Synthesis and structure of lateral halogenated V-shaped liquid crystal molecules based on a 1,7-naphthalene central core and alkylthio tails

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A series of small angle bent-core (V-shaped) mesogens carrying 1,7-naphthalene as a central core linked with lateral halogenated (chlorinated or fluorinated) Schiff-base side wings and alkylthio terminal tails of variable carbon number (n = 12, 16) was synthesised in order to reduce the transition temperature and improve the phase stability of bent-core liquid crystal molecules. Differential scanning calorimetry (DSC), polarising optical microscopy (POM), small-angle X-ray scattering system (SAXS) and two-dimensional X-ray diffractometer were applied to ascertain the mesomorphic structure and phase transition temperatures of the compounds. The results confirm that all the molecules show thermotropic liquid crystalline behaviour and exhibit hexagonal columnar phase (Colh) in a certain temperature range. Compared with the homologous compounds without lateral halogen, the clearing point temperature of lateral halogenated V-shaped compounds generally decrease and the Colh phase ranges are more extensive. The influence of lateral chlorine on the clearing point temperature is more obvious, as well as the effect of lateral fluorine on the range of Colh phase.

Keywords: bent-core mesogens; 1,7-naphthalene; alkylthio tails; lateral halogenated compounds; hexagonal columnar phase; transition temperature

1. Introduction

Since the discovery of unusual switchable mesophases of liquid crystals based on achiral banana-shaped molecules,[1,2] extensive attention has been attracted to synthesise such bent-shaped molecules, in which the bent-shaped molecules based on 1,3-disubstituted benzene and 2,7-disubstituted naphthalene core are usually reported to show unique switchable mesophases (banana phase, B phase).[3–7] The noticeable ferroelectric and anti-ferroelectric responses of these materials are now well documented.[8–10]

Matsuzaki et al. [11,12] were the first to synthesise V-shaped molecules of about 60° based on 1,2-phenylene and 2,3-naphthalene central core, which only show conventional SmA and Nematic phase. Choi [13,14] and Ros et al. [15] have also reported some V-shaped molecules based on the 2,3-naphthalene central unit with ester type side wings, but no B phase appears for these acute-angle liquid crystal materials. In general, the introduction of obtuse angle bent-core had been thought to be essential to form the previously mentioned switchable B phases.

However, Watanabe et al. [16,17] synthesised six kinds of bent-shaped molecules based on naphthalene, the research result is stoked that V-shaped molecules based on 1,7-naphthalene display typical B4 phase. In their subsequent study,[18,19] they found a switchable banana phase (SmAPn), but the temperature range of the switchable phases are averaged from 240°C to 200°C, which makes them very hard to be used at practical applications. On account of the above conclusions, Li et al. [20] synthesise homogeneous V-shaped molecules with alkylthio tails, exhibiting switchable hexagonal columnar phase (Colh) phase. Under the same condition, the switchable Colh phase transition temperatures of the molecules with alkylthio tails obviously decrease, the range of which are from about 146°C to 118°C.

On the other hand, lateral substitution has an essential influence on the sterical and electronical characteristic and thereby on the intermolecular distance. Consequently, it can generate mesophase characteristics different from the related non-substituted mesogen. There are some relevant reports showing that the type and position of substituent have evidently influence on the mesogen behaviour of bent-shaped molecules.[21–24] Certainly, some research have indicated that the introduction of the halogen substituent to the position of the terminal benzene could significantly decrease the phase transition temperatures and improve phase range.[25,26]

In this study, we separately prepared lateral fluorinated or chlorinated V-shaped molecules based on 1,7-dioxynaphthalene with alkylthio tails (Scheme 1) to observe their mesomorphic state and transition temperature. Four compounds uniformly show thermotropic liquid crystalline behaviour and exhibit Colh on cooling. The effect of the introduction of lateral halogenated group and alkylthio tails on the clearing points and scope of Colh phase were investigated.

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2. Experiment

2.1 Measurements

Nuclear magnetic resonance (NMR) spectra and mass spectrum were measured using a Bruker AVANCE III 400 NMR spectrometer and BIFLEX III MALDI-TOF mass spectrometer, respectively. Elemental analyses were performed with an Elementar Vario EL III analyser. Texture observations were conducted under crossed polarisation with polarising optical microscopy (POM) on a Chongqing MIC SZX-5 equipped with a temperature-controlled Weitu WT2100 hot stage. Differential scanning calorimetry (DSC) measurements were made using a Perkin–Elmer DSC 7 calorimeter in a N₂ atmosphere with a heating rate of 10°C/min and cooling rate of 2°C/min. Small-angle X-ray scattering system (SAXS) was performed using Anton paar SAXSess diffraction with Cu Ka radiation. Two-Dimensional X-ray diffraction was carried out by Bruker Nanostar U Scattering system and D8 Discover diffractometer using Cu Ka radiation. Electric field was obtained using high speed bipolar amplifier (NF, BA4825) connected to a SP F05 functional generator. Indium-tin-oxide (ITO) glass cell with 3 μm has neither polymer coating nor rubbing on the surface.

2.2 Synthesis

Scheme 2 outlines a synthetic method leading to the target compounds. The concrete synthetic routes to

Scheme 1. The molecular structure of N(1,7)SRn.

Scheme 2. Synthetic route of N(1,7)SRn.
target compound are as follows in the case of N(1,7) SF12 (R = F, n = 12).

2.2.1 Synthesis of dialdehydes, 1

Samples of 1,7-dihydnaphthalene (2.00 g, 12.5 mmol), 4-carboxybenzaldehyde (4.28 g, 28.5 mmol), 4-dimethylaminoypyridine (3.79 g, 31.0 mmol) and 1,3-dicyclohexylcarbodiimide (6.39 g, 31.0 mmol) were successively added to a round flask with Silica column (CH$_2$Cl$_2$) (90 ml). The mixture was magnetic stirred at 25°C for 3 days, then filtered to remove precipitated materials. CH$_2$Cl$_2$ was used to separate the filtrate, then the target compound was recrystallised from chloroform/ethanol to give 1 (2.03 g, 38%) as a light yellow solid.[16]

1 H-NMR (400 MHz, CDCl$_3$): δ (ppm) 10.16 (s, 1 H), 10.14 (s, 1 H), 8.48 (d, J = 8.4 Hz, 2 H), 8.37 (d, J = 8.4 Hz, 2 H), 8.08–7.42 (m, 10 H).

2.2.2 Synthesis of dodecyl(2-fluoro-4-nitrophenyl) sulfane, 2a

A N,N-dimethylformamide (30 ml) solution of 1,2-difluoro-4-nitrobenzene (3.98 g, 25.0 mmol), 1-dodecanethiol (5.05 g, 25.0 mmol) and potassium carbonate (2.07 g, 15.0 mmol) was stirred at room temperature for 10 h. The mixture was then heated under 90°C for 3 h. After reaction, the saturated NaCl (200 ml) was added to the mixture. The precipitate, namely crude product, was collected through filtration and cleaned by deionised water for two times. Target compound was finally recrystallised from ethanol twice to give 2a (6.19 g, 72.6%) as a yellow crystal.

2a: 1 H-NMR (400 MHz, CDCl$_3$): δ (ppm) 8.02–7.99 (dd, J$_1$ = 2.4 Hz, J$_2$ = 8.8 Hz, 1 H), 7.9–7.87 (dd, J$_1$ = 2.4 Hz, J$_2$ = 8.8 Hz, 1 H), 7.36–7.32 (dd, J$_1$ = 2.4 Hz, J$_2$ = 8.8 Hz, 1 H), 3.01 (t, J = 7.2 Hz, 2 H), 1.72 (quin, 2 H), 1.50–1.26 (m, 18 H), 0.88 (t, J = 6.4 Hz, 3 H).

2b: 1 H-NMR (400 MHz, CDCl$_3$): δ (ppm) 8.02–8.0 (dd, J$_1$ = 1.6 Hz, J$_2$ = 8.8 Hz, 1 H), 7.91–7.88 (dd, J$_1$ = 2 Hz, J$_2$ = 9.6 Hz, 1 H), 7.35–7.31 (dd, J$_1$ = 2.2 Hz, J$_2$ = 8.4 Hz, 1 H), 3.01 (t, J = 7.2 Hz, 2 H), 1.72 (quin, 2 H), 1.49–1.26 (m, 26 H), 0.88 (t, J = 6.8 Hz, 3 H).

2c: 1 H-NMR (400 MHz, CDCl$_3$): δ (ppm) 8.22 (d, J = 2.4 Hz, 1 H), 8.10–8.07 (dd, J$_1$ = 2.4 Hz, J$_2$ = 8.8 Hz, 1 H), 7.26 (d, J = 8.8 Hz, 1 H), 3.01 (t, J = 7.4 Hz, 2 H), 1.77 (quin, 2 H), 152–1.26 (m, 18 H), 0.88 (t, J = 6.4 Hz, 3 H).

2d: 1 H-NMR (400 MHz, CDCl$_3$): δ (ppm) 8.22 (d, J = 2.4 Hz, 1 H), 8.10–8.08 (dd, J$_1$ = 2.4 Hz, J$_2$ = 8.8 Hz, 1 H), 7.26 (d, J = 8.8 Hz, 1 H), 3.01 (t, J = 7 Hz, 2 H), 1.77 (quin, 2 H), 152–1.26 (m, 18 H), 0.88 (t, J = 6.4 Hz, 3 H).

2.2.3 Synthesis of 4-[(dodecylthio)-3-fluoroaniline, 3a

A mixture of 2a (5.12 g, 15.0 mmol), Pd/C (0.52 g) and hydrazine hydrate (80%, 7.5 ml) in ethanol was heated under reflux for 9 h, then another 6 ml hydrazine hydrate was added in order to complete reaction for 5 h. The reaction solution was concentrated and recrystallised from ethanol to give a white solid 3a (2.38 g, 51%).

3a: 1 H-NMR (400 MHz, CDCl$_3$): δ (ppm) 7.23 (quin, 1 H), 6.44–6.40 (m, 2 H), 3.83 (br s, NH$_3$), 2.75 (d, J = 7.2 Hz, 2 H), 1.55 (quin, 2 H), 1.40–1.26 (m, 18 H), 0.90 (t, J = 6.8 Hz, 3 H).

3b: 1 H-NMR (400 MHz, CDCl$_3$): δ (ppm) 7.21 (quin, 1 H), 6.42–6.37 (m, 2 H), 3.81 (br s, NH$_3$), 2.73 (t, J = 9.6 Hz, 2 H), 1.53 (quin, 2 H), 1.24–1.38 (m, 26 H), 0.88 (t, J = 8.4 Hz, 3 H).

3c: 1 H-NMR (400 MHz, CDCl$_3$): δ (ppm) 7.24 (d, J = 8.4 Hz, 1 H), 6.76 (d, J = 2.4 Hz, 1 H), 6.51–6.54 (dd, J$_1$ = 2.4 Hz, J$_2$ = 8.4 Hz, 1 H), 3.74 (br s, NH$_3$), 2.79 (d, J = 7.4 Hz, 2 H), 1.56 (quin, 2 H), 1.40–1.25 (m, 18 H), 0.88 (t, J = 6.8 Hz, 3 H).

3f: 1 H-NMR (400 MHz, CDCl$_3$): δ (ppm) 7.25 (d, J = 8.4 Hz, 1 H), 6.76 (d, J = 2.8 Hz, 1 H), 6.53–6.51 (dd, J$_1$ = 2.4 Hz, J$_2$ = 8.4 Hz, 1 H), 3.74 (br s, NH$_3$), 2.79 (d, J = 7.4 Hz, 2 H), 1.56 (quin, 2 H), 1.41–1.25 (m, 26 H), 0.88 (t, J = 6.8 Hz, 3 H).

2.2.4 Synthesis of 1,7-naphthalenedisulfamido-(4-(4-dodecethylthio-3-fluorophenylimino)methyl)-benzoate, N(1,7)SF12

Compound 1 (0.25 g, 0.6 mmol) and 3a (0.56 g, 1.8 mmol) were uniformly mixed up in CHCl$_3$ (40 ml) under magnetic stirring at 70°C for 24 h. The solvent was volatilised in vacuum. The target compound was recrystallised from ethanol/trichloromethane to receive a yellow solid N(1,7)SF12 (0.41 g, 68%).

N(1,7)SF12: 1 H-NMR (400 MHz, CDCl$_3$): δ (ppm) 8.56 (d, J = 9.2 Hz, 2 H), 8.44 (d, J = 8 Hz, 2 H), 8.35 (d, J = 8.4 Hz, 2 H), 8.09 (d, J = 8 Hz, 2 H), 8.04 (t, J = 6.8 Hz, 3 H), 7.88 (d, J = 7.6 Hz, 1 H), 7.79 (s, 1 H), 7.59 (t, J = 7.6 Hz, 1 H), 7.49–7.39 (m, 4 H), 7.03 (d, J = 9.2 Hz, 4 H), 2.94 (t, J = 7.6 Hz, 4 H), 1.65 (quin, 4 H), 1.44–1.27 (m, 36 H), 0.88 (t, J = 6.4 Hz, 6 H).

MALDI-TOF-MS m/z: Exact mass: 1010.49. Found: 1010.4.

EA: calculated for C$_{66}$H$_{122}$F$_2$N$_2$O$_4$S$_2$: C, 73.63; H, 7.18; N, 2.77. Found: C, 73.46; H, 7.07; N, 2.92.

N(1,7)SF16: 1 H-NMR (400 MHz, CDCl$_3$): δ (ppm) 8.54 (d, J = 9.2 Hz, 2 H), 8.43 (d, 1689 Liquid Crystals 1689
$J = 8.4$ Hz, 2 H), 8.31 (d, $J = 8$ Hz, 2 H), 8.08 (d, $J = 8.4$ Hz, 2 H), 8.02 (t, $J = 7$ Hz, 3 H), 7.86 (d, $J = 7.6$ Hz, 1 H), 7.77 (s, 1 H), 7.57 (t, $J = 7.6$ Hz, 1 H), 7.48–7.37 (m, 4 H), 7.01 (d, $J = 9.6$ Hz, 4 H), 2.92 (t, $J = 7.6$ Hz, 4 H), 1.63 (quin, 4 H), 1.46–1.25 (m, 52 H), 0.88 (t, $J = 6.4$ Hz, 6 H).

**MALDI-TOF-MS m/z:** Exact mass: 1122.62. Found: 1122.8.

**EA:** calculated for C$_{70}$H$_{88}$F$_2$N$_2$O$_4$S$_2$: C, 74.83; H, 7.89; N, 2.49. Found: C, 74.54; H, 7.84; N, 2.49.

N(1,7)SCl$_{12}$

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.55 (d, $J = 9.6$ Hz, 2 H), 8.42 (d, $J = 8.4$ Hz, 2 H), 8.31 (d, $J = 8.4$ Hz, 2 H), 8.07 (d, $J = 8$ Hz, 2 H), 8.04–8.0 (dd, $J_1 = 5.2$ Hz, $J_2 = 8.4$ Hz, 3 H), 7.86 (d, $J = 8.4$ Hz, 1 H), 7.77 (d, $J = 2$ Hz, 1 H), 7.57 (t, $J = 8$ Hz, 1 H), 7.47–7.29 (m, 6 H), 7.19 (t, $J = 2.4$ Hz, 1 H), 7.17 (t, $J = 2.4$ Hz, 1 H), 2.96 (t, $J = 7.6$ Hz, 4 H), 1.71 (quin, 4 H), 1.49–1.26 (m, 36 H), 0.88 (t, $J = 6.4$ Hz, 6 H).

**MALDI-TOF-MS m/z:** Exact mass: 1042.43. Found: 1042.6.

**EA:** calculated for C$_{62}$H$_{72}$Cl$_2$N$_2$O$_4$S$_2$: C, 71.31; H, 6.95; N, 2.68. Found: C, 71.60; H, 6.86; N, 2.60.

**N(1,7)SCl$_{16}$**

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.55 (d, $J = 9.2$ Hz, 2 H), 8.42 (d, $J = 8$ Hz, 2 H), 8.31 (d, $J = 8$ Hz, 2 H), 8.08 (d, $J = 8.4$ Hz, 2 H), 8.02 (d, $J = 8.4$ Hz, 3 H), 7.86 (t, $J = 4.4$ Hz, 1 H), 7.77 (s, 1 H), 7.57 (t, $J = 7.6$ Hz, 1 H), 7.45 (t, $J = 6.8$ Hz, 2 H), 7.31 (t, $J = 7.6$ Hz, 4 H), 7.19 (d, $J = 8$ Hz, 4 H) 2.96 (t, $J = 7.6$ Hz, 4 H), 1.71 (quin, 4 H), 1.49–1.25 (m, 52 H), 0.88 (t, $J = 6.4$ Hz, 6 H).

**MALDI-TOF-MS m/z:** Exact mass: 1154.56. Found: 1154.7.

**EA:** calculated for C$_{70}$H$_{88}$Cl$_2$N$_2$O$_4$S$_2$: C, 72.70; H, 7.67; N, 2.42. Found: C, 72.58; H, 7.43; N, 2.38.

### 3. Results and discussion

From the DSC thermogram of N(1,7)SF$_{16}$ (Figure 1), two transition peaks were observed on cooling, corresponding to two different phase. When slowly cooling the isotropic melt of N(1,7)SF$_{16}$ on a hot stage between untreated glass plates (about 15 μm), a fan-shaped texture appears, as is the characteristic of columnar mesophase.[25,27] We can find that some areas show optically isotropic dark texture which is regarded as column aligned perpendicular to the substrate. While further cooling to 61.8°C, all areas change to a dark blue texture which shows two domain with opposite chirality by the opposite and negative rotations of polariser from the cross position.[28–30]

One dimensional SAXS was employed to further elucidate phase structure of the high-temperature phase, powder samples were kept in an aluminised paper to measure X-ray curve. The X-ray diffraction pattern is shown in Figure 2(a). Three diffraction peaks are

![Figure 1](image_url)

**Figure 1.** (colour online) DSC thermogram (a) and POM textures of N(1,7)SF$_{16}$ on cooling (b–e): Col$_h$ phase at 120°C (b); B4 phase under crossed polariser (c) and B4 phase under uncrossed polariser (d) (e) at 55°C. The lower curve of DSC corresponds to a cooling run.
presented at small angle diffraction region. And the ratio of the corresponding layer spacing is $1:(1/3)^{1/2}:1/2$, which is characteristic of Colh.[27] The three reflections were further indexed to (100), (110) and (200). The hexagonal lattice edge was calculated as 70.4 Å. At lower temperature, we use 2D X-ray diffractometer (Figure 2(b)) to get more detailed reflection information which could be unobvious in 1D SAXS. X-Ray patterns of non-oriented samples in the low-temperature phase show three reflections in the small angle region, which exhibit smectic layer spacing of $d = 43.2$, $38.3$ and $21.6$ Å. There are also several strong broadened reflections in the wide-angle region, and the broad diffuse peak at $d = 4.5$ Å is indicative of liquid crystal phases. The blue colour and X-ray pattern of this phase are indications for B4-like phase.[3] By applying an electric field, the texture didn’t change. Therefore, a phase sequence of Iso-Colh-B4 on cooling is observed for N(1,7)SF16. For the liquid crystal molecules based on 1,7-naphthalene central core and Schiff’s base linkages, B4 phase is the most common phase on low temperature which show dark blue chiral texture.

From the DSC curve of N(1,7)SF12 shown in Figure 3(a), we can find that the cooling curve shows only one obvious peak theoretical corresponding to only one phase transition. However, the change of POM texture shows the existence of another phase which differs from the higher temperature phase below specific temperature. When slowly cooling the compounds, large domains of fan-shaped texture appear as columnar phase below 138.0°C (Figure 3(b)). Figure 4(a) shows the 1D SAXS diffraction pattern of the high-temperature phase, in which inner three reflections having spacing in the ratio of $1:(1/3)^{1/2}:1/2$. Therefore, the high-temperature phase of N(1,7)SF12 is Colh. Further cooling to 58.0°C, the texture slowly turns into completely optical dark domain without obvious transition enthalpy. From the following 2D XRD result (Figure 4(b)), five reflection peaks in the small angle region area are found. According to the related literature, the dark texture may be cubic phase, B4 phase or Colr phase. [27,31] The reflections in the small angle region actually satisfy the feature of cubic phase. Reflection peaks were observed at $d = 58.8$, $48.2$, $41.6$, $33.9$, 31.9 Å.

Figure 2. Powder X-ray diffraction pattern of the compound N(1,7)SF16: (a) Colh phase, (b) B4 phase.

Figure 3. (colour online) DSC thermogram (a) and POM textures of N(1,7)SF12 on cooling (b–c); Colh phase at 100°C (b); Cub phase at 40°C (c). The lower curve of DSC corresponds to a cooling run.
29.4 Å in the small region which were indexed as (110), (111), (200), (211), (220) reflections of the primitive cubic lattice (P-Bravais type). The corresponding cubic lattice was calculated for N(1,7)SF12 is 83.5 Å, which is larger than lattice edge 66.5 Å of Colh phase.

For N(1,7)SCl16 (Figure 5), there are also one transition peak in DSC spectrogram, a Colh exists in the temperature region from 129.1°C to 56°C. Below the critical temperature 56°C, the whole texture of pre-existing fan-shaped phase obviously changed, part area turns into blue colour texture, while the entirety texture still look like column phase.[32] Then we observe the phase texture on a liquid crystal cell with only 3 μm space. The texture of higher temperature phase is still typical fan-shaped domain. It is noteworthy that the phase transition from Colh to lower temperature phase is marked by a distinct lowering of optical birefringence, meanwhile the phase transition temperature are the same with sample observed by the lager space cells. And the phenomenon is same on a 3 μm ITO cell with no coating (Figure 6(a) and (b)). In conjunction with DSC results and POM texture, the lower temperature phase belongs to columnar phase (Colx). By applying a rectangular-wave field, the texture of Colx changed to different fan-shaped texture with higher birefringence (Figure 6(b) and (c)), and it could recover on the field-off state. However, the 2D XRD results in the low-temperature phase show one intense reflection peak in low-angle region and a few peaks in wide angle region. The corresponding spacing are d = 39.0, 9.7, 7.1, 6.5, 4.7, 4.2 and 3.6 Å and a broad diffuse peak around 4.5 Å (Figure 7(b)). According to the number of reflections, the sample kept in an aluminised paper could be partial crystalline due to the effect of covered aluminised paper. The structure which is characteristic of N(1,7)SCl12 is similar with N(1,7)SCl16 and no more repeat (see the Appendices, available as Supplemental Content online). It is noteworthy that the ratio of the Bragg spacing of the former sharp reflections of N(1,7)SCl12 in low-temperature phase might suggest lamellar structure.[33,34]

The phase transition temperatures and associated enthalpies of four compounds are summarised in Table 1 based on the results of DSC in conjunction with POM during cooling. The X-ray spacing data

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**Figure 4.** Powder X-ray diffraction pattern of the compound N(1,7)SF12: (a) Colh phase, (b) Cub phase.

**Figure 5.** (colour online) DSC thermogram (a) and POM textures of N(1,7)SCl16 on cooling (b–c): Colh phase at 100°C (b); Colx phase at 40°C (c). The lower curve of DSC corresponds to a cooling run.
and calculated lattice parameter are summarised in Table 2.

Based on Table 1, we draw a histogram (Figure 8) to compare the transition temperatures of four compounds above with N(1,7)Sn \((n = 12, 16)\). The cleaning point temperatures for lateral chlorinated compounds N(1,7)SCln are obviously lower than that of lateral halogen-free compounds N(1,7)Sn, to reduce the value of 21.2°C and 16.9°C corresponding to carbon number 12 and 16. The decrease value of lateral fluorinated compounds, N(1,7)SFn, is relatively less than that of lateral chlorinated molecules, N(1,7)SCln, to reduce the value of 0.4°C and 4.8°C. The result shows that steric effects play a more important role than substituent polarity for these compounds so that halogenated molecules have lower clearing point temperature owing to the decrease of molecular interaction, meanwhile N(1,7)SCln have a major influence on clearing point temperature in contrast with N(1,7)SFn due to larger steric volume. Lateral halogen compounds have a wider Colh phase extent; the Colh range of N(1,7)SFn \((n = 12, 16)\) is the widest as 80.1°C and 79.4°C, followed by the N(1,7)SCln as 67.3°C and 73.1°C, N(1,7)Sn \((n = 12, 16)\) have the narrowest Colh ranges as 18.9°C and 27.9°C. The compounds of fluoro substituent have the widest Colh phase range depending on the perfect combination of small size, high polarity and strength of C–F bond so as to confer the most excellent phase stability, while the phase stability of lateral chlorinated compounds slightly decrease probably owing to lager size and lower strength of C–Cl.[35] The clearing point and phase transition temperature of these V-shaped molecules will generally rise along with the increase of carbon number in alkylthio tails. The reason could be attributed to the improvement of molecular interaction along with the increase of tail chain length.

Table 1. Transition temperatures and enthalpies of N(1,7)SRn compounds on cooling.

| Compound          | Transition temperature (°C) (enthalpy (kJ mol\(^{-1}\))) |
|-------------------|----------------------------------------------------------|
| N(1,7)S12*        | B4 119.6 (30.0) Colh 138.5 (5.3) Iso                   |
| N(1,7)S16*        | B4 118.1 (30.9) Colh 146.0 (7.0) Iso                   |
| N(1,7)SF12        | Cub 58.0        Colh 138.1 (7.0) Iso                   |
| N(1,7)SF16        | B4 61.8 (7.9)   Colh 141.2 (7.9) Iso                   |
| N(1,7)SCI12       | Colh 50.0       Colh 117.3 (6.4) Iso                   |
| N(1,7)SCI16       | Colh 56.0       Colh 129.1 (7.0) Iso                   |

Note: *data obtained from [20,31].

Figure 6. (colour online) POM texture of N(1,7)SCl16 on ITO cell with 3 μm space; (a) Colh, (b) Colx, (c) texture transformation under a field of ±10 V/μm.

Figure 7. Powder X-ray diffraction pattern of the compound N(1,7)SCl16: (a) Colh phase, (b) Colx phase.
Table 2. XRD data for compounds N(1,7)SRn in their respective mesophases.

| Compound     | Phase | d_{obs} (Å) | d_{calc} (Å) | hkl | a (Å) |
|--------------|-------|-------------|--------------|-----|-------|
| N(1,7)SF12  | Colh  | 57.6        | 57.6         | (100) |
|              |       | 33.3        | 33.2         | (110) | 66.5° |
|              |       | 28.7        | 28.8         | (200) |
|              | Cub   | 58.8        | 58.8         | (110) |
|              |       | 48.2        | 48.0         | (111) |
|              |       | 41.6        | 41.6         | (200) | 83.1° |
|              |       | 33.9        | 33.9         | (211) |
|              |       | 29.4        | 29.4         | (220) |
| N(1,7)SF16  | Colh  | 61.0        | 61.0         | (100) |
|              |       | 35.3        | 35.2         | (110) | 70.4° |
|              |       | 30.5        | 30.5         | (200) |
| B4           |       | 43.2        |              |      |
|              |       | 38.3        |              |      |
|              |       | 21.6        |              |      |
| N(1,7)SCl12 | Colh  | 55.9        | 55.9         | (100) |
|              |       | 32.2        | 32.3         | (110) | 64.6  |
|              |       | 27.9        | 28.0         | (200) |
|              | Colx  | 37.4        |              |      |
|              |       | 18.6        |              |      |
|              |       | 9.7         |              |      |
|              |       | 6.4         |              |      |
|              |       | 4.7         |              |      |
|              |       | 4.2         |              |      |
|              |       | 3.6         |              |      |
| N(1,7)SCl16 | Colh  | 58.7        | 58.7         | (100) |
|              |       | 33.9        | 33.9         | (110) | 67.8° |
|              |       | 29.4        | 29.4         | (200) |
|              | Colx  | 39.0        |              |      |
|              |       | 9.7         |              |      |
|              |       | 7.1         |              |      |
|              |       | 6.5         |              |      |
|              |       | 4.7         |              |      |
|              |       | 4.2         |              |      |
|              |       | 3.6         |              |      |

Note: (a) a is Hexagonal lattice parameter. b is Cubic lattice parameter.
(b) X-ray spacing data of Colh phase was obtained through 1D SAXS, while the X-ray data of B4, Cub, Colx were got through 2D X-ray diffractometer.

4. Conclusions

In this study, we prepared four V-shaped compound based on 1,7-naphthalene central core and alkylthio tails: N(1,7)SF16, N(1,7)SF12, N(1,7)SCl16 and N(1,7)SCl12. All the compounds show the Colh at high temperature on cooling from the isotropic liquid, the mesophase of low temperature are B4, Cub, unidentified Colx, respectively. The clearing point of bent-core can be reduced by the introduction of lateral halogen, especially for the influence of Cl. Meanwhile, wider scope of Colh mesophases could be observed as a result of lateral halogen, and the compounds involving F substituent have a wider Colh range than the molecules of Cl substituent. The clearing point and phase transition temperature of these V-shaped molecules will generally rise along with the increase of carbon number in alkylthio tails.

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Supplemental Data (Appendices)

Supplemental data for this article can be accessed at http://dx.doi.org/10.1080/02678292.2014.948086

References

[1] Niori T, Sekine T, Watanabe J, Furukawa T, Takezoe H. Distinct ferroelectric smectic liquid crystals consisting of banana shaped achiral molecules. J Mater Chem. 1996;6:1231–1233. doi:10.1039/jm9960601231.
[2] Link DR, Natale G, Shao R, Maclennan JE, Clark NE, K€orbliva E, Walba DM. Spontaneous formation of macroscopic chiral domains in a fluid smectic phase of achiral molecules. Science. 1997;278:1924–1927. doi:10.1126/science.278.5345.1924.
[3] Svoboda J, Novotna V, Kozmik V, Glogarova M, Weissflog W, Diele S, Pelzl G. A novel type of banana liquid crystals based on 1-substituted naphthalene-2,7-diol cores. J Mater Chem. 2003;13:2104–2110. doi:10.1039/b302005c.
[4] Reddy RA, Sadashiva BK. Influence of fluorine substituent on the mesomorphic properties of five-ring ester banana-shaped molecules. Liq Cryst. 2003;30:1031–1050. doi:10.1080/0267829031000152978.
[5] Reddy RA, Sadashiva BK. New phase sequences in banana-shaped mesogens: influence of fluorine substituent in compounds derived from 2,7-dihydroxy-naphthalene. J Mater Chem. 2004;14:1936–1947.
[6] Ortega J, De la Fuente MR, Etxebarria J, Folcia CL, Díez S, Gallastegui JA, Gimeno N, Ros MB, Pérez-Jubindo M. Electric-field-induced B1–B2 transition in bent-core mesogens. Phys Rev E. 2004;69:011703. doi:10.1103/PhysRevE.69.011703.
[7] Deb R, Nath RK, Paul MK, Rao NVS, Tuluri F, Shen Y, Shao R, Chen D, Zhu C, Smalyukh II, Clark NA.
Four-ring achiral unsymmetrical bent core molecules forming strongly fluorescent smectic liquid crystals with spontaneous polar and chiral ordered B7 and B1 phases. J Mater. Chem. 2010;20:7332–7336. doi:10.1039/c0jm01539c.

[8] Pelzl G, Diele S, Weissflog W. Banana-shaped compounds – A new field of liquid crystals. Adv Mater. 1999;11:707–724. doi:10.1002/(SICI)1521-4095(199906)11:9<707::AID-ADMA707>3.0.CO;2-D.

[9] Takezoe H, Takanishi Y. Bent-core liquid crystals: their mysterious and attractive world. Jpn J Appl Phys. 2006;45:597–625. doi:10.1143/JJAP.45.597.

[10] Reddy RA, Tschiernke C. Bent-core liquid crystals: polar order, superstructural chirality and spontaneous desymmetrisation in soft matter systems. J Mater Chem. 2006;16:907–961. doi:10.1039/b504400f.

[11] Matsuoka M, Matsunaga Y, Matsuoka H. New mesogenic compounds with unconventional molecular structures 1,2-phenylene and 2,3-naphthylene bis[4-(4-alkoxyphenylmethyl)benzoates] and related compounds. Liq Cryst. 1993;14:105–120. doi:10.1080/02678299308207236.

[12] Kuboshita M, Matsunaga Y, Matsuzaki H. Massorhmic behavior of 1,2-phenylene bis[4-(4-alkoxybenzylidenemino)benzoates]. Mol Cryst Liq Cryst. 1991;199:319–326. doi:10.1080/00268949108030943.

[13] Choi EJ, Cui X, Ohk CW, Zin WC, Lee JH, Lim TK, Jang WG. Smeectic A phase in a new bent-shaped mesogen based on a 2,3-naphthalene central core with an acute-subtended angle. J Mater Chem. 2010;20:3743–3749. doi:10.1039/b919404e.

[14] Choi EJ, Seo YH, Park SB, Zin WC, Song DH, Lee GS, Yoon TH, Lee JH. Electro-optical properties of the nematic phase in V-shaped molecules with a 2,3-naphthalene central unit. J Mater Chem. 2013;1:451–455.

[15] Alonso I, Martinez-Perdiguero J, Ortega J, Folcia CL, Etxebarria J, Gimeno N, Ros MB. The SmA phase of a bent-core V-shaped compound: structure and electric-field response. Liq Cryst. 2010;37:1465–1470. doi:10.1080/02678292.2010.521858.

[16] Lee SK, Naito Y, Shi L, Tokita M, Takezoe H, Watanabe J. Mesomorphic behaviour in bent-shaped molecules with side wings at different positions of a central naphthalene core. Liq Cryst. 2007;34:935–943. doi:10.1080/02678290701541538.

[17] Lee SK, Tokita M, Takezoe H, Watanabe J. Effect of molecular structure on smectic phase structures in two homologues series of bent-shaped molecules with asymmetrical central naphthalene core. Ferroelectrics. 2008;365:1–11. doi:10.1080/00150190802059979.

[18] Lee SK, Shi L, Ishige R, Kang S, Tokita M, Watanabe J. Anti-ferrulectic banana phase in a bent-shaped molecule with a low bend angle of 60°. Chem Lett. 2008;37:1230–1231. doi:10.1246/cl.2008.1230.

[19] Lee SK, Li X, Kang S, Tokita M, Watanabe J. Formation of banana phases in bent-shaped molecules with unusual bent angles as low as 60°. J Mater Chem. 2009;19:4517–4522. doi:10.1021/ja090354a.

[20] Li X, Kang S, Lee SK, Tokita M, Watanabe J. Unusual formation of switchable hexagonal columnar phase by bent-shaped molecules with low bent-angle naphthalene central core and alkylthio tail. Jpn J Appl Phys. 2010;49:121701. doi:10.1143/JJAP.49.121701.

[21] Pelzl G, Diele S, Schröder MW, Weissflog W, Tamba MG, Baumeister U. Structural investigations on B7 phases of new bent-core mesogens including a binary system. Liq Cryst. 2010;37:839–852. doi:10.1080/02678292.2010.488019.

[22] Umadevi S, Radhika S, Sadashiva BK. Polar columnar and lamellar mesophases in homologous bent-core compounds derived from methyl 3,5-dihydroxybenzoate. Liq Cryst. 2013;40:1035–1049. doi:10.1080/02678292.2013.802817.

[23] Gomola K, Guo L, Pociecha D, Aroako F, Ishikawa K, Takezoe H. An optically uniaxial antiferroelectric smectic phase in asymmetrical bent-core compounds containing a 3-aminophenol central unit. J Mater Chem. 2010;20:7944–7952. doi:10.1039/c0jm01241f.

[24] Begum N, Turlapati S, Debnath S, Mohiuddin G, Sarkar DD, Rao Nandiraju VS. Achiral unsymmetrical four-ring bent-core liquid crystals with a polar fluoro or chloro end substituent: synthesis and characterisation. Liq Cryst. 2013;40:1105–1115. doi:10.1080/02678292.2013.795625.

[25] Li X, Zhan M, Wang K. A hexagonal columnar phase formed in lateral fluorinated bent-shaped molecules based on a 1,7-naphthalene central core. New J Chem. 2012;36:1133–1136. doi:10.1039/c2nj21072j.

[26] Li X. Synthesis, structure and properties of V-shaped shaped ferroelectric liquid crystals based on small-angle core. Beijing: Beihang University; 2012.

[27] Gorecka E, Pociecha D, Miezczkowski J, Matraszek J, Guillou D, Donnio B. Axially polar columnar phase made of polycatenar bent-shaped molecules. J Am Chem Soc. 2004;126:15946–15947. doi:10.1021/ja044597k.

[28] Thisayukta J, Nakayama Y, Kawauchi S, Takezoe H, Watanabe J. Distinct formation of a chiral smectic phase in achiral banana-shaped molecules with a central core based on a 2,7-dihydroxynaphthalene unit. J Am Chem Soc. 2000;122:7441–7448. doi:10.1021/ja001370q.

[29] Thisayukta J, Takezoe H, Watanabe J. Study on helical structure of the B4 phase formed from achiral banana-shaped molecule. Jpn J Appl Phys. 2001;40:3277–3287. doi:10.1143/JJAP.40.3277.

[30] Hough LE, Jung HT, Krueker D, Heberling MS, Nakata M, Jones CD, Chen D, Link R, Kraszkiewicz J, Heppke G, Rabe JP, Stocker W, Korblova E, Walba DM, Glaser MA, Clark NA. Helical nanofilament phases. Science. 2009;325:456–460. doi:10.1126/science.1176027.

[31] Kang S, Harada M, Li X, Tokita M, Watanabe J. Notable formation of a cubic phase from small bent-angle molecules based on the 1,7-naphthalene central core and alkylthio tails. Soft Matter. 2012;8:1916–1922. doi:10.1039/c1sm05544h.

[32] Varshney SK, Monobe H, Shimizu Y, Takezoe H, Prasad V. Non-symmetrical discotic liquid crystalline dimers: molecular design, synthesis and mesomorphic properties. Liq Cryst. 2010;5:607–615.

[33] Ponomarenko EA, Tirrell DA, MacKnight WJ. Water-insoluble complexes of poly(l-lysinie) with mixed alkyl sulfates: composition-controlled solid state structures. Macromolecules. 1998;31:1584–1589. doi:10.1021/ma971388u.

[34] Okamoto K, Goto Y, Inagaki S. Self-organization of crystal-like aromatic-silica hybrid materials. J Mater Chem. 2005;15:4136–4140. doi:10.1039/b508818f.

[35] Hird M. Fluorinated liquid crystals – properties and applications. Chem Soc Rev. 2007;36:2070–2095. doi:10.1039/b610738a.