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Effect of Lateral Fluorine Substituent on Mesophase Behavior of Bent-shaped Molecules with Asymmetric Central Naphthalene Core

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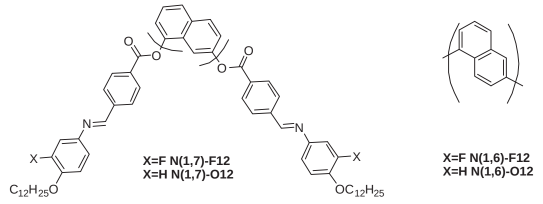
Novel lateral fluorinated bent-shaped molecules based on 1,7- and 1,6-naphthalene central core are prepared. Their mesomorphic properties are discussed in comparison with those of conventional unsubstituted bent-shape molecules.

Bent-shaped liquid crystals have attracted considerable attention over the past few years since its first discovery by Watanabe et al. in 1996.[1] Due to the occurrence of novel polar-ordered structures, supramolecular chirality induced by symmetry breaking in achiral molecules, and the noticeable optical, ferroelectric, or antiferroelectric reponse,[2] extensive research has been carried out in this intriguing field.[3,4] A large number of bent-shaped molecules have been synthesized and characterized, and at least eight types of banana phases (B1–B8) have been identified.[5] One of the major research targets in bent-shaped liquid crystals is to clarify the structure–property relationships. Generally, a bent-shaped molecule consists of three parts: the angular central core, side arms, and terminal chains. Outstanding work where modifications on different parts of the molecule has been analyzed and reported.[6] It is of particular interest to note that the introduction of a fluorine atom to the external phenyl ring has a great effect on the mesomorphic behavior in molecules based on symmetric central core such as 1,3-benzene or 2,7-naphthalene unit.[7,8] Most of the chiral mesophases exhibited by bent-shaped compounds have an antiferroelectric interlayer structure. But the introduction of a fluorine substituent ortho to the terminal *n*-alkoxy chains often results in a ferroelectric switching phase. The mesophase with synclinic tilt of molecules in adjacent layers exhibiting ferroelectric polarization, namely, $\mathrm{SmC_SP_F}$ phase, is formed instead of the original $\mathrm{SmC_SP_A}$ phase in unsubstituted molecules. However, the effect of the lateral fluorine substituent on mesomorphic behaviors of bent-shaped molecules with asymmetric central core has been rarely reported.

Thus, we have synthesized bent-shape molecules with asymmetric central core based on 1,7- or 1,6-naphthalene units and side arms containing Schiff base moieties, designated as N(1,7)-F12 and N(1,6)-F12 (Scheme 1). Polarized optical microscope observation and electrooptical and X-ray diffraction measurements have been carried out to investigate their mesomorphic properties and phase structures, in comparison with those of unsubstituted molecules.

All compounds show enantiotropic transitions. The transition temperatures and associated enthalpy changes were collected from DSC and are listed in Table 1.

It is of interest that for molecules based on 1,7-naphthalene central core, the introduction of the lateral fluorine substituent induces a polar columnar hexagonal mesophase with a phase sequence of Iso-$\mathrm{Col_h}$-B4. On cooling the isotropic liquid of N(1,7)-F12, $\mathrm{Col_h}$ phase appears as a fan-shaped texture (Figure 1a), characteristic of hexagonal molecular arrangement.[9] In some areas, the textures exhibit an optically isotropic zone, indicating columns align vertically to the substrate. On further cooling to B4 phase, two optically active domains with opposite chirality were observed (Figure 1b).



Scheme 1.

Table 1. Transition temperatures and enthalpies (on cooling at a rate of 10 °C min^{-1})

	Transition temperature/°C (enthalpy/kJ mol^{-1})
N(1,7)-F12	B4 87.6 (11.8) $\mathrm{Col_h}$ 147.5 (2.8) Iso
N(1,7)-O12	B4 145.7 (27.4) Iso
N(1,6)-F12	Cr 66.5 (6.3) B2 ($\mathrm{SmC_SP_A}$) 178.2 (23.1) Iso
N(1,6)-O12	Cr 95.8 (2.8) B2 ($\mathrm{SmC_SP_A}$) 193.5 (25.4) Iso

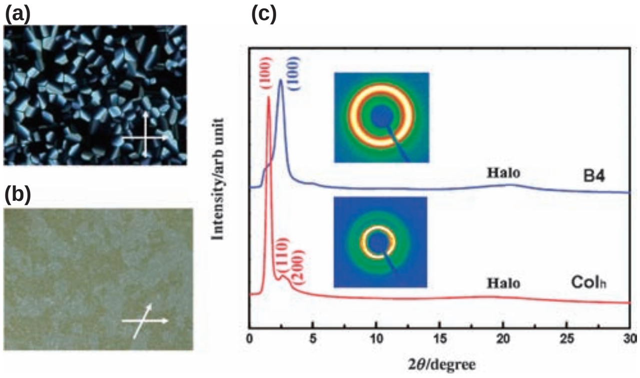


Figure 1. Microphotographs observed in N(1,7)-F12: (a) fan texture of $\mathrm{Col_h}$ phase (at 135 °C), (b) chiral B4 phase under uncrossed polarizers (at 65 °C), and (c) X-ray diffractions.

The columnar nature in $\mathrm{Col_h}$ phase is identified by a characteristic X-ray pattern. The broad diffuse scattering, corresponding to the liquid-like disorder of molecules with a mean distance of 4.5 Å, is detected in the wide angle region. In the small-angle region, three sharp reflections are observed (Figure 1c). They have spacings in the ratio of 1, $(1/3)^{1/2}$, and 2 and are further indexed to (100), (110), and (200) in the two-dimensional hexagonal lattice with *p6mm* symmetry.[10] The hexagonal lattice edge, *a*, is calculated to be 66.9 Å. B4 phase shows only one inner layer reflection, the spacing of which is 35.2 Å. It approximates the molecular length calculated on the most extended conformation.

By applying an electric field to the $\mathrm{Col_h}$ phase, the fan-shaped texture (Figure 2a) immediately disappears and rebuilds to give a zero birefringence (Figure 2b). This indicates the columns reorient their axis vertically to ITO substrates.[9] A single current peak in

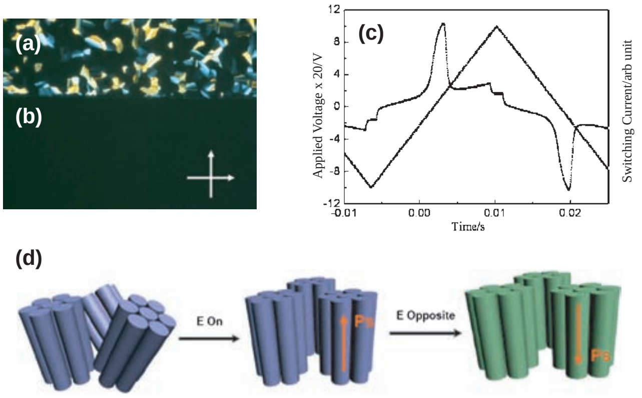


Figure 2. Switching behavior of N(1,7)-F12: (a) fan texture of $\mathrm{Col_h}$ phase exhibited in cell area without electrode part, (b) dark texture under electric field, (c) polarization reversal current under a triangular wave (135 °C, 400 Vpp, 30 Hz), and (d) the switching model.

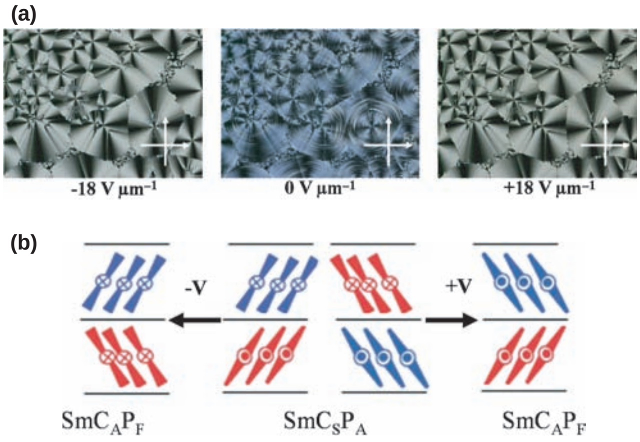


Figure 3. (a) Switching behavior of N(1,6)-F12 at 120 °C, (b) schematic representation of molecular rearrangement.

response to the applied triangular field is observed (Figure 2c). And the spontaneous polarization is about 180 nC cm^{-2}. The switching occurs with no texture change, and the dark texture is maintained after the electric field switches off. This indicates that the polarization exists along the columns and switches along the direction vertical to the ITO plate. The direction of the columns is maintained after the field is off (Figure 2d).

For N(1,6)-F12, typical B2 phase is observed on cooling from the isotropic phase (Figure S1[12]). High birefringent fine-shape domains with extinction directions parallel and perpendicular to the layer normal appeared under rectangular-wave field. When the field is off, dark blue domains with fine stripes were observed, whereas the extinction direction does not change (Figure 3a). By applying a triangular-wave electric field, the B2 phase exhibits two current peaks in half a circle (Figure S2[12]), indicating that it has a racemic $\mathrm{SmC_SP_A}$ structure as a ground state and that the electrooptical switching takes place between $\mathrm{SmC_SP_A}$ and $\mathrm{SmC_AP_F}$ (Figure 3b). On further cooling, a crystal phase is observed. These results are very similar to those of N(1,6)-O12.[11]

As mentioned above, variation of the chemical structure in bent-shaped molecule is very important for interlayer interactions, influencing the formation of banana phases. In this study, a lateral polar fluorine substituent is introduced in the 3-position of Schiff base moiety to bent-shaped molecules with asymmetric naphthalene central core and affects the mesophase structure and properties as follows.

For molecules based on a 1,7-naphthalene unit with an acute angle, the presence of the electron-withdrawing group leads to form a specific hexagonal columnar phase and a dark B4 phase. The column phase has a hexagonal lattice with edges of 66.9 Å and exhibits polar switching with spontaneous polarization along the column axis. By assuming a density of $\rho = 1\,\mathrm{g\,cm^{-3}}$ and a height of the columnar slice of $h = 4.5$ Å, the number of molecules calculated in each column slice is about 10–11. It is of interest how such a number of molecules assemble into one column slice. Our understanding is still at an early stage. A tube-like assembly of molecules and cylindrically symmetric deformation of layers were assumed. The alkyl tails of molecules are protruding outside of the column wall and inside of the enclosed mesogenic layer (Figure S3[12]). The combination of the acute angle central core and the polar fluorine substituent is considered to play an important role, and the clarification of molecular assembly in this phase is now proceeding.

For molecules based on a 1,6-naphthalene unit with an obtuse-angle, although the introduction of fluorine does not change phase sequence, a decrease of the melting temperature (lower by 15 °C) over nonpolar substituent compound has been detected, indicating the presence of the polar substituent tends to prevent the regular packing of molecules. Second, the spacing of the B2 phase in N(1,6)-F12 is larger than that of the unsubstituted molecule (Table S1[12]), whereas the layer spacings of the crystal phase are similar. The tilt angle for N(1,6)-F12 is calculated to be 21°, which is smaller that in N(1,6)-O12, 26°.

In summary, lateral fluorinated bent-shaped molecules based on 1,7- and 1,6-naphthalene core have been studied. All compounds show well-defined fluid smectic mesophases. However, the mesomorphic behavior and phase structure are different from conventional unsubstituted molecules. Although more comprehensive study is required, the combination of the asymmetric central core and the lateral polar fluorine atom could open up prospects for new molecular designs in bent-shaped liquid crystal systems.

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