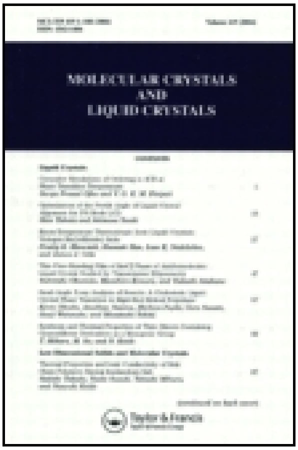

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Hetero Metal Spin-Crossover Complex with LIESST Iron(II) Building Block

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Hetero Metal Spin-Crossover Complex with LIESST Iron(II) Building Block

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LIESST iron(II) spin-crossover mononuclear complex $[Fe(L)(CN)_2]\bullet H_2O$ (**1**) (L is Schiff-base macrocyclic ligand derived from the condensation of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8- diamine) with macro ring and two CN^- bridging ligands was used as optically switchable molecular building blocks. Since the bidentate CN^- ligands in complex **1** can coordinate to other metal compounds, it is possible to build one-dimensional molecular-based photo-magnets. We have synthesized $[Fe(L)(CN)_2][Mn(hfac)_2]$ (**2**) and investigated it by using magnetic susceptibility, Mössbauer spectra and IR spectra mesurements. The complex **2** exhibits spin-crossover behavior ($T_{1/2}$=110 K) on the moieties of the iron sites.

Keywords: spin-crossover; iron(II) complex; LIESST; photo-magnet

INTRODUCTION

A number of spin-crossover iron(II) complexes have been studied. They are important in the development of electronic devices such as molecular switches. Some of them show spin transition from low-spin (S=0) to metastable high-spin (S=2) state by light irradiation at low temperature. This light-induced spin transition effect is termed LIESST (light-induced excited spin-state trapping).[1][2]

The design of photo-induced molecule-based magnet has recently been attracted great attention. Although one prominent example has been reported,[3] the rational design of the molecular photo-magnet is still a challenging issue. In order to construct novel photo-magnets in a rational way, we aimed to develop an optically switchable molecular building block. In our previous work, we have shown that the spin-crossover iron(II) complex, $[Fe(L)(CN)_2]\cdot H_2O$ (**1**), exhibits optical switching (LIESST) effects with highest relaxation temperature (130 K). The compound has two bidentate CN^- ligands, which can coordinate to another metal. Hence, it is expected that the electronic (magnetic) interaction can be mediated between spin sources, when the complex **1** is linked with other metal complexes. Here, we describe one-dimensional molecule-based magnets with homo- or hetero-metal complexes by using the LIESST iron(II) spin-crossover complex **1** as

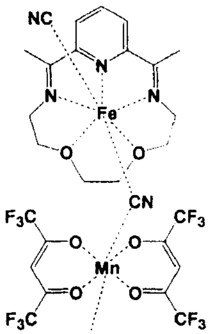

FIGURE 1. Target compound of one dimensional structure.

a photofunctional molecular building block. Our approach will be widely utilized to synthesize a variety of molecule-based magnets.

RESULTS AND DISCUSSION

The complex **1** exhibits spin-crossover behavior (S=0 ↔ S=2) and 'frozen-in' effect by rapid quenching. Furthermore, the complex **1** exhibits LIESST effect, which could be observed even at 130K. The structure of $[Fe(L)(CN)_2]\cdot H_2O$ (**1**) was reported previously.[6] The iron ion is in a pentagonal bipyramidal environment with the macrocycle occupying the pentagonal girdle and the cyanide carbon atoms in the axial positions. The symmetric unit are linked through the water molecules into infinite one-dimensional chains with $[Fe(L)(CN)_2]$ complex along the *a* axis. Since the cyanide ion is bidentate ligand, each nitrogen atom of the axial positions can coordinate another metal. Hence, we have suggested in our previous report that novel one-dimensional photo-induced molecule-based magnets can be constructed by assembling the photo-functional molecular building blocks **1** with homo- or hetero-metal complexes (Figure 1). Along this line, we attempted to build $[Fe(L)(CN)_2][Mn(hfac)_2]$ (**2**) by using $[Fe(L)(CN)_2]\cdot H_2O$ (**1**) and $[Mn(hfac)_2(H_2O)_2]$. The complex **2** could be obtained as powder samples. Elemental analytical data (Anal. Calcd for $C_{17}H_{23}O_3N_5Fe_1$ (**2**): C, 38.05; H, 2.72; N, 8.22 %. Found: C, 38.16; H, 2.56; N, 8.27 %.) show that the 1:1 compositions of $[Fe(L)(CN)_2]$ and $[Mn(hfac)_2]$.

The IR spectra of **1** and **2** were analyzed to gain the variation of the ν(C-N) mode in the complexes. Figure 2 shows the IR spectra measured at room temperature. Strong two resonances due to ν(C-N) were observed for **1** at 2106 and 2102 cm^{-1}, while a storong signal due to ν(C-N) was observed for **2** at 2133 cm^{-1}. The band due to ν(C-N) for **2** was different from that for **1**, indicating the formation of one-dimensional chain in complex **2** as shown in Figure 1.

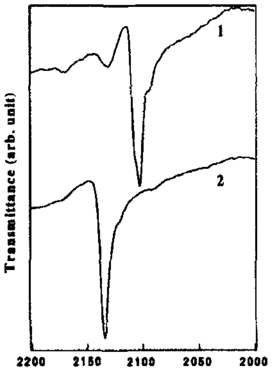

FIGURE 2. IR spectra for 1 and 2 at r.t.

The temperature dependence of the magnetic moment for **2** was investigated Quantum Design MPMS-5S SQUID magnetometer (Figure 3). The value of the magnetic moment at 300 K is equal to 7.46 B.M., which corresponds to the high-spin states for iron(II) and manganese(II) ions. On cooling, the value of the moment abruptly decreases from 130 to 100 K ($T_{1/2}$↓ = 110 K). The spin transition temperature, $T_{1/2}$, is defined as the temperature at which complexes show a population of 50 % in the high-spin and 50 % in the low-spin states. At 50 K, the value of the moment is close to 6.1 B.M. The complex **2** exhibits no thermal hysteresis and 'frozen-in' effect.[5][6][7]

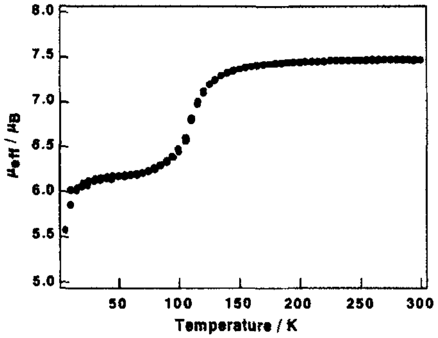

FIGURE 3. Temperature dependence of effective magnetic moments for 2.

The IR spectra of **2** before and after spin transition were shown in

Figure 4. At 300 K, a strong resonance due to ν(C-N) in the Fe(II, high-spin)-CN-Mn(II, high-spin) state was found at 2133 cm^{-1}. With decreasing temperature, the intensity of ν(C-N) in the Fe(II, high-spin)-CN-Mn(II, high-spin) state was diminished and a new signal arising from ν(C-N) in Fe(II, low-spin)-CN-Mn(II, high-spin) state appeared at 2128 cm^{-1}.

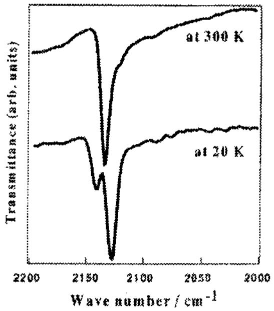

FIGURE 4. Temperature dependence of IR spectra for 2.

The temperature dependence of the Mössbauer spectra of **2** is shown in Fig. 5. The spectra at room temperature show a doublet of the absorption with qsuadrupole splitting (*Q.S.*) = 2.99 mms^{-1} and isomer shift (*I.S.*) = 0.87 mms^{-1}, which can be assigned to the high-spin state. At 13 K, the spectra can be divided into two parts. The outer doublet with *Q.S.* = 3.26 mms^{-1} and *I.S.* = 0.95 mms^{-1} can be assigned to the high-spin state. The indoublet, characterized by *Q.S.* = 1.50 mms^{-1} and *I.S.* = 0.27 mms^{-1}, which gains intensity with decreasing temperature, is ascribable to a low-spin isomer. The temperature dependence of the spectra is characteristic of spin-crossover complexes and is in good agreement with the magnetic data.

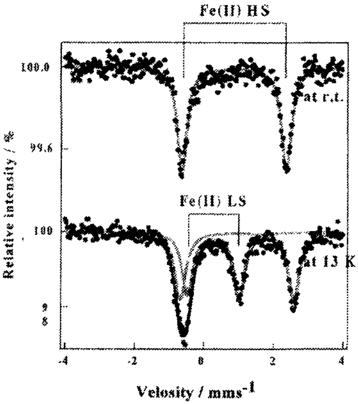

FIGURE 5. Temperature dependence of the Mossbauer spectra for 2.

CONCLUSIONS

The complex $[Fe(L)(CN)_2][Mn(hfac)_2]$ (**2**) was investigated. The composition was identified by elemental analysis. IR spectra suggest that $Fe(L)(CN)_2$ is linked with $Mn(hfac)_2$ via bidentate CN ligand. The complex **1** exhibits spin-rossover behavior, thermal hysteresis ($T_{1/2}\uparrow$=225 K and $T_{1/2}\downarrow$=198 K), 'frozen-in' effect and LIESST effect. On the other hand, the complex **2** does not show thermal hysteresis and 'frozen-in' effect, although it exhibits spin-crossover behavior ($T_{1/2}$=110 K). The complex **2** might be suitable for LIESST experiments due to using LIESST iron(II) complex **1**. These properties will be detailed in a subsequent paper.

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