Nanometer-scale ordering in cast films of columnar metallomesogen as revealed by STM observations†

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STM observations were performed on a cast film of a columnar metallomesogen ([Cr(5C$_8$)$_3$]; 5C$_8$ = 1-(3,4,5-trioctyloxyphenyl)-3-(3,4-dioctyloxyphenyl)propane-1,3-dionate anion) on a graphite surface, revealing the nanometer-scale surface ordering into an oblique lattice (a = 10.5 nm, b = 11.5 nm, α = 55°) possibly due to the ΔΛ-chiral interactions.

Microscopic ordering in molecular assemblies has attracted extensive interest because it plays a central role in a number of chemical and physical processes such as nonlinear optics, ferroelectric properties, and catalytic functions. Surface observation techniques such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM) have been favorably employed to detect these ordering phenomena.[1,2]

When liquid crystalline (LC) materials are subject to such observations, nano-scale ordered structures, if observed in the LC films, may be thought of as a two-dimensional (2D) manifestation of intricate interactions in their bulk phases. Previous studies on LC films of columnar triphenylene derivatives[3–5] have even unraveled surface induced chirality in suitably alkylated cases. In contrast, metallomesogenic molecules contain characteristically rigid coordination structures such as planar, tetrahedral, and octahedral ones. Of particular interest to us are the octahedral mesogens which are expected to express a certain regularity arising from their stereoselective packing involving the ΔΛ-chirality.[6–8]

An interesting proposal by Swager[6] states that, in a hexagonal columnar (Col$_h$) mesophase of labile complexes, microdomains may form where a Δ- or Λ-isomer dominates. This is based on an assumption that the phase consists of persistently homochiral columns, which would lead to a typically frustrated system. It is suggestive of segregation of chiral domains under favorable conditions, but no *direct* verification has been presented. It came to us that exploration in the 2D hexagonal framework might serve as a test for the feasibility. The present paper reports on the first example of surface ordering in the cast film of [Cr(5C$_8$)$_3$] (Fig. 1) on highly ordered pyrolytic graphite (HOPG). The formation of a nanometer-scale structure found at a vertical resolution of less than 0.05 nm is interpreted as a possible manifestation of the chiral interactions.

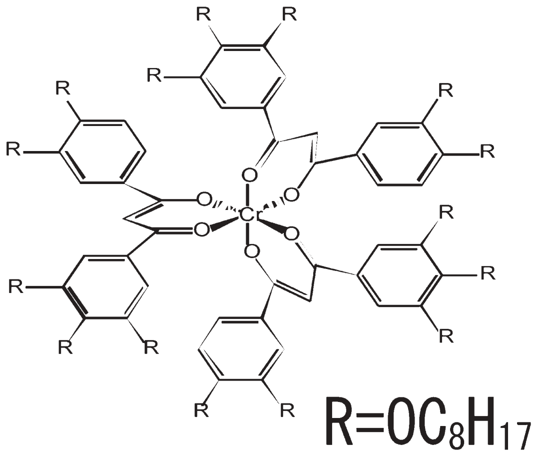

Fig. 1 Model structure of [Cr(5C$_8$)$_3$].

[Cr(5C$_8$)$_3$] was prepared following literature procedures with some modifications.‡ The product could be a mixture of *mer*- and *fac*-isomers, but the isolated sample is likely to be the former from steric considerations (a total of 15 octyloxy chains must be distributed as in 8/7 instead of 9/6 along the pseudo-C_3 axis). Accordingly, its DSC thermogram displayed sharp transitions both on heating and cooling for Col$_h$–I at 115 °C (ΔH = 3.5 kJ/mol), which is reasonable compared to the literature data (*ca.* 100 °C for the dodecyl homologue).[7,8] Focal conic fan texture was observed under a polarized light microscope at 109 °C, which is also consistent with the mesophase identification. On the other hand, no clear transition was observed for crystal-to-Col$_h$. According to the previous studies on analogous compounds ([Fe(5C$_{12}$)$_3$]),[6] this class of metallomesogen has a tendency for supercooling due to their large masses and the relatively low clearing temperature. Thus, no solidification exotherm was recorded in cooling runs.

STM observations were performed with a Nanoscope III (Digital Instruments) scanning tunneling microscope. A sample was prepared by casting a chloroform solution of [Cr(5C$_8$)$_3$] (1 × 10^{-3} M) onto a freshly cleaved HOPG (0.8 cm × 0.8 cm). The tunneling current was IT = 2.0 nA. The images were recorded in the constant current mode at a scanning rate of 20 lines per second at air and room temperature. Fig. 2A shows a 25 nm × 25 nm STM image at a sample tunnel voltage of Vs = 766 mV. Bright spots in a 2D lattice of estimated dimensions 2.0–2.3 nm are clearly visible, and this should indicate the molecular arrangement on the HOPG surface considering the molecular dimension (*ca.* 2 nm, Fig. 1). The unit cell can be regarded as hexagonal with a = 2.28 nm, while the image appears as somewhat compressed towards a centered rectangular lattice.

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† Electronic supplementary information (ESI) available: focal conic fan texture and DSC thermogram. See http://www.rsc.org/suppdata/cc/b4/b419429b/

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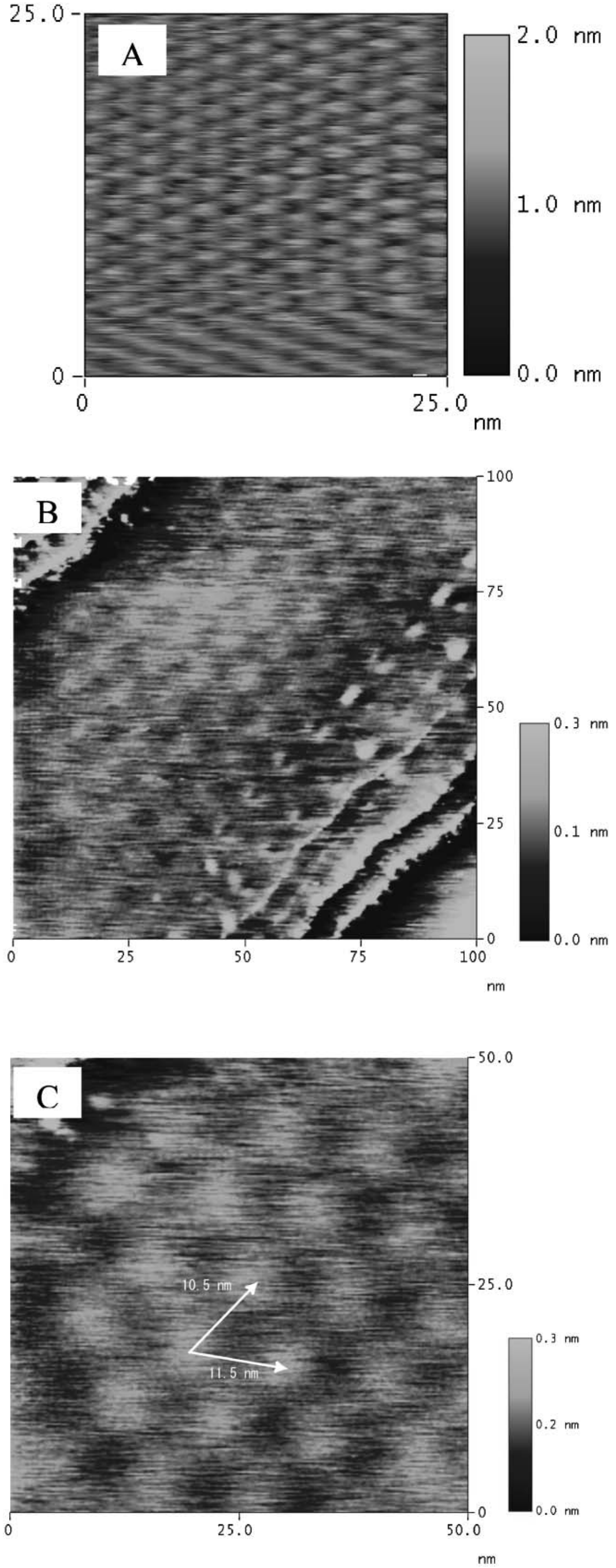

Fig. 2 STM images of the cast film of [Cr(5C_8)$_3$] on HOPG. The conditions were V = 766 mV, I = 2.0 nA.

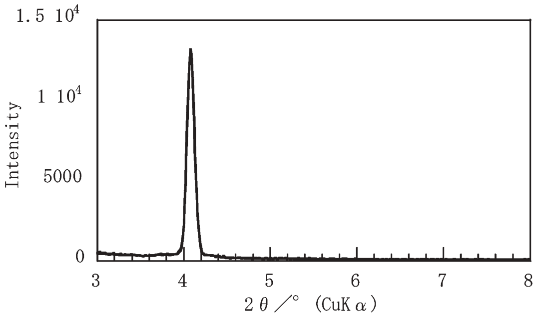

Fig. 3 XRD peaks of the cast film of [Cr(5C_8)$_3$].

X-ray diffraction measurements were then performed with a Rigaku Rint Ultima System. Fig. 3 shows the diffraction pattern, showing a peak at 2.23 nm, which is close to the above lattice constant. This peak is assignable to the (100) diffraction from the hexagonal lattice, as observed in the Col_h phases of a higher homologue.[8] This experiment gives an assurance that the molecules of [Cr(5C_8)$_3$] will sit on HOPG with their pseudo-C_3 axes parallel to the substrate normal. The image in Fig. 2A suggests that the monomolecular layer of [Cr(5C_8)$_3$] is rotationally disordered as in its Col_h phase.

Fig. 2B shows a 100 nm × 100 nm STM image for a different sample at tunnel voltage of Vs = 766 mV. No molecular images were obtained in this region. On the right-hand side, a large rough area was observed due to multi-layer formation. On the left-hand side, however, there emerged a regular array of bright domains of nanometer scale. When a 50 nm × 50 nm area is enlarged as in Fig. 2C, a definite periodicity in the 2D arrangement of bright spots shows up. It fits to an oblique lattice (a = 10.5 nm, b = 11.5 nm, α = 55°), and can also be approximated as hexagonal. From the measurements of height profiles, the bright regions were only 0.05 nm higher than the dark regions. Such periodic regions span over the length of 50–70 nm.

The structure as observed in Fig. 2C may be interpreted on the basis of a triangular Ising net. We start with a chiral lowest-energy state (Fig. 4a). A hexagon in the lower part of Fig. 4a indicates seven molecules arranged in the hexagonal base network (six at peripheral sites and one at the center). The triangle marking for the

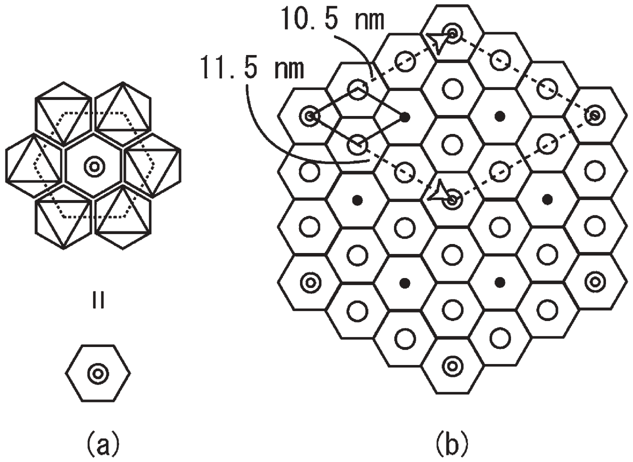

Fig. 4 Schematics showing (a) a chiral 2D hexagonal arrangement of [Cr(5C_8)$_3$] octahedra with thick lines indicating the ligands, and (b) a possible arrangement of them on HOPG. The rhombic lattice drawn in solid line is the $\sqrt{3} \times \sqrt{3}$ superlattice and the lattice drawn in dashed line is three times larger than the $\sqrt{3} \times \sqrt{3}$ superlattice.

peripheral six molecules is to be viewed as the top plane of [Cr(5C$_8$)$_3$], and then the up and down triangles correspond to the Δ- and Λ-enantiomers, respectively. They must alternate for close packing. The central molecule, however, cannot be fixed as either one of the enantiomers, since it is impossible for that molecule to form racemic pairs with all its neighbours. Because of this frustration, the molecule at the hexagonal site marked by a double circle can have random orientations. Fig. 4b shows the 2D hexagonal network with such a double circle site at the center, and $\sqrt{3} \times \sqrt{3}$ superlattice sites relative to it are indicated by circles (the rhombic lattice is drawn as a solid line in Fig. 4b). In fact, in the case of a triangular triphenylene derivative with suitable alkyl chains, the $\sqrt{3} \times \sqrt{3}$ superlattice was observed as bright spots in STM images.[4] In order to explain the present nanometer scale periodicity as observed in Fig. 2C, it is further assumed that a rhombic unit as indicated by dashed lines in Fig. 4b provides the contrast in STM images. Then three times expansion would result in a superlattice that is $3\sqrt{3}$ (= 5.2) times greater in length than the original triangular net, and this dimension is close to what was observed in Fig. 2C.§ At present, however, it is not clear why the ordering is suppressed on such a large scale, unlike in triphenylene derivatives. The system also involves vertical frustration related to the packing of 15 octyloxy chains, and the small contrast reported above may reflect surface undulation due to the partitioning of 8 *vs.* 7 chains along the normal. Thus the problem may be better treated by a coupled XY-Ising model.[9] Further experiments are now in progress to obtain more STM images hopefully with (sub)molecular resolution. Preparation of enantiomerically enriched materials is also under way.

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Notes and references

‡ [Cr(5C$_8$)$_3$] was prepared by reacting 1.0 g of [Cr(acac)$_3$] (10 mmole) and 3.0 g of 5C$_8$H (30 mmole) in a Teflon vessel at 180 °C for 12 hours. The brown product was dissolved in methanol and eluted on a column packed with silica gel (C500, Wako). The eluted fraction was further purified chromatographically on an HPLC column (Capcel Pack, Shiseido). The eluting solvent was 1 : 1 (v/v) acetonitrile/benzene. The collected fraction was analyzed by MS: *m*/*e* = 2645 (calc: 2644.92).

§ We have a reservation that smaller lattices may emerge if the images are processed. However, the results reported herein are what we have observed repeatedly and to the best of our resolution.

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