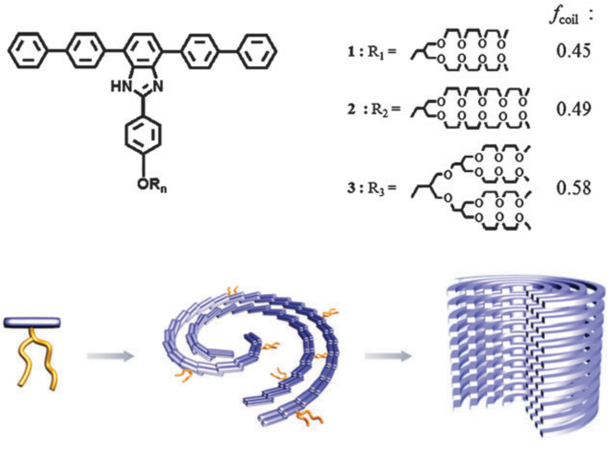

Fig. 1 Schematic representation of spiral columns and molecular structure of **1–3**.

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segments within the aromatic domains with an inter-rod distance of 5.1 Å.[12]

Considering the calculated rod length of 2.4 nm, the *a* and *b* dimensions are too much deviated to be interpreted as a perpendicular arrangement of the rods to the column axis. Therefore, parallel arrangements of the rods along the column axis would be an appropriate model, similar to other laterally grafted rods.[5] Based on the lattice constants and measured densities, the average numbers of rod units per cross section of the column are calculated to be ~8 for all the samples (Table S2†). Taking the lattice parameters into account, this number of molecules suggests that four rods are faced parallel to each other to produce a brick-like rectangular solid which subsequently stacks together with an overlap of an approximately half of the rod length to form stepped columns (Fig. 2b, 3b). The bricks have a thickness of 1.54 nm and widths of 2.94 nm, 3.45 nm, and 3.78 nm for **1**, **2**, and **3**, respectively. These dimensions indicate that the lateral chains are located in the side faces of the rectangular solid. This packing arrangement of rod segments is similar to how stepped column structure is formed from the laterally grafted elongated aromatic rods.[5a]

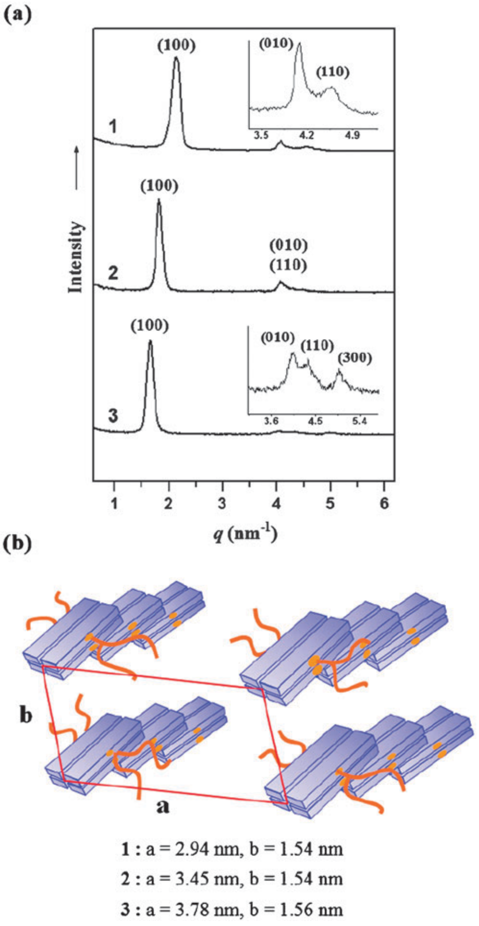

Fig. 2 (a) SAXS patterns of **1–3** plotted against q (= $4\pi \sin\theta\lambda^{-1}$) (Inset: magnified SAXS reflections in the range of q = 3.5–5.5 nm^{-1}). (b) Schematic representation of a 2D rectangular structure.

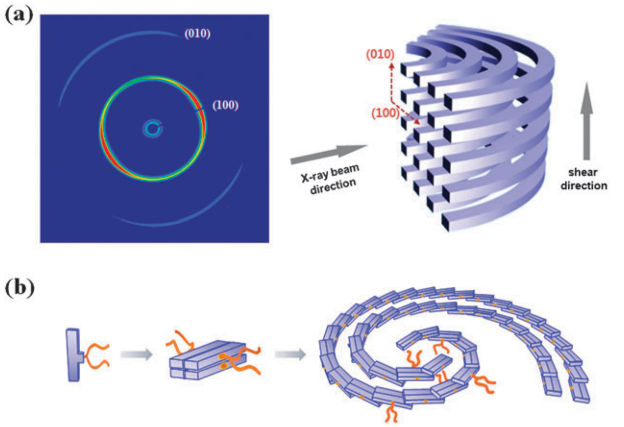

Fig. 3 (a) 2D-SAXS pattern obtained from the sheared sample of **1** at 25 °C. The X-ray pattern was recorded on the sample along a direction perpendicular to the shear. The diffraction pattern shows {100}, {010} reflections. (b) Schematic representation of the packing model of **1**.

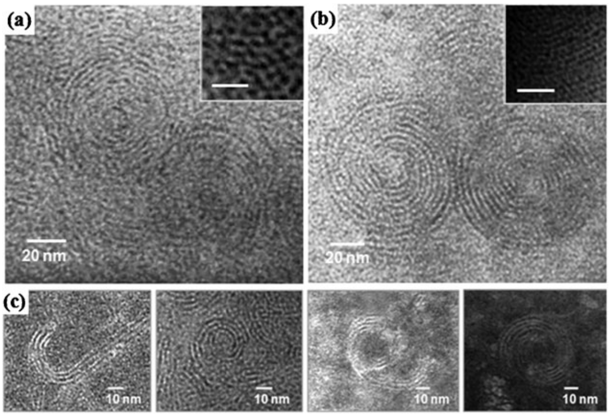

Fig. 4 (a) The high magnification image of the cross-section shows spiral columns from **1**. (b) TEM image of **2**. The insets in (a) and (b) are high-magnification images of the cross-section. Scale bar (a) 10 nm and (b) 20 nm. (c) TEM micrographs of intermediate structures kinetically trapped by quick quenching from the melt of **2**. TEM analysis was performed on thin films cryo-microtomed at −70 °C. TEM images of the cross sections from the experiment show the intermediate structures between straight and spiral column.

At room temperature, the sample could be mechanically aligned by shearing on a polyimide film, as observed in the 2D X-ray diffraction pattern (Fig. 3a). When the X-ray beam is oriented perpendicular to the shear direction, a pair of (100) reflections is diffracted along the equator, while the (010) reflections are diffracted in the cross direction at an angle of 90°. This result indicates that 2D ordered columns adopt an orientation perpendicular to the shear direction, as opposed to conventional columnar structures in which the columns are aligned parallel to the shear direction.[13]

To further investigate the unusual 2D supramolecular structure, transmission electron microscopy experiments were performed with the cryo-microtomed films of **1** and **2**. Remarkably, the columns of both samples are curved to form spirals, as revealed by TEM images in Fig. 4. The images of **1** and **2** stained with RuO_4 show curved columns of a regular thickness of ~3 nm with a spiral arrangement throughout the samples. These dimensions are consistent with those obtained from SAXS. The periodic dimensions of ~3 nm in the spiral packing suggest that the columns bend toward rod–coil junctions, that is, the side face of the rectangular solid. The side view image shows a dimensional array of dark aromatic spots in a matrix of light oligo(ethylene oxide) chains (Fig. 4a,b, inset).

The transmission electron microscopy observations together with the X-ray results lead to the structural model of the spiral structure as shown in Fig. 3. The rod segments self-assemble into a rectangular brick with lateral chains in the side faces which stacks together with a half overlap of the rod length to form stepped columns. Subsequently, the resulting stepped column bends toward the rod–coil junctions through staggering between the bricks at a certain angle to form a spiral columnar structure with a 2D rectangular lattice. Considering that the laterally grafted rods based on ether linkages in rod–coil junctions form linear columns without curvature,[5a] hydrogen bonding interactions between the imidazole units in this system seem to play an important role in the curved structure. This was confirmed by FT-IR spectroscopy that shows characteristic bands associated with hydrogen bonding of imidazole units (Fig. S5†).

To elucidate the formation mechanism of the curved columns from the melt, we have investigated the cryomicrotomed films of **2** with different annealing times (Fig. 4c). When quickly quenched from the melt by blowing cold argon, the TEM images show the loosely bent columns together with non-curved columns. However, when the films were cooled slowly from the melt to ambient temperature, we observed closely packed spirals throughout the image area. This result implies that the molecule first assembles into a linear columnar structure which subsequently bends into spirals.

The results described here demonstrate that the aromatic rods with a lateral branched chain self-assemble into a 2D spiral columnar structure, where the rod segments are arranged parallel to the column axis in a stepped fashion. Although the definitive driving forces responsible for this curvature are not clear at present, a delicate balance between the energetic gain obtained through maximized hydrogen bonding together with π–π stacking interactions and the penalty associated with large mismatch between the cross sectional area of rod and coil seems to play a crucial role in the formation of a curved columnar structure.[14] Compared to the scrolls in laterally grafted rods based on a linear chain,[7] this result indicates that the scrolls break up along the rod direction into spiral columns with increasing cross-sectional area of the flexible chains. This is similar to how nanostructures with interfacial curvatures are formed in preference to lamellar structures in linear rod–coil systems with increasing volume fraction of flexible chains.[3a,4,15] The spiral bending of elongated columns is in marked contrast to structural behavior of repeated 2D structures.[13,16] In this respect, this system provides access to a large variety of theoretical and experimental investigations to expand the scope of curved nanostructures formed in the bulk of self-assembling molecules.

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