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The Light-induced Excited Spin State Trapping Effect on Ni(dmit)$_2$ Salt with an Fe(III) Spin-crossover Cation: [Fe(qsal)$_2$][Ni(dmit)$_2$]$\cdot$2CH$_3$CN

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The Ni(dmit)$_2$ salt with an Fe(III) spin-crossover cation, Fe(qsal)$_2$, was prepared and showed a cooperative spin transition based on π–π interactions between π-ligands. The light-induced excited spin state trapping effect on this complex was also observed.

Recently spin-crossover (SC) complexes have aroused a considerable attention in molecular materials scientists. Since the spin conversion between the low-spin (LS) and high-spin (HS) states can be induced by external perturbations such as temperature, pressure, and light, the introduction of the SC component is expected to give a switching ability to a molecular solid. In particular, the first observation of the light-induced excited spin state trapping (LIESST) effect on an Fe(II) SC complex[1] has focused much interest on the SC complex as a promising candidate for photo-switchable functional molecular materials. In spite of a large number of reports of the LIESST effect on Fe(II) complexes, Fe(II) ions are considered to be not so stable against oxidative surroundings such as coexistence of organic stable radicals and electrochemical oxidation in order to prepare conducting molecular complexes. On the other hand, the number of the reports of the LIESST effect on Fe(III) complexes is very rare. Therefore, realization of the LIESST in an Fe(III) SC component may be the first step to develop various photo-switchable molecular materials.

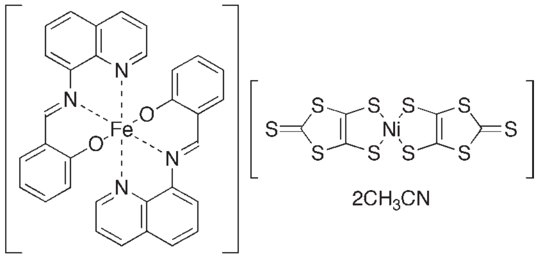

Figure 1. Molecular structure of [Fe(qsal)$_2$][Ni(dmit)$_2$]$\cdot$2CH$_3$CN.

In order to realize a photo-switching of the spin states in an Fe(III) ion, we have picked up the Fe(III) SC cation, Fe(qsal)$_2$ [qsalH = *N*-(8-quinolyl)salicylaldimine], because [Fe(qsal)$_2$]SeCN$\cdot$MeOH or CH$_2$Cl$_2$ was reported to display a large hysteresis loop originating from a cooperative phenomenon based on strong π–π interactions.[2] Such a strong cooperativity is considered to be essential to produce the LIESST effect on the Fe(III) SC complex.[3] Since the Fe(qsal)$_2$ ion is an univalent cation, Ni(dmit)$_2$ salt[4] [dmit = 4,5-dithiolato-1,3-dithiole-2-thione] was selected as a potential component affording magnetic or conducting crystals. Concerning the possibility of the development of conducting SC Fe(III) complexes, TCNQ anion radical salt[5] [TCNQ = 7,7,8,8-tetracyanoquinodimethane] and, quite recently, Ni(dmit)$_2$ salt[6] involving the Fe(III) SC ion as a counter cation, which showed a hysteresis loop based on π–π interactions, have been reported. However, no one has ever described the LIESST effect on the corresponding Fe(III) SC complexes. In this paper, we will present the observation of the LIESST effect on [Fe(qsal)$_2$][Ni(dmit)$_2$]$\cdot$2CH$_3$CN.

The complex was synthesized by metathesis between [Fe(qsal)$_2$]Cl$\cdot$1.5H$_2$O[7] and (Bu$_4$N)[Ni(dmit)$_2$][8] in acetonitrile. The composition of [Fe(qsal)$_2$][Ni(dmit)$_2$]$\cdot$2CH$_3$CN was determined by microanalysis. This complex is hereafter designated as the 1:1 complex. The crystal structure analysis was performed at 273 K by using a Rigaku Mercury CCD diffractometer with a confocal mirror X-ray source (Figure 2).[9] There are one crystallographically independent Fe(qsal)$_2$ cation and one Ni(dmit)$_2$ anion within unit cell. Coordination bond lengths around an Fe(III) ion [Fe···O: 1.912–1.913, Fe···N: 2.125–2.151 Å] are longer than those in the LS state reported previously [Fe···O: 1.869–1.879, Fe···N: 1.941–1.991 Å],[2] suggesting the Fe(III)

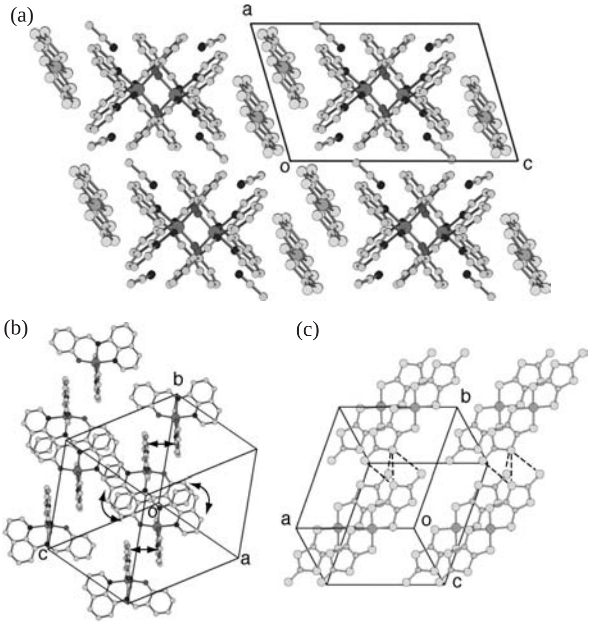

Figure 2. (a) Crystal structure of [Fe(qsal)$_2$][Ni(dmit)$_2$]$\cdot$2CH$_3$CN. Hydrogen atoms are omitted to clarify; (b) Fe(qsal)$_2$ arrangement, arrows indicate the existence of π–π interactions; (c) Ni(dmit)$_2$ arrangement, broken lines indicate the existence of S···S short contacts.

ion will be in the HS state. Despite the apparent dimeric arrangement of Ni(dmit)$_2$ anions, there is no S···S short contact within the dimer. Short S···S contacts (3.565–3.708 Å) are observed on the 1,3-dithiol-2-thione moieties of an Ni(dmit)$_2$ anion along the *b* axis, affording one-dimensional chains of Ni(dmit)$_2$ anions. Furthermore, there is the shortest S···S contact [S···S: 3.425 Å] between these one-dimensional chains. On the other hand, one-dimensional chain of Fe(qsal)$_2$ cations is formed by π–π overlapping between the π-ligands along the *b* axis [C(7)···C(7′)(65602): 3.345 Å, C(23)···C(23′)(66602): 3.304 Å] and, however, there is no short contact between these one-dimensional chains due to the existence of solvent molecules. These strong π–π interactions indicate the possibility of cooperative SC phenomenon.

Temperature dependence of $\chi_M T$ was measured by using a Quantum Design MPMS-7XL SQUID susceptometer (Figure 3a). The $\chi_M T$ value of the 1:1 complex was 4.15 emu K mol^{-1} at 300 K, suggesting that the Fe(III) ion is almost in the high spin state and the spins on the Ni(dmit)$_2$ anions are antiferromagnetically coupled with each other, which is consistent with an Ni(dmit)$_2$ arrangement. On lowering the temperature, the $\chi_M T$ value gradually decreased at around 200 K, accompanying a small step. The spin conversion from the HS to the LS states was completed at around 150 K ($T_{1/2}\downarrow = 194$ K). After the spin transition, the $\chi_M T$ value became 0.77 emu K mol^{-1}, indicating that about 10% of the 1:1 complex remained in the HS state. These HS/LS ratios were also confirmed by Mössbauer spectra.[10] In heating process, an abrupt increase in $\chi_M T$ was observed at about 230 K ($T_{1/2}\uparrow = 231$ K). On the other hand, repeating the cooling and heating processes, the hysteresis-like loop disappeared, and only an abrupt change and its tail in $\chi_M T$ were observed in the cooling process. This means that the virgin sample was in the metastable state and after the first spin transition the sample turned to be in the thermodynamically stable state, which is hereafter designated as the "aged" sample. In any case, a strong cooperative interaction between the Fe(III) sites was revealed to exist. Preliminary crystal analysis of this complex at 90 K also suggested the preservation of π–π interactions.

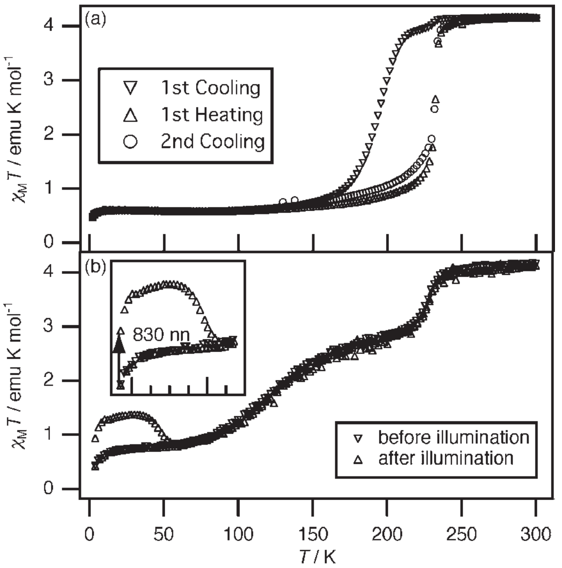

Figure 3. $\chi_M T$ vs T plot of [Fe(qsal)$_2$][Ni(dmit)$_2$]·2CH$_3$CN: (a) Bulk sample, (b) the LIESST experiment of ground sample with an adhesive tape by using a diode laser (830 nm).

The LIESST experiment was carried out on an "aged" sample. The sample was fixed with an adhesive transparent tape. The difference in magnetization curve (Figure 3b) was ascribed to that of sample preparation. The sample for the LIESST experiment was ground in order to illuminate a wider area of the complex. Although the grinding effect usually results in relatively gradual magnetic transition,[11] the magnetic properties of the complex are considered to be essentially unchanged, because the transition temperature is similar to that of polycrystalline sample. On illumination with a diode laser (830 nm) at 5 K, the magnetization of the complex gradually increased, indicating that the light-induced metastable HS state could be trapped. On heating after saturation of magnetization with light illumination, the relaxation from the metastable HS to the ground LS states was observed at around 40 K ($T_{\mathrm{LIESST}} = 46$ K). The magnetization curve of the annealing sample followed that before illumination. This indicates that the change by light is completely reversible. The similar increase in magnetization was observed by using an Hg-Xe lamp passing through a band path filter (500–600, > 640 nm) as a light source, whereas the magnetization was not changed by using a diode laser (980 nm). This means that the change by light proceeds via the photon mode not the photo-thermal mode. Furthermore, the decease in magnetization by illuminating the metastable HS state with a diode laser (980 nm) suggests that the magnetism of the 1:1 complex can be controlled by light irradiation.

In summary, we have demonstrated a cooperative spin transition, and the LIESST effect on [Fe(qsal)$_2$][Ni(dmit)$_2$]·2CH$_3$CN. These observations reveal that an Fe(qsal)$_2$ cation is a promising building block for photo-switchable molecular materials. Preparation and characterization of the conducting mixed-valenced complexes derived from the 1:1 complex are now in progress.

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9 Crystal structure data for [Fe(qsal)$_2$][Ni(dmit)$_2$]·2CH$_3$CN: C$_{42}$H$_{28}$FeN$_6$NiO$_2$S$_{10}$, MW = 1083.87, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.409(2)$, $b = 12.435(2)$, $c = 17.875(3)$ Å, $\alpha = 105.749(3)$, $\beta = 99.422(3)$, $\gamma = 109.537(3)^\circ$, $V = 2207.7(7)$ Å^3, $T = 273$ K, $Z = 2$, $\rho_{\mathrm{calc}} = 1.630$ g/cm^3, Of the 23704 reflections that were collected, 9871 were unique ($R_{\mathrm{int}} = 0.037$), $R1 = 0.039$, $wR2 = 0.103$, using reflections with $I > 3\sigma(I)$, GOF = 1.013.
10 Mössbauer Parameters; 293 K: HS (100%) I.S. = 0.276, Q.S. = 0.745; 9 K: HS (13%) I.S. = 0.32, Q.S. = 0.68, LS (87%) I.S. = 0.07, Q.S. = 2.74.
11 P. Gütlich, A. Hauser, and H. Spiering, *Angew. Chem., Int. Ed. Engl.*, **33**, 2024 (1994), and references herein.

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