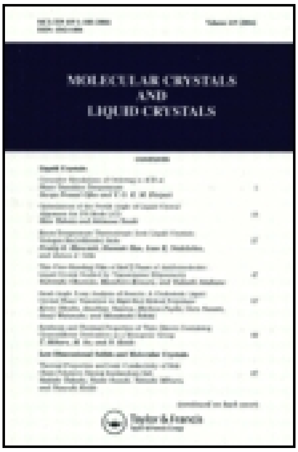

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Switchable Columnar Phase Formed from Bent-Shaped Molecules with Low Bent-Angle Naphthalene Central Core and Alkylthio Tail

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Switchable Columnar Phase Formed from Bent-Shaped Molecules with Low Bent-Angle Naphthalene Central Core and Alkylthio Tail

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Novel low-angle bent molecules with 1,7-naphthalene central core and alkylthio tails form the hexagonal columnar phase as well as the well-known B4 phase. The columnar phase has a large two-dimensional hexagonal lattice of 65–70 Å and exhibits the antiferroelectric switching with the spontaneous polarization along the column axis. The column is considered to be constructed by the cylindrically enclosed layer.

Keywords Banana molecule; Columnar phase; Hexagonal lattice; Layer deformation; tube-like assembly; antiferroelectric switching

1. Introduction

Since the discovery of spontaneous formation of liquid crystal phases with unique polarity and supermolecular chirality in bent-shaped (or banana) molecules,[1,2] a number of these banana molecules have been synthesized and characterized[3–5] to clarify the structure-property relationships. The most important factor for the design of banana molecules is to find the central bent core with an appropriate bent angle. A 1,3-disubstituted benzene ring, 2,6-disubstituted pyridine ring, 2,7-disubstituted naphthalene unit and 1,3′-disubstituted biphenyl unit have been used. In these molecules, the bent angle is approximately 120° although some angular variation is allowed through the rotation of the linkage group to the side wings. It is assumed that the bent angles in a range of 100° to 140° are favorable to form the typical banana phases.[6]

When molecules have bent angle much smaller than 120°, calamitic mesophases with a U-shape packing are mostly formed. Matsuzaki *et al.*[7,8] studied the molecules based on 1,2-phenylene and 2,3-naphthalene units with a bent angle of about 60°, and found that only conventional nematic and smectic phases are formed. However, Watanabe *et al.*, recently synthesizing six kinds of bent-shaped molecules with typical Schiff-base side wings substituted at various positions of a central naphthalene core,[9–12] found that the molecules composed of a 1,7-naphthalene central core form typical banana phases such as B4 and $\mathrm{SmAP_A}$ irrespective of its low bent angle of approximately 60°. These studies have opened a new area to exploit the new type of banana phases.

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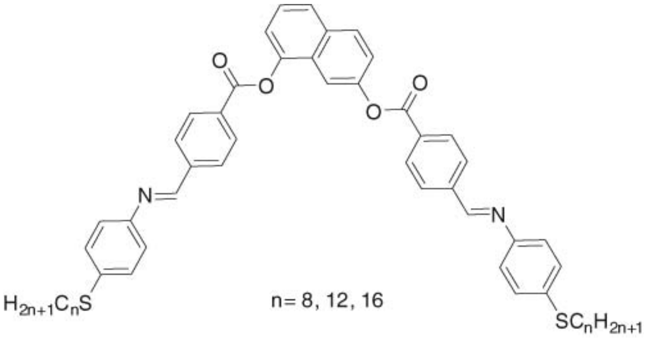
In this study, we report a homologous series of bent-shaped molecules with 1,7-naphthalene central core and alkylthio tail, namely, 1,7-naphthalene-bis[4-(4-alkylthiophenyliminomethyl)]benzoate shown below.



The compounds are designated here as N(1,7)-Sn where n indicates the number of carbons in alkylthio tails. Of interest is that the introduction of alkylthio tail in place of the alkoxy tail induces a switchable hexagonal columnar phase (Col_h) as a new type of self assembly. Switchable Col_h phase is rather rare, there are only a few molecular systems up to now. One is exhibited in polycatenar bent–shaped molecules discovered by Gorecka *et al*,[13] and the other appears in urea derivatives synthesized by Kishikawa *et al.*[14] Both of these two systems contain branched alkoxy tails which play an important role in forming columnar phase with a discotic-like assembly of molecules. In contrast, the column in this study is constructed by a tube-like assembly of molecules, *i.e.* the cylindrically enclosed layer. This is a new type of columnar assembly of banana molecules exhibiting antiferroelectric switching.

2. Experiments

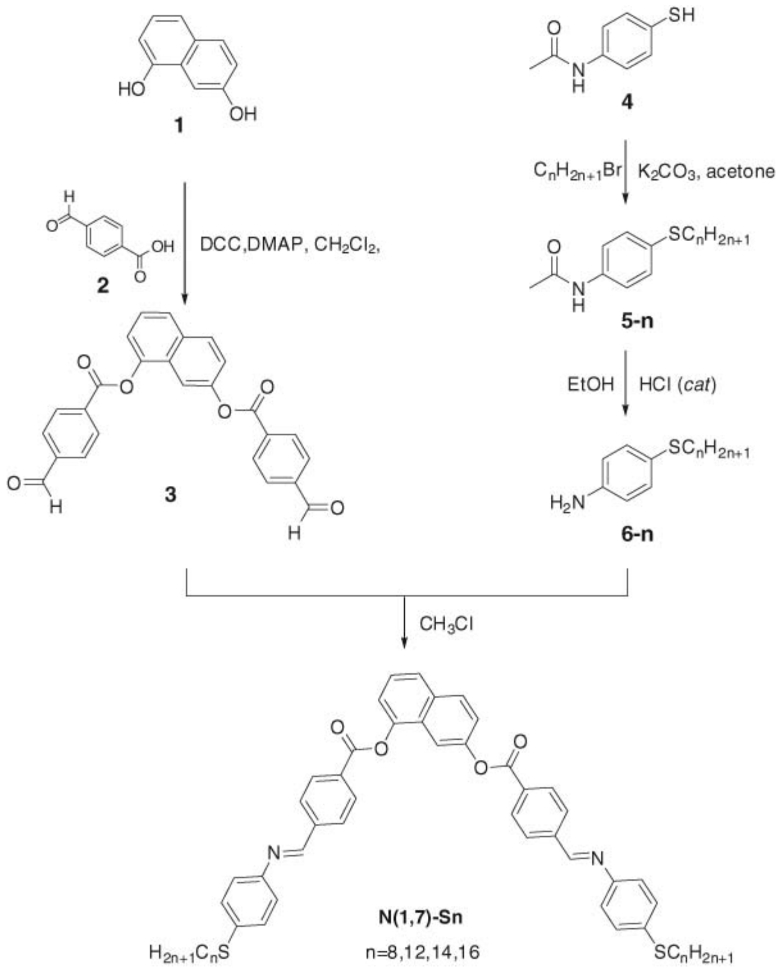
Synthesis

N(1,7)-Sn molecules were synthesized according to the routes illustrated in Scheme 1.[12] All reagents including bis(*p*-hydroxyphenyl)methane were purchased from TCI (Tokyo Kasei kogyo Co, Ltd) and used without further purification. Solvents were purified by normal procedures and handled under a moisture-free atmosphere.

Methods

Optical textures were observed under a crossed polarizer using an Olympus BX50 polarizing optical microscopy (POM) system equipped with a temperature-controlled Mettler Toledo FP 82 hot stage. Transition temperatures and corresponding enthalpies were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC 7 calorimeter.

Wide-angle X-ray diffraction (WAXD) measurements were performed using a Rigaku-Denki RINT-2500 X-ray generator with monochromic Cu-Kα radiation from the graphite crystal of the monochromator and a flat-plate-type imaging plate. Powder X-ray investigations were carried out with samples kept in glass capillary tubes with a diameter of 1.5 mm. The aligned sample for X-ray measurements was prepared on a glass



Scheme 1. Synthetic route of N(1,7)-Sn.

substrate coated with commercially available organosilane N,N-dimethyl-n-octadecyl-3-aminotropyltrimethoxysilyl chloride (DMOAP).

Electro-optic switching was observed by using a high-speed voltage amplifier (FLC Electronics, F20A) connected to a function generator (NF Electronic Instruments, WF1945A). The sample was sandwiched between two glass plates with a transparent indium tin oxide (ITO) electrode. Neither polymer coating nor rubbing was made on the substrate surface.

3. Results and Discussion

All the compounds, N(1,7)-Sn with n = 8, 12, 14 and 16, show enantiotropic transitions as shown in Figure 1. Their transition temperatures and associated enthalpy changes are listed in Table 1. While the shortest homologue N(1,7)-S8 exhibits direct transition from

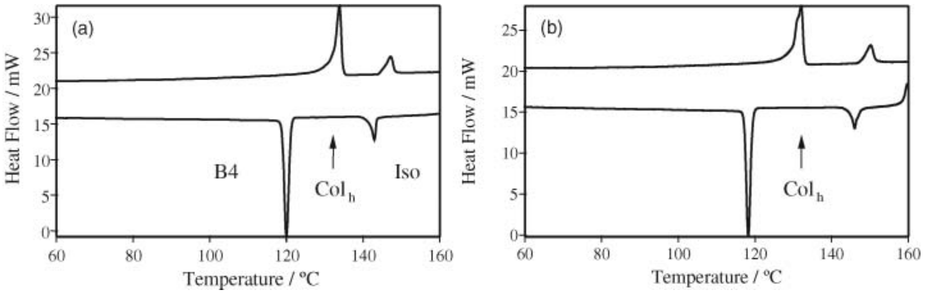


Figure 1. Representative DSC thermograms of N(1,7)-Sn materials. (a) n = 14 and (b) n = 16. (Heat flow of endotherm is upper direction.)

the isotropic liquid to B4 phase, N(1,7)-S12 and N(1,7)-S16 show an additional Col$_h$ phase with a sequence of Iso-Col$_h$-B4 on decreasing the temperature.

When cooling from the isotropic liquid between untreated glass plates, Col$_h$ phase appears as a smooth fan textures with extinction brushes aligned along the polarizers (Figure 2b). In some part, textures include the optically isotropic zone. On further cooling to B4 phase, all parts change dark blue texture including two optically active domains with opposite chirality which was recognized by clockwise and anticlockwise rotations of polarizer from the cross polarization position (Figure 2a).

The columnar nature in Col$_h$ phase is firmly identified by the chraracteristic X-ray pattern with the outer broad diffuse scattering of 4.6 Å corresponding to the liquid-like lateral packing of molecules, and inner three sharp reflections (see Figure 3). As listed in Table 1, the later three reflections have the spacings in the ratio of 1, $3^{1/2}$ and 2, and they are indexed to (100), (110) and (200) of the two dimensional hexagonal lattice. The hexagonal lattice edge, *a*, is 65.0 Å for N(17)-S12, 67.3 Å for N(17)-S14 and 70.0 Å for N(17)-S16. The lower-temperature B4 phase shows only a layer reflection, the spacings of which are 28.3, 33.6, 36.1 and 39.2 Å for N(1,7)-S8, N(1,7)-S12, N(17)-S14 and N(1,7)-S16, respectively. These approximate to the molecular lengths calculated for the most extended conformation, as listed in Table 2.

To elucidate the more detailed structure of the Col$_h$ phase, we examined the X-ray pattern for a droplet of the material deposited onto a silane coupling glass plate. It was initially heated up to the isotropic melt and then cooled to the Col$_h$ phase at a rate of 1°C/min. By this surface treatment, the highly birefringent fan-like texture is observed, showing that the colums take a planar orientation with their long axes parallel to the glass surface. Figure 4a shows the X-ray photographs taken for this sample by the irradiations

Table 1. Transition temperatures and enthalpies of N(1,7)-Sn compounds

Compounds	Transition temperature/°C[a] (*enthalpy/kJmol^{-1}*)
N(1,7)-S8	B4 113.1 (*29.1*) Iso
N(1,7)-S12	B4 119.6 (*30.0*) Col$_h$ 138.5 (*5.3*) Iso
N(1,7)-S14	B4 119.9 (*28.1*) Col$_h$ 143.0 (*5.7*) Iso
N(1,7)-S16	B4 118.1 (*30.9*) Col$_h$ 146.0 (*7.0*) Iso

[a] Based on cooling DSC curves.

Table 2. X-ray data and elucidated lattice parameter of N(1,7)-Sn compounds

Compounds	Phase	d_{obs}/Å	*hkl*	d_{calc}/Å	a^a/Å	Molecular Length[b]
N(l,7)-S8	B4	28.3	*001*	—	—	31.5
N(1,7)-S12	Colh	56.3	*100*	56.3		
		32.6	*110*	32.5	65.0	
		28.2	*200*	28.2		
	B4	33.6	*001*			38.2
N(l,7)-S14	Colh	58.3	*100*	58.3	67.3	
		33.4	*110*	33.6		
		29.2	*200*	29.2		
	B4	36.1	*001*			41.5
N(l,7)-S16	Colh	60.6	*100*	60.6		
		34.8	*110*	34.9	70.0	
		30.4	*200*	30.3		
	B4	39.2	*001*			44.9

[a] *a:* hexagonal lattice parameter, [b] Based on the most extended chains.

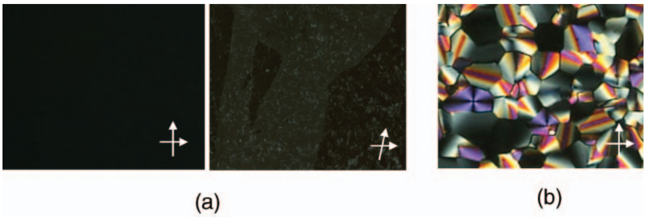

(a) (b)

Figure 2. Microscopic photographs of (a) the dark texture of B4 phase at 100°C (left) showing the chiral domains under uncrossed polarizers (right), and (b) the fan-like texture of Col_h phase (at 130°C) in N(1,7)-S14.

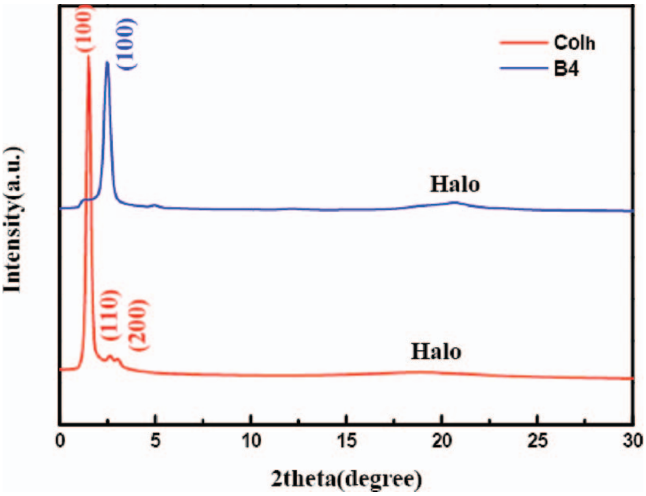


Figure 3. X-ray diffraction profiles taken for the Col_h and B4 phases of powder sample in N(1,7)-S14.

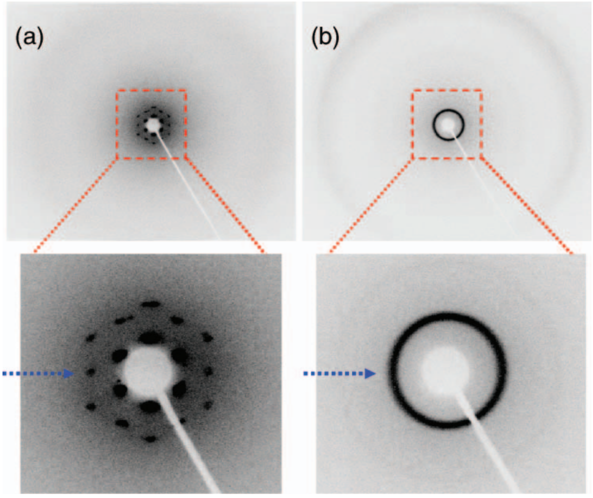


Figure 4. X-ray diffraction patterns of (a) Col_h phase and (b) B4 phase, which is prepared on the homeotoropically surface-treated glass. Using a Rigaku-Denki RINT-2500 X-ray generator with monochromic Cu-Kα radiation from the graphite crystal of the monochromator, the X-ray beam is irradiated along the direction parallel to the glass surface and the diffraction patterns are corrected on a flat-plate-type imaging plate. The arrow indicates the glass surface direction.

parallel to the glass surface. All of (100), (110) and (200) reflections appear as six spots. For example, a pair of (100) reflection spots are observed strongly on the equatorial direction (i.e. the direction perpendicular to the glass surface), and other pairs of spots are located every 60° along the azimuthal direction. On the other hand, no orientation is detected in the X-ray photograph taken with a beam perpendicular to the glass surface. Such characteristic patterns can be explained by the planar orientation of columns in which the hexagonal (100) planes are parallel to the glass surface, but the column axes are randomly displaced. On cooling to the B4 phase, the orientation disappears completely as observed in the B4 phase of usual banana molecular systems (see Figure 4b).[15,16]

Electro-optic switching was observed for the sample which was sandwiched between two glass plates with a transparent indium tin oxide (ITO) electrode. Neither polymer coating nor rubbing was made on the substrate surface. By applying an electric field on the columnar phase, the texture with fan-shaped domains immediately disappears and is rebuilt to give a zero birefringence (Figure 5a). In response to the applied triangular field, a dark homeotropic texture is maintained (Figures 5b and 5c) and a clear current is detected as a single peak (Figure 5d). Thus, we suggest that the Col_h phase may be ferroelectric; the polarization exists along the columns, and on reversing the field the molecules within a column rotate their polar axis to the opposite direction to maintain the columnar axis along the field. On the other, it should be noted that the SHG signal observed in field-on state disappears on field-off state. This indicates that it is not ferroelectric, but actually antiferroelectric.

Figure 6 shows the temperature dependence of the spontaneous polarization (Ps) of N(1,7)-S12 against the temperature measured at 25.0 Hz. A maximum Ps value of 160 nC/cm^2 is attained immediately after the transformation of B4 to the columnar phase. It decreases with an increase in temperature and becomes zero on the transformation to the

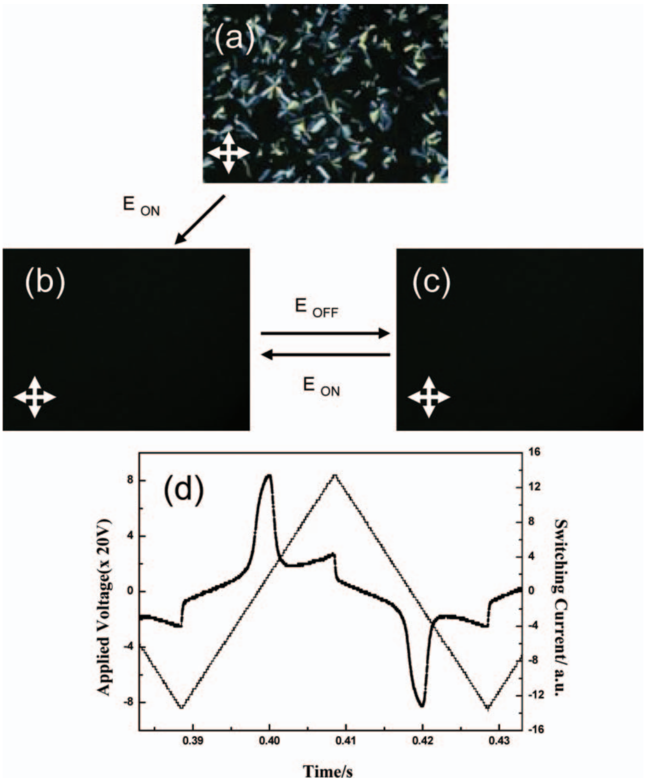


Figure 5. Electro-optic (EO) switching behavior observed for N(1,7)-S12 in the Col_h phase. (a) Optical microscopic virgin texture of fan-like domain and optically isotropic domain cooled from isotropic liquid prepared within a cell, (b) Optically isotropic texture transformed under applied electric field. (c) No substantial textural change was accepted between E_{off} and E_{on}. (d) Polarization reversal current in the Col_h phase under the application of triangular wave gives a single reversal current peak (Temperature: 135°C, Voltage: 340 Vpp, Frequency: 25 Hz and Cell gap: 4.5 μm).

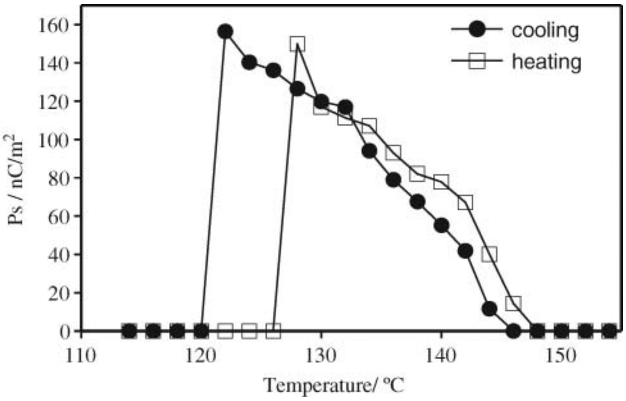


Figure 6. Temperature dependence of the spontaneous polarization observed in N(1,7)-S12 (Voltage: 340 Vpp, Frequency: 25 Hz and Cell gap: 4.5 μm).

isotropic melt. Currently, there exists no explanation for this strong temperature dependence of Ps.

How is each column constructed by the bent molecules? Four key results help us figure up the molecular assembly into the column forming the $\mathrm{Col_h}$ phase. First, as observed above in X-ray pattern of Figure 4a, there is no preferential orientation of molecules on the projection along the column. This point is also supported by zero birefringence in the homeotropic sample with the column axis aligned perpendicularly to the film sample (see Figure 5b). Second, alkyl silane coupling surface treatment, promoting the homeotropic alignment of molecules, results in the planar orientation of columns. This suggests that the alkyl tails of molecules are protruding out of the side wall of the column. Third, the hexagonal lattice edge, *a*, is approximately two times the layer thickness of the B4 phase. Fourth, the antiferroelectric switching takes place along the column axis; probably, the bent direction of molecules is perpendicular to the column axis at the electric field-off state whereas it becomes perpendicular on the field-on. These results are substantiated if the column is constructed by a tube-like assembly of molecules, as illustrated in Figure 7a. The construction is similar to a cylindrically enclosed layer, whereby the alkyl tails are protruding outside and inside of the enclosed mesogenic layer.

Cylindrically symmetric deformation of layers can be caused by the packing asymmetry in two side rigid arms (refer to Figures 7a–7c). The present molecules have the asymmetric shape because of the use of the 1,7-substituted naphthalene core. Hence, when the asymmetric molecules are packed into a layer with a same directionality (Figure 7a),

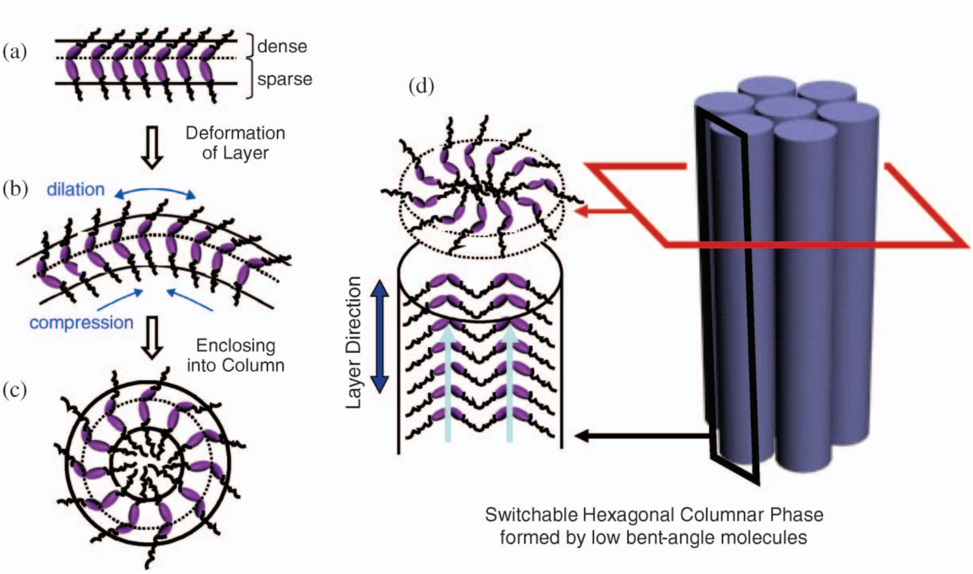


Figure 7. Schematic illustration of (a)–(c) column formation by the winding of layer and (d) packing of banana molecules within a column. Two rigid side-arms of asymmetric banana molecule take a different orientation to the layer normal which produces the significant difference in the density if the layer is flat. Hence, a dilation occurs in one half-layer (upper part divided by the dotted line in (a)) while a compression in the other half (lower part). This frustration can cause cylindrically enclosing deformation of layer as in (b) and (c). By assuming a density of $\rho = 1$ g·cm^{-3} and a height of the columnar slice of 4.6 Å (corresponding to the average distance between molecules), the number of molecules included in each column slice is calculated to be $\sim$11.

the two side rigid arms orient differently and then two parts of layer have the different densities if the layer is flat. This frustration, a dilation in one half-layer and a compression in the other half, can be reduced by cylindrical enclosing of layers (Figures 7b and 7c). By assuming a density of $\rho = 1$ gcm^{-3} and a height of the columnar slice of h (corresponding to the average distance between molecules), the number of molecules, n, included in each column slice is calculated to be n = 2.4 h (Figure 7d). If h is assumed to be 4.6 Å (the spacing of the outer broad reflection), n is 11 as an average. It should be noted here that by such a large number of molecules in a unit slice we cannot build up the assembly model of bent molecules into a disk-shaped object reported by Gorecka *et al.*[13] and Kishikawa *et al.*[14]

However, it has been never reported that the cylindrically enclosed column is stably isolated to form the hexagonal columnar phase in the banana molecular system. This is due to the difficult accommodation of alkyl tail groups in a space between the columns. At this aspect, it is important to state that the rotational freedom of thio-ether linkage in the alkylthio tail is considerably higher than that of ether linkage in the alkoky tail. Figure 8 shows the relative energy diagram as a function of dihedral angle around the C-S bond in phenyl-S and C-O bond in phenyl-O. Here, dodecylthiobenzene and dodecyloxybenzene were used for simple calculation. Two stable conformations are found in both compounds (dihedral angle: 0 or 180°). But the path from one stable conformer to the other is different. The path for C-O is obstructed by high energy barrier (13.2 kJ mol^{-1}, in position of dihedral angle: 90°). In contrast, the potential barrier for C-S is lower (1.88 kJ mol^{-1}, in position of dihedral angle: 50 and 130°) although metastable conformer exists at 90°. These particularly low barriers of the alkylthio terminal chain enable the compound to change the conformation more easily and make their accommodation into the tube-like layer possible.

In summary, we found that novel low-angle bent molecules with 1,7-naphthalene central core and alkylthio tails are able to form a columnar phase as a new type of self-assembly of bent molecules. This columnar phase is switchable; the spontaneous polarization exists along the column axis and the antiferroelectric switching takes place without changing the long column axis. The combination of asymmetric low-bent-angle 1,7-naphathalen core

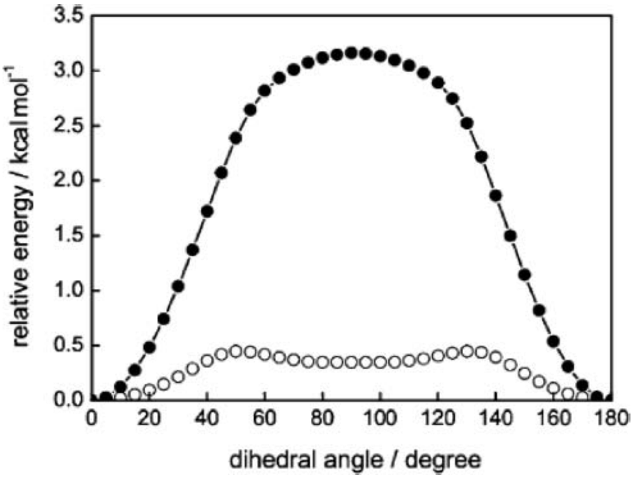


Figure 8. Internal rotation energy against the dihedral angles around C-S bond in pheny-S (open circles) and C-O bond in phenyl-O (closed circles).

and flexible alkylthio tails is considered to be responsible for the formation of switchable columnar phase.

Acknowledgement

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