Unconventional layered mesophase-like TGBA phase in non-chiral α-(4′-propoxyphenylbenzyl-4-ylthio)-ω-(4′-butoxyphenybenzyl-4-ylthio)perfluorohexane

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Existence of a stable unconventional mesophase-like twist grain boundary smectic A (TGBA) phase was found in a wide temperature range for non-chiral α-(4′-propoxyphenylbenzyl-4-ylthio)-ω-(4′-butoxyphenylbenzyl-4-ylthio)-perfluorohexane (3BF6B4), which may be a consequence of the boomerang shape of the molecules.

Recently the generation and structure of TGB (twist grain boundary) phases have been investigated by several researchers[1–4] because of their unique packing structure. TGBA and TGBC phases can be regarded as smectic A and C variants composed of small SmA or SmC domains, respectively. The layer planes of the domains are arranged helically to form a macroscopic helical structure. Since the discovery of TGBA phases in (*R*)- or (*S*)-1-methylheptyl-4′-{[(4″-alkoxyphenyl)-propioloyl]oxy}biphenyl-4-carboxylate by Goodby *et al.*,[4] several liquid crystalline (LC) compounds exhibiting TGB phases have been reported, but, up to now, only chiral LC compounds were found to generate TGB phases, to our knowledge, with the chiral moiety causing a frustration of smectic ordering, so resulting in the helical ordering of the smectic domains. In this work, we have found unconventional layered mesophase-like TGBA (hereafter, simply denoted TGBA) phase in non-chiral α-(4′-propoxyphenylbenzyl-4-ylthio)-ω-(4′-butoxyphenylbenzyl-4-ylthio)perfluorohexane (3BF6B4, Fig. 1),† which is stabilized over a wide temperature range.

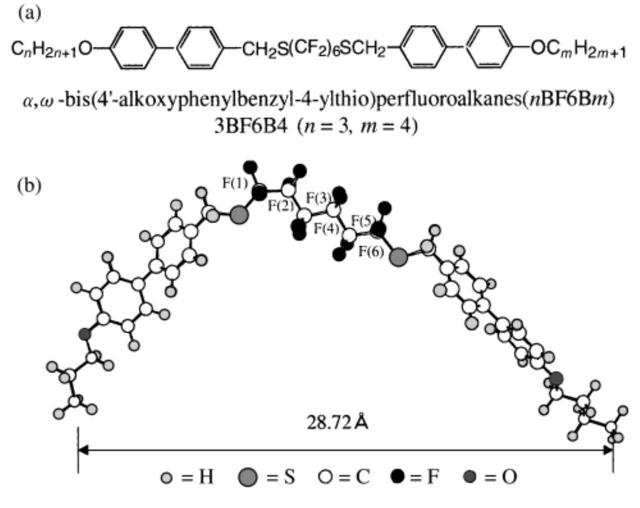

Fig. 1 Chemical structure of *n*BF*x*B*m* compounds (a) and the molecular model of 3BF6B4 obtained by PM3 calculation, where $–CF_2(1)–CF_2(2)–$ and $–CF_2(5)–CF_2(6)–$ bonds are in *gauche* and *trans* conformation, respectively (b).

Fig. 2(c) shows DSC curves of 3BF6B4.‡ For the first heating, the 3BF6B4 crystallites (Cr phase) melt to a TGBA state at 78.4 °C which changes into the isotropic liquid (I) phase at 99.4 °C. It is noted that the TGBA phase exists in the wide temperature range from 78.4 to 99.4 °C. The identification of the TGBA phase was made from texture observations; Fig. 3 shows a cylindrical domain (CC) texture when the two glass plates are untreated [Fig. 3(a)] and a spiral filament texture when the two plates are rubbed parallel to the plane [Fig. 3(b)], this result indicating that the mesophase is a TGBA phase.[6] Moreover, we find an endothermic peak near 81.9 °C on heating of the DSC curve of Fig. 2(c), suggesting the presence of two TGBA phases, TGBA1 below 81.9 °C and TGBA2 above 81.9 °C; the TGBA textures of Fig. 3 were observed over the temperature range exhibiting the TGBA 1 and 2 phases and did not show any change between TGBA1 and TGBA2, hence it is believed that both phases essentially belong to the TGBA state. In Fig. 2(a), the X-ray scattering intensity (*I*) is plotted *vs.* the scattering angle (2θ) for 3BF6B4, as a function of temperature.‡ In the crystalline state (61 °C), the *I vs.* 2θ curve shows several sharp peaks, but only three peaks are seen at *ca.* 3.0, 6.0 and 9.0° for TGBA1 (78 °C) and at *ca.* 3.1, 6.1 and 9.2° for TGBA2 (90 °C). These three peaks are attributable to reflections from SmA layers of thickness 29.23 and 28.85 Å, respectively. A conformational structure was calculated for 3BF6B4, using PM3 (parametric method). As shown in Fig. 1(b), assuming a *gauche* conformation for $–CF_2(1)–CF_2(2)–$ a *trans* conformation for $–CF_2(5)–CF_2(6)–$, and a *trans* conformation for all the other bonds, the molecule is boomerang-shaped and the molecular length is estimated as 28.72 Å.[7] When the $–CF_2(1)–CF_2(2)–$ and $–CF_2(5)–CF_2(6)–$ bonds are in *trans* and *gauche*

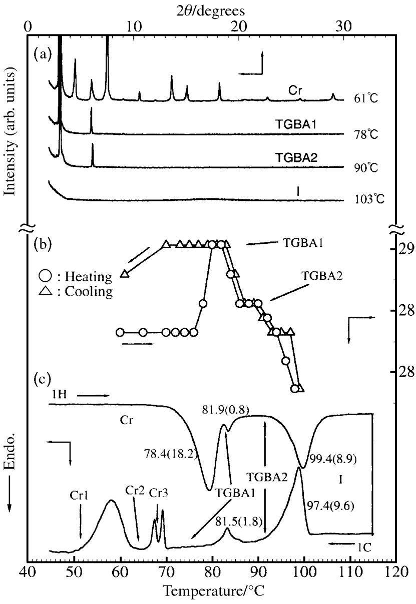

Fig. 2 X-Ray diffraction patterns of 3BF6B4 (a) and the temperature dependence of the spacing *d* (b) and DSC thermograms of 3BF6B4 (c). 1H: 1st heating, 1C: 1st cooling; Cr: crystalline state, I: isotropic phase. These figures in (c) denote the phase transition temperatures (°C) and enthalpy changes (kJ mol^{-1}).

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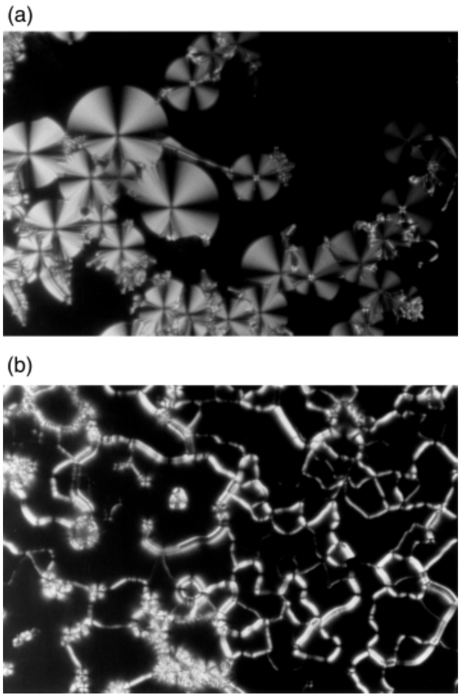

Fig. 3 The cylindrical domain (CC) texture of the TGBA phase at 92.5 °C (a) and spiral filament texture of the TGBA phase at 93.7 °C (b) in 3BF6B4 under a polarized microscope (magnification ×100).

conformation, respectively, the molecular length is estimated as 28.43 Å. Both molecular lengths are well consistent with the layer thickness obtained from the X-ray data.[8] From these results, both TGBA1 and TGBA2 phases can be tentatively concluded to be TGBA phases consisting of SmA domains. In Fig. 2(b), the spacing (*d*) is plotted *vs.* temperature. On heating, the value of *d* changes from 28.66 to 29.23 Å near the Cr–TGBA1 phase transition temperature, and suddenly decreases to 29.04 Å near the TGBA1–TGBA2 transition temperature, and rapidly decreases approaching the TGBA2–isotropic liquid (I) phase transition temperature. The decrease of *d* in the TGBA2 phase with increasing temperature may be caused by either the packing of 3BF6B4 molecules in the SmA layer being disturbed or the packing of the long molecular axes of 3BF6B4 molecules at a tilt angle to the layer normal (TGBC). At present, we infer that the former packings may be responsible for the appearance of TGBA2, since the texture of TGBA2 is similar to that in TGBA1.

In conclusion, this work has revealed the existence of a TGBA phase in non-chiral 3BF6B4, as a consequence of its boomerang-molecular shape, reminiscent of the generation of ferroelectricity in banana-shaped molecules.[9]

We are investigating the phase transition behaviors of *n*BF6B*m* homologues (Fig. 1), and at present, find the existence of TGBA phases in 3BF6B3, 3BF6B4 and 3BF6B5. Further studies will be published elsewhere in the near future.

Notes and references

† *Synthesis* of 3BF6B4: 4-*n*-propoxyphenylbenzylthioalcohol[5] (0.5 g, 0.002 mol) and 4-*n*-butoxyphenylbenzylthio (0.53 g, 0.002 mol) in THF (50 ml) was added to a soution of NaH (0.186 g, 0.0048 mol) in THF (30 ml) under N_2, to give a muddy white mixture. Dodecafluoro-1,6-diiodohexane (1.3 g, 0.0024 mol) was added dropwise to this mixture which was stirred at room temperature for 10 h. The crude product was obtained by evaporation to dryness after extraction into diethyl ether. The product was purified by column chromatography [silica gel, benzene–hexane (1 : 2.5)] and further by recrystallization from ethanol, giving 3BF6B4 (white powder, yield:18%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (3H, t, CH_3, *J* 7.6), 1.06 (3H, t, CH_3, *J* 7.6), 1.26 (2H, m, CH_2), 1.82 (4H, m, CH_2), 3.97 (2H, t, CH_2, *J* 6.6), 4.01 (2H, t, CH_2, *J* 6.3), 4.21 (4H, s, CH_2), 6.97 (4H, d, Ph-H, *J* 8.8), 7.39 (4H, d, Ph-H, *J* 8.3), 7.50 (4H, d, Ph-H, *J* 8.8), 7.53 (4H, d, Ph-H, *J* 8.3); 19F NMR (400 MHz, $CDCl_3$): δ 68.28, 35.99, 34.52.

‡ Phase transition parameters were measured by differential scanning calorimetry (Seiko Denshi DSC-210, SSC-5000) at a scanning rate of 5 K min^{-1}. The texture of the mesophase was observed by use of a polarizing microscope (NIKON OPTIPHOT-POL) equipped with a Mettler FP-82 hot stage. Wide-angle X-ray diffraction measurements were performed as a function of temperature with a Rigaku, Rinto 200 diffractometer equipped with a home-made cell using Cu-Kα radiation (40 kV, 30 mA), where the scattering intensities detected with a scintillation counter incorporating a pulse-height analyser.

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