Thermo-Responsive Chiral Column by Scissoring Motion from Rigid-Flexible Aromatic Rod Assembly

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Abstract: Here, we report thermo-responsive chiral columns from self-assembled coil-rod-coil molecules. The rigid rods self-assemble into multiplying dimers which stack on the top of one another to form non-chiral columnar crystal. Notably, the achiral crystal transforms into 2D hexagonally ordered liquid crystal with supramolecular chirality as heating. The reversible chiral switching behavior within columnar structures arises from scissoring motion from neighbored molecules driven by high thermal entropy of flexible chains relative to stiff-rod.

Keywords: π stacking; self-assembly; chirality control; helical stacking; optical switch

The sensor of chirality based on self-aggregated helix has been of growing interest both for life and materials science due to their wide application potentials in interdisciplinary areas combining chemistry, biology and optical physics.¹⁻⁸ In the living system, it is known that DNA and proteins can produce mechanical signals through spontaneous motions in response to external stimuli. Like human DNA, generally, the artificial supramolecular nano-helix can be constructed by the assembly process of chiral molecules through hydrogen bonding,^{9,10} π - π stacking,¹¹ solvophobic effects,¹² and electrostatic interactions.^{13,14} Among them, chirality control of the helical architectures is one of the highlighted topics to mimic the molecular motions of complicated biological systems. The majority of these studies are reported in polymers, liquid crystalline phases, or host-guest complexes systems by changing the

external conditions such as solvent,^{15,16} temperature,^{17,18} light,¹⁹⁻²¹ pH,²²⁻²⁵ or by interaction with specific guests.²⁶⁻²⁹ The senses of chirality in self-assembled systems can be ascribed to a change of helical twisting power (HTP) or a conformational change of the molecular backbones due to supramolecular aggregations. Previously, we have prepared a switchable helical fiber with reversible chiral-nonchiral states from the self-assembly of rigid flexible amphiphiles through intermolecular spring motion.³⁰ We have also reported a tunable 2D organization of dumbbell-shaped amphiphiles based on different cross-sectional flexible segments by scissoring motion.³¹ The manipulation of 2D growth was attributed to the degree of twisted angle between two neighboring stacked rigid segments. Moreover, introducing chirality into flexible segment would produce a switchable column between crystal and liquid crystals resulting in the competition of microphase separation and π - π interaction. Beyond the molecular design, herein, we report the formation of temperature-responsive chiral columns self-assembled from the dumbbell-shaped coil-rod-coil triggered by molecular scissoring motion. For comparison, we investigated the derivative **2** based on strongly π stacked aromatic anthracene (scheme 1).

Scheme 1. Chemical structure of rigid-flexible amphiphiles **1** and **2**.

The synthesis of **1** was performed stepwise according to previously reported methods, and meanwhile, **2** was synthesized from the preparation of anthracene bi-boronic acid and 9-arylcarbazole aromatic scaffold according to the procedure described previously.³² The final compound was successfully synthesized by Suzuki coupling with the adaptive boronic acid. These resulting molecules **1** and **2** were characterized by ¹H and ¹³C NMR spectroscopy, and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy and the data were shown to be in full agreement with the structures presented.

Molecule **1** which consists of dumbbell-shaped stiff rod block and flexible dendritic coil block can self-assemble into an aggregated structure due to microphase separation between each block on the solid film. Subsequently, the aggregation behavior of **1** in solid state was investigated by means of DSC,

Fig. 1. a) The absorption spectra of **1** in CHCl₃ (17 μ M, black), and in solid film measured at 30 $^{\circ}$ C (red); b) CD spectra of **1** measured at 30 $^{\circ}$ C (black), at 70 $^{\circ}$ C (red), and **2** measured at 30 $^{\circ}$ C (green).

thermal optical polarized microscopy, UV-Vis spectroscopy, circular dichroism (CD), and X-ray scattering. Similar to the one described previously, **1** in chloroform (17 μ M) shows an absorption maximum at 325 nm (π - π^* transition) and two emissions at 397 and 410 nm, suggesting the carbazole plane was twisted with hexa-*p*-phenylene at molecular dissolved state.³⁰ In the solid film, the UV shows two maximum absorptions at 358 and 373 nm and fluorescence quenching (Fig. 1a and Fig. S1, Supplementary Information). The red shift can be ascribed to the existence of the effective conjugated length, indicating that the twisted aromatic rod transforms into co-planar conformations to induce strong aggregation in solid state. On slow cooling from the isotropic liquid to room temperature (RT), a fernlike texture which corresponds to a typical columnar mesophase was observed (Fig. S2, Supplementary Information). Interestingly, when the column on a quartz plate was subjected to circular

Fig. 2. X-ray diffraction patterns measured at different temperatures plotted against q ($= 4\pi\sin 2\theta/\lambda$) in the oblique columnar structure at 30 °C, and the hexagonal columnar structure at 70 °C for **1**.

dichroism (CD) measurements at 30 °C, no CD signals could be detected, indicating that the columnar objects are non-chiral even though **1** contains chiral side groups (Fig. 1b). To further understand the molecular packing within a column, we performed X-ray scattering experiments. The small-angle X-ray diffraction (SAXS) pattern of **1** displayed a number of sharp reflections at 30 °C with some peaks at wide angle, an indication of the existence of a highly ordered nanoscopic structure with three distinct lattice parameters (Fig. 2). These reflections indeed can be indexed to an oblique columnar crystalline structure with a characteristic angle of $\gamma = 65^\circ$ and lattice parameters $a = 2.7$ nm, $b = 3.2$ nm, $c = 1.2$ nm (Table S1, Supplementary Information). In order to better

understand the packing structure, we calculated the number (n) of molecules in one column. From the measured density ($1.17 \text{ g}\cdot\text{cm}^{-3}$) and the lattice volume (Table 1), it is estimated that approximately two molecules were filled in a slice of each column. Based on the extended aromatic length (3.5 nm by Corey-Pauling-Koltun (CPK) molecular model) and 002, 102, 312, 422 such as three dimensional peaks which observed in wide angle (Fig. 2), we consider that the neighbored two molecules are stacked along c axis with alternative arrangement through strong π - π stacking to form crystalline ordering, thus frustrating the chiral transfer from the side groups to the aromatic cores, leading to a non-chiral column.

Table 1. Thermal transtions of dumbbell-shaped molecules (data are from heating and cooling scans) ^[a]

Molecules	ρ ^[b] [g/cm^3]	f_{rod} ^[c]	Phase transition [$^{\circ}\text{C}$] and corresponding enthalpy changes [kJ/mol]	
			Heating	Cooling
1	1.17	0.27	Cr 63.6(5.1) Hc 111.1(9.3) i	I 100.8(-8.9) Hc 46.2(-5.2) Cr
2	1.14	0.28	Cr 123.5(6.8) i	I 109.4(-8.2) Cr

[a] Data are from heating and cooling scans. Cr: alternartively stacked crystal;Hc: helical columnar liquid crystal.

[b] ρ = molecular density. [c] f_{rod} = rod volume fraction.

The formation of multiplying rod packing with the flexible dendritic exterior suggests that the columnar crystals would exhibit thermo-responsive behavior because the higher entropy of flexible chains relative to the stiff-rod segments requires a larger interfacial area to reduce enhanced space crowding in the flexible domains. Indeed, the DSC thermograms showed that crystal **1** melts

into anisotropic liquid crystals at 64 °C followed by isotropic liquid (Fig. S3, Supplementary Information). In contrast to low temperature, the CD at liquid crystalline phase gives positive cotton effect in the spectral range of the aromatic units (Fig. 1), indicative of the formation of helical stacks of the rod segments with a preferred handedness³³. To understand the 2D structures, we performed X-ray scattering experiment at high temperature. As heating, the several reflections of **1** in the wide-angle gradually defused with some new peaks at small angle, suggesting a liquid crystal was formed with reduced π - π interaction between neighbored rods. However, it is notable that both of the X-ray scattering patterns, regardless of temperature, showed a reflection at the same position about 10.7 nm⁻¹ (Fig. 2 and Fig. S4, Supplementary Information), indicating the π stacking distance of neighboring rods is nearly unchanged. Upon heating to 70 °C, both 100 and 010 peaks merged into a new reflection accompanied by two peaks at middle-angle and these three diffractions at high temperature could be indexed as a 2D hexagonal columnar structure with a lattice constant of 2.9 nm (Table S2, Supplementary Information). Compared with the oblique columnar, the hexagonal ordering has an increased parameter ratio (a/b), whereas a decreased anisotropic ability, suggesting the reduced π interaction take place in column plane.

Based on these results, the unique feature of chiral induction can be explained by the competition between π - π stacking and microphase separation. The rod segments within columnar structure at lower temperature have a strong tendency of anisotropic crystalline ordering to drive the rod segments to aggregate in one dimension with ABAB arrangement through microphase

separation between incompatible components and π - π stacking interaction, thus, frustrating the chiral transfer from the side groups to the aromatic cores, leading to a non-chiral column. As heating, however, higher thermal motion of flexible chains relative to the stiff-rod block requires a larger interfacial area. To reduce this enhanced crowding at interphase, the alternatively stacked rod separated more to reduce anisotropic interaction leading to neighbored rod rotated one dimension to minimize a steric repulsion between bulky dendritic segments.

To gain insight into the role of the π - π stacking interactions between neighbored aromatic segments in the switchable behavior of chirality, compound **2** based on an anthracene aromatic unit was prepared with the aim of frustration of chiral amplification by strong anisotropic interaction. The dumbbell-shaped molecule **2** was also observed form columnar crystals that melt into isotropic liquid upon 87 °C. As expected, the solid film based on self-assembly of **2** did not show any CD signal in columnar crystalline phase (Fig. 1b). To obtain more structure information of the solid phase, the WAXD analysis was performed at RT. Both in small- and wide-angle a number of diffractions were observed. The summary of the diffraction peaks and their indexation can be found in the supporting information. In the small-angle, **2** shows two kinds of equidistant reflections that can be indexed based on a 2D oblique lattice: $a = 2.4$ nm, $b = 3.8$ nm, $\gamma = 71^\circ$ (Fig. S5, Supplementary Information). The large number of (hkl) diffractions at wide-angle, particularly those with $l \neq 0$, suggests the existence of crystalline nature of the columns. These (hkl) with (001)

diffractions confirm that there is repetitive periodicity with 0.82 nm along c^* axis. According to the cell parameter, two molecules were calculated within one unit cell of the columnar crystals. From the molecular parameters, it is apparent that the molecular core covers the a,b plane allowing neighbored molecules along c^* axis with strong anisotropic interaction to produce periodic columnar crystals (Fig. S6, Supplementary Information). The comparison between **1** and **2**, strongly supports the appropriate competition based on π stacking and microphase separation plays a crucial role in the reversible chiral switching in columnar aggregates.

Fig. 3. Schematic representation of thermo-responsive organization of **1**.

In summary, we have demonstrated herein that the coil-rod-coil molecules can self-assemble into multi-twisted ordering. At room temperature, the neighboring molecules show strong π interaction to self-assemble into alternatively stacked columnar crystals. The multiplying crystals were shown to

be temperature-responsive to convert into helical columnar liquid crystals by scissoring motion of neighbored molecules (Fig. 3). It is notable that the switching behavior of chirality within columnar structure by dynamic molecular motion represents a remarkable contrast to other helical columnar structures that dissolve into molecular components. Such optical switch by mechanical motion on thin film may provide a new strategy for the construction of dynamic nano devices or optical motor with desired functions.

Acknowledgements

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Graphical abstract

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Assembly

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