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## Molecular Crystals and Liquid Crystals

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## Synthesis and Mesomorphic Behavior of Novel Liquid-Crystalline Thiophene Derivatives

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# Synthesis and Mesomorphic Behavior of Novel Liquid-Crystalline Thiophene Derivatives

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*A new class of thiophene-based cholesteryl and ferrocenyl derivatives was synthesized and characterized by common analytical techniques. Liquid-crystalline properties were investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Thiophene-based cholesteryl derivatives show homeotropic liquid-crystalline phase sequence crystal  $\rightarrow$  smectic A  $\rightarrow$  cholesteric  $\rightarrow$  isotropic, whereas the ferrocenyl derivative is nonmesomorphic. The effects of thiophene ring, terminal group, and length of the polymethylene spacers on the mesomorphic behavior are discussed.*

**Keywords** Cholesterol; ferrocene; Sonogashira coupling; thiophene-based liquid crystal

## Introduction

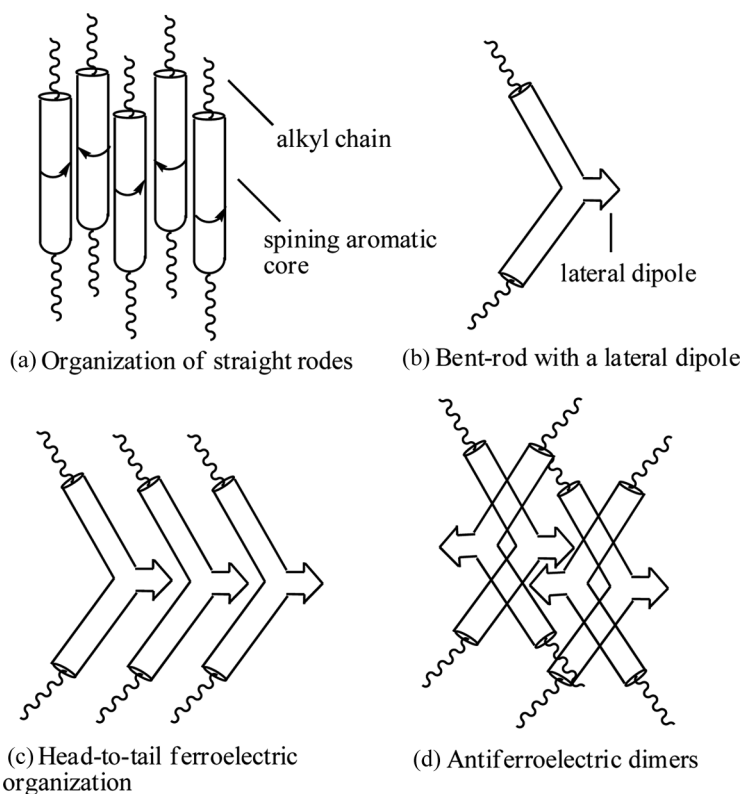
Thiophene derivatives have been used widely as conducting materials, which are chemically more stable than other aromatic compounds [1]. In particular, 2,5-thienylene derivatives are structurally planar and electrically conducting. The use of  $\pi$ -conjugated polymers and oligomers has stimulated enormous interest in recent years for molecular electronic, photonic, and electroluminescent devices [2]. Seed *et al.* synthesized the polarizable thiophene derivatives for use in nonlinear optical applications and showed that thiophene-containing materials, which are highly birefringent, can be used in electrooptic devices [3]. In their earlier studies they showed that the incorporation of thiophene into the molecular core can substantially increase the optical anisotropy and provide molecules with relatively low melting points [4,5]. Hiyama *et al.* synthesized and explored the liquid-crystalline (LC) properties of thiophene derivatives. They observed a nematic phase when azobenzene moiety is in *trans* form, whereas no LC phase was exhibited by the *cis* conformer [6]. The electrical and structural properties of thiophene derivatives have been explored extensively by other groups. The photoresponsive properties were also explored with an intension to develop photonic materials by using electron polarization of  $\pi$ -conjugated units [7].

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The simplest and most technologically important liquid-crystalline phase is the nematic phase [8]. Thermotropic nematic liquid crystals are generally optically uniaxial materials composed of rigid rods or discs that can undergo rapid rotation, to give a uniformly disrotated orientation along one axis (Fig. 1(a)). In an effort to achieve new nematic phases with potential biaxial optical properties, we became interested in bent-rod structures with lateral dipole (Fig. 1(b)). Rotation of a bent-rod structure about its long axis will require a larger displacement of the neighboring molecules and thereby increase the rotational activation barrier relative to a rod mesogen. The addition of lateral dipoles also has the potential to produce head-to-head ferroelectric organization, as in a MacMillan type smectic C structure (Fig. 1(c)) [9] or arrange in an antiferroelectric dimerized structure (Fig. 1(d)).

The structures and interactions necessary to create stable liquid-crystalline phases from bent-rod systems are not fully understood. It is generally found that materials with severely bent structures display liquid-crystalline phases with lower thermodynamic stability than their straight-rod relatives [10]. To produce a bent-rod structure with liquid-crystalline property, Swager *et al.* [11] synthesized nematic liquid crystals with a range of lateral dipoles with the thiophene cores. In continuation of our recent work in cholesterol-based liquid crystals [12], we decided to focus on materials with a thiophene as a central core of the mesogens. Here we report our results.



**Figure 1.** Different dipolar organization of dimers.

## Results and Discussion

### Synthesis

The synthetic route for the new class of bent-rod liquid crystals (**9a, b**), is depicted in Scheme 1.

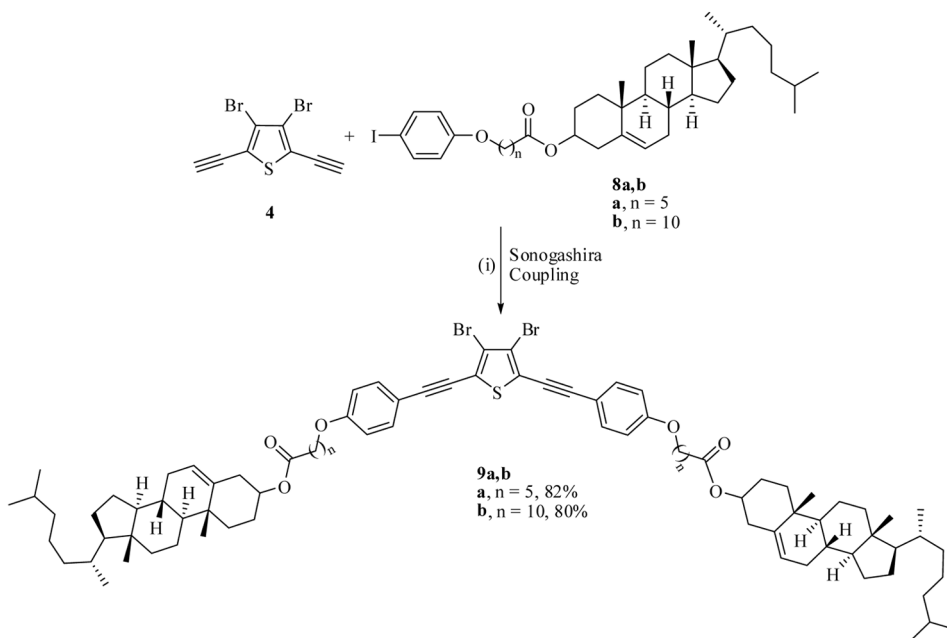
The required precursor **4** was synthesized by deprotection of the trimethylsilane (TMS) group of compound **3** using KF-MeOH. Compound **3** was in turn prepared by Sonogashira coupling of compound **2** with trimethylsilylacetylene. Compound **2** was prepared by the bromination of thiophene with slow addition of bromine in  $\text{CHCl}_3$  following a standard literature procedure [13] (Scheme 2).

The other precursors **8a, b** were synthesized from naturally occurring cholesterol. Esterification of cholesterol (**5**) with the bromoalkanoylchlorides (**6a, b**) was carried out in tetrahydrofuran (THF) in the presence of pyridine to afford the compounds **7a, b**. The cholesteryl 4-iodo alkyl esters (**8a, b**) were prepared by the reaction of compounds **7a, b** with 4-iodophenol in refluxing acetone in the presence of anhydrous  $\text{K}_2\text{CO}_3$  [14] (Scheme 3).

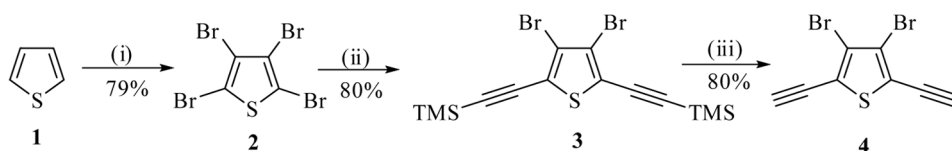
Finally, the target compounds (**9a, b**) were successfully obtained by Sonogashira coupling between compound **4** and compounds **8a, b** by using  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (10 mol%) as catalyst, CuI (12 mol%) as co-catalyst, and *N,N*-Diisopropylethylamine (DIPEA) as base in THF.

The methodology for the synthesis of thiophene derivatives containing ferrocenyl moiety is depicted in Scheme 4.

Ferrocene (**10**) was first converted to 6-bromohexyloyl ferrocene (**11**) by treatment with acid chloride (**6a**) in dry chloroform in the presence of anhydrous aluminium chloride. Compound **11**, on treatment with zinc amalgam in the presence of concentrated hydrochloric acid in benzene-water under refluxing condition,



**Scheme 1.** Reagent and conditions: (i)  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ , CuI, DIPEA, THF, rt, 12 h.



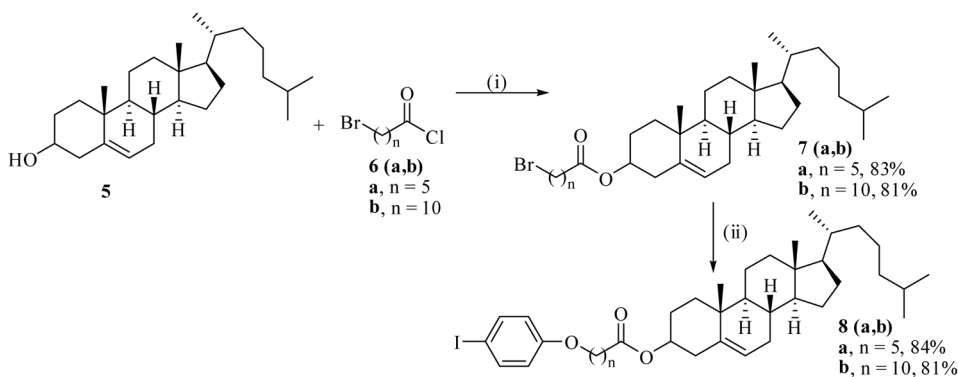
**Scheme 2.** Reagent and conditions: (i)  $\text{Br}_2$ ,  $\text{CHCl}_3$ , rt, 6 h (ii) Trimethylsilylacetylene,  $\text{Pd}(\text{PPh}_3)_2\text{Cl}$ ,  $\text{CuI}$ ,  $\text{DIPEA}$ ,  $\text{THF}$ , rt, 12 h (iii)  $\text{KF}$ ,  $\text{MeOH}$ , 2 h.

afforded compound **12** [12c]. Compound **12** on reaction with 3,4,5-trihydroxyethylbenzoate and anhydrous potassium carbonate in refluxing acetone followed by subsequent hydrolysis of the ester function with ethanolic potassium hydroxide afforded the acid derivative **14**. The acid derivative **14** on esterification with *p*-iodophenol afforded the iodo derivative **15**. The target compound **16** was successfully synthesized by Sonogashira coupling of compound **4** and compound **15** by using  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (15 mol%) as catalyst,  $\text{CuI}$  (20 mol%) as co-catalyst, and  $\text{DIPEA}$  as base in  $\text{THF}$ .

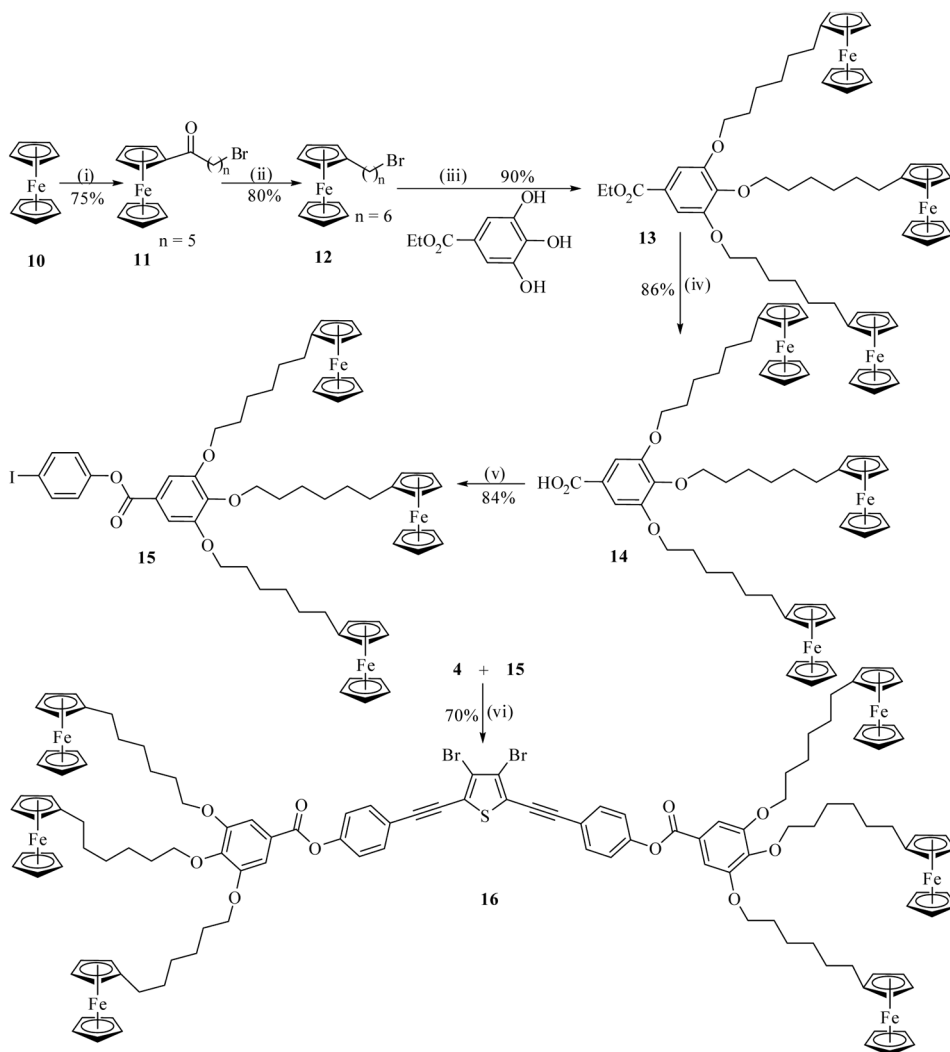
### Mesomorphic Behavior

Thiophene derivatives containing cholesteryl moiety (**9a, b**) show mesomorphic behavior, whereas thiophene derivative **16** containing ferrocenyl moiety did not exhibit any mesomorphic behavior. The phase transitions of the bent-rod liquid crystals **9a, b** were measured using differential scanning calorimetry (DSC) at a heating rate of  $5^\circ\text{C min}^{-1}$ . The transition temperatures and associated enthalpies are shown in Table 1.

Textural analysis was carried out with the help of a polarizing optical microscope (POM). Compound **9a** showed enantiotropic phase sequence of crystal  $\rightarrow$  smectic A  $\rightarrow$  cholesteric  $\rightarrow$  isotropic. When the hexamethylene spacer of **9a** was replaced by an undecamethylene spacer, compound **9b** also displayed the same phase sequence. On cooling the isotropic phase of compound **9a**, an oily streak texture appeared, which instantly transformed to a fan-like texture, the characteristic texture of  $\text{N}^*$  phase (Fig. 2(a)). On further cooling the sample, the homeotropic texture of



**Scheme 3.** Reagent and conditions: (i)  $\text{THF}$ , pyridine, rt, 12 h (ii) *p*-Iodophenol,  $\text{K}_2\text{CO}_3$ , acetone, reflux, 12 h.



**Scheme 4.** Reagents and Conditions, (i) 6-bromohexanoyl chloride, AlCl<sub>3</sub>, CHCl<sub>3</sub>, rt, 2 h (ii) Zn-Hg, Conc. HCl, benzene-water, reflux, 36–48 h (iii) acetone, K<sub>2</sub>CO<sub>3</sub>, reflux, 12 h (iv) C<sub>2</sub>H<sub>5</sub>OH, KOH, reflux, 2 h (v) *p*-iodophenol, DCC, DMAP, CHCl<sub>3</sub>, rt, 2 h (vi) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl, CuI, DIPEA, THF, rt, 12 h.

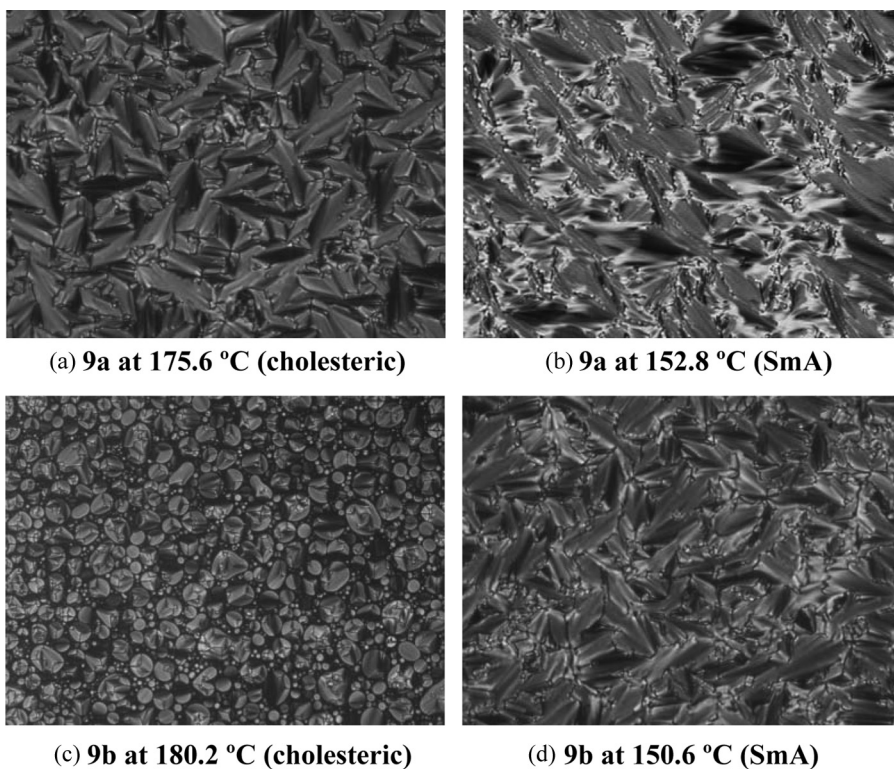
SmA phase, as characterized by the focal conic texture (Fig. 2(b)), appeared. Compound **9b** also showed similar phase transitions as indicated in Fig. 2(c) (cholesteric droplets) and Fig. 2(d) (focal conic texture of SmA phase). But compound **16** did not show any mesomorphic behavior even when placed in a thin cell with a cell gap of  $d = 5 \pm 0.2 \mu\text{m}$  with homogeneous planar boundary conditions.

In conclusion, we have synthesized a new class of bent-shaped liquid crystals containing thiophene as a core moiety. Compounds containing cholesteryl moiety show N\* phase over a wide temperature range along with SmA phase. When ferrocenyl moiety was introduced in place of the cholesteryl moiety, the resulting compound becomes nonmesomorphic.

**Table 1.** Phase transition temperatures ( $^{\circ}\text{C}$ ) and associated enthalpies ( $\Delta H$ ,  $\text{KJ mol}^{-1}$ ) of the compounds in the heating and cooling cycles are summarized below

| Compound  | Phase transition (heating cycle) |             | Enthalpy | Phase transition (cooling cycle) |             | Enthalpy |
|-----------|----------------------------------|-------------|----------|----------------------------------|-------------|----------|
|           |                                  | Temperature |          |                                  | Temperature |          |
| <b>9a</b> | Cr-SmA                           | 113.4       | 34.9     | I-N*                             | 225.5       | 2.3      |
|           | SmA-N*                           | 169.4       | 0.68     | N*-SmA                           | 159.1       | 0.5      |
|           | N*-I                             | 226.5       | 2.7      | SmA-Cr                           | 91.1        | 26.7     |
| <b>9b</b> | Cr-SmA                           | 114.2       | 35.7     | I-N*                             | 225.9       | 2.5      |
|           | SmA-N*                           | 171.5       | 1.1      | N*-SmA                           | 159.4       | 0.87     |
|           | N*-I                             | 226.4       | 2.8      | SmA-Cr                           | 91.2        | 28.1     |

Cr = Crystalline phase, Sm = Smectic phase, N = nematic phase, I = isotropic phase.

**Figure 2.** Polarizing micrographs of compound **9a,b**.

## Experimental

### General

All the chemicals were procured from either Sigma Aldrich Chemicals Pvt. Ltd. or Spectrochem, India. Silica gel (60–120 mesh) was used for chromatographic

separation. Silica gel G (E-Merck, Mumbai, India) was used for thin layer chromatography (TLC). Petroleum ether refers to the fraction boiling between 60°C and 80°C. IR spectra were recorded on a Perkin-Elmer L 120-000A spectrometer ( $\nu_{\max}$  in  $\text{cm}^{-1}$ ) on KBr disks.  $^1\text{H}$ -NMR spectra were determined for solutions in  $\text{CDCl}_3$  with TMS as internal standard on a Bruker DPX-400 and Bruker DPX-300.  $^{13}\text{C}$ -NMR spectra were determined for solutions in  $\text{CDCl}_3$  on a Bruker DPX-400. Carbon hydrogen nitrogen (CHN) was recorded on 2400 series II CHN analyzer (Perkin Elmer) from the Chemistry Department of Kalyani University. The liquid-crystalline properties were established by thermal microscopy (Nikon polarizing microscope LV100POL attached to an Instec hot and cold stage HCS302, with STC200 temperature controller configured for HCS302) and the phase transitions were confirmed by differential scanning calorimetry (Perkin-Elmer Diamond DSC Pyris1 system).

*Synthesis of Compound 3.* Nitrogen gas was purged through a solution of compound **2** (1 g, 2.50 mmol), trimethylsilylacetylene (0.54 g, 5.50 mmol), and DIPEA (4 mL) in dry THF (10 mL) for 30 min. Then catalyst  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (175.6 mg, 0.250 mmol) and cocatalyst  $\text{CuI}$  (57.2 mg, 0.300 mmol) were added and stirred for 12 h at room temperature. THF was removed followed by extraction with  $\text{CHCl}_3$  ( $3 \times 30$  mL) and the extract was washed with  $\text{H}_2\text{O}$  ( $2 \times 20$  mL) followed by brine (10 mL), dried ( $\text{Na}_2\text{SO}_4$ ), and the solvent was evaporated to give the crude product, which was purified by column chromatography over silica gel by EA:PE (1:99) as elutant to afford compound **3**.

Yellow solid, yield 80%. IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\max}$ : 2151;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 0.26$  (s, 18 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 0.0, 95.4, 105.9, 121.5, 129.4$ . MS: ( $m/z$ ) = 432 ( $\text{M}^+$ ), 434 ( $\text{M} + 2$ ), 436 ( $\text{M} + 4$ ). Anal. Calcd. for  $\text{C}_{14}\text{H}_{18}\text{Br}_2\text{SSi}_2$ : C, 38.71; H, 4.18%. Found: C, 38.85; H, 4.23%.

*Synthesis of Compound 4.* A mixture of compound **3** (1 g, 2.30 mmol) and KF (1.34 g, 23.0 mmol) in MeOH (10 mL) was stirred for 2 h at room temperature. After removal of the solvent, the reaction mixture was extracted with  $\text{CHCl}_3$  ( $3 \times 20$  mL) and the extract was washed with  $\text{H}_2\text{O}$  ( $2 \times 10$  mL) followed by brine (10 mL), dried ( $\text{Na}_2\text{SO}_4$ ), and the solvent was evaporated to give compound **4**.

Yellow solid, yield 80%. IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\max}$ : 2101;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 3.67$  (s, 2 H). MS: ( $m/z$ ) = 288 ( $\text{M}^+$ ), 290 ( $\text{M} + 2$ ), 292 ( $\text{M} + 4$ ). Anal. Calcd. for  $\text{C}_8\text{H}_2\text{Br}_2\text{S}$ : C, 33.14; H, 0.70%. Found: C, 33.23; H, 0.76%.

### **General Procedure for the Synthesis of Bent-Rod Liquid Crystals **9a,b** via Sonogashira Coupling**

Nitrogen gas was purged through a solution of compound **4** (100 mg, 0.345 mmol), **8a** (385 mg, 0.759 mmol), and DIPEA (4 mL) in dry THF (10 mL) for 30 min. Then catalyst  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (25 mg, 0.035 mmol) and cocatalyst  $\text{CuI}$  (8 mg, 0.041 mmol) were added and stirred for 12 h at room temperature. THF was removed followed by extraction with  $\text{CHCl}_3$  ( $3 \times 30$  mL) and the extract was washed with  $\text{H}_2\text{O}$  ( $2 \times 20$  mL) followed by brine (10 mL), dried ( $\text{Na}_2\text{SO}_4$ ), and the solvent was evaporated to give the crude product, which was purified by column chromatography over silica gel by EA:PE (1:99) as elutant to afford compound **9a**. Similar treatment of **8b** with compound **4** afforded compound **9b**.



**Compound 9a.** White solid, yield 82%. IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{max}}$ : 2935, 2202, 1731, 1518;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 0.60–2.27 (m, 102 H), 3.92 (t,  $J$  = 6.4 Hz, 4 H), 4.51–4.59 (m, 2 H), 5.31 (d,  $J$  = 4.0 Hz, 2 H), 6.80 (d,  $J$  = 8.7 Hz, 4 H), 7.41 (d,  $J$  = 8.4 Hz, 4 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 11.9, 18.7, 19.3, 21.0, 22.6, 22.8, 23.8, 24.3, 24.7, 25.6, 27.8, 28.0, 28.2, 28.8, 29.7, 31.8, 31.9, 34.6, 35.8, 36.2, 36.6, 37.0, 38.2, 39.5, 39.7, 42.3, 50.0, 56.1, 56.7, 67.8, 73.9, 79.9, 98.9, 113.8, 114.7, 118.3, 121.3, 122.7, 133.3, 133.5, 139.7, 159.9, 173.0. Anal. Calcd. for  $\text{C}_{86}\text{H}_{118}\text{Br}_2\text{O}_6\text{S}$ : C, 71.74; H, 8.26%. Found: C, 71.87; H, 8.32%.

**Compound 9b.** Yellow solid, yield 80%. IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{max}}$ : 2929, 2203, 1734, 1519;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 0.67–2.29 (m, 122 H), 3.98 (t,  $J$  = 6.4 Hz, 4 H), 4.53–4.61 (m, 2 H), 5.37 (d,  $J$  = 4.0 Hz, 2 H), 6.89 (d,  $J$  = 8.7 Hz, 4 H), 7.48 (d,  $J$  = 8.4 Hz, 4 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 11.9, 18.7, 19.3, 21.0, 22.6, 22.8, 23.9, 24.3, 25.1, 26.0, 27.8, 28.0, 28.2, 29.0, 29.1, 29.2, 29.3, 29.4, 31.9, 34.7, 35.8, 36.2, 36.6, 37.0, 38.2, 39.5, 39.7, 42.3, 50.0, 56.1, 56.7, 68.1, 73.7, 79.9, 98.9, 113.8, 114.7, 118.3, 121.3, 122.7, 133.3, 133.5, 139.7, 160.0, 173.3. Anal. Calcd. for  $\text{C}_{96}\text{H}_{138}\text{Br}_2\text{O}_6\text{S}$ : C, 72.98; H, 8.80%. Found: C, 73.09; H, 8.88%.

### Procedure for the Synthesis of Compound 16

Nitrogen gas was purged through a solution of compound **4** (100 mg, 0.345 mmol), **15** (893 mg, 0.759 mmol), and DIPEA (4 mL) in dry THF (10 mL) for 30 min. Then catalyst  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (36.5 mg, 0.052 mmol) and cocatalyst  $\text{CuI}$  (13.2 mg, 0.069 mmol) were added and stirred for 12 h at room temperature. THF was removed followed by extraction with  $\text{CHCl}_3$  ( $3 \times 30$  mL) and the extract was washed with  $\text{H}_2\text{O}$  ( $2 \times 20$  mL) followed by brine (10 mL), dried ( $\text{Na}_2\text{SO}_4$ ), and the solvent was evaporated to give the crude product, which was purified by column chromatography over silica gel by EA:PE (1:99) as elutant to afford compound **16**.

**Compound 16.** Reddish solid, yield 80%. IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{max}}$ : 2931, 2214, 1735, 1513;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 1.39–1.55 (m, 36 H), 1.82–1.85 (quin,  $J$  = 7.3 Hz, 12 H), 2.33 (t,  $J$  = 7.8 Hz, 12 H), 4.02–4.04 (m, 36 H), 4.08 (s, 30 H), 7.22 (d,  $J$  = 8.7 Hz, 4 H), 7.39 (s, 4 H), 7.62 (d,  $J$  = 8.6 Hz, 4 H). Anal. Calcd. for  $\text{C}_{130}\text{H}_{138}\text{Br}_2\text{Fe}_6\text{O}_{10}\text{S}$ : C, 65.40; H, 5.83%. Found: C, 65.51; H, 5.88%.

### Acknowledgments

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