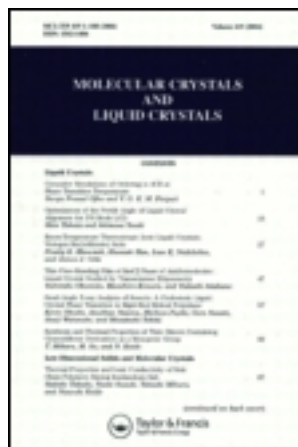


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Spin Transition Induced by Mesophase Transition in the Cobalt(II) Compounds with Branched Alkyl Chains

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Cobalt(II) compounds [Co(C10C8C2-terpy)](BF₄)₂ (1) and [Co(C12C10C2-terpy)](BF₄)₂ (2) (C_xC_yC_z-terpy = 4'-5'''-Alkyl-1'''-alkoxy-2,2':6',2''-terpyridine) with branched alkyl chains, based on a terpyridine frame, was synthesized. The cobalt(II) compounds 1 and 2 exhibit the spin transition between low-spin and high-spin with thermal hysteresis loop at the liquid crystal transition temperature (T_{1/2}↑ = 275 K and T_{1/2}↓ = 250 K for 1 and T_{1/2}↑ = 307 K and T_{1/2}↓ = 296 K for 2), and the spin transition is induced by crystal-mesophase transition. The bifunctional materials show synchronizing both spin transition and liquid crystal transition.

Keywords: cobalt(II) complex; coupled phase transition; metallomesogen; spin transition

I. INTRODUCTION

Liquid crystals are fascinating functional materials, and are important in the field of advanced materials such as electro optic devices. Organic liquid crystals are diamagnetic and can be easily oriented by an electric field. Liquid crystals of transition metal complexes,

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called *metallomesogens*, have attracted a great deal of attention at a point of view of multi-functionality [1]. The development of *metallomesogens* with multi-functions (spin-crossover, mixed-valence, magnetism, conductivity etc.) is very important in order to achieve the co-occurrence of various physical properties in the functional molecular-based materials.

The spin-crossover (SCO) phenomenon occurs when transforming between high-spin (HS) and low-spin (LS) states reversibly, stimulated by external perturbations (e.g., temperature, pressure, magnetic field or light) [2]. Galyametdinov *et al.* reported such a SCO iron(III) compound ($S = 1/2 \leftrightarrow S = 5/2$) with liquid-crystal properties [3]. This compound consists of an iron(III) ion coordinated to Schiff-base ligands with long alkyl chains, and exhibits a rod-like geometry. The SCO behavior was gradual in the temperature range of 50 K – 300 K, and the smectic A mesophase was observed between 380 K and 418 K. We have also observed a photo-induced spin transition (LIESST effect) below about 60 K in the SCO iron(II) compounds, which displays the mesophase above about 350 K [4–6]. The development of novel compounds exhibiting LIESST is one of the main challenges in this field. It may be possible that both the SCO and mesophase transition can be synchronized. Fujigaya *et al.* have reported a one-dimensional iron(II) compound with triazole derivatives, which exhibits SCO and liquid-crystal behavior in the same temperature region [7,8]. However, the supposed mesomorphism of the complexes has not been confirmed. Gaspar *et al.* have been investigating the possibility of synchronizing both transitions in the iron(II) complexes which are 1-D compounds based on triazole ligands [9–11]. They have reported that thermochromic liquid crystals operating in the room-temperature region exhibited SCO behavior in the temperature range at which the materials show a discotic columnar mesophase. Furthermore, the controlling the SCO characteristics of 1-D iron(II) compounds by an amphiphilic phase transition have also reported [12,13].

Hence, in order to develop a variety of switchable molecules which exhibit a spin transition induced by a crystal-mesophase transition, we propose the strategies as following; (i) the SCO compounds are necessary in order to transform the spin states even by subtle structural changes in the ligands or molecules, (ii) the SCO compounds with $T_{1/2}$ above room temperature are necessary because the liquid-crystal transition temperature is generally higher than room temperature for the *metallomesogens* or (iii) the liquid-crystal transition temperature should be adjusted to $T_{1/2}$ in the SCO compounds by changing the length or type of the alkyl chains. Based on the strategy (i)–(iii), we aimed at construction of the spin transition compounds which occurred

at liquid crystal transition temperature. The SCO *metallomesogens* have been investigated for only iron(II) or iron(III) compounds so far. The SCO *metallomesogens* for other metal compounds, cobalt(II) and so on, have been also interesting.

II. EXPERIMENTAL

We focused on the cobalt(II) compounds $[\text{Co}(\text{C10C8C2-terpy})_2](\text{BF}_4)_2$ (**1**) and $[\text{Co}(\text{C12C10C2-terpy})_2](\text{BF}_4)_2$ (**2**) ($\text{CxCyCz-terpy} = 4'-5'''$ -Alkyl-Alkyl-1'''-alkoxy-2,2':6',2''-terpyridine) with branched alkyl chains. The branched alkyl chains were introduced in order to down the mesophase transition temperature and synchronize the liquid-crystal and spin transition temperatures in the compounds **1** and **2** [14]. The ligand C12C10C2-terpy was synthesized by mixing 2-Decyl-1-tetradecanol (1.38 g, 3.43 mmol), 2,6-bis(2-pyridyl)-4(1H)-pyridone(0.57 g, 2.29 mmol) and K_2CO_3 (0.63 g, 4.58 mmol) in DMF (70 ml) at 80°C for 12 h. The ligand C10C8C2-terpy was also synthesized by the same method. The compounds **1** and **2** were obtained as brown powder by reacting $\text{Co}(\text{BF}_4)_2$ with the ligands, and the compositions for **1** and **2** were confirmed by elemental analysis. Anal. Calcd. for $\text{C}_{70}\text{H}_{102}\text{N}_6\text{O}_2\text{B}_2\text{F}_8\text{Co}_1$ (**1**): C, 65.07 H, 7.96 N, 6.50. Found: C, 65.23 H, 8.02 N, 6.73. Anal. Calcd. for $\text{C}_{78}\text{H}_{118}\text{N}_6\text{O}_2\text{B}_2\text{F}_8\text{Co}_1$ (**2**): C, 66.71 H, 8.47 N, 5.98. Found: C, 66.83 H, 8.72 N, 5.73. A rod-like geometry is proposed for the molecular structure of **1** and **2** (Fig. 1).

III. RESULTS AND DISCUSSION

Liquid-crystalline properties for **1** and **2** were confirmed by powder X-ray diffraction (XRD), and polarizing optical microscopy (POM).

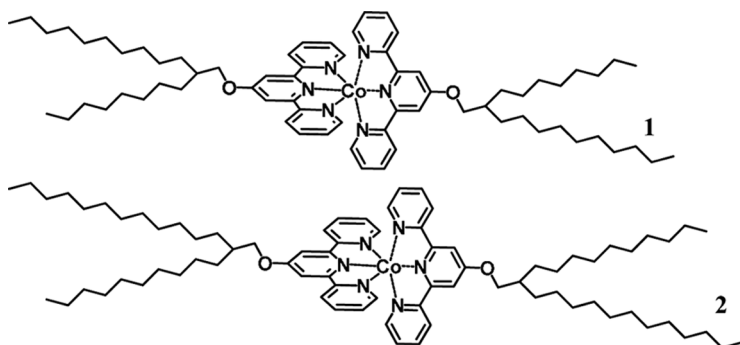


FIGURE 1 Chemical structures of the cations in **1** and **2**.

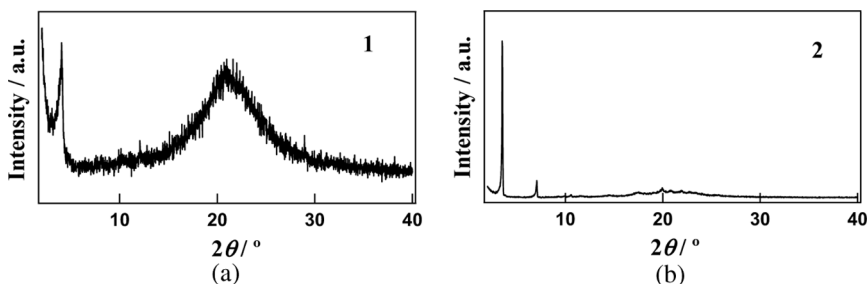


FIGURE 2 Powder XRD patterns for **1** at 300 K and **2** at 400 K.

Powder XRD measurements for **1** and **2** were carried out to confirm this mesophase. Figure 2 (**1**) shows the XRD pattern of the mesophase state observed at 300 K. The pattern displays a diffuse and broad scattering halo, centered at 4.2 \AA ($2\theta = 21.0^\circ$) in the wide-angle region, and indicative of a liquid-like order of the aliphatic chains and thus of the fluid-like nature of the phase. In the small-angle region, the XRD pattern displayed the reflections of a lamellar phase with a periodicity $d = 21.9 \text{ \AA}$ ($2\theta = 4.0^\circ$). Figure 2 (**2**) shows the XRD pattern of the mesophase state observed at 470 K. The pattern displays a diffuse and broad scattering halo, centered at 4.4 \AA ($2\theta = 20.0^\circ$) in the wide-angle region, and indicative of a liquid-like order of the aliphatic chains and thus of the fluid-like nature of the phase. In the small-angle region, the XRD pattern displayed the reflections of a lamellar phase with a periodicity $d = 25.1 \text{ \AA}$ ($2\theta = 3.5^\circ$).

The textures of **2** at 310 K and 350 K are shown in Figures 3(a) and (b), and a typical fan-shaped texture was observed at 350 K. For **2**, the assigning the mesophase M_1 was difficult. On the other hand,

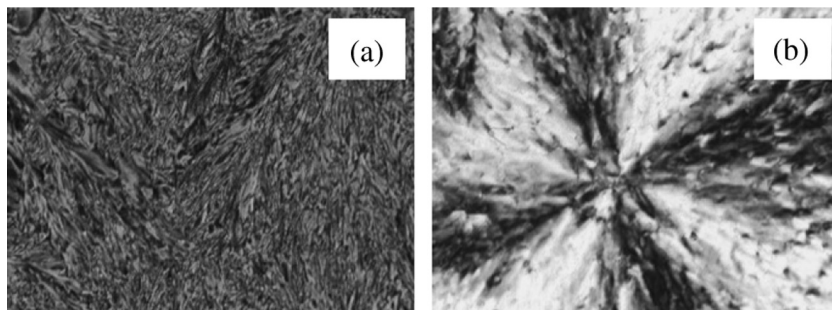


FIGURE 3 The textures of **2** at 310 K (a) and 350 K (b).

the mesophase M_2 was identified as a smectic A (SmA) mesophase based on the texture observed by POM and the powder XRD pattern.

Spin transition between the high-spin and low-spin states for **1** and **2** was followed by measurements of the molar magnetic susceptibility χ_m as a function of temperature (Fig. 4). The $\chi_m T$ value for **1** is equal to $0.53 \text{ cm}^3 \text{ Kmol}^{-1}$ at 5 K, which is in the range of values expected for LS cobalt(II) ions. As the temperature is increased from 5 K, the $\chi_m T$ product remained practically constant from 5 K to 80 K, then abruptly increased around $T_{1/2\uparrow} = 275 \text{ K}$. The $\chi_m T$ value at 400 K was $1.80 \text{ cm}^3 \text{ Kmol}^{-1}$, showing that the spin transition from the LS to the HS state was induced. The spin transition is directly related to the mesophase transition. On cooling, the $\chi_m T$ value for **1** was decrease gradually from 400 K to 300 K, then abruptly dropped at around $T_{1/2\downarrow} = 250 \text{ K}$, showing that the HS moieties were restored to the LS state with hysteresis loop ($\Delta T = 25 \text{ K}$). Additional thermal cycles did not modify the thermal hysteresis loop. The $\chi_m T$ value for **2** is equal to $0.52 \text{ cm}^3 \text{ Kmol}^{-1}$ at 5 K, which is in the range of values expected for LS cobalt(II) ions. As the temperature is increased from 5 K, the $\chi_m T$ product remained practically constant from 5 K to 70 K, then abruptly increased around $T_{1/2\uparrow} = 307 \text{ K}$. The $\chi_m T$ value at 400 K was $1.95 \text{ cm}^3 \text{ Kmol}^{-1}$, showing that the spin transition from the LS to the HS state was induced. The spin transition is also directly related to the mesophase transition. On cooling, the $\chi_m T$ value for **2** was decrease gradually from 400 K to 310 K, then abruptly dropped at

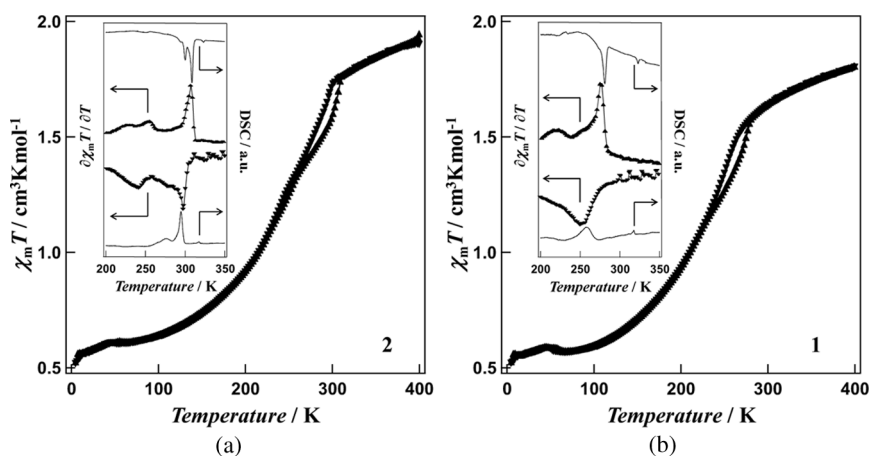


FIGURE 4 $\chi_m T$ versus T plots (\blacktriangle : heating mode, and \blacktriangledown : cooling mode) for **1** and **2**. The insert graph shows the derivative $\partial\chi_m T/\partial T$ plot as a function of the temperature.

TABLE 1 Phase Transition Temperatures of **1** and **2**

Compound	Phase $\xrightarrow{T/K}$ Phase						
1	K_1	$\xrightarrow{275K}$	M_1	$\xrightarrow{323K}$	SmA	$\xrightarrow{479K}$	I.L.
2	K_1	$\xrightarrow{298K}$	K_2	$\xrightarrow{307K}$	M_1	$\xrightarrow{323K}$	SmA $\xrightarrow{453K}$ I.L.

Phase nomenclature: K = crystal, I.L. = isotropic liquid, M_1 = unknown mesophase, SmA = smectic A mesophase.

around $T_{1/2\downarrow} = 296$ K, showing that the HS moieties were restored to the LS state with hysteresis loop ($\Delta T = 11$ K). Additional thermal cycles did not modify the thermal hysteresis loop.

Phase transition temperatures for **1** and **2** obtained by differential scanning calorimetry (DSC) measurements are summarized in Table 1. The DSC analysis showed that unknown two mesophases, M_1 and M_2 , were included in the compound **1**. On heating, the crystal K_1 phase transforms to the M_1 phase at 275 K, and transforms from M_1 phase to the M_2 (smectic A: SmA) phase at 323 K. Further heating, the mesophase-to-isotropic liquid transition temperature for **1** was observed at 479 K. On the other hand, the polymorphism includes two crystal forms K_1 and K_2 , and two mesophase M_1 and M_2 in the compound **2** [15]. On heating, the crystal K_1 phase transforms to the K_2 phase at 298 K, and transforms from K_2 phase to the unknown M_1 phase at 307 K. Further heating, the M_1 phase transforms to the M_2 (SmA) phase at 323 K. The mesophase-to-isotropic liquid transition temperature for **2** was observed at 453 K. The complicated phase transition and relaxation behavior can be rationally explained by using the G-T diagram (Fig. 5) [16].

The insert of Figures 4(a) and (b) shows the extreme of the derivative $\partial\chi_m T/\partial T$ in the spin transition behavior and DSC curves measured at scan rate the same as magnetic measurement (2 Kmin^{-1}) for **1** and **2**. The extremes of the derivative $\partial\chi_m T/\partial T$ agree with the peaks in DSC curves. On heating, the spin transition temperature was observed at 275 K for **1** and at 307 K for **2**, and the temperature agrees with crystal-to-mesophase transition temperature. On the other hand, the extremes of the derivative $\partial\chi_m T/\partial T$ were observed at 250 K for **1** and 296 K for **2** on cooling, and the mesophase-to-crystal transitions occur in the same temperature range. It has been known that the cobalt(II) compounds with terpy derivative ligands exhibit gradual SCO behavior between $S = 1/2$ and $S = 3/2$ [17–20]. Therefore, it has been thought that the LS specie transforms to HS species induced by crystal-mesophase transition. These results demonstrate that the spin transitions for **1** and **2** are triggered by crystal-mesophase transition.

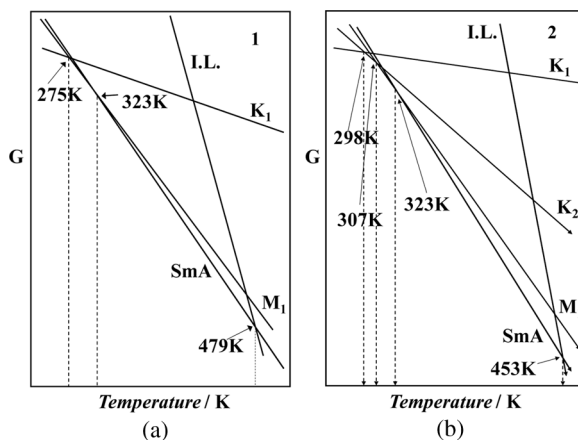


FIGURE 5 Schematic free energy versus temperature (G-T) diagram of **1** and **2**.

IV. CONCLUSION

In summary, we have succeeded in synchronizing mesophase and spin transitions for the cobalt(II) compounds $[\text{Co}(\text{C}8\text{C}6\text{C}2\text{-terpy})_2](\text{BF}_4)_2$ (**1**), $[\text{Co}(\text{C}10\text{C}8\text{C}2\text{-terpy})_2](\text{BF}_4)_2$ (**2**), and $[\text{Co}(\text{C}12\text{C}10\text{C}2\text{-terpy})_2](\text{BF}_4)_2$ (**3**) by using branched alkyl chains in the ligand around room temperature. In this way, the phenomenon that one phase transition causes another phase transition is very interesting, and will become important in future in the field of materials science. Furthermore, metallo-mesogens with multi functions will play an important role in the field of materials science in next generation.

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