

Complimentary Gearing of Molecular Swirls Resolved by X-ray Diffraction

The connection between liquid crystalline and constituent molecules becomes an attracting topic in science for hundreds of years. The crystalline-liquid states resulted from the structure of molecules play a significant role in this field. Through structure design depending on the interactions between molecules, interesting shapes of liquid crystalline shall emerge to our sight. Herein swirl-like gears in molecular scale (< 1 nm) have been prepared through molecular design. Cooperative gearing of the molecules extends in three dimensions resolved by powder X-ray diffraction and scanning tunnelling microscopy.

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Columnar liquid crystalline materials continuously attract interests because of their cooperative physical properties that lead to many technological applications. As for the design principles of columnar mesogenic materials, the molecular core planarity and chain density are usually the two main considerations, which resulted in that columnar supra-structures generated mainly by planar disc-like mesogens with strong $\pi - \pi$ core attractions and assisted by intermolecular forces, such as hydrogen bonding and dipole-dipole interactions. Recently, Meijer *et al.* reported substituted star-like hexaarylbenzene compounds showing columnar packing in liquid crystalline states. Scanning tunnelling microscopic (STM) studies revealed molecular rosettes of specific chain "rotation directions" at a solid-liquid interface. We recently demonstrated that the side-arm rotation could be restricted and thus the inter-disc interactions were improved by introducing an additional chain *ortho* to the original chain of one side-arm in hexakis (alkoxyphenylethynyl) benzene.¹

The rotations of the six peripheral phenyls in hexa (phenylethynyl) benzene can be limited in the molecular design of the novel mesogen **1** which was synthesized and exhibited a columnar liquid crystalline phase. The rotation of peripheral phenyls, restricted but not rigid, endows structural flexibility for **1** to favour a cooperative fashion of chain arrangement giving a molecular swirl geometry, i.e. a molecular rosette (Fig. 1), to minimize intramolecular steric congestion. Hence, the inter-disc $\pi - \pi$ attractions along the column are enhanced. Moreover, along the disc plane, packing of molecules of the same swirl sense, i.e. a gearing or lock-in mechanism of molecular swirls, will be favoured to minimize steric crowded-

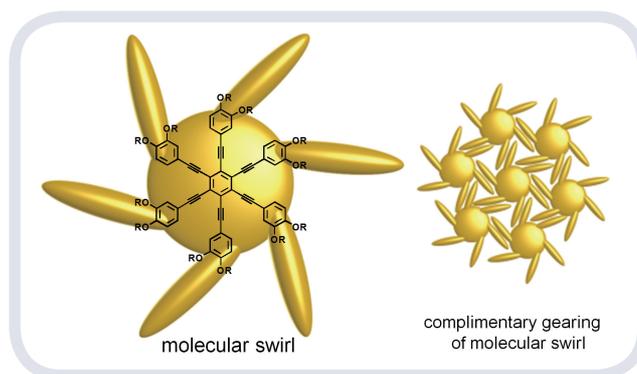


Fig. 1: Left panel: chemical structure of compound **1** and schematic molecular geometry representations of compounds **1** showing molecular swirl conformation. Right panel: cooperative packing of molecular swirls.

ness and in-plane inter-chain van der Waals (VDW) interactions can be maximized.²

The above mentioned inter-disc packing pattern was confirmed by X-ray diffraction investigations on aligned **1** prepared by filament extrusion. For comparison, Figs. 2(a) and 2(b) show the XRD investigations on the unaligned sample of **7e**. Figure 2(c) shows the 2D XRD pattern of an extruded filament of **1**. For the aligned sample shown in Fig. 2(c), in the small angle regime, a pair of sharp and intense arcs along the equator, corresponding to intercolumnar correlations, is found. Each arc is consisted of two overlapped reflections of d_{11} and d_{20} . Since the filament was placed vertically, these small angle equatorial reflections correspond to the inter-columnar order. In the wide angle regime, in addition to the broad alkyl halo at 4.6 Å, a pair of diffuse reflections, corresponding to a long $\pi - \pi$ stacking distance of peripheral phenyls at 3.9 Å with an averaged

tilting angle of 52° , appears at both sides of the meridian as shown in Fig. 2(b). The fact that the meridian-centered alkyl halos are perpendicular to the equator-centered intercolumnar reflections proves the out-of-plane chain bending model to be invalid as described previously. At middle angles, a very weak diffuse reflection at 7.2 \AA was detected, which cannot be derivative signals of the rectangular lattice due to its very diffuse nature. The azimuthal scan of this scattering revealed the reflection centered along meridian rather than along the equator, indicative of a modulation of electronic density along columns (Fig. 2(d)). The distance is ca. two $\pi - \pi$ stacking distances, indicating that

every 3rd disk within a column is rotationally correlated. With a C_6 rotational axis along the disk normal of **1** with a cooperative in-plane chain bending, such a correlation can be realized by rotating each successive stacked disk by $360^\circ/6/2 = 15^\circ$ about the C_6 axis to give a helical stacking with every other disk to be rotationally eclipsed (Fig. 2(e)). Thus, the helical pitch can be determined to be $7.2 \text{ \AA} \times 6 = 43.2 \text{ \AA}$. The packing pattern derived from XRD investigations was also corroborated by scanning tunnelling microscopy.

Beamline 17A1 XRPD end station

References

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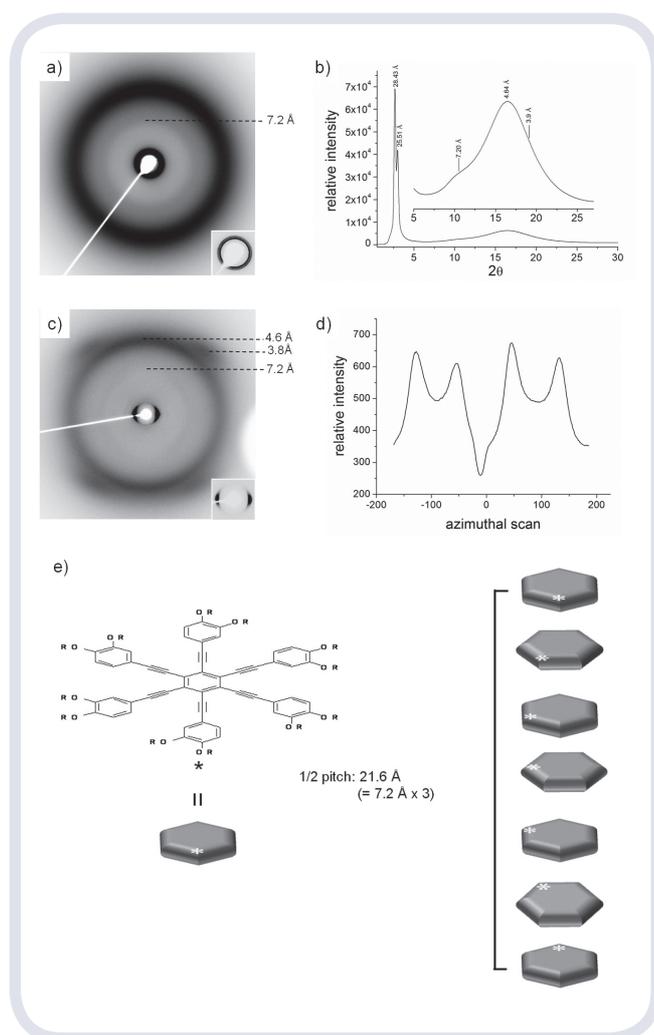


Fig. 2: Structural investigations of **1** by (a) the 2D PXR pattern of unaligned sample at 180°C (inset: 2D PXR of small angle scatterings); (b) respective intensity/ 2θ plot of (a); (c) the 2D PXR pattern of a sample aligned by filament extrusion at 105°C (inset: 2D PXR of small angle scatterings); (d) the azimuthal integration of the scattering intensity corresponding to the π -stacking distance; and (e) the schematic illustration of the intramolecular arrangement of **7e** within a helical column (the "*" indicates a reference point on each disk to better illustrate the helical conformation within a column).