Spin-crossover Transition in a Mesophase Iron(II) Thiocyanate Complex Chelated with 4-Hexadecyl-*N*-(2-pyridylmethylene)aniline

Yuya Oso and Takayuki Ishida*

Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182-8585

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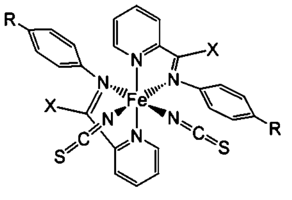
The title compound was a high-spin molecule for a morph as synthesized but exhibited a spin-crossover transition at 176 K in its mesophase after annealing above the mesophase transition at 353 K. The hexyl derivative in place of the hexadecyl group showed a reversible spin-crossover at 117 K, while the unsubstituted derivative had a sturdy high-spin state.

Spin-crossover (SCO) phenomenon is a reversible low-spin/high-spin transition by external stimuli such as heat.[1] We often find SCO in iron(II) compounds with an FeN_6 octahedral configuration.[2] Bistability with a wide thermal hysteresis, hopefully near room temperature, is a key to future applications to memories and displays.[3] Multifunctional materials are of increasing interest,[4] including liquid-crystalline SCO materials.[4,5] We have recently reported that $[Fe^{II}(L_{py})_2(NCS)_2]$ showed a very wide irreversible thermal loop (L_{py} = 4-alkyl-*N*-(di-2-pyridylmethylene)anilines, Chart 1), when long alkyl chains were introduced ($\Delta T_C = 90$ K for R = n-$C_{16}H_{33}$).[6] This system seems versatile, as shown by the present results on a simplified family $[Fe^{II}(L_H)_2(NCS)_2]$ (L_H = 4-alkyl-*N*-(2-pyridylmethylene)anilines). After being annealed, a derivative with R = n-$C_{16}H_{33}$ has a low-spin state stabilized (this work), whereas the corresponding L_{py} derivative a high-spin state stabilized.[6]

Ligands (L_H) were easily prepared from condensation of 2-formylpyridine with alkylanilines.[6–8] The complexation of iron(II) thiocyanate with L_H was conducted with a molar ratio of 1/2 in methanol under a nitrogen atmosphere, according to a method similar to that of known **1**.[7] The products were characterized by means of elemental analysis and spectroscopic methods.[9] The specimens did not involve any solvated molecules. The IR spectrum showed absorptions characteristic of N-bonded thiocyanates.[7] The molecular structure is plausibly assumed as illustrated in Chart 1, where the thiocyanates are located at a cis position like analogous compounds.[6,10]

Magnetic study of powder specimens on a SQUID magnetometer revealed that **1** almost had a high-spin state ($S = 2$) down to 10 K, being compatible with the previous report.[7] On the other hand, **2** exhibited SCO behavior ($S = 0 \rightarrow S = 2$) at $T_{1/2} = 117$ K on heating (Figure 1a). Cooling from 400 K showed the inverse transition without any hysteresis. The data on repeated measurements traced the same curve.



$[Fe(L_{py})_2(NCS)_2]$: X = 2-pyridyl
$[Fe(L_H)_2(NCS)_2]$: X = H
1 : X = H, R = H
2 : X = H, R = n-C_6H_{13}
3 : X = H, R = n-$C_{16}H_{33}$

Chart 1. Molecular structures for $[Fe(L_X)_2(NCS)_2]$ (X = py and H).

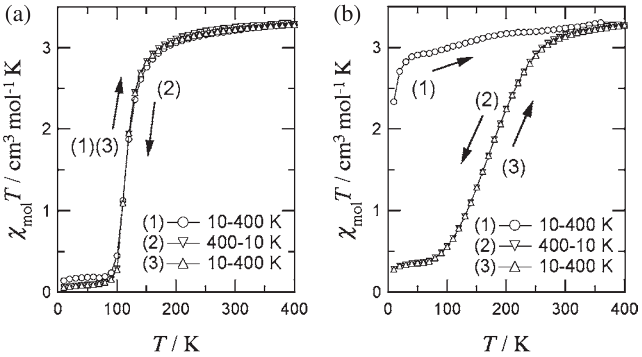


Figure 1. The $\chi_{mol}T$ vs. T plots for (a) **2** and (b) **3**. Temperature scan sequences are denoted with arrows. A static filed of 5000 Oe was applied.

More interestingly, a thermal irreversible curve was drawn in a similar experiment on **3** (Figure 1b). The first heating run did not show any spin transition. After **3** was heated to 400 K and then cooled, clear SCO behavior was observed around $T_{1/2} = 176$ K. Once the SCO appeared, repeated experiments reproduced the SCO.

The elemental and spectral analyses of the specimen of **3** recovered from the above magnetic study clarified no decomposition below 400 K.[9] The thermogravimetry of **3** supported the absence of any solvated molecule in the as-synthesized form.

A phase transition was found to occur at 353 K for **3**, as indicated by an intense and irreversible exothermic peak in differential scanning calorimetry (DSC; Figure 2a). Another peak was found at 413 K and attributed to a melting point. To clarify the character of these phases, we measured the temperature-variable powder X-ray diffraction (XRD) of **3** (Figure 2b). The XRD profiles were drastically changed across 353 K; many diffractions found at room temperature (296 K) disappeared at 370 K. Instead, new diffractions appeared at $2\theta = 3.48$ and $6.84°$, corresponding to an interlayer distance of 12.7 Å. This feature implies that this specimen is in a mesophase such as a liquid-crystalline state. The XRD profile remained almost the same after cooling down to room temperature, supporting that the mesophase transition is irreversible. When the specimen was heated again to 420 K, the diffractions completely disappeared in the XRD.

As illustrated in the G vs. T diagram (Figure 3), the irreversible phase transition of **3** is attributed to a supercooling of the mesophase, where we named the phases as S (a crystalline solid), M (a mesophase), and L (an isotropic liquid). A mesophase transition temperature is denoted as T_m. The thermal cycle of **3** (Figure 1b) is interpreted as: $S_{hs} \rightarrow (T_m) \rightarrow M_{hs}$ on heating and $M_{hs} \rightarrow (T_m) \rightarrow M_{hs} \rightarrow (T_{1/2}) \rightarrow M_{ls}$ on cooling.

In general, a solid phase possesses tighter molecular packing, a stronger ligand-field, and accordingly a lower-lying low-spin state than a mesophase does. The present result of **3** appa-

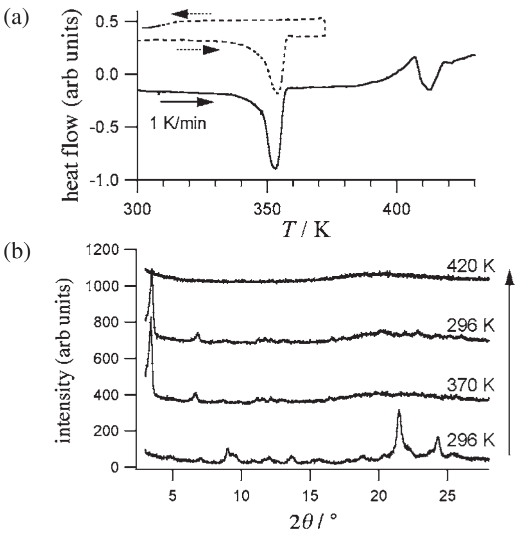


Figure 2. (a) DSC measurements on as-synthesized specimens of **3**. A small thermal cycle is shown with a dotted line. (b) The XRD profiles sequentially measured at 296, 370, 296, and 420 K.

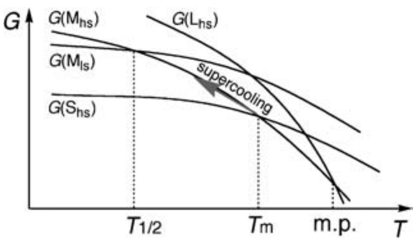


Figure 3. Free energy diagram for **3**.

rently violates this trend. A possible explanation is that the arrangement of the alkyl chains during annealing might settle down into a coordination sphere that is conducive to the SCO. The displacement of the alkyl groups is rather drastic (Figure 2), leading to facile supercooling.

Kahn and co-workers introduced R = Ph and PhC_2 in L_H (Chart 1) and improved thermal hysteresis.[11] While such rigid aromatic groups increase intermolecular interaction and SCO hysteresis widths, long alkyl chains have been proven to be useful as well for development of wide thermal loops. Very recently Gütlich et al. proposed three categories with respect to coupled or uncoupled systems between SCO and liquid-crystalline phase transitions.[12] They intensively studied metallomesogens where the mesophase transition was highly reversible.[12,13] On the other hand, **3** exhibited an irreversible mesophase transition, thus forming a new class of bistable magnetic materials. A potential utility might be, for instance, a write-once information storage medium.

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8 L_H (R = n-C_6H_{13}): ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.71 (ddd, J = 4.9, 1.6, 0.8 Hz, 1H), 8.63 (s, 1H), 8.20 (ddd, J = 8.1, 1.1, 0.8 Hz, 1H), 7.80 (ddd, J = 8.1, 7.6, 1.6 Hz, 1H), 7.35 (ddd, J = 7.6, 4.9, 1.1 Hz, 1H), 7.25–7.22 (m, 4H), 2.63 (t, J = 7.6 Hz, 2H), 1.63 (quint, J = 7.6 Hz, 2H), 1.32 (brs, 6H), 0.89 (t, J = 6.2 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 159.61, 154.78, 149.64, 148.43, 141.89, 136.60, 129.18, 124.93, 121.75, 121.10, 35.54, 31.70, 31.42, 29.96, 22.58, 14.07. L_H (R = n-$C_{16}H_{33}$): Mp 45–46 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.72 (ddd, J = 4.9, 1.6, 0.8 Hz, 1H), 8.63 (s, 1H), 8.21 (ddd, J = 8.4, 1.1, 0.8 Hz, 1H), 7.81 (ddd, J = 8.4, 7.6, 1.6 Hz, 1H), 7.35 (ddd, J = 7.6, 4.9, 1.1 Hz, 1H), 7.25–7.23 (m, 4H), 2.63 (t, J = 7.6 Hz, 2H), 1.59 (quint, J = 7.6 Hz, 2H), 1.26 (brs, 26H), 0.88 (t, J = 6.5 Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 159.61, 154.79, 149.65, 148.44, 141.90, 136.60, 129.18, 124.93, 121.76, 121.10, 35.55, 31.91, 31.47, 29.68 (3C), 29.64 (2C), 29.62 (2C), 29.59, 29.51, 29.35, 29.31, 22.67, 14.11.

9 **2**: Mp 421 °C (DSC). Anal. Calcd for $C_{38}H_{44}FeN_6S_2$: C, 64.76; H, 6.29; N, 11.92; S, 9.10%. Found: C, 64.45; H, 6.51; N, 11.61; S, 9.33%. IR (KBr disk): 2925, 2854, 2058, 1502, 1441 cm^{-1}. **3** (as-synthesized): Mp 413 °C (DSC). Anal. Calcd for $C_{58}H_{84}FeN_6S_2$: C, 70.70; H, 8.59; N, 8.53; S, 6.51%. Found: C, 70.41; H, 8.81; N, 8.28; S, 6.48%. IR (KBr disk): 2918, 2850, 2360, 2332, 2060, 1506 cm^{-1}. **3** (after-annealing): Anal. Found: C, 70.72; H, 8.34; N, 8.32; S, 6.70%.

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