

## Single-crystal-like chiral organic droplets exhibiting unidirectional rotating sliding

Bridging the gap between the nanoscale (e.g., molecules) and macroscopic (e.g., materials that can be taken in the hand) words is a key issue in science and technology. For instance, the construction of organic materials with ultralong-range structural order on a scale of several millimeters or even several centimeters, i.e., beyond the nanometer scale that can be achieved by general molecular self-assembly, is one of the ultimate goals of soft materials science and engineering as well as thin-film device technology. Furthermore, if it becomes a reality, it might lead to discoveries of unknown behaviors of molecules in the condensed phase.

Here, we report a surprising finding of a very unique soft material that exhibits not only three-dimensional (3D) structural integrity like a single crystal but also fluidity [1]. In general, single crystals have a well-defined polyhedral shape and consist of a continuous and regular assembly of 3D unit cells [2]. However, when heated to their melting temperature and subsequently cooled, organic molecules generally solidify into polycrystals with multiple grain boundaries. Even for a liquid crystal, its macroscopic entity usually comprises many discontinuous microdomains, with the exception of a nematic phase [3]. Unlike those materials, our material can be obtained as a millimeter-size macroscopic droplet by the spontaneous assembly of a molecule upon simply heating a bulk solid sample to the melting temperature and subsequently cooling.

The structure of the obtained droplets is characterized by high positional and orientational ordering and 3D structural integrity similar to that of single crystals. One molecule that shows such a superb self-assembly property is a discotic triphenylene derivative with six chiral 2-pentyl groups as side chains (Fig. 1(a)). When a bulk sample of an enantiomerically pure molecule was placed in a glass capillary (Fig. 1(b)) and exposed to an X-ray beam at SPring-8 BL45XU at the mesophase temperature, regularly arranged diffraction spots clearly appeared in the resulting through-view two-dimensional (2D) XRD image (Fig. 1(b)). This molecule exhibits a single-domain mesophase in a size regime greater than 1 mm, where 2D sheets, formed by the herringbone-like packing of the triphenylene core, stack into a multilayer structure with a one-dimensional (1D) structural correlation, resulting in 3D periodic order (Figs. 1(b,c)). The mesophase was identified as the H\* phase (i.e., chiral H phase), which has never been reported even for the very widely investigated rod-

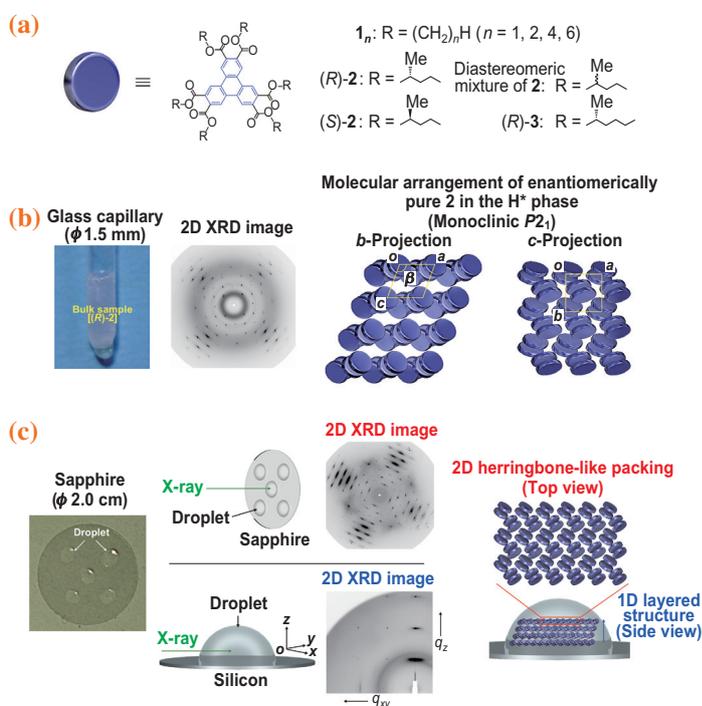


Fig. 1. (a) Chemical structures of triphenylenes. (b) Photograph, 2D XRD image, and schematic illustration of the arrangement of the triphenylene core of enantiomerically pure 2 in its H\* phase with a monoclinic P2<sub>1</sub> space-group symmetry. (c) Photograph, 2D XRD images, and schematic illustration of the arrangement of enantiomerically pure 2 in a droplet.

shaped liquid-crystalline molecules.

Surprisingly, under the force of gravity, the droplet can flow without impairing the internal 3D structure. In common sense, crystals, in which the position and orientation of the constituent elements are rigorously determined, do not show fluidity. Plastic crystals, in which the constituent molecules are rotating but fixed at their positions, do not generally behave like a fluid. In liquid crystals that exhibit fluidity, although the constituent molecules have orientational order, their positions are not fixed owing to translational and rotational motion. According to this general notion of the phases of organic materials, the present molecular assembly is surprising: it exhibits flowability despite its well-defined positional and orientational order. X-ray imaging using a synchrotron radiation X-ray beam (beamline BL45XU) showed that under the force of gravity, droplets of this chiral triphenylene in the mesophase can flow without impairing the internal structure while unidirectionally rotating clockwise or

counterclockwise in accordance with the chirality of the side chains (Fig. 2(a), bottom).

The intriguing fluid nature allowed us to reveal the occurrence of synchronous and collective asymmetric molecular motion controlled by small molecular chirality. This result demonstrates that the “small” point chirality of a molecule can control the movement direction of the “macroscopic” molecular assembly. Rheological measurements indicated that the unidirectional rotational flow behavior originates from the difference in yield stress between the enantiomers. Furthermore, the chiral triphenylene assembly was found to possess very unusual rheological properties that exhibit comparable storage and loss elastic moduli at values greater than  $10^4$  Pa (Fig. 3). This delicate balance between elasticity and viscosity accounts for the unique fluid nature of the droplet.

We assume that the “2D + 1D” structure is essential for both the spontaneous formation of the single-crystal-like droplet and the macroscopic asymmetric collective motion of the molecules in the H\* phase. In the past, we reported that a large-area single-crystalline order was achieved in layered materials in which constituent molecules assemble into a sheet with a 2D structural correlation [4,5]. This structural pattern holds true for the order in the H\* phase of the molecules. The 1D structural correlation between the 2D sheets also plays a role in the collective molecular motion with enantiospecific unidirectional rotation (Fig. 2(b)).

The discovery of the unprecedented soft material that exhibits spontaneous ultralong-range ordering as well as synchronous and collective asymmetric movement will update the fundamental understanding of the structure formation, motility, and phase of organic materials.

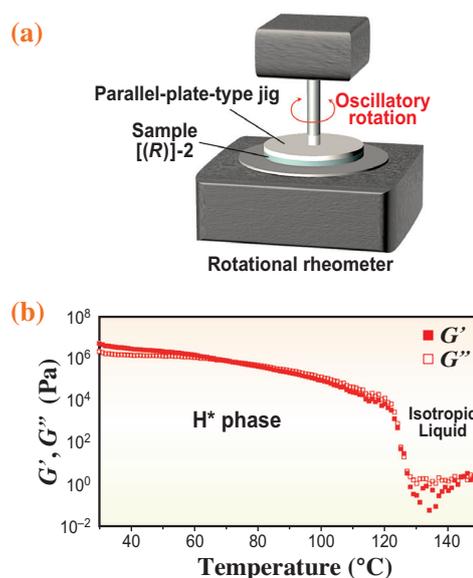


Fig. 3. (a) Schematic illustration of a rheometer equipped with a parallel-plate jig for the dynamic viscoelasticity measurement of (R)-2. (b) Temperature dependence of the storage elastic modulus ( $G'$ ) and loss elastic modulus ( $G''$ ) of (R)-2.

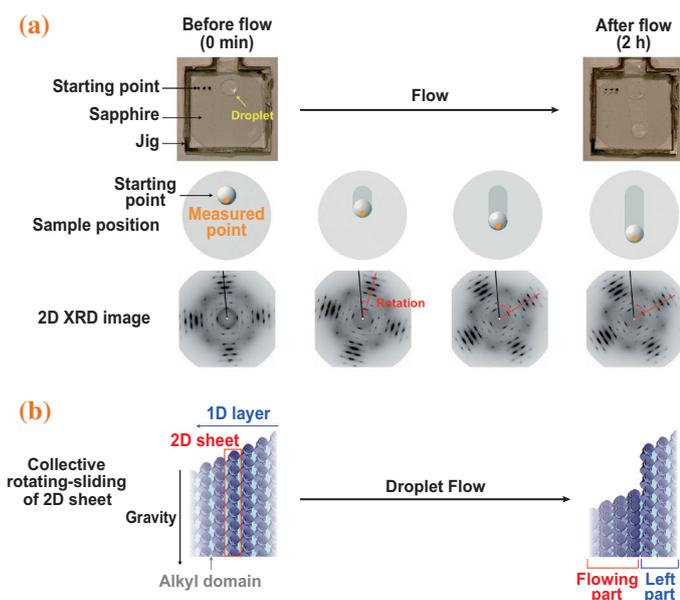


Fig. 2. (a) Photographs and 2D XRD images of (R)-2 droplets on a vertical sapphire substrate before and after flow. (b) Schematic illustration of the rotating-sliding motion in a sliding droplet.

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