LIESST Effect and Cooperativity of a 2-D Hofmann-type Compound

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2-D Hofmann-type compound [Fe(4-phpy)$_2$Ni(CN)$_4$]•H$_2$O (4-phpy = 4-phenylpyridine) was synthesized and characterized by magnetic susceptibility measurements. The compound exhibited spin-crossover behavior with thermal hysteresis loop and LIESST effect. The activation energy and the tunneling rate constant were estimated as $E_a = 773\,(\mathrm{cm}^{-1})$ and $k_{\mathrm{HL}}(T\rightarrow 0) = 4.51 \times 10^{-6}\,(\mathrm{s}^{-1})$ for the compound.

Spin-crossover (SCO) compounds are one of the representative examples of molecular bistability. The high-spin (HS) and low-spin (LS) states in SCO compounds are interconvertible by several different physical perturbations such as thermal, pressure and light irradiation.[1] While SCO behavior is essentially a phenomenon of a single molecule, the intermolecular interactions in SCO compounds are an important factor to govern SCO properties such as the abruptness of the spin transition with hysteresis and LIESST (light-induced exited spin state trapping) effect, which are important properties for applications such as information storage, molecular switching, and visual display. From this viewpoint, the synthetic design of SCO compounds exhibiting interactions between spin transition sites is of current interest. Along this line, polymeric SCO compounds with bridging ligands and mononuclear SCO compounds exhibiting intermolecular interactions such as hydrogen bonding or π–π stacking have been extensively investigated.[2] In dimensional SCO compounds, 2-D and 3-D SCO Hofmann-type compounds were reported by Kitazawa et al. and Real et al.[3]

Hence, in order to develop a variety of optically switchable molecular solids, one of the strategies to prevent such a rapid relaxation from a metastable state to a ground state is the introduction of dimensionality in molecular compounds. It is thought that the cooperativity resulting from the dimensionality operates to increase the activation energy for the relaxation processes, enabling the observation of a long-lived metastable state after illumination. Here, we report the LIESST effect for 2-D Hofmann-type SCO compound [Fe(4-phpy)$_2$Ni(CN)$_4$]•H$_2$O (**1**) (4-phpy = 4-phenylpyridine) (Figure 1).[4]

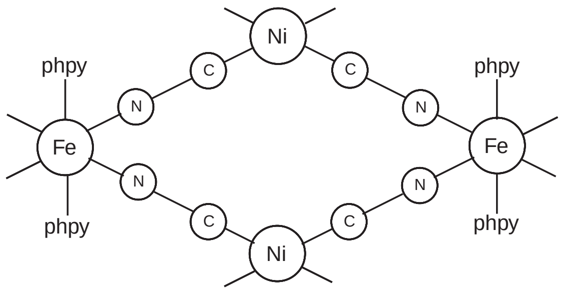

Figure 1. Perspective view of the 2-D Hofmann-like structure for **1**.

Magnetic properties show that the value of $\chi_m T$ (μ_{eff} value) for **1** at room temperature is equal to $3.59\,\mathrm{cm}^3\,\mathrm{K\,mol}^{-1}$ (5.36 BM), which corresponds to what is expected for the high-spin state in iron(II) compounds (Figure 2). On cooling, the value of $\chi_m T$ drops abruptly around $T_{1/2}\downarrow = 134\,\mathrm{K}$. The $\chi_m T$ value at 60 K is equal to $1.02\,\mathrm{cm}^3\,\mathrm{K\,mol}^{-1}$ (2.86 BM), representing the low-spin state. On heating, an abrupt variation of $\chi_m T$ was observed around $T_{1/2}\uparrow = 143\,\mathrm{K}$. Fairly abrupt transition with a hysteresis loop ($\Delta T = 9\,\mathrm{K}$) shows the presence of strong cooperative interaction. The magnetic behavior after light irradiation was recorded for compound **1** in order to investigate photomagnetic properties. A green laser ($\lambda = 532\,\mathrm{nm}$, 150 mW) was used as a light source in the investigation of illumination effects. The light was guided via an optical fiber into the SQUID. The sample was placed over the edge of the optical fiber. When the sample was illuminated at 5 K, an increase in the dc susceptibility was observed for **1** (Figure 2). The change in the magnetization persisted for many hours, even after the illumination was stopped. This increase suggests that the transition from the LS state to the HS state was induced by the illumination. This fact suggests that SCO compound **1** exhibited LIESST effect. As Létard et al. have reported photomagnetic properties, the temperature dependence of $\chi_m T$ after irradiation shows that the magnetization decreases with the increase in temperature and that the relaxation to the ground state occurs with $T(\mathrm{LIESST}) = 64\,\mathrm{K}$ for **1**.[5]

The dynamics of the HS → LS relaxation was investigated over the temperature range 10–65 K. The decay of the HS molar fraction γ_{HS} vs. time at various temperatures was measured.[6]

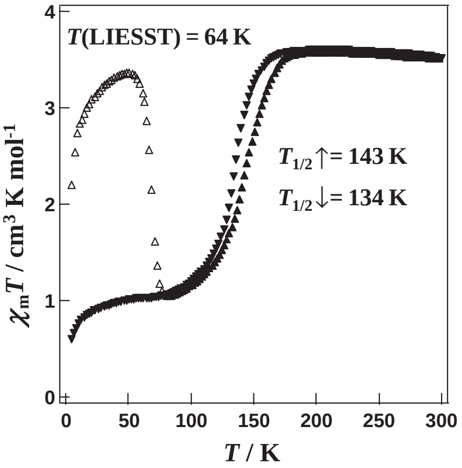

Figure 2. $\chi_m T$ vs. T plots for **1**. Sample was cooled from 300 to 5 K (▼) and then warmed from 5 to 300 K (▲) at a rate of $2\,\mathrm{K\,min}^{-1}$. Sample was warmed at a rate of $2\,\mathrm{K\,min}^{-1}$ after irradiated at 5 K (△).

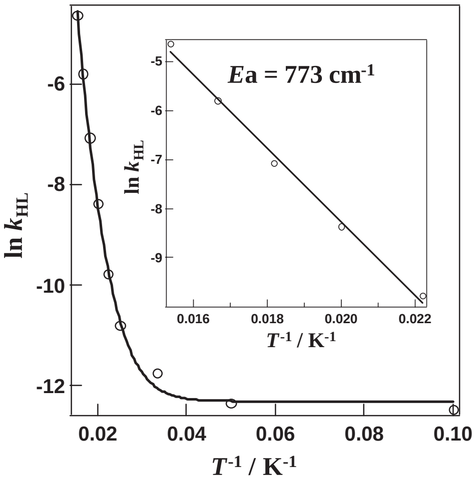

Figure 3. ln $k_{HL}(T)$ vs. $1/T$ curve for **1**. The solid line shows Huang–Rhys factor $S = 44.1$. The insert graph shows Arrhenius plots for $T \geq 45$ K.

The HS → LS rate constant k_{HL} was determined by fitting the data according to the expression: $\gamma_{HS} = \exp[k_{HL}(T)t]$. Figure 3 presents the $\ln[k_{HL}(T)]$ vs. $1/T$ plots for **1**. A thermally activated relaxation behavior at elevated temperatures and a nearly temperature-independent relaxation behavior at low temperatures can be observed. For $T \geq 45$ K, the $\ln[k_{HL}(T)]$ vs. $1/T$ plot gives a straight line and can be satisfactorily fitted to an Arrhenius plot with $E_a = 773\,\text{cm}^{-1}$. For $T \leq 40$ K, the $\ln[k_{HL}(T)]$ vs. $1/T$ plot gives a straight line with a zero slope, and the tunneling region for **1** can be observed below 40 K with a tunneling rate smaller than $k_{HL}(T \rightarrow 0) = 4.51 \times 10^{-6}\,\text{s}^{-1}$. In compound **1** the $k_{HL}(T \rightarrow 0)$ value is in the range of those for iron(II) SCO compounds (10^{-5}–$10^{-10}\,\text{s}^{-1}$).[7] Furthermore, Huang–Rhys factor S parameter is for the horizontal displacement of the potential wells of the two spin states.[8] The S values estimated with $S = 44.1$ for **1** and are in good agreement with what is expected for iron(II) SCO compounds.

The relationship between LIESST effect and cooperativity is important in order to understand the LIESST effect for **1** such as 2-D and 3-D SCO Hofmann-type compounds. The first work based on a comparison of T(LIESST) temperatures was made by Létard et al. In this study, the magnetic and the photomagnetic properties of SCO compounds were determined; that is, the thermal spin transition $T_{1/2}$ as well as the T(LIESST) temperatures. They proposed a general equation, $T(\text{LIESST}) = T_0 - 0.3T_{1/2}$ for the LIESST compounds and suggested that the different T_0's depend on the chemical nature of the ligand involved in the inner coordination sphere; $T_0 = 100$, 120, 150, 180, and 200 K for monodentate (FeL_6), bidentate (FeL_3), tridentate (FeL_2), macrocyclic ligands, and Prussian blue analogous, respectively.[9] Compound **1** exhibited SCO at $T_{1/2}\downarrow = 134$ K and $T_{1/2}\uparrow = 143$, and LIESST at $T(\text{LIESST}) = 64$ K. The values for **1** are located in the $T_0 = 100$ line for monodentate mononuclear compounds in spite of being a 2-D compound. Compound **1** forms 2-D and exhibits abrupt SCO with hysteresis loop. It is thought that there is a strong interaction between the SCO centers in **1**. On the other hand, it is thought that compound **1** behaves as a monodentate mononuclear compound in the relationship of the $T_{1/2}$ and T(LIESST) because the iron(II) ions and the nickel(II) ions are arranged in alternation, and the nickel(II) ions play a role of dilution matrix.

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4 To prepare **1**, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (0.80 g, 2 mmol) and 4-phenylpyridine (0.62 g, 5.15 mmol) were solved in the 10-mL mixture of $CH_3OH:H_2O = 1:1$, and added a little ascorbic acid for avoiding oxidation of Fe^{II}. In addition, $K_2[Ni(CN)_4] \cdot H_2O$ (0.53 g, 2 mmol) in water (10 mL) was dropped to the mixture and stirred for 1 h at room temperature. Then, yellow powder of **1** was gained (yield: 0.89 g). Anal. Calcd for $C_{26}H_{20}N_6O_1Fe_1Ni_1$: C, 57.03; H, 3.69; N, 15.36%. Found: C, 56.65; H, 3.40; N, 15.42%.

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