An unusual phase sequence of iso liq-blue phase-smectic A observed for novel binaphthyl mesogenic derivatives†

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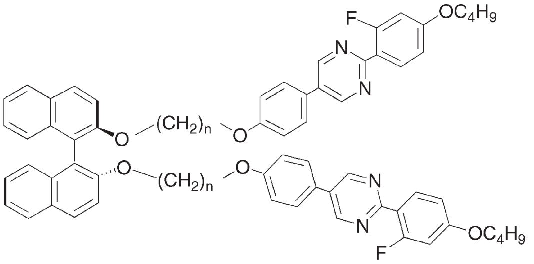
A homologous series of novel chiral dimeric compounds, (*R*)-2,2′-bis{6-[4-(2-(2-fluoro-4-butyloxyphenyl)pyrimidine-5-yl)phenyloxy]alkyloxy}-1,1′-binaphthyl, has been prepared and the physical properties investigated. The binaphthyl derivatives with an even number of atoms in the spacers showed a chiral nematic phase, however, those with an odd number of atoms showed an unusual direct blue phase to smectic A phase transition.

Investigation of chirality in liquid crystals is one of the most exciting areas of liquid crystal science. Frustrated phenomena induced by chirality have been reported. Twist grain boundary (TGB) phases, blue phases, and smectic Q phases have been observed and structure–property correlations investigated.[1] Blue phases are of particular interest because they have a fluid lattice structure that is stabilized by lattice defects. Appearance of blue phases results from the competition between the chiral twisting force and the desire for molecules to pack in ways such that they fill space uniformly. Theoretical and experimental works have demonstrated that chiral nematic liquid crystals of short pitch can form up to three distinct blue phases, *i.e.* blue phase I (BPI), blue phase II (BPII) and blue phase III (BPIII).[2–4] Blue phases are normally found in a very narrow (*ca.* 1 °C) temperature range between the isotropic liquid and a chiral nematic (N*) phase of sufficiently short pitch, except in a few cases where a SmA to BPI transition has been observed.[5–7] Double twist cylinders are believed to exist in BPI and BPII. Meiboom *et al.* discovered that the local free energy of most chiral nematic liquid crystals could be reduced by a double twist structure.[8] Such a structure requires energetically unfavourable disclinations between separate double twist regions. As the liquid crystals approach the isotropic transition, the energy cost of disclinations lowers and a network of the double twist structures with disclinations might be more stable than the helical N* phase. Li *et al.* reported the observation of a different phase sequence I-BPs-TGBA-TGBC-SmC* in a fluoro-substituted chiral tolane derivative.[9,10] Recently, there has also been experimental evidence for a smectic blue phase, which is observed between the isotropic and smectic phases.[11,12] From the viewpoint of applications, blue phases are interesting for fast light modulators or tunable photonic crystals. However, the narrow temperature range is a critical problem. Kikuchi *et al.* reported polymer-stabilized blue phases in which a temperature range is extended to more than 60 °C and they demonstrated a fast electro-optical switching for the stabilized blue phase.[13] On the other hand, many kinds of liquid-crystalline materials possessing a centre of chirality have been investigated. Recently compounds possessing an axis or a plane of chirality have been reported.[14–17] A single chiral compound with a wide blue phase-temperature range has never been obtained. Theoretical work suggests that biaxiality plays an important role in the blue phases.[18] However, the biaxiality in most chiral nematic liquid crystals is slight, and as a result the double twist structure cannot exist in a wide temperature range.

We reported an U-shaped molecule that induces a smectic-like layer ordering in the nematic phase and noted the possibility that the nematic (N) phase has biaxiality.[19] Thus we have designed coupling between axial chirality and the U-shaped system. The designed system is expected to induce unusual order in the N* phase. In the present study, we have prepared a homologous series of dimeric liquid-crystalline compounds possessing a binaphthyl group ((*R*)-***n***) and found an unusual phase sequence of iso-BP- SmA. A few examples of binaphthyl derivatives have been reported[20,21] and some of them show chiral smectic phases,[21] however, a N* phase has not been observed for binaphthyl mesogenic derivatives.



(*R*)-n

Experimental

Spectroscopic analysis

Purification of final products was carried out using column chromatography over silica gel (63–210 μm) (Kanto Chemical,

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† Electronic supplementary information (ESI) available: Analytical data for compounds (*S*)-**9**, (*R*)-**6**, (*R*)-**7**, (*R*)-**8**, (*R*)-**10**, (*R*)-**11** and (*R*)-**12**. Photomicrograph of a contact region between compounds (*R*)-**9** (right-hand side) and (*R*)-**10** (left-hand side) at 118.5 °C. Photomicrograph of a contact region between mixtures of achiral host material, 5-octyl-2-(4-hexyloxyphenyl)pyrimidine, and 5 wt% of each chiral compound, *i.e.* compound (*R*)-**9** (left-hand side) and compound (*R*)-**10** (right-hand side) at 63.5 °C in the N* phase. See http://www.rsc.org/suppdata/jm/b4/b410931g/

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Tokyo, Japan) using dichloromethane or a dichloromethane–ethyl acetate mixture as the eluent, followed by recrystallization from ethanol. The purities of final compounds were checked by thin layer chromatography (TLC, aluminium sheets, silica gel 60 F254 from Merck, Elmsford, NY, USA). Dichloromethane was used as the solvent. Detection of products was achieved by UV irradiation (λ = 254 and 365 nm). The purities of the final compounds were also checked by normal phase HPLC (Intersil SIL 150A-5 column). A dichloromethane–isopropylalcohol (85 : 15) mixture was used as eluent. Detection of products was achieved by UV irradiation (λ = 254 nm).

The structures of the final products were elucidated by infrared (IR) spectroscopy (BIO RAD FTS-30) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (JEOL JNM-GX270). Elemental analysis (Perkin Elmer 2400II, CHN analyzer) was obtained for each final compound.

Preparation of materials

The binaphthyl derivative (*R*)-**n** was prepared by the synthesis outlined in Scheme 1. Optically active (*R*)-2,2′-dihydroxy-1,1′-binaphthyl and (*S*)-2,2′-dihydroxy-1,1′-binapthyl were obtained from Aldrich Chemical Company, Milwaukee, WI, USA. 5-(4-Hydroxy)phenyl-2-(2-fluoro-4-butyloxyphenyl)-pyrimidine was obtained from Midori Kagaku Co., Ltd., Tokyo, Japan.

(*R*)-2,2′-Bis{6-[4-(2-(2-fluoro-4-butyloxyphenyl)pyrimidine-5-yl)phenyloxy]nonyloxy}-1,1′-binaphthyl, (*R*)-9

Potassium carbonate (0.41 g, 3.0 mmol) was added to a solution of 5-(4-hydroxy)phenyl-2-(2-fluoro-4-butyloxyphenyl)pyrimidine (1.0 g, 3.0 mmol) and 1,9-dibromononane (1.1 g, 4.0 mmol) in cyclohexanone (15 ml). The reaction mixture was stirred at 80 °C for 6 h. After the filtration of precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with dichloromethane. The intermediate product, 5-{4-(6-bromononyl)}phenyl-2-(2-fluoro-4-butyloxyphenyl)pyrimidine, was obtained. Yield 0.79 g (1.4 mmol, 49%).

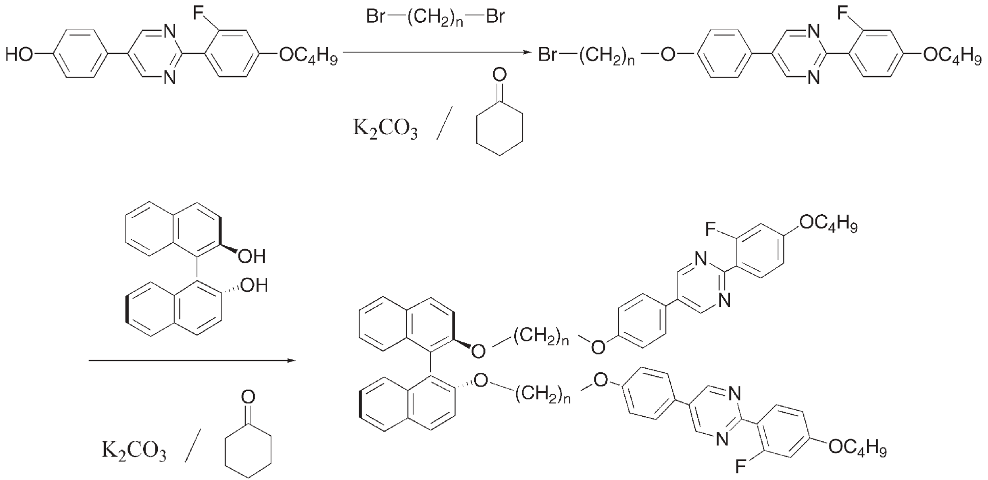
Potassium carbonate (0.14 g, 1.0 mmol) was added to a solution of 5-{4-(6-bromononyl)}phenyl-2-(2-fluoro-4-butyloxyphenyl)pyrimidine (0.54 g, 1.0 mmol) and (*R*)-2,2′-dihydroxy-1,1′-binaphthyl (0.14 g, 0.50 mmol) in cyclohexanone (10 ml). The reaction mixture was stirred at 140 °C for 9 h. After the filtration of precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with (39 : 1) dichloromethane–ethylacetate. Recrystallization from ethanol gave the desired product. Yield 0.23g (0.19 mmol, 38%).

^{1}H NMR (270 MHz, solvent CDCl$_3$, standard TMS) δ_H/ppm: 9.00(s, 4H, Ar–**H**), 8.12(t, 2H, Ar–**H**, *J* = 8.9 Hz), 7.90(d, 2H, Ar–**H**, *J* = 8.9 Hz), 7.83(d, 2H, Ar–**H**, *J* = 8.1 Hz), 7.54(d, 4H, Ar–**H**, *J* = 8.6 Hz), 7.39(d, 2H, Ar–**H**, *J* = 8.9 Hz), 7.32–7.16(m, 6H, Ar–**H**), 7.03(d, 4H, Ar–**H**, *J* = 8.6 Hz), 6.84–6.71(m, 4H, Ar–**H**), 4.03(t, 4H, Ar–OC**H**$_2$–, *J* = 6.5 Hz), 4.00–3.84(m, 4H, –C**H**$_2$O–), 4.00(t, 4H, Ar–OC**H**$_2$–, *J* = 6.5 Hz), 1.85–0.89 (m, 42H, aliphatic–**H**); IR (KBr) ν_{max}/cm^{-1}: 2932, 2855, 1621, 1439, 1430, 1248; Purity: 100%. Elemental analysis: Found: C, 77.35; H, 6.89; N, 4.75. Calc. for $C_{78}H_{84}F_2N_4O_6$: C, 77.26; H, 6.93; N, 4.62%.

The other compounds presented in this paper were obtained by a similar method to that for (*R*)-**9**. Analytical data for the other compounds are listed in Electronic Supplementary Information.†

Liquid-crystalline and physical properties

The initial assignments and corresponding transition temperatures for the final products were determined by thermal optical microscopy using a Nikon Optiphot POL polarizing microscope equipped with a Mettler FP82 microfurnace and FP80 control unit. The heating and cooling rates were 5 °C min^{-1}, unless otherwise indicated. Temperatures and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 6200 calorimeter. The material was studied at a scanning rate of 5 °C min^{-1}, for both heating and cooling cycles, after being encapsulated in aluminium pans. The helical pitch in the N* phase was measured by the Cano wedge method for a chiral nematic mixture consisting of



(*R*)-**n**

Scheme 1 Synthesis of compound (*R*)-**n**.

nematic liquid-crystalline material, 4-hexyl-4′-cyanobiphenyl (**6CB**) (purchased from BDH, Dorset, UK) and each chiral additive. The mixtures were studied using the contact method and their chiral nematic helical twist senses were established. The helical pitches were measured at room temperature. The definition of the helical twist senses used in this article is the same as that of Goodby.[22]

Results and discussion

The phase transition behaviour of compound (*R*)-**9** was investigated by optical microscopy. On cooling (5 °C min^{-1}) the isotropic liquid exhibited a blue colour of low birefringence and then showed a platelet texture composed of blue and slight red plates. This transition behaviour is indicative of blue phase I (Fig. 1a). On further cooling the BP changed to a smectic A (SmA) phase without appearance of a N* phase (Fig. 1b). The temperature range of the BP was about 4 °C. On heating from the SmA phase, a SmA to BP phase transition was observed.

We investigated the effect of chirality on the transition behaviour of compound (*R*)-**9**. A contact study between compound (*R*)-**9** and its (*S*)-isomer was carried out. The texture in the contact region is shown in Fig. 2. A Schlieren texture is seen in the central region, indicating that this region is an N phase. On decreasing the optical purity, the blue phase of the single compound changed to the N* phase and then to the N phase in its racemic mixture. Transition behaviour of the racemic mixture of compounds (*R*)-**9** (50 wt%) and (*S*)-**9** (50 wt%) on cooling was I 121 °C N 115 °C SmA.

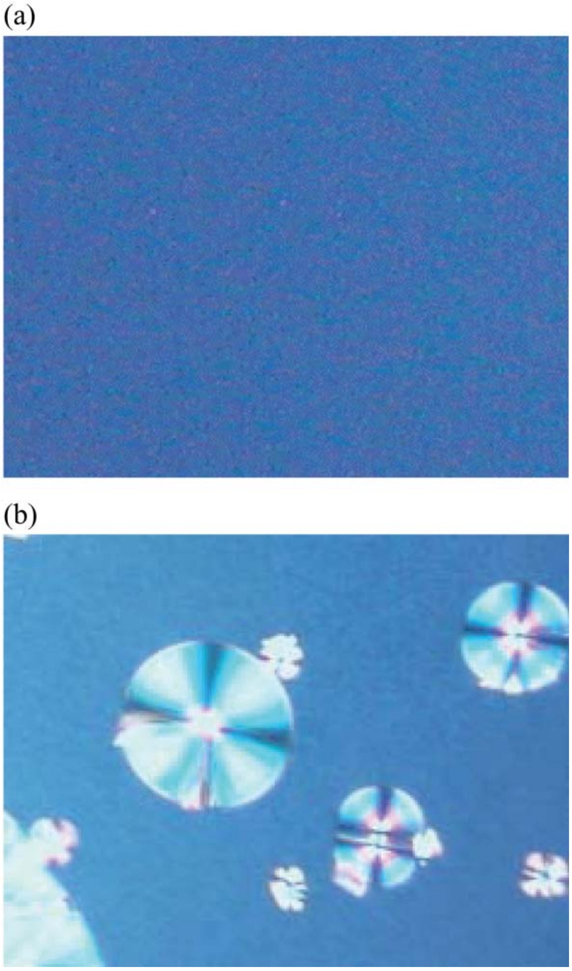


Fig. 1 Photomicrographs of (a) the blue phase at 118 °C and (b) the blue phase to SmA phase transition at 116 °C of a homogeneously aligned sample of compound (*R*)-**9**. Magnification 100 ×.

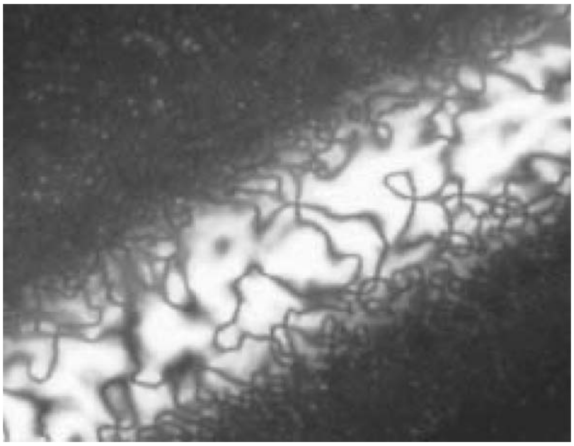


Fig. 2 Photomicrograph of a contact region between compounds (*R*)-**9** and (*S*)-**9** at 118 °C. Magnification 200 ×.

We investigated the effect of spacers on the phase transition behaviour of the binaphthyl derivatives. Temperatures and enthalpies of transition determined for the (*R*)-**n** compounds by optical microscopy and differential scanning calorimetry (DSC) are compared in Table 1. The binaphthyl derivatives with an even number of atoms in the spacers showed a chiral nematic phase, whereas those with an odd number of atoms showed a blue phase. The remarkable odd–even effect on chirality-dependent phase transition was observed for the binaphthyl mesogenic derivatives. As the spacer length increases, the stability of the SmA phase increases. Eventually, compound (*R*)-**12** showed only a SmA phase.

In order to understand the spacer effect on the transition behaviour, we investigated twisting power of each chiral compound. The helical pitch values and their helical twist senses in the N* phases are listed in Table 2.

The results of induced pitches in a host nematic liquid crystal doped with each chiral material indicate that twisting power of the odd dimers is smaller than that of the even dimers. Helical twist sense for compounds (*R*)-**6**, (*R*)-**7**, (*R*)-**8** and (*R*)-**9** was right-handed, however, that for compounds

Table 1 Transition temperatures (°C) on cooling and enthalpies (kJ mol^{-1}) of transition (in brackets) for compounds (*R*)-***n***

n	SmA	N*	BP	I	mp[a]
6	• 63 (0.7)	• 113 (1.4)		•	99
7	• 94 (6.7)		• 103(2.0)	•	54
8	• 105 (5.2)	• 124 (3.2)		•	100
9	• 116 (8.6)		• 120 (2.2)	•	46
10	• 108 (3.5)	• 122 (2.5)		•	41
11	• 127[b]		• 127[b]	•	62
12	• 135 (9.4)			•	74

[a] The melting points were measured by DSC. [b] The I-BP and BP-SmA transitions occurred simultaneously. The total value of both transition enthalpies was 5.9 kJ mol^{-1}.

Table 2 Helical pitch in the N* phase for a chiral nematic mixture of 6CB and 2 wt% of each chiral compound and the helical twist senses, *i.e.* right-handed (RH) or left-handed (LH)

n	Pitch/μm	Sense
6	8.4	RH
7	21.9	RH
8	8.5	RH
9	too long to be observed	RH
10	8.2	LH
11	too long to be observed	LH
12	16.1	LH

(*R*)-**10**, (*R*)-**11** and (*R*)-**12** was left-handed. The chiral materials producing the opposite handedness in the mixtures, *i.e.*, compounds (*R*)-**9** and (*R*)-**10**, were contacted. The contact region between the blue phase of compound (*R*)-**9** and the N* of compound (*R*)-**10** was discontinuous.† In order to confirm the opposite handedness, mixtures composed of achiral host material, 5-octyl-2-(4-hexyloxyphenyl)pyrimidine, and 5 wt% of each chiral compound, *i.e.* compound (*R*)-**9** and compound (*R*)-**10** were also contacted. A nematic phase was found to be induced in the central region between the two mixtures in the N* phase, indicating that the helical senses for compounds (*R*)-**9** and (*R*)-**10** are opposite in the N* phase.† Further investigation is necessary to clear origin of the helical twist inversion.

Interesting odd–even effects were observed for chiral properties of dimeric liquid crystals.[23–25] Blatch, Fletcher and Luckhurst reported that blue phase I behaviour was observed in a very narrow temperature range (0.6 °C) between isotropic liquid and N* phases for the odd non-symmetric dimers, whereas a direct I–N* transition was observed for the even non-symmetric dimers.[26] There is no marked difference in twisting power between the odd and even dimers, whereas the helical pitch for the odd dimer in its N* phase is significantly smaller than for the even dimers. The authors noted that the odd–even effect on the appearance of blue phase I is related to the smaller twist elastic constant of the odd dimers.

An optically pure 2,2′-substituted 1,1′-binaphthyl molecule can exist in two conformations, either cisoid or transoid.[27] MM2 calculations of (*R*)-**n** suggest that the cisoid conformation is more stable than the transoid. The energy difference between the cisoid and transoid conformers of compounds (*R*)-**6** and (*R*)-**7** were estimated to be 11.2 kJ mol^{-1} and 13.2 kJ mol^{-1}, respectively. We assumed the cisoid conformer and *all trans* configuration of the spacer for the initial molecular configuration for the calculation. MM2 models of compounds (*R*)-**6** and (*R*)-**7** show that configuration of the mesogenic groups of the odd dimer is more twisted than that of the even dimer (Fig. 3). Thus the axial chirality and the twist configuration of the mesogenic groups are thought to play an important role in the appearance of the blue phase.

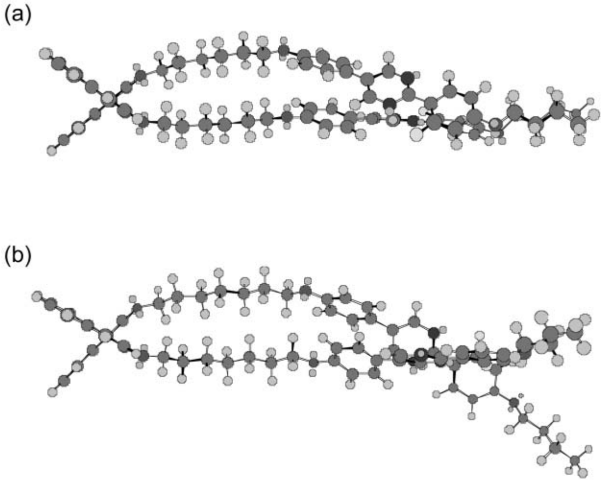


Fig. 3 MM2 models of (a) compound (*R*)-**6** with even-numbered spacers and (b) compound (*R*)-**7** with odd-numbered spacers.

Conclusion

We have observed a blue phase in a relatively wide temperature range between the isotropic and SmA phases of the novel binaphthyl mesogenic derivatives. Coupling between the axial chirality of the binaphthyl group and the twist configuration of the two 2-fluorophenyl-5-phenylpyrimidine moieties can produce the blue phase. The present chiral U-shaped system is thought to be a new molecular design for the appearance of blue phases. Furthermore, a new type of helical twist inversion was observed for the novel chiral system.

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References

1 J. W. Goodby, in *Handbook of Liquid Crystals*, ed. D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, vol. 1, ch V, pp. 115–132.
2 H. Stegemeier, T. H. Blümel, K. Hiltop, H. Onusseit and F. Porsch, *Liq. Cryst.*, 1986, **1**, 3.
3 J. Thoen, *Phys. Rev. A*, 1988, **37**, 1754.
4 P. P. Crooker, *Liq. Cryst.*, 1989, **5**, 751.
5 H. Onusseit and J. Stegemeier, *Z. Naturforsch., A*, 1984, **392**, 658.
6 H.-T. Nguyen, C. Sallen, A. Babeau, J. M. Galvan and C. Destrade, *Mol. Cryst. Liq. Cryst.*, 1987, **154**, 147.
7 V. V. Vashchenko, L. A. Kutulya, M. N. Pivenko and N. I. Shkolnikova, *Russ. Chem. Bull. Int. Ed.*, 2003, **52**, 2406.
8 S. Meiboom, J. P. Sethna, W. P. Anderson and W. F. Brinkman, *Phys. Rev. Lett.*, 1981, **46**, 1216.
9 M. -H. Li, H. -T. Nguyen and G. Sigaud, *Liq. Cryst.*, 1996, **20**, 361.
10 P. Jamee, G. Pitsi, M.-H. Li, H.-T. Nguyen, G. Sigaud and J. Thoen, *Phys. Rev. E*, 2000, **62**, 3687.
11 B. Pansu, E. Grelet, M.-H. Li and H.-T. Nguyen, *Phys, Rev. E*, 2000, **62**, 658.
12 Y. Takanishi, T. Ogasawara, A. Yoshizawa, J. Umezawa, T. Kusumoto, T. Hiyama, K. Ishikawa and H. Takezoe, *J. Mater. Chem.*, 2002, **12**, 1325.
13 H. Kikuchi, M. Yokota, Y. Hisakado, H. Yang and T. Kajiyama, *Nature Mater.*, 2002, **1**, 64.

14 G. Solladie and R. Zimmermann, *Ang. Chem., Int. Ed. Engl.*, 1985, **24**, 4062.

15 R. Lunkwitz, C. Tschierske, A. Langhoff, F. Gießelmann and P. Zugenmaier, *J. Mater. Chem.*, 1997, **7**, 1713.

16 K. Yang and R. F. Lemieux, *Mol. Cryst. Liq. Cryst.*, 1995, **260**, 247.

17 L. Ziminski and J. Malthete, *J. Chem. Soc., Chem. Commun.*, 1990, 1495.

18 D. C. Wright and N. D. Mermin, *Rev. Mod. Phys.*, 1989, **61**, 385.

19 A. Yoshizawa and A. Yamaguchi, *Chem. Commun.*, 2002, 2060.

20 J. C. Bhatt, S. S. Keast, M. E. Neubert and R. G. Petschek, *Liq. Cryst.*, 1995, **18**, 367.

21 K. Kanazawa, I. Higuchi and K. Akagi, *Mol. Cryst. Liq. Cryst.*, 2001, **364**, 825.

22 J. W. Goodby, *J. Mater. Chem.*, 1991, **1**, 307.

23 A. Yoshizawa, K. Matsuzawa and I. Nishiyama, *J. Mater. Chem.*, 1995, **5**, 2131.

24 C. C. Yelamaggad, S. A. Nagamani, U. S. Hiremath, D. S. S. Rao and S. K. Prasad, *Liq. Cryst.*, 2001, **28**, 1581.

25 I. Nishiyama, J. Yamamoto, J. W. Goodby and H. Yokoyama, *J. Mater. Chem.*, 2002, **12**, 1709.

26 A. E. Blatch, I. D. Fletcher and G. R. Luckhurst, *J. Mater. Chem.*, 1997, **7**, 9.

27 L. Pu, *Chem. Rev.*, 1998, **98**, 2405.