Tuning Mesomorphic Properties and Handedness of Chiral Calamitic Liquid Crystals by Minimal Modification of the Effective Core

ANHUA LIU, QIMING SUN, JIAXI CUI, JIA ZHENG, WENJIAN LIU,* AND XINHUA WAN*

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing, People’s Republic of China

ABSTRACT Two pairs of calamitic liquid crystalline molecules, (+)-2-[4’-(S)-sec-butoxyphenyl]-5-(4’-hexoxyphenyl)toluene ((+)-S1) and (+)-2-[4’-(S)-sec-butoxyphenyl]-5-(4’-hexoxyphenyl)toluene ((+)-S2), (+)-2-[4’-(R)-sec-butoxyphenyl]-5-(4’-hexoxyphenyl)toluene ((–)-R1) and (–)-2-[4’-hexoxyphenyl]-5-[4’-(R)-sec-butoxyphenyl]toluene ((–)-R2), have been designed and synthesized. Each of the molecules consists of a β-terphenyl core substituted with a methyl group on the middle ring, a chiral sec-butoxy tail, and an achiral n-hexoxy tail. The geometrical difference between (+)-S1 ((–)-R1) and (+)-S2 ((–)-R2) lies only in the location of the methyl group on the effective mesogenic core. Yet, such a small change in the structure gives rise to remarkable differences in mesogenic properties and handedness. Both (+)-S1 and (–)-R1 have an enantiotropic cholesteric phase (N*) and a monotropic twist grain boundary C* phase (TGBC*), whereas (+)-S2 and (–)-R2 exhibit only a monotropic N* phase. Moreover, (–)-S1 ((–)-R1) and (+)-S2 ((–)-R2) have opposite handedness in the N* phase, and (+)-S1 and (–)-R1 even have a helical inversion from N* to TGBC* phase through a non-helical chiral mesophase. Chirality 23:E74–E83, 2011. © 2011 Wiley Periodicals, Inc.

KEY WORDS: cholesteric phase; twist grain boundary C* phase; handedness; rotational isomer; molecular modeling

INTRODUCTION

Precise control and manipulation of chiroptical properties of chiral molecules, macromolecules, and supramolecules are theoretically important and practically useful. Molecular media usually play important roles in chirality generation and transformation. In this regard, liquid crystal (LC) is unique for its ability of transferring and magnifying molecular chirality. Introduction of a chiral center in the molecules of nematic (N) and smectic C (SmC) LCs is known to induce a helical ordering along the long axes of the constituent molecules, which has been utilized in high-resolution digital displays, optical storages, and sensors. Chiral LC phase can also be generated by doping with chiral nonracemic molecules. Biaryl atropisomeric compounds are simply examples of dopants with a high twisting power by virtue of the large steric coupling between guest and host molecules.

An important aspect of chiral LCs has been concerned with the relationship between the molecular feature and the helical sense. Early investigations on cholesteric LCs by Gray and Mcdonnell led to an empirical Sol-Rel, Sed-Rod alternation rule, which describes the dependence of the rotation direction of plane-polarized light through a helical mesophase, clockwise (+, dextro) or counterclockwise (–, laevo), on the absolute spatial configuration (R or S) of the chiral center, the distance of the chiral center with respective to the effective mesogenic core (odd and even numbers or o and e), and the electronic nature of the substituents attached to the chiral center. Later, Goodby et al. found that the rule was also applicable to other liquid crystalline mesophases, like helicoidal smectics. More recent investigations have shown that, for certain types of chiral LCs, the twist sense also depends on temperature, which induces the change in the population of conformational isomers.

For example, a thermotropic LC compound, 4′-propoxymethylene-2′-fluoro-4-[2(3S)-3-propylloxiran-2-ylmethoxy]-1,1′,4′,1′,3'5,5,3'-octyloxy-2,3-difluorobiphenyl-4′-yl3-fluoro-4(2fluorooctanoyloxy)benzoate induces a twist inversion in the N* phase.

β-Terphenyl has frequently been used in building LCs due to its rod-like shape and strong π-π interaction among aromatic rings, which favor self-organization of the constituted molecules. As β-terphenyl has three benzene rings and two...
inter-ring C–C bonds, the competition between the conjugative and steric effects results in a helical conformation and an alternately twisted conformation around the inter-ring C–C bonds, which interconvert rapidly in solution and in isotropic melt. The interconversion barriers increase with the dimensions of the ortho substituents. Formation of a stable rotational isomer also depends on its local environment. Hamilton and coworkers used functionalized 3,2,2'-terphenyl derivatives to mimic the structure and function of extended regions of an α-helix protein. It was found that the terphenyl conformation was sensitive to the complementary recognition site.

Herein, we report synthesis, mesomorphic properties, and handedness in the LC states of two pairs of p-terphenyl based compounds, (+)-2-(4(S)-sec-butoxyphenyl)-5-(4′-hexoxyphenyl)toluene ((+)-S1) and (-)-2-(4′-hexoxyphenyl)-5-(4′-S)-sec-butoxyphenyl)toluene ((-)-S2). Each pair of the compounds differs only by the location of the methyl group relative to the effective mesogenic core. We think that although a single methyl substituent on the middle ring cannot itself stabilize the conformers of p-terphenyl by restricting the rotation of the inter-ring C–C bonds as in LCs with an atropisomeric structure, their different twist angles in the terphenyl group may affect the mesophase structure and screw sense of the chiral LC phase. A combination of different techniques including differential scanning calorimetry (DSC), circular dichroism (CD), and ferroelectricity measurement was used to characterize the structures and handedness of the mesophases. It’s interesting to see that the small change in the location of the methyl group relative to the effective mesogenic core influences not only the mesomorphic property but also the supramolecular chirality.

**EXPERIMENTAL**

**Materials and Reagents**

2-Iodo-5-bromotoluene (98%, Aldrich), 3,4-dihydro-2H-pyran (99%, Acros), trimethyl borate (99%, Acros), (-)-R-sec-butanol (99%, [α]D 20 = −13.00 (neat), Acros), (-)-S-sec-butanol (99%, [α]D 20 = +13.00 (neat), Acros), triphenylphosphine (99%, Acros), azodicarboxylic acid diethyl ester (DEAD, 40% in toluene, TCI), and 1-bromohexane (99%, Acros) were used as purchased. Tetrahydrofuran (THF, 99.9%, Beijing Chemical Reagents) for Grignard reaction was refluxed first in calcium hydride for at least 8 h and then refluxed with diphenyl ketone over sodium under argon until the solvent became deep blue and was further distilled out just before use. Other reagents and solvents were purchased from Beijing Chemical Reagents and used as obtained unless otherwise specified.

4-Hexoxyphenylboronic acid and 4-(2-(2H)-tetrahydropropyloxy)phenylboronic acid were prepared according to the literature procedures.

**Measurements**

1H spectra were obtained with a Bruker ARX 400 MHz and Varian 300-MHz NMR spectrometer with CDCl3 as the solvent and tetramethylsilane (TMS) as the internal reference. Mass spectra were recorded with a Finnigan-MAT ZAB-HS spectrometer. Elemental analyses were made on an Elemental Vario EL instrument. DSC traces were obtained with a TA DSC Q100 at a heating and cooling rate of 5 °C min⁻¹. The crystal state was introduced by heating the polyimide-coated and parallel rubbed sandwich-type cell by capillary action in order to obtain the plane texture to fit for CD measurement. Polarized optical microscopy (POM) observation was performed on Leica DML POM microscope with Mettler-Toledo hot stage (FB 82 HT with a FP-90 central processor) as temperature control. The pitch of the (+)-S1 and (+)-S2 in the N* phase was estimated with Cano’s wedge method, using a POM equipped with Mettler-Toledo hot stage (heating and cooling rate of 10 °C min⁻¹). The length of the Cano cell (North Liquid Crystal Engineering R&D Center, China) was 10 mm, the thickness of one side was 3 µm and another side was 40 µm. The alignment of the Cano cell was antiparallel.

The polarization measurements were measured by applying triangular voltage-wage (50 V, 0.5–2 Hz) using Instec automatic liquid crystal tester equipment in conjunction with the Mettler-Toledo hot stage (FB 82 HT with a FP-90 central processor). The sample was introduced into parallel polyimide-coated ITO glass cell (LC-5.0, Instec) with 4-µm space, which produced surface stabilized ferroelectric liquid crystal (SSFLC) films suitable for measurement of ferroelectric properties.

To prepare the homeotropically anchoring LC cells, glass wafers (1.5 cm × 1 cm) were ultrasonically cleaned for 5 min in succession with acetone and ethanol. After drying in a stream of nitrogen, the wafers were placed into a solution of octadecyltrimethoxysilane (1.0 g) in ethanol (19.0 g) and allowed to stand in the solution for 1 min. The wafers were heated at 100 °C for 1 h. After cooling to room temperature, the wafers were cleaned ultrasonically in chloroform for 2 min and then rinsed with ethanol. The surface modified glass wafers were obtained after drying in a stream of nitrogen.

**Synthesis of (+)-S-1 and (-)-R-1**

1. **2-(4′-Hydroxyphenyl)-5-bromotoluene.** Into a 500 ml three-necked round-bottom flask were added 2-iodo-5-bromo-toluene (33.7 mmol, 10.0 g), 4-hexoxyphenylboronic acid (7.5 mmol, 1.7 g), Pd(PPh3)4 (0.4 mmol, 0.5 g), benzene (8 ml), ethanol (2.00 g, 7.61 mmol), 2-(4′-hydroxyphenyl)-5-bromotoluene (6.3 mmol, 2.0 g), 4-hexoxyphenylboronic acid (7.5 mmol, 1.7 g), Pd(PPh3)4 (0.4 mmol, 0.5 g), benzene (8 ml), ethanol (2.00 g, 7.61 mmol), 4-(2-(2H)-tetrahydropyran-2-yl)toluene (2.00 mmol), NaHCO3 (100 ml 3 M) and HI solution (100 ml 3 M) and DI water (100 ml 3 M) and DI water (100 ml 3 M). The solution was mixed with THF (80 ml), methanol (20 ml), and concentrated hydrochloric acid (20 ml) in a round-bottom flask. The mixture was stirred at room temperature for 18 h. Then, 200 ml of DI water was added into the reaction mixture for dilution. The reaction mixture was extracted with CH2Cl2 (100 ml × 3) and the combined organic phase was washed with 5% aqueous solution of NaHCO3 (100 ml × 3) and DI water (100 ml × 3). After drying over sodium sulfate, the solvent was removed under reduced pressure. The crude product was further purified by column chromatography (Silica gel, CH2Cl2 as eluant) and afforded 61.1 g of white solids. Yield: 68%.

2. **1H NMR (300 MHz, [D1]CDCl3, 25 °C, TMS) δ = 7.39 (3H, 1H), 7.33 (d, 1H), 7.14 (2H), 7.05 (d, 1H), 6.86 (2H), 4.97 (s, 1H), 2.23 ppm (3H).**

3. **Synthesis of (+)-S-1 and (-)-R-1**

1. **2-(4′-Hydroxyphenyl)-5-bromotoluene.** Into a 100 ml one-necked round-bottom flask were added 2-(4′-hydroxyphenyl)-5-bromo-toluene (2.00 g, 7.61 mmol), (-)-R-sec-butanol (0.56 g, 7.61 mmol), PPh3 (1.99 g, 7.61 mmol), and THF (40 ml). The mixture was cooled to 0 °C, and azodicarboxylic acid diethyl ester (1.053, 7.61 mmol) was added dropwise over 5 min. After being stirred for 12 h, the solution was concentrated. The crude product was purified by column chromatography on silica gel using CH2Cl2 as eluant and afforded 1.70 g of colorless liquid. Yield: 70.7%.

2. **1H NMR (300 MHz, [D1]CDCl3, 25 °C, TMS) δ = 7.38 (s, 1H), 7.32 (d, 1H), 7.15–7.20 (d, 2H), 7.04–7.06 (d, 1H), 6.91–6.94 (d, 2H), 4.27–4.36 (m, 2H), 2.34 ppm (3H).**

3. **2-(4′-S)-sec-Butoxyphenyl]-5-bromotoluene.** To a 100 ml three-neck round-bottom flask were added (+)-2-(4′-S)-sec-butoxyphenyl]-5-bromotoluene (6.53 mmol, 2.0 g), 4-hexoxyphenylboronic acid (7.5 mmol, 1.7 g), Pd(PPh3)4 (0.4 mol mmol, 0.5 g), benzene (8 ml), ethanol (8 ml), and 1.5 M Na2CO3 aqueous solution (15 ml). The reaction mixture was vigorously stirred and refluxed for 24 h under argon atmosphere. The reaction mixture was extracted with CH2Cl2 (300 ml), hexane (20 ml), and concentrated hydrochloric acid (20 ml) in a round-bottom flask. The mixture was stirred at room temperature for 18 h. Then, 200 ml of DI water was added into the reaction mixture for dilution. The reaction mixture was extracted with CH2Cl2 (100 ml × 3) and DI water (100 ml × 3). After drying over sodium sulfate, the solvent was removed under reduced pressure. The crude product was further purified by column chromatography on silica gel using CH2Cl2 as eluant and afforded 1.70 g of colorless liquid. Yield: 70.7%.

4. **1H NMR (300 MHz, [D1]CDCl3, 25 °C, TMS) δ = 7.38 (s, 1H), 7.32 (d, 1H), 7.15–7.20 (d, 2H), 7.04–7.06 (d, 1H), 6.91–6.94 (d, 2H), 4.27–4.36 (m, 2H), 2.23 ppm (3H).**

5. **Chirality DOI 10.1002/chir**
fied by chromatography on silica gel using CH_2Cl_2 as eluant, followed by recrystallization in hexane to obtain pure target molecules in 98% yield. 

^1^H NMR (400 MHz, [D_1]CDCl_3, 25 °C, TMS) δ = 7.53–7.56 (d, 2H), 7.45 (s, 1H), 7.41–7.43 (d, 1H), 7.26–7.29 (q, 3H), 6.94–6.99 (t, 4H), 4.27–4.36 (m, 1H) 3.99–4.02 (t, 2H), 2.23 (s, 3H), 0.83–1.81 ppm (m, 19H). Mass spectrum (m/e): 416, 354, 276, and 186. Elemental analysis calculated (%) for C_{30}H_{38}O_2: C, 83.61; H, 8.71. Found: C, 83.37; H, 8.71.

(–)-2'-(4'-R)-sec-butoxyphenyl]-5-(4'-hexoxyphenyl)toluene (–)-(–)-R-1). The compound was prepared in a similar way to (+)-S-1. ^1^H NMR (400 MHz, [D_1]CDCl_3, 25 °C, TMS) δ = 7.53–7.56 (d, 2H), 7.45 (s, 1H), 7.41–7.43 (d, 1H), 7.26–7.29 (q, 3H), 6.94–6.99 (t, 4H), 4.27–4.36 (m, 1H) 3.99–4.02 (t, 2H), 2.23 (s, 3H), 0.83–1.81 ppm (m, 19H). Mass spectrum (m/e): 416, 354, 276, and 186. Elemental analysis calculated (%) for C_{30}H_{38}O_2: C, 83.61; H, 8.71. Found: C, 83.37; H, 8.70.

**Synthesis of (+/-)-2 and (–/-)-R-2**

2'-4'-Hexoxyphenyl]-5-bromotoluene. Into a 250-ml three-necked round-bottomed flask were added 2'-4'-Hexoxyphenyl]-5-bromotoluene (16.9 mmol, 5.0 g), 4'-hexoxyphenylboronic acid (21.1 mmol, 4.7 g), Pd(PPh_3)_4 (0.8 mmol, 0.9 g), benzene (40 mL), ethanol (20 mL), and 1.5 M Na_2CO_3 aqueous solution (40 mL). The reaction mixture was vigorously stirred and refluxed for 3.5 h under argon atmosphere.

After the reaction was finished, reaction mixture was extracted with CH_2Cl_2 (50 ml). The mixture was cooled to 0 °C, and azodicarboxylic acid diethyl ester (0.76 g, 5.6 mmol) was added dropwise over 5 min. After being stirred for 12 h, the solution was concentrated. The crude product was purified by column chromatography on silica gel using CH_2Cl_2 as eluant and afforded colorless liquid in 75% yield. ^1^H NMR (400 MHz, [D_1]CDCl_3, 25 °C, TMS) δ = 7.53–7.56 (d, 2H), 7.45 (s, 1H), 7.41–7.43 (d, 1H), 7.26–7.29 (q, 3H), 6.94–6.99 (t, 4H), 4.27–4.36 (m, 1H) 3.99–4.02 (t, 2H), 2.23 (s, 3H), 0.90–1.82 ppm (m, 19H). Mass spectrum (m/e): 416, 354, 276 and 247; Elemental analysis calculated (%) for C_{30}H_{38}O_2: C, 83.61; H, 8.71. Found: C, 83.37; H, 8.71.

(–)-2'-4'-Hexoxyphenyl]-5-(4'-S)-sec-butoxyphenyl]toluene (–)-(–)-S-2). Into a 100-ml one-necked round-bottom flask were added 2'(4'-hexoxyphenyl]-5-(4'-hydroxyphenyl)toluene (2.00 g, 5.6 mmol), (–)-R-sec-butanol (0.41 g, 5.6 mmol), PPh_3 (1.46 g, 5.6 mmol), and THF (30 ml). The mixture was cooled to 0 °C, and azodicarboxylic acid diethyl ester (0.76 g, 5.6 mmol) was added dropwise over 5 min. After being stirred for 12 h, the solution was concentrated. The crude product was purified by column chromatography on silica gel using CH_2Cl_2 as eluant and afforded colorless liquid in 75% yield. ^1^H NMR (400 MHz, [D_1]CDCl_3, 25 °C, TMS) δ = 7.53–7.56 (d, 2H), 7.45 (s, 1H), 7.41–7.43 (d, 1H), 7.26–7.29 (q, 3H), 6.94–6.99 (t, 4H), 4.27–4.36 (m, 1H) 3.99–4.02 (t, 2H), 2.23 (s, 3H), 0.90–1.82 ppm (m, 19H). Mass spectrum (m/e): 416, 354, 276 and 247; Elemental analysis calculated (%) for C_{30}H_{38}O_2: C, 83.61; H, 8.71. Found: C, 83.37; H, 8.71.

**RESULTS AND DISCUSSION**

**Synthesis**

By taking the advantage of the quite different reactivity of bromine and iodine toward boronic acid,^30,37^ two pairs of enantiomers, (–)-(–)-R-1 and (–)(–)-R-2, were
prepared via multiple synthetic routes as shown in Schemes 1 and 2, respectively. The synthesis of (+)-S1 and (-)-R1 started from Suzuki-cross coupling reaction of 2-iodo-5-bromotoluene with 3,4-dihydro-2H-pyran protected 4-hydroxyphenylboronic acid, followed by deprotection, Mitsunobu etherification with sec-butanol, and the second Suzuki-cross coupling reaction with 4-hexoxyphenylboronic acid. The synthetic strategy of (+)-S2 and (-)-R2 differed from (+)-S1 and (-)-R1 only by the sequence of the coupling reactions, i.e., 2-iodo-5-bromotoluene reacted first with 4-hexoxyphenylboronic acid instead of protected 4-hydroxyphenylboronic acid. The key intermediates and target compounds were characterized by proton NMR spectroscopy, mass spectrometry, and elemental analysis. All the data agreed thoroughly with the expected structures. The absolute configurations of the target molecules were predetermined by the reaction pathway through which they were prepared from the starting materials with known absolute configurations. The Mitsunobu reaction allows the conversion of secondary alcohol to phenyl ether with inversion of configuration at the alcohol carbon. Therefore, (-)-R-sec-butanol led to (+)-S1 and (+)-S2, whereas (+)-S-sec-butanol to (-)-R1 and (-)-R2. Although each pair of calamitic compounds, (+)-S1/(-)-S2 and (-)-R1/(-)-R2, had identical structure except for the methyl position on the effective mesogenic core, their optical rotations varied remarkably (Table 1), reflecting the influence of the location of methyl group in middle ring of p-terphenyl on the optical activity of the composed molecule even though in solution.

**Mesomorphic Properties**

The thermal behaviors of the four compounds were characterized by a variety of techniques, including DSC, POM, and WAXD. The results are summarized in Table 1. Figure 1 shows the DSC traces of (+)-S1. During heating scanning, the compound presented two endothermic peaks. One was at 64.5 ± 0.8 °C, whereas the other at 76.5 ± 0.8 °C. The enthalpy value for the higher temperature transition was 0.45 kJ mol⁻¹, which was of the same order of magnitude as that from nematic to isotropic state, implying the formation of N phase after melting. During cooling scanning, three exothermic peaks were identified at 75.7, 35.0, and 26.1 ± 0.8 °C, respectively. The small enthalpy value of 0.6 kJ mol⁻¹ of the highest temperature transition also indicated the formation of N phase. It was apparent based on the DSC results that (+)-S1 had one

---

**TABLE 1. Phase transitions of the four liquid crystalline compounds**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Heating</th>
<th>Cooling</th>
<th>[α]365°/°C</th>
<th>αβ(^{\text{a}})°/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)-S1</td>
<td>K64.5N° + 76.5I</td>
<td>I76.6N° + 35.0TGBC*</td>
<td>-6.1K</td>
<td>53.0</td>
</tr>
<tr>
<td>(-)-R1</td>
<td>K64.0N° + 77.2I</td>
<td>I76.6N° + 35.7TGBC*</td>
<td>-4.0K</td>
<td>-50.7</td>
</tr>
<tr>
<td>(+)-S2</td>
<td>K67.8I</td>
<td>165.7N° + 47.4K</td>
<td>42.6</td>
<td></td>
</tr>
<tr>
<td>(-)-R2</td>
<td>K68.0I</td>
<td>166.9N° + 46.3K</td>
<td>-40.0</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)K: crystal; N*: chiral nematic phase; I: isotropic phase; TGBC*: twist grain boundary C* phase.

\(^{b}\)Specific optical rotation measured in THF. c = 2.0 g L⁻¹

---

**Fig. 1.** DSC curves of (+)-S1 recorded during first heating and cooling scans at a rate of 5 °C min⁻¹ under nitrogen atmosphere.
enantiotropic N phase and one monotropic mesophase with higher order.

Figure 2 displays thermograms of (+)-S2. Unlike (+)-S1, (+)-S2 had only one endothermic melting peak during heating scanning. On subsequent cooling, the sample presented at least three exothermic transitions. The first peak at 66°C had a quite small enthalpy value (0.8 kJ mol⁻¹), suggesting again the possible N phase formation. The third peak at the lowest temperature 46°C corresponded to crystallization. The second peak was so close to crystallization that it was difficult to know its nature. The compounds (−)-R1 and (−)-R2 presented almost identical DSC profiles with their enantiomers (+)-S1 and (+)-S2, respectively.

Upon cooling slowly from the isotropic phase to just below its clearing point, (+)-S1 enclosed between two pieces of clean cover glasses displayed a N* fingerprint texture (Fig. 3a). In the temperature range from 35.0 to −6.1°C, the sanded-schlieren texture was observed (Fig. 3c). When put into polyimide-coated and parallel rubbed sandwich-type glass cells, the N* phase showed single color reflecting Grandjean textures (Fig. 3b), while the monotropic mesophase of (+)-S1 with higher order exhibited a uniformly oriented ferroelectric domain texture (Fig. 3d), suggesting the formation of the chiral Smectic (Sm C*)-like mesophase. In homeotropic anchoring glass cell, the N* phase displayed fingerprint texture at high temperature, which diminished with reducing temperature and coexisted with pseudo-isotropic texture (Fig. 3e). When cooled to 35°C, the fingerprint domains disappeared completely and no birefringence was observed, indicating the gradual pitch increase of the N* phase due to the decreased twist power with reduced temperature. Being cooled further to 35°C, the fingerprint texture appeared again and transferred into pseudo-isotropic immediately (Figs. 3f and 3g). By a combination of POM observations under planar and homeotropic conditions, the higher ordered phase of (+)-S1 was tentatively considered as twist grain boundary C* phase (TGBC*). The easiness of forming a pseudo-isotropic texture under homeotropic anchoring condition might be due to the small angle between the local vector n and the normal k of Sm C* grain layer. This will be further demonstrated by the 1D-WAXD and CD results to be presented below.

Upon cooling, (+)-S2 displayed fingerprint N* texture and Grandjean texture, separately, depending on the examination condition (Fig. 4).

Temperature-variable 1D-WAXD was used to further identify the phase structures of the four compounds. Figure 5 shows the 1D-WAXD patterns of (+)-S1 at 60 and 34°C, respectively. There was only one weak peak at 2θ = 3.76° in the low angle region at 60°C, the corresponding d spacing value of 2.35 nm was comparable to the full length (2.48 nm) of molecule. Although in the wide angle region, only a scattering peak was present. The result indicated that the mesophase exhibited solely orientational order and no long-range positional order of constituent molecules. This was consistent with the results obtained with DSC and POM. At 34°C, two sharp peaks located respectively at 2θ = 3.97 and 7.72° were observed in the low angle region. The d-spacing ratio of the two diffractions was about 2/1, indicating a layer-like arrangement of the molecules. The d-spacing (2.22 nm) of the first diffraction was less than the full length (2.48 nm) of molecule, suggesting a Sm C* like phase with a small angle between the local vector n and the normal k of Sm C* grain
layer. (+)-S2 in the N* phase had a 1D-WAXD pattern similar to that of (+)-S1 (not shown).

To convincingly prove the existence of Sm C* grains in the TGBC* phase of (+)-S1, ferroelectricity measurement was also carried out in a 5.0 µm thick ITO glass cell with parallel rubbed polyimide anchoring surface, which produced a bookshelf-oriented LC layer. The photomicrographs in Figure 6 show the switching behavior of (+)-S1 at 32°C by application of an electric field. In the absence of a field, the compound displayed fan-shaped domains.41,42 By applying a triangular wave voltage, the texture remained unchanged except for a slight birefringence color change, indicating a bistable switching between the Sm C* states. In the mean time, a single switching current peak in a half cycle was observed, an indicative of ferroelectric phase (Fig. 7). The square wave current background was due to the LC cell being a capacitor.43

**Handedness of Mesophase**

CD spectroscopy is a commonly used technique to probe screw sense of N* phase, which depends on the sign of the Cotton effect and its position relative to the pitch of mesophase.44 To measure the cholesteric pitches of (+)-S1 and (+)-S2, Cano’s wedge method was used.33–35 Figure 8 shows the temperature dependence of the pitches of (+)-S1 and (+)-S2 in the N* phase. The pitch of (+)-S1 increased as temperature decreased, which was consistent with the POM results, and became infinite at the point where the phase transition from N* to TGBC* took place. Nonetheless, the pitch of (+)-S2 in the N* phase remained almost unchanged with decreasing temperature.

The temperature variable CD spectra of (+)-S1 and (+)-S2 under the planar condition are shown in Figure 9a. Neither (+)-S1 nor (+)-S2 displayed a Cotton effect in the isotropic state. Upon cooling down to the N* phase from isotropic melt, (+)-S1 exhibited a strong negative Cotton effect in the absorption region of p-terphenyl, implying the formation of a left-handed helix.44 The intensity of the Cotton effect decreased with reducing temperature and finally inversed from negative to positive at the N* to TGBC* transition, implying that the handedness of (+)-S1 changed from left to right in the N* phase, right-handedness in the TGBC* state, and right-handed helical LC phase.16–24 Although (+)-S2 was similar to (+)-S1 in structure, it displayed a positive Cotton effect in the N* phase, an implication of right-handed helix formation.

In the TGBC* phase, there is a superposition of N*-like and Sm C* -like helical structures with the axes perpendicular to each other. The handedness of Sm C* grains was also examined by the CD spectroscopy. When a Sm C* sample is subjected to a homeotropic boundary condition, the smectic layer plane is oriented parallel to the substrate planes, and the helix axis is perpendicular to the substrate. This is similar to the N* phase under the planar boundary condition. As a result, the rotation direction of plane-polarized light through it changes in the same way provided that the twisting senses of the two helices are the same.45 The CD spectrum of (+)-S1 in the TGBC* phase at 34°C under the homeotropical condition is displayed in Figure 9b. The positive selective reflection region and negative absorption region appeared at 446 and 325 nm, respectively. It indicated that the Sm C* grain of the TGBC* phase was left-handed helical and the pitch was 297 nm (if refractive index n was 1.5). The right-handedness under the planar condition against left-handedness under the homeotropic condition for the same sample suggested that the higher ordered mesogenic structure of (+)-S1 was at the TGBC* phase. It should be noted that no square pattern, a characteristic texture of the TGBC* phase under a planar state, was observed for (+)-S1 regardless of thermal condi-

---

**Fig. 4.** Polarized photomicrographs of (+)-S2 taken at 61°C during cooling process: (a) fingerprint texture; (b) Grandjean texture.

**Fig. 5.** 1D-WAXD patterns of (+)-S1 recorded at different temperature during cooling process.

---

Chirality DOI 10.1002/chir
tion. It might be attributed to the short pitch of the $S_m\text{C}^*$ grains in the TGBC$^*$ state.

The two enantiomers of a given compound have the same LC properties, and chiral properties of the same magnitude and opposite sign (The minor differences of liquid crystalline properties and chiroptical properties between pairs of enantiomers might origin from experimental errors or the stereostructural ($ee\%$) distinctness caused during Mitsunobu reaction.).

**Role of the Methyl Group on $\pi$-Terphenyl on Phase Structure**

Based on the results presented above, it was clear that the location of the methyl group relative to the effective mesogenic core had significant effects on the structure and handedness of the systems studied here. Both (+)-S1 and (-)-R1 had an enantiotropic N* phase and a monotropic TGBC$^*$ phase, whereas (+)-S2 and (-)-R2 had only one monotropic N* phase. (+)-S1/(-)-R1 and (+)-S2/(-)-R2 had opposite handedness in the N* phase and (+)-S1/(-)-R1 even experienced a helical inversion from the N* to TGBC$^*$ phase transition. It’s evident that the presently observed changes in the handedness could not be explained by the empirical Sol-Rel, Sed-Rod alternation rule.\textsuperscript{12} The absolute spatial configurations of the asymmetric carbon atoms of both compounds were S and the parities were even (e).

According to the above rule, a left-hand helical phase should be formed by the two compounds, i.e., the rotation direction of plane-polarized light through them should be dextrorotatory.

It is well documented in the literature that one of the most important contributions to the twisting sense of chiral dopants (or mesogens) is the interplay of anisotropy and chirality of intermolecular mediated by the chiral surface of the dopant.\textsuperscript{11,25,46} Chiral biphenyls are challenging systems because they are able to induce twisting mesophases with different pitch and handedness as a consequence of relatively small structural changes in the homochiral biphenyl unit. For the bridged biphenyl dopants, Ferrarini, Spada and their coworkers established a link between molecular feature and macroscopic response in terms of molecular surface, atom charges, and distributed polarizabilities. Unbridged biphenyl mesogens as (+)-S1/(-)-S2 and (-)-R1/(-)-R2 are even more complex systems due to the arbitrary dimension and flexible groups. We have tried to make some theoretical analyses to understand the above interesting findings. The low-energy conformers of (+)-S1 and (+)-S2 were first located by using molecular mechanical force fields (The molecular mechanics calculation were performed with PCMODEL for windows, version 7.0, Serena Software.). It turned out that the conformers were energetically indistinguishable and geometrically characterized by three nearly coplanar

---

![Fig. 6](image-url). Texture change of (+)-S1 in TGBC$^*$ at 32°C under the application of a triangular-wave voltage.

![Fig. 7](image-url). Ferroelectric response of (+)-S1 in TGBC$^*$ at 32°C under the application of a triangular-wave voltage.

![Fig. 8](image-url). Temperature dependence of pitches of (+)-S1 (▼) and (+)-S2 (●) measured by Cano wage method during cooling cycle. The inset shows the polarized optical micrograph of Grandjean steps of (+)-S2 at 68°C.
fragments \( P_1: \text{C3-C4-C5-C6-C7}, \ P_2: \text{C8-C9-C10-C11}, \ P_3: \text{C12-C13-C14-C15-C16}, \) as depicted in Figure 10. Furthermore, the twisting angles between planes \( P_1 \) and \( P_2 \) (cf. Fig. 10; denoted as \( \theta_1 \)) and between \( P_2 \) and \( P_3 \) (denoted as \( \theta_2 \)) were about 45 and 30°, respectively. To further investigate the rotations around the inter-ring \( \text{C—C} \) bonds, density functional theory calculations were carried out at the B3LYP/6-31G** level. (Geometry optimization was carried out at
not discriminate conformers of each compound. It meant polarity in the type conformers, the two systems had the same and opposite strongly polarized to almost the same extent. As for the B-molecular axis the A-type conformers of both systems were whereas those of ( although (moments, the 16 conformers of ( were taken from the molecular modeling. Again, the so optimized conformers were energetically degenerate within 0.5 kJ/mol. The optimal twisting angles and the corresponding dipole moments were documented in Table 2. It can be seen that the 16 conformers of each molecule could be classified into two groups, denoted as A and B, according to whether plane 1 was almost perpendicular or parallel to P2. It was concluded from the geometries that these low energy conformers resulted from the competition of the steric and conjugative effects. Along the long molecular axis (z-direction, see Fig. 10), the 16 conformers of ( had no polarity, whereas those of ( had discernible dipole moment components. In the directions perpendicular to the long molecular axis the A-type conformers of both systems were strongly polarized to almost the same extent. As for the B-type conformers, the two systems had the same and opposite polarity in the y and z-directions, respectively. However, although ( was more polar than (1), the small differences in dipole moments ruled out any significant role of the dipole moment. Unlike the small differences in dipole moments, the 16 conformers of ( displayed remarkable distinct conformations to ( as evidenced by θ1 and θ2 values, which therefore gave rise to various chiral shape. This might be the reason behind the different behavior of the liquid crystalline phases formed by ( and (2). Unfortunately, our preliminary calculations could not discriminate 16 conformers of each compound. It meant the explanation of twisting power requires an accurate sampling of the conformational space. This work is under way.

CONCLUSIONS

We have achieved two pairs of new chiral LC compounds, (1) and (2) and ( and (2). The subtle difference in the location of the methyl group on the terphenyl core led to remarkable variations of mesomorphic properties in two aspects. One aspect was the mesogenic properties. The molecules of (1) and (2) had an enantiotropic N* phase and a monotropic TGBC* phase, while (2) and (2) displayed only one monotropic N* phase. The other aspect was the opposite handedness of each pair of the compounds in the N* phase and (1) and (2) had a helical inversion through a nonhelical chiral mesophase from the N* to TGBC* state. Although the optimized structures were energetically degenerate within 0.5 kJ/mol and gave 16 conformers for each compound, (1) differed (2) by twisting angles between phenyl rings based on the preliminary computer calculations. Thus obtained various chiral shapes might rationalize the different behavior of the liquid crystalline phases formed by two pairs of compounds. The present investigation may not only add our understanding of the relationship between the molecular feature and the helical sense of chiral LCs but also provide a facile way to tune the chirality of supramolecular systems.

LITERATURE CITED


36. Gray GW, Hird M, Lacey D, Toyne KJ. The synthesis and transition temperatures of some 4,4'-dialkoxy- and 4,4'-alkoxyalkyl1,1'-4',1'-terphenyls with 2,2'-or 2,3'-disubstituted side chains and their biphenyl analogues. J Chem Soc Perkin Trans II 1989;2001:2041–2053.


