Cite this: New J. Chem., 2012, 36, 1133–1136

A hexagonal columnar phase formed in lateral fluorinated bent-shaped molecules based on a 1,7-naphthalene central core†

Xiaodong Li, Mao-sheng Zhan* and Kai Wang*

Received (in Montpellier, France) 29th December 2011, Accepted 23rd February 2012 DOI: 10.1039/c2nj21072j

Lateral fluorinated bent-shaped molecules based on a 1,7-naphthalene central core and alkoxy tails can form a switchable hexagonal columnar phase and B₄ phase. The columnar phase has a large two-dimensional hexagonal lattice of 65–70 Å and exhibits ferroelectric switching with spontaneous polarization along the column axis.

Hexagonal columnar liquid crystals have attracted considerable interest owing to their distinctive structure and potential application in the fields such as photovoltaics,^{1–3} light-emitting diodes⁴ and field effect transistors.^{5,6} Compared with nematic and smectic liquid crystals, fewer structural skeletons have been found to exhibit a hexagonal columnar phase. Disk-like aromatic compounds such as triphenylene, porphyrin and phathalocyanine with mutiple tails have been known to exhibit hexagonal columnar liquid crystal properties.⁷

Recently not only simple disklike molecules but also a variety of molecular shapes such as rings, fans, cones or bows are utilized to form hexagonal columnar self-assemblies.⁸ In particular, some bent-shaped molecular systems exhibit hexagonal columnar phases. Kishikawa *et al.* prepared urea derivatives based on an abuse-angle central core and three alkoxy tails on each terminal benzene ring. The molecules are connected linearly through hydrogen bonds to form columns.⁹ Gorecka *et al.* synthesized polycatenar bent-shaped molecules with 2,6-pyridine central units and three alkoxy tails on each side. And the molecules can be assembled into a conical-shaped unit that forms columns.¹⁰ Both of these cases contain mutiple alkoxy tails, which is assumed to be a necessary structural characteristic to induce a hexagonal columnar stacking nature.

In the previous research, we prepared bent-shaped molecules with a 1,7-dioxynaphthalene central core and a single alkylthio tail in each side wing.¹¹ Surprisingly, the material exhibits a hexagonal columnar phase although neither flat aromatic backbones nor multiple tails are involved in the molecular structure. The relatively flexible alkylthio tail and the low bent-angle central core are considered to play a significant role. In this study, we prepared



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

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

	Transition temperature ^{a} / $^{\circ}$ C (enthalpy/kJ mol ⁻¹)
N(1,7)-F12 N(1,7)-F14 N(1,7)-F16	B ₄ 87.6 (11.8); Col _h 147.5 (2.8); iso B ₄ 84.9 (14.1); Col _h 142.3 (2.7); iso B ₄ 82.3 (15.9); Col _h 137.1 (2.2); iso
^a Based on cooli	ng DSC data.

lateral fluorinated bent-shaped molecules based on the same central core but with a single alkoxy tail in each side wing. And the fluorine substituent is introduced at the position 3 of the terminal phenyl ring. The compound was designated as N(1,7)-Fn, where n indicates the number of carbon atoms in the alkoxy tails (Scheme 1). Interestingly, the introduction of the fluorine substituent has also induced a specific hexagonal columnar mesophase, which exhibits ferroelectric switching under electric field.

The synthetic route to N(1,7)-Fn is described in Scheme S1 (ESI[†]). All compounds exhibited a hexagonal columnar phase (Col_h) with a phase sequence of Iso–Col_h–B₄ upon decreasing temperature (Table 1). Their transition temperatures and associated enthalpy changes are listed in Table 1. When slowly cooling the isotropic liquid of N(1,7)-F14 on an untreated glass slide under POM, large domains of dendritic texture were observed (Fig. 1a), as is characteristic of the columnar mesophase.¹⁰ While on homogeneously rubbing glass, a uniform birefringent texture was detected while the rubbing direction is tilted from the polarizer's direction (Fig. 1b), which additionally supports the one-dimensional organization of the Col_h phase. Upon further cooling to the B₄ phase, dark blue textures were exhibited (Fig. 1c). Two optically active domains with opposite chirality were observed, in which the brightness was interchanged

Beijing University of Aeronautics and Astronautics, Beijing, P.R.China. E-mail: zhanms@buaa.edu.cn, wangkai@buaa.edu.cn; Fax: +86 1082317120; Tel: +86 1082317120, +86 1082338557 † Electronic supplementary information (ESI) available. See DOI: 10.1039/c2nj21072j

100



Fig. 1 Microphotographs observed for N(1,7)-F14 (a) dendritic texture of the Col_h phase on an untreated glass substrate (at 120 °C), (b) texture of the Col_h phase on a homogenous rubbing cell, while the rubbing direction is 30° tilted from the polarizer's direction. (c) The B₄ phase on an untreated glass substrate (at 60 °C), (d) chiral domains in the B₄ phase under uncrossed polarizers.

by positive and negative rotations of the polarizer from the cross polarization position (Fig. 1d). These characteristics of the B_4 phase have been explained by the twisted grain boundary (TGB) alignment¹² or helical nanofilaments of the layers.¹³

The columnar nature in the Col_h phase is firmly identified by a characteristic X-ray pattern (Fig. 2). Powder X-ray investigations were carried out with samples kept in glass capillary tubes. By slowly cooling the compound from isotropic liquid to the Col_h phase, a broad halo scattering is detected in the wide angle region, corresponding to the liquid-like disorder of molecules with a mean distance of 4.5 Å. In the small-angle region, three sharp reflections corresponding to layer spacings in the ratio of 1, $(1/3)^{1/2}$ and 2 were identified (Table 2). They were further indexed to (100), (110) and (200) in the two-dimensional hexagonal lattice with p6mm symmetry.¹⁰ The hexagonal lattice constant, a, is calculated to be 66.9 Å, 67.6 Å, 70.1 Å for N(1,7)-F12, N(1,7)-F14 and N(1,7)-F16 respectively, showing steady increment with the growth of *n*. Upon further cooling to the B₄ phase, a few equidistant smectic layer reflections and outer reflections of 4.5 Å were exhibited, as generally observed in B₄ phases.¹⁴

To elucidate more detailed structure of the Col_h phase, an oriented X-ray pattern of the compound was obtained. By slowly cooling a droplet of the compound N(1,7)-F14 deposited onto a homogeneously rubbing glass slide, the diffraction pattern of a



Fig. 2 Powder X-ray diffraction patterns of the Col_h phase (at 120 °C) and the B_4 phase (at 60 °C) observed in N(1,7)-F14.

N(1,/)-Fn					
Compound	Phase	$d_{ m obs}/{ m \AA}$	$d_{ m cal}/{ m \AA}$	hkl	$a^a/\text{\AA}$
		57.9	57.9	100	
N(1,7)-F12	Col_h	33.6	33.4	110	66.9
		28.8	28.9	200	
	B_4	35.2	_	100	
		58.6	58.6	100	
N(1,7)-F14	Col _h	34.0	33.8	110	67.6
		29.3	29.3	200	
	B_4	38.4		100	
		59.2	59.2	100	
N(1,7)-F16	Colh	34.0	34.1	110	70.1
		29.6	29.6	200	

41.3

Table 2 X-Ray spacing data and calculated lattice parameter of

^a Hexagonal lattice parameter.

B₄



Fig. 3 X-Ray diffraction patterns of the Col_h phase (at 120 °C) and the B₄ phase (at 60 °C) observed in N(1,7)-F14 on a homogeneously rubbing substrate. The X-ray beam is irradiated parallel to the rubbing direction.

well-aligned Col_h could be observed (Fig. 3), which clearly proves the existence of a hexagonal columnar phase. Fig. 3 illustrates the X-ray photographs taken upon irradiation parallel to the rubbing direction of the glass substrate. In the small angle region, well-aligned sharp spots of (100), (110), and (200) reflections clearly appeared. For instance, a pair of (100) reflection spots was observed in the meridional direction, and the additional pairs of spots are located every 60° along the azimuthal direction, confirming the hexagonal packing of molecules. However, in contrast to the high orientation of the inner reflections, the outer broad reflection appeared as a diffuse ring pattern similar to that of the non-oriented sample. Thus, it is concluded that there is no long range orientational correlation in the adjacent molecules on the projection along the column axis. Upon further cooling to the B₄ phase, the orientation with respect to the inner reflections disappeared completely as observed in the B4 phase of usual bent-core molecular systems.¹⁴

Electro-optic switching was observed for samples sandwiched between two glass plates with a transparent ITO electrode. The substrate surface was neither polymer coated nor rubbed. Fan-shaped domains were first observed upon cooling the isotropic liquid to the Col_h phase (Fig. 4a). By applying an electric field on the Col_h phase, the fan-shaped texture immediately disappeared and was rebuilt to give a zero birefringence (Fig. 4b). Thus, an electric field induced the



Fig. 4 Switching behaviour observed for N(1,7)-F12. (a) Microscopic fan-like texture of the Col_h phase originally prepared within a cell. (b) Dark texture observed under the applied electric field. (c) Polarization reversal current under the application of triangular wave (135 °C, 400 Vpp, 30 Hz, cell gap: 4.0 μ m). (d) The switching model.

homeotropic alignment of columns with their axes perpendicular to the ITO substrate. A single current peak in response to the applied triangular field was observed (Fig. 4c), indicating that the columnar phase is ferroelectric.^{9,10} The spontaneous polarization was calculated to be about 180 nC cm⁻². The switching occurred with no texture change, and the dark texture was maintained after the electric field switched off. This indicates that the polarization exists along the columns and switches along the direction vertical to the ITO plate (Fig. 4d). At the field-on state, the molecules rotate around its long axis and the bent direction of molecules is parallel to the column can rotate their polar axis to the opposite direction to maintain the columnar axis along the field. And the direction of the columns is maintained after the field is off.

The examples shown in this paper give evidence of the subtle relationship between the chemical structure and mesomorphic properties of the bent-shaped liquid crystals. The introduction of a lateral fluorine substituent at position 3 on the terminal phenyl rings leads to a drastic change in mesomorphic behaviour since a switchable hexagonal columnar mesophase is observed, while the non-substituted homologous N(1,7)-On only exhibited the B_4 phase.¹⁵ Also, in contrast to the typical molecular structures which form a hexagonal columnar phase, neither flat aromatic backbones nor multiple tails are involved in the N(1,7)-Fn compound. It is assumed that the molecular organisation of bent-shaped compounds results in a complex balance between the electro-static interactions and the van der Waals interactions developed by the aliphatic chain.¹⁶ Thus the distribution of the electrostatic potential extrema along the molecule will strongly influence the molecular arrangement and the nature of the mesophases. Electrostatic potential maps of N(1,7)-Fn and N(1,7)-On were calculated by the B3LYP/6-31G* method with Spartan 08 V1.12 software (Fig. 5). The presence of the fluorine substituents on the outer rings modifies the distribution of the potential extrema (Table 3). In the N(1,7)-Fn series, the fluorine substitution slightly reduces the electrostatic potential around the Schiff base and the ester group but largely reinforces the negative potential between the fluorine substituted phenylene group and the alkoxy group. This small difference might be able to induce different molecular arrangement and result in formation of different mesophases.



Fig. 5 Electrostatic potential maps of the N(1,7)-Fn series (the electrostatic potential was calculated by the B3LYP/6-31G* method with Spartan 08 V1.12). The correlation of the colour and electron density is on the right side bar.

Table 3 Values of the calculated electrostatic potential (kcal mol^{-1}) on the different parts of the molecule

Series	N(1,7)-F <i>n</i>	N(1,7)-On
Central ring	-67	-69
0	-60	-71
C=O	-185	-197
Intermediate ring	-42	-57
CH=N	-137	-148
Outer ring	-85	-107
O at the end of side wing	-157	-130

At present time, our understanding of how molecules in this study construct hexagonal columnar assembly is still at an early stage. The value of the lattice parameter a (the diameter of the column) was approximately two-fold larger than the layer thickness of the B₄ phase. By assuming a density of $\rho = 1 \text{ g cm}^{-3}$ and a height of the columnar slice of h = 4.5 Å (corresponding to the average distance between molecules), the number of molecules calculated in each column slice is found to be 10-11. This value is relatively large, so we believe that the column formation involving disc-like stacking by a conical assembly of bent-core molecules reported by Kishikawa et al.⁹ and Gorecka et al.¹⁰ is unlikely in our case. Based on the broad diffuse scattering observed in the wide-angle region of the wellaligned sample, it is concluded that there is no preferential orientation of molecules on the projection along the column.¹¹ One possible model is that the column is shaped with slices containing 10-11 molecules. The groups (or ribbons) of parallel molecules packed without any orientational correlation along the column axis (Fig. S2a, ESI⁺), which is similar to the selfassembly proposed for phasmidic molecules.¹⁷ Another possible model is that the column is constructed from a tube-like assembly of molecules and cylindrically symmetric deformation of layers was assumed (Fig. S2b, ESI⁺). The alkoxy tails of molecules are protruding outside of the column wall and inside of the enclosed mesogenic layer respectively. In this case, the column includes a very high curvature and the concentration of the aliphatic chains in the central part is quite high. However, such a high curvature is not unusual since it is generally observed in the smectic layers to form the focal conic defects.¹³ Further clarification of the molecular assembly in this phase is now proceeding.

In summary, lateral fluorinated bent-shaped molecules based on a 1,7-dioxynaphthalene central core have been studied. The material can form a switchable hexagonal columnar phase and B_4 phase. The columnar phase has a large two-dimensional hexagonal lattice of 65–70 Å and exhibits ferroelectric switching with spontaneous polarization along the column axis. The number of molecules calculated in each column slice is found to be 10–11. It is assumed that the combination of the acute angle central core and the lateral polar fluorine substituent cooperates to generate a hexagonal columnar self-assembly, although the molecule itself only has one single alkoxy tail on each side wing. This could open up prospects for new molecular designs in hexagonal columnar liquid crystal systems.

Experimental

The synthetic routes are illustrated in Scheme S1 (ESI†). All reagents including 1,7-dihydroxynaphthalene 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. ¹H-NMR and ¹³C-NMR spectra were recorded on a JEOL FT-NMR AL400 (400 MHz) spectrometer using CDCl₃ as an internal standard. Elemental analysis was determined by a CHN corder MT-6.

Optical textures were observed under a crossed polarizer using an Olympus BX51 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-Ka 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. 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 performed on the substrate surface.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 51073007). X. Li is grateful to Prof. Junji Watanabe in Tokyo Institute of Technology for the stay in his lab on the exchange research.

Notes and references

- T. N. Y. Hoang, D. Pociecha, M. Salamonczyk, E. Gorecka and R. Deschenaux, *Soft Matter*, 2011, 7, 4948–4953.
- 2 J. Wu, W. Pisula and K. Müllen, Chem. Rev., 2007, 107, 718-747.
- 3 L. Schmidt-Mende, A. Fechtenkotter, K. Mullen, E. Moons, R. H. Friend and J. D. MacKenzie, *Science*, 2001, 293, 1119–1122.
- 4 E. Y. Elgueta, M. L. Parraa, J. Barberáb, J. M. Vergaraa and J. A. Ulloaa, *Supramol. Chem.*, 2011, 23, 721–730.
- 5 H. S. Kim, S. M. Choi, J. H. Lee, P. Busch, S. J. Koza, E. A. Verploegen and B. D. Pate, *Adv. Mater.*, 2008, 20, 1105–1109.
- 6 A. Calo, P. Stoliar, M. Cavallini, S. Sergeyev, Y. H. Geerts and F. Biscarini, J. Am. Chem. Soc., 2008, 130, 11953–11958.
- 7 S. Kumar, Chem. Soc. Rev., 2006, 35, 83-109.
- 8 (a) T. Kato, N. Mizoshita and K. Kishimoto, Angew. Chem., Int. Ed., 2006, 45, 38–68; (b) B. Donnio, S. Buathong, I. Bury and D. Guillon, Chem. Soc. Rev., 2007, 36, 1495–1513.
- 9 K. Kishikawa, S. Nakahara, Y. Nishikawa, S. Kohmoto and M. Yamamoto, J. Am. Chem. Soc., 2005, **127**, 2565–2571.
- 10 E. Gorecka, D. Pociecha, J. Mieczkowski, J. Matraszek, D. Guillon and B. Donnio, J. Am. Chem. Soc., 2004, 126, 15946–15947.
- 11 X. Li, S. Kang, S. K. Lee, M. Tokita and J. Watanabe, Jpn. J. Appl. Phys., 2010, 49, 121701–121706.
- 12 J. Thisayukta, H. Takezoe and J. Watanabe, Jpn. J. Appl. Phys., 2001, 40, 3277–3281.
- 13 L. É. Hough, H. T. Jung, D. Kruerke, M. S. Heberling, M. Nakata, C. D. Jones, D. Chen, D. R. Link, J. Zasadzinski, G. Heppke, J. P. Rabe, W. Stocker, E. Korblova, D. M. Walba, M. A. Glaser and N. A. Clark, *Science*, 2009, **325**, 452–456.
- 14 J. Thisayukta, Y. Nakayama, S. Kawauchi, H. Takezoe and J. Watanabe, J. Am. Chem. Soc., 2000, **122**, 7441–7448.
- 15 S. K. Lee, Y. Naito, L. Shi, M. Tokita, H. Takezoe and J. Watanabe, *Liq. Cryst.*, 2007, 34, 935–943.
- 16 J. P. Bedel, J. C. Rouillon, J. P. Marcerou, M. Laguerre, H. T. Nguyen and M. F. Achard, *J. Mater. Chem.*, 2002, **12**, 2214–2220.
- 17 (a) J. Malthête, H. T. Nguyen and C. Destrade, *Liq. Cryst.*, 1993,
 13, 171–187; (b) H. T. Nguyen, C. Destrade and J. Malthête, *Adv. Mater.*, 1997, 9, 375; (c) J. Malthête, A. Collet and
 A. M. Levelut, *Liq. Cryst.*, 1989, 5, 123.