

# Synthesis and Characterization of Ferrocene-Containing Liquid Crystalline Materials with a Bromo-phenyl Moiety<sup>†</sup>

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Ten ferrocene-containing liquid crystalline materials,  $p$ -FcC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>N = CHC<sub>6</sub>H<sub>4</sub>O<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>BrOC<sub>n</sub>H<sub>2n+1</sub> (type I) and  $p$ -FcC<sub>6</sub>H<sub>4</sub>N = CHC<sub>6</sub>H<sub>4</sub>O<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>BrOC<sub>n</sub>H<sub>2n+1</sub> (type II), were synthesized by condensation reactions of two ferrocene-substituted amines,  $p$ -FcC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (4) and  $p$ -FcC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (5) (Fc: ferrocenyl) with five bromo-substituted benzaldehydes (3) (H<sub>2n+1</sub>C<sub>n</sub>OC<sub>6</sub>H<sub>3</sub>BrCOOC<sub>6</sub>H<sub>4</sub>CHO,  $n = 2, 4, 6, 8$  and  $10$ ). Their mesogenic behaviors were studied by hot-stage polarized optical microscopy and differential scanning calorimetry. The effects of structure (rigid core, terminal chain length) on the phase transition behaviors were discussed.

**Keywords** organometallic complex, liquid crystal, ferrocene

## Introduction

Recently, ferrocene has been attracting widespread investigation in the field of liquid crystalline materials.<sup>1</sup> One important reason for this is that the methods for the synthesis of ferrocene derivatives offer ample opportunities for structure variations. Deschenaux<sup>2-5</sup> reported the first example of electron-transfer induced mesomorphism in the ferrocene-ferrocenium redox system, fullerene-ferrocene mixed liquid-crystalline materials and polymethacrylate thermotropic liquid crystal of ferrocene-containing side-chain. Bruce<sup>6</sup> succeeded in synthesizing a thermotropic metallomesogenic polymers with a poly (ferrocenylsilanes) main chain; Cook<sup>7</sup> succeeded in communicating a liquid

crystalline ferrocenyl-phthalocyanine discotic mesogen. We have discovered<sup>8</sup> organometallic liquid crystals with ferrocenyl building block containing not any soft terminal chain. Here we report the synthesis and characterization of mono-substituted ferrocene-containing liquid crystalline materials and the effect of structure (rigid core, chain length) on the mesogenic behaviors and try to explore the structure-liquid crystal properties relationship of these compounds. A series of novel ferrocene-containing liquid crystals with a bromo-phenyl moiety were synthesized according to the route shown in Scheme 1.<sup>1</sup>

## Experimental

### Instrument and chemical reagents

<sup>1</sup>H NMR spectra were recorded on a Bruker ACE-200 Spectrometer with CDCl<sub>3</sub> as the solvent and TMS as the internal standard. IR spectra were recorded on a Nicolet Magna-IR 500 Spectrometer Series II. Elemental analyses were performed on a Carlo Erba 1106 elemental analysis apparatus. Perkin-Elmer 7 series differential scanning calorimeter was used for thermal analysis, with heating rate 10 °C/min. Orthlux-II Polbk polarized optical microscopy with hot-stage was used for the melting point determination, clearing point measurement, as well as liquid crystal phases and textures characterization.

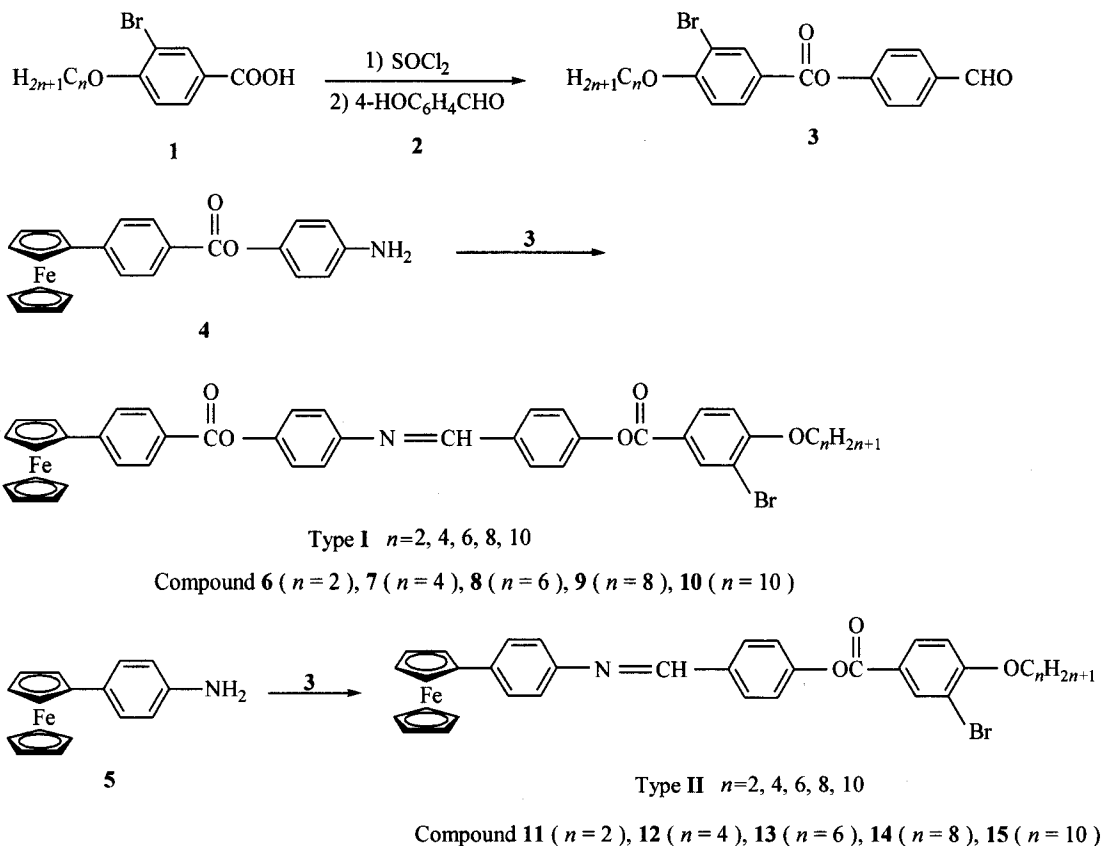
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## Scheme 1



*p*-Hydroxybenzaldehyde and  $\text{SOCl}_2$  were of chemical grade. Other chemicals and solvents were of analytical grade and used without further purification.

#### Syntheses of compounds 1, 4 and 5

Compounds **1**<sup>9</sup>, **4**<sup>8</sup> and **5**<sup>10</sup> were prepared according to the literature.

#### Syntheses of compounds 3

3-Bromo-4-alkoxybenzoic acid **1** (1 mmol) was added to excess of  $\text{SOCl}_2$  and the mixture was heated under reflux for 5 h. After the reaction was completed, the excess amount of  $\text{SOCl}_2$  was distilled off under reduced pressure to get an oily chloride. The chloride was dissolved in dry benzene, pyridine and *p*-hydroxybenzaldehyde, and the solution was heated to reflux. After being cooled, the precipitate was collected by filtration. The product was purified by recrystallization from benzene with yields of 61%—70%. The analytic data of a series

of compounds **3** are as follows:

**4-Formylphenyl 3-bromo-4-ethoxybenzoate** ( $\text{H}_5\text{C}_2\text{-OC}_6\text{H}_3\text{BrCO}_2\text{C}_6\text{H}_4\text{CHO}$ ) White solid, m. p. 131—132 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 10.02 (s, 1H, CHO), 7.40 (d,  $J = 8.6$  Hz, 2H,  $\text{C}_6\text{H}_4$ ), 7.93 (d,  $J = 8.6$  Hz, 2H,  $\text{C}_6\text{H}_4$ ), 6.90—8.37 (m, 3H,  $\text{C}_6\text{H}_3$ ), 4.07—4.21 (q,  $J = 6.8$  Hz, 2H,  $\text{OCH}_2$ ), 1.42—1.49 (t,  $J = 6.6$  Hz, 3H,  $\text{CH}_3$ ); IR (KBr)  $\nu$ : 1725, 1697, 1283, 1246  $\text{cm}^{-1}$ .

**4-Formylphenyl 3-bromo-4-butoxybenzoate** ( $\text{H}_9\text{C}_4\text{-OC}_6\text{H}_3\text{BrCO}_2\text{C}_6\text{H}_4\text{CHO}$ ) White solid, m. p. 102—103 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 10.01 (s, 1H, CHO), 7.40 (d,  $J = 8.6$  Hz, 2H,  $\text{C}_6\text{H}_4$ ), 7.92 (d,  $J = 8.6$  Hz, 2H,  $\text{C}_6\text{H}_4$ ), 6.95—8.40 (m, 3H,  $\text{C}_6\text{H}_3$ ), 4.10—4.17 (t,  $J = 6.6$  Hz, 2H,  $\text{OCH}_2$ ), 0.88—1.96 (m, 7H,  $\text{C}_3\text{H}_7$ ); IR (KBr)  $\nu$ : 1727, 1699, 1284, 1248  $\text{cm}^{-1}$ .

**4-Formylphenyl 3-bromo-4-hexyloxybenzoate** ( $\text{H}_{13}\text{C}_6\text{-OC}_6\text{H}_3\text{BrCO}_2\text{C}_6\text{H}_4\text{CHO}$ ) White solid, m. p. 95—96 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 10.02 (s, 1H,

CHO), 7.40 (d,  $J = 8.6$  Hz, 2H,  $C_6H_4$ ), 7.93 (d,  $J = 8.6$  Hz, 2H,  $C_6H_4$ ), 6.93—8.39 (m, 3H,  $C_6H_3$ ), 4.11—4.18 (t,  $J = 6.5$  Hz, 2H,  $OCH_2$ ), 0.88—1.93 (m, 11H,  $C_5H_{11}$ ); IR (KBr)  $\nu$ : 1726, 1698, 1282, 1246  $cm^{-1}$ .

4-Formylphenyl 3-bromo-4-octyloxybenzoate ( $H_{17}C_8-OC_6H_3BrCO_2C_6H_4CHO$ ) White solid, m.p. 97.5—98.5  $^{\circ}C$ ;  $^1H$  NMR ( $CDCl_3$ , 200 MHz)  $\delta$ : 10.04 (s, 1H, CHO), 7.39 (d,  $J = 8.6$  Hz, 2H,  $C_6H_4$ ), 7.93 (d,  $J = 8.6$  Hz, 2H,  $C_6H_4$ ), 6.923—8.37 (m, 3H,  $C_6H_3$ ), 4.08—4.14 (t,  $J = 6.4$  Hz, 2H,  $OCH_2$ ), 0.84—1.91 (m, 15H,  $C_7H_{15}$ ); IR (KBr)  $\nu$ : 1725, 1697, 1281, 1246  $cm^{-1}$ .

4-Formylphenyl 3-bromo-4-decyloxybenzoate ( $H_{21}C_{10}-OC_6H_3BrCO_2C_6H_4CHO$ ) White solid, m.p. 91—92  $^{\circ}C$ ;  $^1H$  NMR ( $CDCl_3$ , 200 MHz)  $\delta$ : 10.00 (s, 1H, CHO), 7.39 (d,  $J = 8.6$  Hz, 2H,  $C_6H_4$ ), 7.93 (d,  $J = 8.6$  Hz, 2H,  $C_6H_4$ ), 6.92—8.37 (m, 3H,  $C_6H_3$ ), 4.07—4.14 (t,  $J = 6.6$  Hz, 2H,  $OCH_2$ ), 0.83—1.95 (m, 19H,  $C_9H_{19}$ ); IR (KBr)  $\nu$ : 1724, 1698, 1281, 1244  $cm^{-1}$ .

#### Syntheses of compounds 6—10

4 (0.25 mmol) and 3 (0.25 mmol) were dissolved in 10 mL of ethanol and the mixture was heated under reflux for 5 h. After cooling, the precipitate was collected by filtration and purified by chromatography on silica gel (eluent: benzene:acetone = 5:1,  $V:V$ ) and recrystallized from benzene-petroleum (60—90  $^{\circ}C$ ). Yield 82.5%—85%. All compounds of type I are orange crystal. The analytical data of type I, are as follows:

6 m.p. 246.8  $^{\circ}C$ ;  $^1H$  NMR ( $CDCl_3$ , 200 MHz)  $\delta$ : 1.43—1.50 (t,  $J = 7.0$  Hz, 3H,  $CH_3$ ), 4.09—4.23 (q,  $J = 6.8$  Hz, 2H,  $OCH_2$ ), 4.08 (s, 5H,  $C_5H_5$ ), 4.45 (s, 2H, FcH), 4.77 (s, 2H, FcH), 8.52 (s, 1H, CH = N), 7.28—7.36 (m, 4H, C =  $NC_6H_4$ ), 7.60 (d,  $J = 8.4$  Hz, 2H,  $FeC_6H_4$ ), 8.06 (d,  $J = 8.4$  Hz, 2H,  $FeC_6H_4$ ), 7.43 (d,  $J = 8.8$  Hz, 2H, N =  $CC_6H_4$ ), 7.97 (d,  $J = 8.8$  Hz, 2H, N =  $CC_6H_4$ ), 6.96—8.40 (m, 3H,  $O_2CC_6H_3$ ); IR (KBr)  $\nu$ : 1728, 1732, 1266, 1196, 1624  $cm^{-1}$ ; Anal. calcd for  $C_{39}H_{30}NO_5BrFe$ : C 64.28, H 4.12, N 1.92; found C 64.32, H 4.10, N 1.82.

7 m.p. 199.0  $^{\circ}C$ ;  $^1H$  NMR ( $CDCl_3$ , 200 MHz)  $\delta$ : 4.06—4.13 (t,  $J = 6.4$  Hz, 2H,  $OCH_2$ ), 0.90—1.87 (m, 5H,  $C_3H_7$ ), 4.05 (s, 7H,  $C_5H_5$ ), 4.41 (s, 2H, FcH), 4.74 (s, 2H, FcH), 8.53 (s, 1H, CH = N),

7.26—7.34 (m, 4H, C =  $NC_6H_4$ ), 7.35 (d,  $J = 8.7$  Hz, 2H, N =  $CC_6H_4$ ), 7.88 (d,  $J = 8.7$  Hz, 2H, N =  $CC_6H_4$ ), 7.55 (d,  $J = 8.3$  Hz, 2H,  $FeC_6H_4$ ), 8.01 (d,  $J = 8.3$  Hz, 2H,  $FeC_6H_4$ ), 6.90—8.37 (m, 3H,  $O_2CC_6H_3$ ); IR (KBr)  $\nu$ : 1728, 1731, 1265, 1194, 1624  $cm^{-1}$ ; Anal. calcd for  $C_{41}H_{34}NO_5BrFe$ : C 65.08, H 4.50, N 1.85; found C 65.00, H 4.55, N 1.80.

8 m.p. 162.6  $^{\circ}C$ ;  $^1H$  NMR ( $CDCl_3$ , 200 MHz)  $\delta$ : 0.85—1.86 (m, 11H,  $C_5H_{11}$ ), 4.06—4.13 (t,  $J = 6.5$  Hz, 2H,  $OCH_2$ ), 4.42 (s, 2H, FcH), 4.75 (s, 2H, FcH), 4.07 (s, 5H,  $C_5H_5$ ), 8.50 (s, 1H, CH = N), 7.26—7.34 (m, 4H, C =  $NC_6H_4$ ), 7.62 (d,  $J = 8.4$  Hz, 2H,  $FeC_6H_4$ ), 8.08 (d,  $J = 8.4$  Hz, 2H,  $FeC_6H_4$ ), 7.40 (d,  $J = 8.7$  Hz, 2H, N =  $CC_6H_4$ ), 7.92 (d,  $J = 8.7$  Hz, 2H, N =  $CC_6H_4$ ), 6.96—8.42 (m, 3H,  $O_2CC_6H_3$ ); IR (KBr)  $\nu$ : 1725, 1730, 1268, 1197, 1626  $cm^{-1}$ ; Anal. calcd for  $C_{43}H_{38}NO_5BrFe$ : C 65.82, H 4.85, N 1.78; found C 65.78, H 4.88, N 1.73.

9 m.p. 154.0  $^{\circ}C$ ;  $^1H$  NMR ( $CDCl_3$ , 200 MHz)  $\delta$ : 0.84—1.87 (m, 15H,  $C_7H_{15}$ ), 4.05—4.11 (t,  $J = 6.5$  Hz, 2H,  $OCH_2$ ), 4.05 (s, 5H,  $C_5H_5$ ), 4.41 (s, 2H, FcH), 4.74 (s, 2H, FcH), 8.50 (s, 1H, CH = N), 7.26—7.34 (m, 4H, C =  $NC_6H_4$ ), 7.58 (d,  $J = 8.3$  Hz, 2H,  $FeC_6H_4$ ), 8.04 (d,  $J = 8.3$  Hz, 2H,  $FeC_6H_4$ ), 7.40 (d,  $J = 8.7$  Hz, 2H, N =  $CC_6H_4$ ), 7.93 (d,  $J = 8.7$  Hz, 2H, N =  $CC_6H_4$ ), 6.94—8.40 (m, 3H,  $O_2CC_6H_3$ ); IR (KBr)  $\nu$ : 1727, 1731, 1265, 1195, 1624  $cm^{-1}$ ; Anal. calcd for  $C_{45}H_{42}NO_5BrFe$ : C 66.50, H 5.17, N 1.72; found C 66.35, H 5.21, N 1.66.

10 m.p. 123.5  $^{\circ}C$ ;  $^1H$  NMR ( $CDCl_3$ , 200 MHz)  $\delta$ : 4.07—4.14 (t,  $J = 6.5$  Hz, 2H,  $OCH_2$ ), 0.83—1.90 (m, 19H,  $C_9H_{19}$ ), 4.43 (s, 2H, FcH), 4.77 (s, 2H, FcH), 4.05 (s, 5H,  $C_5H_5$ ), 8.52 (s, 1H, CH = N), 7.27—7.36 (m, 4H, C =  $NC_6H_4$ ), 7.42 (d,  $J = 8.8$  Hz, 2H, N =  $CC_6H_4$ ), 7.95 (d,  $J = 8.8$  Hz, 2H, N =  $CC_6H_4$ ), 7.60 (d,  $J = 8.4$  Hz, 2H,  $FeC_6H_4$ ), 7.60 (d,  $J = 8.4$  Hz, 2H,  $FeC_6H_4$ ), 6.92—8.39 (m, 3H,  $O_2CC_6H_3$ ); IR (KBr)  $\nu$ : 1729, 1732, 1266, 1196, 1627  $cm^{-1}$ ; Anal. calcd for  $C_{47}H_{46}NO_5BrFe$ : C 67.14, H 5.48, N 1.67; found C 67.25, H 5.42, N 1.66.

#### Syntheses of imine compounds 11—15

Compounds 11—15 were prepared according to the above method. Yield 68%—72%. All compounds of type II are orange crystal. The analytical data of type II are as fol-

lows:

**11** m.p. 219.9 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ: 4.11—4.24 (q, *J* = 6.7 Hz, 2H, OCH<sub>2</sub>), 1.45—1.52 (t, *J* = 6.8 Hz, 3H, CH<sub>3</sub>), 4.06 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.31 (s, 2H, FcH), 4.64 (s, 2H, FcH), 8.51 (s, 1H, CH = N), 7.34 (d, *J* = 8.6 Hz, 2H, N = CC<sub>6</sub>H<sub>4</sub>), 7.97 (d, *J* = 8.6 Hz, 2H, N = CC<sub>6</sub>H<sub>4</sub>), 7.21 (d, *J* = 8.3 Hz, 2H, FcC<sub>6</sub>H<sub>4</sub>), 7.49 (d, *J* = 8.3 Hz, 2H, FcC<sub>6</sub>H<sub>4</sub>), 6.93—8.39 (m, 3H, O<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>); IR (KBr) ν: 1722, 1295, 1627 cm<sup>-1</sup>; Anal. calcd for C<sub>32</sub>H<sub>26</sub>NO<sub>3</sub>BrFe: C 63.16, H 4.28, N 2.30; found C 63.09, H 4.20, N 2.20.

**12** m.p. 179.8 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ: 4.10—4.17 (t, *J* = 6.4 Hz, 2H, OCH<sub>2</sub>), 0.86—1.89 (m, 7H, C<sub>3</sub>H<sub>7</sub>), 4.04 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.31 (s, 2H, FcH), 4.64 (s, 2H, FcH), 8.51 (s, 1H, CH = N), 7.34 (d, *J* = 8.6 Hz, 2H, N = CC<sub>6</sub>H<sub>4</sub>), 7.96 (d, *J* = 8.6 Hz, 2H, N = CC<sub>6</sub>H<sub>4</sub>), 6.92—8.40 (m, 3H, O<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>), 7.18 (d, *J* = 8.4 Hz, 2H, FcC<sub>6</sub>H<sub>4</sub>), 7.49 (d, *J* = 8.4 Hz, 2H, FcC<sub>6</sub>H<sub>4</sub>); IR (KBr) ν: 1725, 1298, 1627 cm<sup>-1</sup>; Anal. calcd for C<sub>34</sub>H<sub>30</sub>NO<sub>3</sub>BrFe: C 64.15, H 4.72, N 2.20; found C 64.25, H 4.72, N 2.21.

**13** m.p. 171.1 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ: 4.09—4.15 (t, *J* = 6.4 Hz, 2H, OCH<sub>2</sub>), 0.84—1.87 (m, 11H, C<sub>5</sub>H<sub>11</sub>), 4.30 (s, 2H, FcH), 4.60 (s, 2H, FcH), 4.03 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 8.51 (s, 1H, CH = N), 7.33 (d, *J* = 8.6 Hz, 2H, N = CC<sub>6</sub>H<sub>4</sub>), 7.95 (d, *J* = 8.6 Hz, 2H, N = CC<sub>6</sub>H<sub>4</sub>), 7.19 (d, *J* = 8.4 Hz, 2H, FcC<sub>6</sub>H<sub>4</sub>), 7.47 (d, *J* = 8.4 Hz, 2H, FcC<sub>6</sub>H<sub>4</sub>), 6.92—8.39 (m, 3H, O<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>); IR (KBr) ν: 1721, 1298, 1623 cm<sup>-1</sup>; Anal. calcd for C<sub>36</sub>H<sub>34</sub>NO<sub>3</sub>BrFe: C 65.06, H 5.12, N 2.11; found C 65.06, H 5.15, N 2.09.

**14** m.p. 146.3 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ: 4.07—4.14 (t, *J* = 6.6 Hz, 2H, OCH<sub>2</sub>), 0.84—1.92 (m, 15H, C<sub>7</sub>H<sub>15</sub>), 4.01 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.29 (s, 2H, FcH), 4.60 (s, 2H, FcH), 8.49 (s, 1H, CH = N), 7.30 (d, *J* = 8.6 Hz, 2H, N = CC<sub>6</sub>H<sub>4</sub>), 7.93 (d, *J* = 8.6 Hz, 2H, N = CC<sub>6</sub>H<sub>4</sub>), 6.90—8.37 (m, 3H, O<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>), 7.17 (d, *J* = 8.4 Hz, 2H, FcC<sub>6</sub>H<sub>4</sub>), 7.45 (d, *J* = 8.4 Hz, 2H, FcC<sub>6</sub>H<sub>4</sub>); IR (KBr) ν: 1720, 1295, 1620 cm<sup>-1</sup>; Anal. calcd for C<sub>38</sub>H<sub>38</sub>NO<sub>3</sub>BrFe: C 65.90, H 5.49, N 2.02; found C 65.95, H 5.45, N 1.99.

**15** m.p. 120.9 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ: 4.10—4.17 (t, *J* = 6.8 Hz, 2H, OCH<sub>2</sub>), 0.84—1.93 (m, 19H, C<sub>9</sub>H<sub>19</sub>), 4.04 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.31 (s, 2H, FcH), 4.64 (s, 2H, FcH), 8.51 (s, 1H, CH = N), 7.33 (d, *J* = 8.6 Hz, 2H, N = CC<sub>6</sub>H<sub>4</sub>), 7.95 (d, *J* = 8.6 Hz,

2H, N = CC<sub>6</sub>H<sub>4</sub>), 7.19 (d, *J* = 8.4 Hz, 2H, FcC<sub>6</sub>H<sub>4</sub>), 7.47 (d, *J* = 8.4 Hz, 2H, FcC<sub>6</sub>H<sub>4</sub>), 6.92—8.39 (m, 3H, O<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>); IR (KBr) ν: 1723, 1297, 1625 cm<sup>-1</sup>; Anal. calcd for C<sub>40</sub>H<sub>42</sub>NO<sub>3</sub>BrFe: C 66.67, H 5.83, N 1.94; found C 66.53, H 5.91, N 1.96.

## Results and discussion

The thermal analytical results of compounds **6**—**15** were listed in Table 1. Among these compounds, compounds **6**—**10** with four phenyl groups in the molecules showed the characteristics of smectic liquid crystal (Fig. 1). Compounds **11**—**15** have three phenyl rings in the molecules, among which compound **11** has not mesomorphism, because the terminal chain (*n* = 2) of the molecule is shorter. When the terminal chain of molecules becomes the longer, compounds show the different liquid crystalline properties. Compounds **12** and **13** were monotropic mesogens, and compounds **14** and **15** were enantiotropic mesogens, thus, the

**Table 1** Phase transition temperatures and enthalpies for the synthesized compounds

Compd.	Phase transition <sup>a</sup>	Temp. (°C)	Δ <i>H</i> (kJ/mol)
<b>6</b>	C—S	246.77	34.62
	S—I	286.1	80.37
<b>7</b>	C—S	199.03	28.53
	S—I	301.6	97.91
<b>8</b>	C—S	162.57	29.21
	S—I	277.41	1.72
<b>9</b>	C—S	153.96	36.66
	S—I	259.83	1.45
<b>10</b>	C—S	123.54	15.21
	S—I	232.58	1.16
<b>11</b>	C—I	219.9	36.67
<b>12<sup>b</sup></b>	C—I	179.8	34.51
	I—S	160.70	-1.44
<b>13<sup>b</sup></b>	C—I	171.1	36.93
	I—S(1)	156.75	-1.47
	S(1)—S(2)	122.41	-2.92
	S(2)—S(3)	106.55	-2.40
<b>14</b>	C—S	146.3	44.97
	S—I	149.0	2.32
<b>015</b>	C—S	120.9	23.49
	S—I	134.5	1.27

<sup>a</sup> C, crystal; I, isotropic liquid; S, smectic phase. <sup>b</sup> Monotropic liquid crystal.

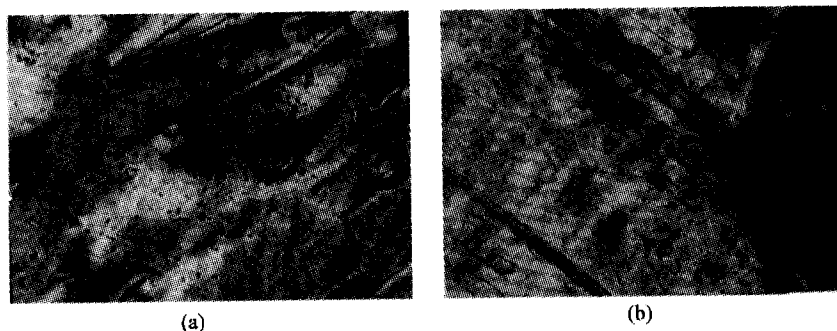


Fig. 1 Typical textures of compounds **10** (a) and **15** (b) under polarized microscopy. (a) Compound **10**, 210 °C,  $\times 250$ ; (b) compound **14**, 149 °C,  $\times 250$ .

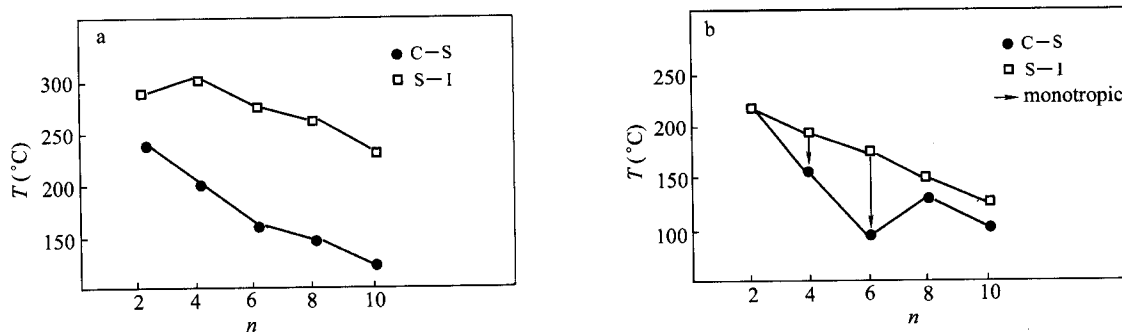


Fig. 2 Influence of terminal carbon number ( $n$ ) on the liquid crystal properties. (a) Type I compound; (b) type II compound.

stabilities of mesogenic phases of **14** and **15** were higher than those of **12** and **13**. These results can be explained by the facts that ferrocenyl unit is a bulky group which needs to be compensated by the molecular length. The longer the rigid core, the more stable the liquid crystal phase is.

Fig. 2 shows the influence of  $n$  (number of carbon atom in their terminal chain) on the liquid crystal properties. The melting and clearing points turn lower as the  $n$  increases. This trend coincides with the principal of liquid crystal. As for the cubic shaped mesogenic molecules, the mesomorphism depends not only on the ratio of length and width of molecules, but also on the length ratio of rigid core and terminal chain. When the rigid core becomes longer (from three phenyl rings to four phenyl rings), the temperature range of phase transition becomes wider.

Contrast to their analogy compounds<sup>8</sup> without bromo-substitution, **6**–**10** have lower melting and clearing points and slightly narrower liquid crystalline temperature ranges. Bromine atom is much bigger than hydrogen atom (0.114 nm and 0.037 nm in atomic radii) in size, and disfavor for the closing package of molecules. The bromine substituent decreases intermolecular forces, weaker intermolecular forces led to lower melting and clearing points. So bromine-substi-

tuent can lower the phase transformation temperatures of ferrocene liquid crystals.

## Conclusions

We have reported the synthesis and liquid crystal properties of ten ferrocene compounds with four and three phenyl rings. The bulkiness of ferrocene is compensated by the length of the molecule. In comparison with our reported results,<sup>8</sup> due to the fact that the bromine atom has a larger steric effect, the bromine-substituent in structure caused loose package in crystal, thus lowered melting and clearing points of liquid crystals.

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