

## 单取代二茂铁西佛碱型液晶化合物的合成及介晶性研究

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**摘要** 报道了两个系列二茂铁衍生物,  $\text{FcC}_6\text{H}_4\text{N}-\text{CHC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$  (系列 I) 和  $\text{FcC}_6\text{H}_4\text{N}-\text{CHC}_6\text{H}_4\text{O}_2\text{CC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$  (系列 II) ( $\text{Fc}$ : ferrocenyl;  $n=2, 4, 6, 8, 10, 12, 14, 16$ ), 并通过 DSC 和热台偏光显微镜对其介晶性进行了研究。系列 I 不具有介晶性, 系列 II 呈较窄的液晶温度范围。其结果显示分子的刚性部分长度对介晶性有重要影响。

**关键词** 金属有机, 二茂铁, 液晶

## Synthesis and Mesogenic Behavior Studies of Monosubstituted Ferrocene-containing Schiff Base Liquid Crystals

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**Abstract** Two series of ferrocene compounds with structure of  $\text{Fc}-\text{C}_6\text{H}_4-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{OC}_n\text{H}_{2n+1}$  (series I) and  $\text{Fc}-\text{C}_6\text{H}_4-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{OC}_n\text{H}_{2n+1}$  (series II) ( $\text{Fc}$ : ferrocenyl;  $n=2, 4, 6, 8, 10, 12, 14, 16$ ) were prepared. Their mesogenic behaviors were studied with DSC and polarized optical microscopy. The results show that series I compounds do not possess liquid crystalline properties, while series II compounds have narrow liquid crystal temperature range. These results prove that the length of the rigid core in the molecule has an important effect on the mesogenic properties.

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

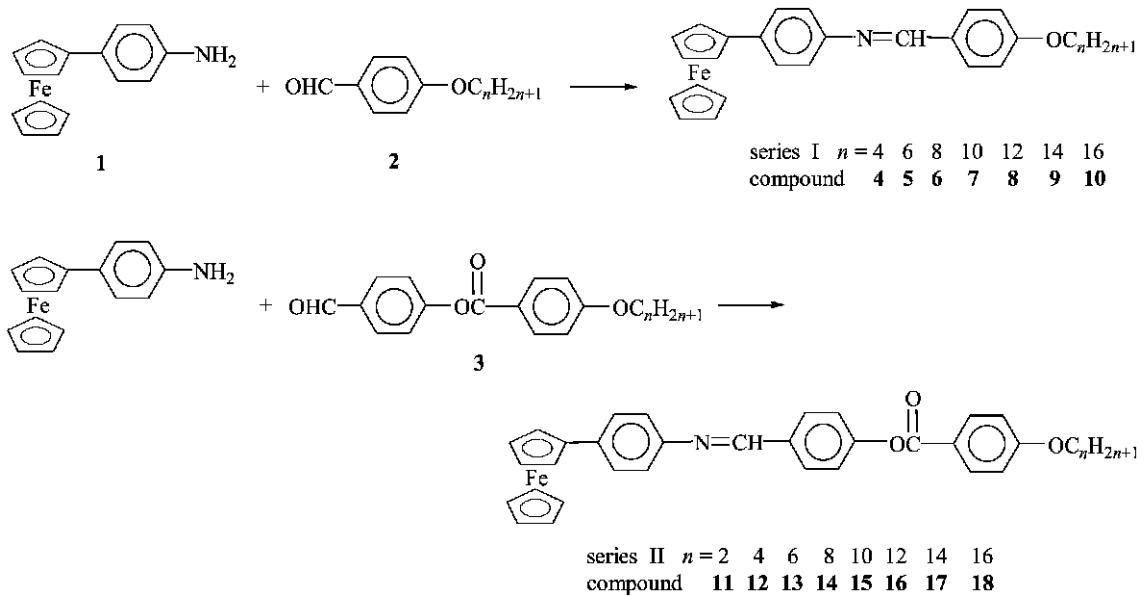
液晶是通过分子间相互作用, 将分子聚集在一起形成的各相异性的超分子流体。有机液晶通过偶极-偶极和色散力相互作用, 而金属有机液晶还可能存在分子间金属-金属、金属-配体相互作用, 呈现介晶性。因而, 金属有机液晶已成为蓬勃发展的有机和无机超分子化学的重要组成部分<sup>[1~4]</sup>。

二茂铁及其衍生物由于其独特的性能而在非线性光学材料、磁性材料、液晶材料等领域受到重

视<sup>[5]</sup>, 二茂铁液晶因其独特的稳定性和易于衍生化受到研究人员的青睐, 目前报道的化合物其介晶相温度较窄, 结构多以茂环 1,1-和 1,3-双取代为主<sup>[6~12]</sup>。我们曾经报道 1-单取代的二茂铁液晶的合成与介晶性<sup>[13]</sup>。这里我们进一步报道二茂铁金属有机液晶分子的刚性部分长度对介晶性的影响。合成路线如下:

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## 1 实验部分

### 1.1 仪器与试剂

核磁共振谱仪 Brucker ACE-300 spectrometer 和 Varian INOVA-400 spectrometer,  $\text{CDCl}_3$  作溶剂. 红外光谱仪 Nicolet Magna-IR 500 Spectrometer, Series II, KBr 压片. 元素分析仪 WRS-IA, Carlo Erba 1106. 热分析仪 Perkin-Elmer 7 Series ( $\text{N}_2$  气氛, 升温速度 10 / min). 偏光显微镜 Orthlux-II Polbk, 热台自制. 所用试剂均为国产化学纯. 溶剂在使用前按标准方法干燥、蒸馏处理.

### 1.2 合成

化合物**1** 按文献[14]方法合成, 化合物**2** 按文献[15]方法合成, 化合物**3** 按文献[13]方法合成.

#### 1.2.1 系列 I 化合物(4~10)的合成

将 0.28 g (1 mmol) 化合物**1** 与 1 mmol 4-烷氧基苯甲醛溶于 25 mL 乙醇中, 搅拌回流 5 h. 反应中逐渐析出黄色固体, 反应毕, 冷却, 过滤得粗品; 用石油醚(90~120  $^{\circ}\text{C}$ )重结晶, 得橙黄色晶体, 产率 70%~80%. 波谱分析数据如下:

化合物**4**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) : 4.02 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.31 (s, 2H,  $\text{C}_5\text{H}_2$ ), 4.63 (s, 2H,  $\text{C}_5\text{H}_2$ ), 8.44 (s, 1H,  $\text{CH}=\text{N}$ ), 6.95 (d,  $J = 8.6$  Hz, 2H,  $\text{OC}_6\text{H}_2$ ), 7.83 (d,  $J = 8.6$  Hz, 2H,  $\text{OC}_6\text{H}_2$ ), 7.16 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ), 7.45 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ), 4.02 (t,  $J = 6.8$  Hz, 2H,  $\text{OCH}_2$ ), 1.71~1.82 (m, 2H,  $\text{OCCH}_2$ ), 1.34~1.45 (m, 2H,  $\text{CH}_2$ ), 1.15 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ); IR (KBr) : 3106, 3083, 2921, 2868, 2852,

1624, 1608, 1573, 1520, 1106, 1002, 820  $\text{cm}^{-1}$ .  
Anal. calcd for  $\text{C}_{27}\text{H}_{27}\text{ONFe}$ : C 74.14, H 6.18; found C 74.01, H 6.12.

化合物**5**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) : 4.03 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.30 (s, 2H,  $\text{C}_5\text{H}_2$ ), 4.63 (s, 2H,  $\text{C}_5\text{H}_2$ ), 8.43 (s, 1H,  $\text{CH}=\text{N}$ ), 6.96 (d,  $J = 8.6$  Hz, 2H,  $\text{OC}_6\text{H}_2$ ), 7.84 (d,  $J = 8.6$  Hz, 2H,  $\text{OC}_6\text{H}_2$ ), 7.17 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ), 7.49 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ), 4.04 (t,  $J = 6.8$  Hz, 2H,  $\text{OCH}_2$ ), 1.79~1.89 (m, 2H,  $\text{OCCH}_2$ ), 1.31~1.55 (m, 6H,  $\text{C}_3\text{H}_6$ ), 0.93 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ); IR (KBr) : 3102, 3087, 2929, 2857, 2849, 1623, 1611, 1573, 1522, 1106, 999, 822  $\text{cm}^{-1}$ .  
Anal. calcd for  $\text{C}_{29}\text{H}_{31}\text{ONFe}$ : C 74.84, H 6.67; found C 74.73, H 6.60.

化合物**6**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) : 4.03 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.30 (s, 2H,  $\text{C}_5\text{H}_2$ ), 4.62 (s, 2H,  $\text{C}_5\text{H}_2$ ), 8.42 (s, 1H,  $\text{CH}=\text{N}$ ), 6.95 (d,  $J = 8.6$  Hz, 2H,  $\text{OC}_6\text{H}_2$ ), 7.85 (d,  $J = 8.4$  Hz, 2H,  $\text{OC}_6\text{H}_2$ ), 7.13 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ), 7.47 (d,  $J = 8.6$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ), 3.98 (t,  $J = 6.8$  Hz, 2H,  $\text{OCH}_2$ ), 1.74~1.83 (m, 2H,  $\text{OCCH}_2$ ), 1.27~1.52 (m, 10H,  $\text{C}_5\text{H}_{10}$ ), 1.02 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ); IR (KBr) : 3104, 3084, 2924, 2868, 2854, 1622, 1606, 1570, 1520, 1511, 1106, 1002, 821  $\text{cm}^{-1}$ .  
Anal. calcd for  $\text{C}_{31}\text{H}_{35}\text{ONFe}$ : C 75.46, H 7.10; found C 75.41, H 7.09.

化合物**7**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz) : 4.03 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.30 (s, 2H,  $\text{C}_5\text{H}_2$ ), 4.63 (s, 2H,

$\text{C}_5\text{H}_2$ ), 8.43 (s, 1H,  $\text{CH}=\text{N}$ ), 6.95 (d,  $J = 8.6$  Hz, 2H,  $\text{OC}_6\text{H}_2$ ), 7.82 (d,  $J = 8.6$  Hz, 2H,  $\text{OC}_6\text{H}_2$ ), 7.14 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ), 7.48 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ), 3.95 (t,  $J = 6.5$  Hz, 2H,  $\text{OCH}_2$ ), 1.77~1.88 (m, 2H,  $\text{OCCH}_2$ ), 1.26~1.55 (m, 14H,  $\text{C}_7\text{H}_{14}$ ), 0.91 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ); IR (KBr) : 3113, 2921, 2868, 2850, 1624, 1612, 1577, 1511, 1105, 1001, 818  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{33}\text{H}_{39}\text{ONFe}$ : C 76.01, H 7.49; found C 75.80, H 7.51.

**化合物 8**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) : 4.04 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.30 (s, 2H,  $\text{C}_5\text{H}_2$ ), 4.63 (s, 2H,  $\text{C}_5\text{H}_2$ ), 8.43 (s, 1H,  $\text{CH}=\text{N}$ ), 6.96 (d,  $J = 8.6$  Hz, 2H,  $\text{OC}_6\text{H}_2$ ), 7.84 (d,  $J = 8.6$  Hz, 2H,  $\text{OC}_6\text{H}_2$ ), 7.15 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ), 7.48 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ), 4.03 (t,  $J = 6.8$  Hz, 2H,  $\text{OCH}_2$ ), 1.74~1.85 (m, 2H,  $\text{OCCH}_2$ ), 1.26~1.52 (m, 18H,  $\text{C}_9\text{H}_{18}$ ), 0.89 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ); IR (KBr) : 3109, 3083, 2919, 2858, 1622, 1612, 1573, 1520, 1513, 1104, 1001, 818  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{35}\text{H}_{43}\text{ONFe}$ : C 76.50, H 7.83; found C 76.39, H 7.80.

**化合物 9**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) : 4.03 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.31 (s, 2H,  $\text{C}_5\text{H}_2$ ), 4.64 (s, 2H,  $\text{C}_5\text{H}_2$ ), 8.43 (s, 1H,  $\text{CH}=\text{N}$ ), 6.95 (d,  $J = 8.6$  Hz, 2H,  $\text{OC}_6\text{H}_2$ ), 7.83 (d,  $J = 8.6$  Hz, 2H,  $\text{OC}_6\text{H}_2$ ), 7.14 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ), 7.47 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ), 3.99 (t,  $J = 6.8$  Hz, 2H,  $\text{OCH}_2$ ), 1.76~1.86 (m, 2H,  $\text{OCCH}_2$ ), 1.26~1.49 (m, 22H,  $\text{C}_{11}\text{H}_{22}$ ), 0.88 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ); IR (KBr) : 3101, 3072, 2920, 2852, 1622, 1607, 1573, 1522, 1107, 1005, 819  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{37}\text{H}_{47}\text{ONFe}$ : C 76.95, H 8.14; found C 76.88, H 8.11.

**化合物 10**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) : 4.02 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.30 (s, 2H,  $\text{C}_5\text{H}_2$ ), 4.63 (s, 2H,  $\text{C}_5\text{H}_2$ ), 8.42 (s, 1H,  $\text{CH}=\text{N}$ ), 6.95 (d,  $J = 8.6$  Hz, 2H,  $\text{OC}_6\text{H}_2$ ), 7.84 (d,  $J = 8.6$  Hz, 2H,  $\text{OC}_6\text{H}_2$ ), 7.16 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ), 7.48 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ), 3.97 (t,  $J = 6.8$  Hz, 2H,  $\text{OCH}_2$ ), 1.77~1.87 (m, 2H,  $\text{OCCH}_2$ ), 1.26~1.49 (m, 26H,  $\text{C}_{13}\text{H}_{26}$ ), 0.89 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ); IR (KBr) : 3103, 3086, 2919, 2869, 2851, 1623, 1610, 1573, 1523, 1105, 1002, 818  $\text{cm}^{-1}$ .

Anal. calcd for  $\text{C}_{39}\text{H}_{51}\text{ONFe}$ : C 77.36, H 8.43; found C 77.29, H 8.41.

### 1.2.2 系列 II 化合物(11~18)的合成

将 0.28 g (1 mmol) 化合物 1 与 1 mmol 化合物 3 反应. 实验方法与系列 I 化合物类似, 得到橙黄色晶体, 产率 78%~82%. 波谱分析数据如下:

**化合物 11**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) : 4.04 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.31 (s, 2H,  $\text{C}_5\text{H}_2$ ), 4.65 (s, 2H,  $\text{C}_5\text{H}_2$ ), 8.52 (s, 1H,  $\text{CH}=\text{N}$ ), 7.32 (d,  $J = 8.8$  Hz, 2H, N=CC<sub>6</sub>H<sub>2</sub>), 7.97 (d,  $J = 8.8$  Hz, 2H, N=CC<sub>6</sub>H<sub>2</sub>), 6.97 (d,  $J = 8.6$  Hz, 2H, O<sub>2</sub>CC<sub>6</sub>H<sub>2</sub>), 8.14 (d,  $J = 8.6$  Hz, 2H, O<sub>2</sub>CC<sub>6</sub>H<sub>2</sub>), 7.15 (d,  $J = 8.4$  Hz, 2H, FcC<sub>6</sub>H<sub>2</sub>), 7.50 (d,  $J = 8.4$  Hz, 2H, FcC<sub>6</sub>H<sub>2</sub>), 4.12 (q,  $J = 6.8$  Hz, 2H, OCH<sub>2</sub>), 1.45 (t,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>); IR (KBr) : 3094, 2920, 2857, 1724, 1621, 1602, 1580, 1521, 1259, 1106, 1010, 821  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{32}\text{H}_{27}\text{O}_3\text{NFe}$ : C 72.59, H 5.10; found C 72.53, H 5.09.

**化合物 12**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) : 4.02 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.30 (s, 2H,  $\text{C}_5\text{H}_2$ ), 4.65 (s, 2H,  $\text{C}_5\text{H}_2$ ), 8.53 (s, 1H,  $\text{CH}=\text{N}$ ), 7.33 (d,  $J = 8.8$  Hz, 2H, N=CC<sub>6</sub>H<sub>2</sub>), 7.98 (d,  $J = 8.8$  Hz, 2H, N=CC<sub>6</sub>H<sub>2</sub>), 6.95 (d,  $J = 8.6$  Hz, 2H, O<sub>2</sub>CC<sub>6</sub>H<sub>2</sub>), 8.14 (d,  $J = 8.6$  Hz, 2H, O<sub>2</sub>CC<sub>6</sub>H<sub>2</sub>), 7.16 (d,  $J = 8.4$  Hz, 2H, FcC<sub>6</sub>H<sub>2</sub>), 7.50 (d,  $J = 8.4$  Hz, 2H, FcC<sub>6</sub>H<sub>2</sub>), 4.03 (t,  $J = 6.8$  Hz, 2H, OCH<sub>2</sub>), 1.72~1.83 (m, 2H, OCCH<sub>2</sub>), 1.35~1.46 (m, 2H, CH<sub>2</sub>), 1.16 (t,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>); IR (KBr) : 3095, 2918, 2854, 1732, 1625, 1604, 1581, 1521, 1282, 1102, 1007, 821  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{34}\text{H}_{31}\text{O}_3\text{NFe}$ : C 73.25, H 5.56; found C 73.10, H 5.56.

**化合物 13**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) : 4.04 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.30 (s, 2H,  $\text{C}_5\text{H}_2$ ), 4.64 (s, 2H,  $\text{C}_5\text{H}_2$ ), 8.53 (s, 1H,  $\text{CH}=\text{N}$ ), 7.31 (d,  $J = 8.8$  Hz, 2H, N=CC<sub>6</sub>H<sub>2</sub>), 7.98 (d,  $J = 8.8$  Hz, 2H, N=CC<sub>6</sub>H<sub>2</sub>), 6.95 (d,  $J = 8.6$  Hz, 2H, O<sub>2</sub>CC<sub>6</sub>H<sub>2</sub>), 8.15 (d,  $J = 8.6$  Hz, 2H, O<sub>2</sub>CC<sub>6</sub>H<sub>2</sub>), 7.17 (d,  $J = 8.4$  Hz, 2H, FcC<sub>6</sub>H<sub>2</sub>), 7.49 (d,  $J = 8.4$  Hz, 2H, FcC<sub>6</sub>H<sub>2</sub>), 4.01 (t,  $J = 6.8$  Hz, 2H, OCH<sub>2</sub>), 1.77~1.88 (m, 2H, OCCH<sub>2</sub>), 1.32~1.56 (m, 6H, C<sub>3</sub>H<sub>6</sub>), 0.94 (t,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>); IR (KBr) : 3101, 2952, 2872, 1732, 1626, 1606, 1581, 1521, 1269, 1106, 1003, 819  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{36}\text{H}_{35}\text{O}_3\text{NFe}$ : C 73.85, H 5.98; found C 73.76, H 5.96.

**化合物 14**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) : 4.05 (s, 5H,  $\text{C}_5\text{H}_5$ ) , 4.30 (s, 2H,  $\text{C}_5\text{H}_2$ ) , 4.64 (s, 2H,  $\text{C}_5\text{H}_2$ ) , 8.54 (s, 1H,  $\text{CH}=\text{N}$ ) , 7.33 (d,  $J = 8.8$  Hz, 2H,  $\text{N}=\text{CC}_6\text{H}_2$ ) , 8.00 (d,  $J = 8.8$  Hz, 2H,  $\text{N}=\text{CC}_6\text{H}_2$ ) , 6.94 (d,  $J = 8.6$  Hz, 2H,  $\text{O}_2\text{CC}_6\text{H}_2$ ) , 8.13 (d,  $J = 8.6$  Hz, 2H,  $\text{O}_2\text{CC}_6\text{H}_2$ ) , 7.17 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ) , 7.50 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ) , 3.95 (t,  $J = 6.8$  Hz, 2H,  $\text{OCH}_2$ ) , 1.74 ~ 1.85 (m, 2H,  $\text{OCCH}_2$ ) , 1.26 ~ 1.52 (m, 10H,  $\text{C}_5\text{H}_{10}$ ) , 0.89 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ) ; IR (KBr) : 3083, 2949, 2868, 1729, 1621, 1602, 1573, 1510, 1264, 1106, 1001, 818  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{38}\text{H}_{39}\text{O}_3\text{NFe}$ : C 74.39, H 6.36; found C 74.36, H 6.37.

**化合物 15**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz) : 4.04 (s, 5H,  $\text{C}_5\text{H}_5$ ) , 4.31 (s, 2H,  $\text{C}_5\text{H}_2$ ) , 4.65 (s, 2H,  $\text{C}_5\text{H}_2$ ) , 8.53 (s, 1H,  $\text{CH}=\text{N}$ ) , 7.31 (d,  $J = 8.8$  Hz, 2H,  $\text{N}=\text{CC}_6\text{H}_2$ ) , 7.98 (d,  $J = 8.8$  Hz, 2H,  $\text{N}=\text{CC}_6\text{H}_2$ ) , 6.96 (d,  $J = 8.8$  Hz, 2H,  $\text{O}_2\text{CC}_6\text{H}_2$ ) , 8.15 (d,  $J = 8.8$  Hz, 2H,  $\text{O}_2\text{CC}_6\text{H}_2$ ) , 7.16 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ) , 7.51 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ) , 4.04 (t,  $J = 6.5$  Hz, 2H,  $\text{OCH}_2$ ) , 1.74 ~ 1.86 (m, 2H,  $\text{OCCH}_2$ ) , 1.27 ~ 1.53 (m, 14H,  $\text{C}_7\text{H}_{14}$ ) , 0.87 (t,  $J = 6.3$  Hz, 3H,  $\text{CH}_3$ ) ; IR (KBr) : 3100, 2922, 2857, 1731, 1621, 1605, 1578, 1511, 1268, 1108, 1004, 822  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{40}\text{H}_{43}\text{O}_3\text{NFe}$ : C 74.88, H 6.71; found C 75.12, H 6.66.

**化合物 16**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) : 4.03 (s, 5H,  $\text{C}_5\text{H}_5$ ) , 4.30 (s, 2H,  $\text{C}_5\text{H}_2$ ) , 4.64 (s, 2H,  $\text{C}_5\text{H}_2$ ) , 8.52 (s, 1H,  $\text{CH}=\text{N}$ ) , 7.31 (d,  $J = 8.8$  Hz, 2H,  $\text{N}=\text{CC}_6\text{H}_2$ ) , 7.97 (d,  $J = 8.8$  Hz, 2H,  $\text{N}=\text{CC}_6\text{H}_2$ ) , 6.95 (d,  $J = 8.6$  Hz, 2H,  $\text{O}_2\text{CC}_6\text{H}_2$ ) , 8.14 (d,  $J = 8.6$  Hz, 2H,  $\text{O}_2\text{CC}_6\text{H}_2$ ) , 7.15 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ) , 7.49 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ) , 3.95 (t,  $J = 6.8$  Hz, 2H,  $\text{OCH}_2$ ) , 1.72 ~ 1.83 (m, 2H,  $\text{OCCH}_2$ ) , 1.24 ~ 1.49 (m, 18H,  $\text{C}_9\text{H}_{18}$ ) , 0.87 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ) ; IR (KBr) : 3080, 2921, 2852, 1732, 1622, 1604, 1577, 1511, 1268, 1108, 1004, 822  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{42}\text{H}_{47}\text{O}_3\text{NFe}$ : C 75.34, H 7.02; found C 75.28, H 6.95.

**化合物 17**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) : 4.04 (s, 5H,  $\text{C}_5\text{H}_5$ ) , 4.31 (s, 2H,  $\text{C}_5\text{H}_2$ ) , 4.65 (s, 2H,  $\text{C}_5\text{H}_2$ ) , 8.53 (s, 1H,  $\text{CH}=\text{N}$ ) , 7.32 (d,  $J = 8.8$

Hz, 2H,  $\text{N}=\text{CC}_6\text{H}_2$ ) , 7.98 (d,  $J = 8.8$  Hz, 2H,  $\text{N}=\text{CC}_6\text{H}_2$ ) , 6.96 (d,  $J = 8.6$  Hz, 2H,  $\text{O}_2\text{CC}_6\text{H}_2$ ) , 8.15 (d,  $J = 8.6$  Hz, 2H,  $\text{O}_2\text{CC}_6\text{H}_2$ ) , 7.16 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ) , 7.51 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ) , 3.95 (t,  $J = 6.8$  Hz, 2H,  $\text{OCH}_2$ ) , 1.72 ~ 1.83 (m, 2H,  $\text{OCCH}_2$ ) , 1.26 ~ 1.50 (m, 22H,  $\text{C}_{11}\text{H}_{22}$ ) , 0.88 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ) ; IR (KBr) : 3087, 2922, 2851, 1733, 1623, 1603, 1579, 1511, 1269, 1106, 1003, 822  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{44}\text{H}_{51}\text{O}_3\text{NFe}$ : C 75.75, H 7.32; found C 75.66, H 7.30.

**化合物 18**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) : 4.03 (s, 5H,  $\text{C}_5\text{H}_5$ ) , 4.32 (s, 2H,  $\text{C}_5\text{H}_2$ ) , 4.66 (s, 2H,  $\text{C}_5\text{H}_2$ ) , 8.52 (s, 1H,  $\text{CH}=\text{N}$ ) , 7.33 (dd,  $J = 8.8$  Hz, 2H,  $\text{N}=\text{CC}_6\text{H}_2$ ) , 7.99 (d,  $J = 8.8$  Hz, 2H,  $\text{N}=\text{CC}_6\text{H}_2$ ) , 6.94 (d,  $J = 8.6$  Hz, 2H,  $\text{O}_2\text{CC}_6\text{H}_2$ ) , 8.13 (d,  $J = 8.6$  Hz, 2H,  $\text{O}_2\text{CC}_6\text{H}_2$ ) , 7.15 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ) , 7.50 (d,  $J = 8.4$  Hz, 2H,  $\text{FcC}_6\text{H}_2$ ) , 3.95 (t,  $J = 6.8$  Hz, 2H,  $\text{OCH}_2$ ) , 1.72 ~ 1.83 (m, 2H,  $\text{OCCH}_2$ ) , 1.27 ~ 1.51 (m, 26H,  $\text{C}_{13}\text{H}_{26}$ ) , 0.89 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ) ; IR (KBr) : 3088, 2922, 2851, 1732, 1623, 1605, 1578, 1510, 1264, 1107, 1003, 819  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{46}\text{H}_{55}\text{O}_3\text{NFe}$ : C 76.14, H 7.59; found C 76.01, H 7.53.

## 2 结果与讨论

### 2.1 产物结构表征

IR 光谱中, 系列 I 和 II 化合物在 1000, 1100  $\text{cm}^{-1}$  左右均出现单取代二茂铁的特征吸收峰; 在 820  $\text{cm}^{-1}$  左右有对位取代苯的特征峰, 1625  $\text{cm}^{-1}$  左右为  $\text{CH}=\text{N}$  的伸缩振动峰; 系列 II 化合物在 1730, 1270  $\text{cm}^{-1}$  左右出现两个强的吸收峰, 表明有酯基的存在。在  $^1\text{H}$  NMR 谱中, 两系列化合物  $\text{CH}=\text{N}$  中质子峰出现在 8.5 左右; 未取代茂环的质子化学位移在 4.0 左右, 而单取代环茂的质子化学位移在 4.3 ~ 4.7; 所有苯环的偶合情况均表现出对位取代的特征, 为两组双重峰, 其化学位移值也在合理的范围; 另外, 烷氧基尾链的波谱也符合其应有特征。

### 2.2 化合物的介晶性

按传统的液晶结构理论, 棒状分子的液晶性与分子的长宽比有关, 一般要求大于 4。在本文中, 通过 DSC 和偏光显微镜研究结果显示, 尽管系列 I 化

合物的末端 C 原子数从 2 增加到 16, 长宽比逐渐增加, 按照 CPK 分子模型,  $n = 10$  时, 分子长宽比已大于 4, 仍未出现介晶相。这可能是对于棒状液晶分子而言, 除要求一定的长宽比外, 我们进而观察到分子的刚性部分 (Rigid Core, 指分子中对位取代苯环通过中心桥键相连接起来的部分) 的长度与分子宽度之比对介晶性有重要影响, 这一点在过去的文献中被忽视了, 该系列化合物没有介晶性是由于其刚性部分还不够长和不够刚性所致。因此对于这类化合物, 只是分子长径比达到要求还不足以产生介晶性。表 1 中列出了各系列化合物的相变温度和焓变。

系列 II 化合物均出现介晶相。与系列 I 比较, 系列 II 化合物分子中增加了一个中心桥键酯基和一个苯环, 显然分子的刚性部分增长了。这说明刚性部

分长度对介晶相产生的影响。虽然化合物 11 ( $n=2$ ) 的末端尾链较短, 但它不仅有介晶性, 而且介晶相温度范围却还宽, 因此对该类化合物而言, 分子中刚性部分长度比尾链长度对介晶性贡献更明显: 刚性部分长度不够时, 即便尾链长度较长, 也不具有介晶性; 刚性部分达到一定长度时, 才可能出现介晶相, 此时尾链长度的影响不明显。这主要是因为二茂铁体积较大, 较长的刚性部分可以起到平衡作用, 更有利于分子的排列和取向, 有利于液晶相的生成。当然, 引入的中心桥键酯基也会改变分子间的相互作用, 对诱导介晶相的形成也有重要的影响。图 1 中列出了系列 II 化合物末端碳原子数与相变温度的关系。典型化合物液晶织构图见图 2。

表 1 系列 I (4~10) 和系列 II (11~18) 化合物相变温度和焓变<sup>a</sup>

Table 1 Temperature for phase transformation and enthalpy transition of compounds 4~18

化合物系列 I	相变 (C—I) <i>t</i> /	焓变 <i>H</i> /(kJ·mol <sup>-1</sup> )	化合物系列 II	相变	<i>t</i> /	焓变 <i>H</i> /(kJ·mol <sup>-1</sup> )	介晶相温度范围	
							—	11
4	173.38	-9.24	12	C—I	217.58	49.68	15.38	(单变)
	185.8	29.06		I—M	202.2	-2.23		
5	145.40	3.13	13	M—C	171.46	-40.06	1.19	
	148.69	40.83		C—M	190.43	32.65		
6	140.72	42.76	14	M—I	193.62	0.80	6.77	
				C—M	176.67	34.98		
7	127.96	42.39	15	M—I	183.44	1.35	17.03	
				C—M	155.82	40.08		
8	107.77	34.54	16	M—I	172.85	1.22	11.31	
				C—M	152.86	35.89		
9	105.32	40.37	17	M—I	164.17	1.18	35.59	
				C—M	122.01	43.05		
10	76.70	50.27	18	M—I	157.59	1.23	30.17	
				C—M	118.58	42.82		
				M—I	148.75	1.14		

<sup>a</sup> C, 晶体; I, 各向同性液体; M, 介晶相。

n	M—I (t/°C)	C—M (t/°C)
2	235	200
4	230	195
6	210	185
8	195	175
10	185	165
12	175	155
14	165	135
16	155	105

图 1 系列 II 化合物末端碳原子数与相变温度

Figure 1 Relationship between number of carbons (*n*) and phase transformation temperature of series II compounds

图 2 化合物 18 偏光显微镜下液晶织构图 (130 , ×125)

Figure 2 Liquid crystal texture of compound 18 under polarized microscopy (130 , ×125)

系列 I 化合物不出现介晶相,但熔点随末端碳链的增长而降低,这与分子的非极性部分的增大,使分子间作用力减小有关。相关系列 II 化合物, $n=2$  是一个特殊情况(化合物 11 的尾链最短,而相变温度范围较宽)。 $n=4$ (化合物 12)到 $n=16$ 的化合物(化合物 18)呈现出一定规律性:熔点和清亮点均随碳原子数增加而降低,相变温度范围亦随之变化,当 $n=4$ 时,是单变液晶,由此尾链长度对介晶性开始起作用,随着尾链的增长,变为互变液晶,并维持一定的相变温度范围。当 $n$ 由 14 到 16 时,相变温度范围有所加大,尾链作用稍显突出,这可能是熔点下降较清亮点下降更快所致。这些都符合液晶分子结构与介晶性关系规律。

本文采用简便、有效的合成方法,设计、合成了分子中刚性部分长度不同的两个系列单取代二茂铁化合物。DSC 和偏光显微镜研究结果显示系列 I 化合物不具有液晶性,系列 II 化合物在较窄的温度区间出现介晶相,观察到了分子刚性部分长度对介晶性的重要影响。随着末端碳原子数的增加,熔点和清亮点均呈下降趋势。这些结果为进一步研究二茂铁液晶材料分子结构与介晶性的关系,以及设计、合成二茂铁实用液晶提供了一点素材。

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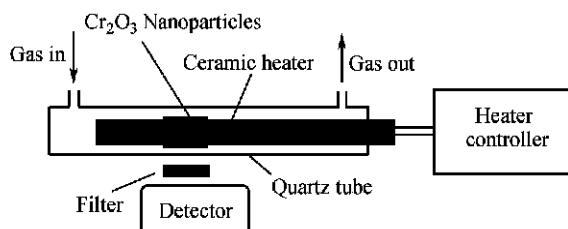
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**Study of Cataluminescence Characteristics of NH<sub>3</sub> on the Surface of Nanosized Materials**

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*Acta Chimica Sinica* 2002, 60(9), 1668



Schematic illustration of the detection system.

**Spectrofluorimetric Analysis Combined with Microdialysis Sampling for Studying Binding of Thioguanine to Protein**

WANG, Chang; LU, Jia-Gen; ZHANG, ZhuJun

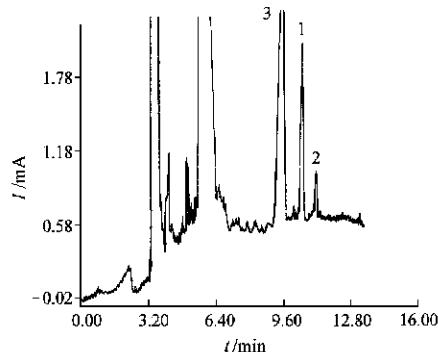
*Acta Chimica Sinica* 2002, 60(9), 1672

The binding of thioguanine ( $\delta$ -TG) to bovine serum albumin was studied using the technique of microdialysis combined with spectrofluorimetric analysis. In the presence of NaOH,  $\delta$ -TG can be oxidized by KMnO<sub>4</sub> to 2-amino- $\delta$ -guanine sulfate acid, which produces higher fluorescence emission. The estimated association constant ( $K$ ) and the number of the binding sites ( $n$ ) on one of BSA were  $1.02 \times 10^{-4}$  (mol L<sup>-1</sup>)<sup>-1</sup> and 1.63 (Scatchard equation), respectively.

**Determination of Excitatory Amino Acids in Cerebrospinal Fluid Following Cerebral Injury by Capillary Electrophoresis**

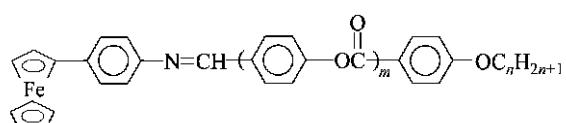
LU, HaoJie; GUO, YinLong; LIANG, Bing; OU, Qing Yu

*Acta Chimica Sinica* 2002, 60(9), 1677



Analysis of excitatory amino acids in cerebrospinal fluid following cerebral injury was achieved by capillary electrophoresis. The limitation of detection was less than  $1.7 \times 10^{-7}$  mol/L under the optimum conditions with benzene carboxylic acid as an internal standard. The reproducibility was also satisfactory with the relative standard deviation less than 2 %.

**Synthesis and Mesogenic Behavior Studies of Monosubstituted Ferrocene-containing Schiff Base Liquid Crystals**



$m = 0, 1; n = 2, 4, 6, 8, 10, 12, 14, 16$

HU, Ping; ZHAO, KeQing; XU, HongBo; ZHANG, LiangFu

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