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Spin Crossover

Synergistic Spin Transition between Spin Crossover and Spin-Peierls-like Singlet Formation in the Halogen-Bonded Molecular Hybrid System: $[Fe(Iqsal)_2][Ni(dmit)_2]\cdot CH_3CN\cdot H_2O$[**]

Kappei Fukuroi, Kazuyuki Takahashi, Tomoyuki Mochida, Takahiro Sakurai, Hitoshi Ohta, Takashi Yamamoto, Yasuaki Einaga, and Hatsumi Mori*

Abstract: *To introduce halogen-bond interactions between a cation and an anion, a novel Fe*^{III} *complex from iodine-substituted ligands involving a paramagnetic nickel dithiolene anion was prepared and characterized. The compound exhibited the synergy between a spin-crossover transition and a spin-Peierls-like singlet formation. The halogen-bond interactions between the iodine and the sulfur atoms stabilized the paramagnetic state of* π*-spins and played a crucial role in the synergistic magnetic transition between d- and* π*-spins. In addition, the compound showed the light-induced excited spin state trapping effect.*

A spin crossover (SCO) phenomenon between a high-spin (HS) and low-spin (LS) state is usually observed in octahedrally coordinated transition-metal complexes under an appropriate ligand field. Since the SCO conversion can be induced by external stimuli, such as temperature, pressure, and light, SCO compounds have aroused a great deal of attention for their potential use in externally controllable molecular materials anticipating future applications for magnetic memory, display, and switching devices.[1] The development of multifunctional SCO compounds has been an active research field over the past decade. The synergy between an SCO conversion and electronic properties such as conductivity, magnetism, and optics will provide an opportunity to control the electronic properties of a molecular solid by external stimuli. Although a number of molecular hybrid systems combining an SCO with an electronic functional component have been reported, the coupling of the SCO conversion to changes in electronic properties has rarely been exploited.[2]

We recently developed SCO conductors, in which the conductivity modulation was coupled to the SCO conversion.[2a,b] The intermolecular π-stacking interactions between the SCO cations in an SCO layer play a key role in inducing the SCO transition. To develop new functional SCO hybrid systems, however, the intermolecular interactions between ions with the same charge are not always utilized, because the Coulomb repulsion may prevail against such intermolecular interactions. Therefore, we have focused on intermolecular interactions between a cation and an anion to induce an SCO transition.

Halogen-bond interactions are noncovalent directional intermolecular interactions between halogen atoms, except F, and electronegative atoms, such as O, N, and S. The interaction energies are considered to be of a magnitude similar to that of π-stacking interactions.[3] Kato et al. recently reported a unique paramagnetic molecular metal comprising a magnetic layer and a conducting layer from the same $[Ni(dmit)_2]$ molecules (dmit = 4,5-dithiolato-1,3-dithiole-2-thione).[4] The difference of the molecular arrangement in each layer was derived from two kinds of directional I···S interactions with an iodine-substituted countercation. This result implies that the arrangement of $[Ni(dmit)_2]$ molecules could be tuned by means of halogen-bond interactions.

We have previously reported the SCO compounds involving a spin-singlet Ni dithiolate anion dimer.[5] To control both the spin state and molecular arrangement of the paramagnetic $[Ni(dmit)_2]$ anions by halogen-bond interactions, we designed a molecular hybrid compound that includes a potential SCO cation containing the iodine-substituted ligand, $[Fe(Iqsal)_2]^+$ (HIqsal = 5-iodo-*N*-(8′-quinolyl)-salicylaldinine). We herein report the preparation, crystal structures, and magnetic properties of the molecular hybrid compound, $[Fe(Iqsal)_2][Ni(dmit)_2]\cdot CH_3CN\cdot H_2O$ (**1**). Compound **1** exhibited a synergistic spin transition between an SCO conversion and a spin-Peierls (SP)-like singlet formation of the paramagnetic $[Ni(dmit)_2]$ anions stabilized by halogen-bond interactions. To our knowledge, this is the first SCO magnetic compound where d-spins are coupled to π-spins by means of the cation–

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[*] K. Fukuroi, Prof. Dr. K. Takahashi, Prof. Dr. T. Mochida
Department of Chemistry, Kobe University
1-1 Rokkodai, Kobe 657-8501 (Japan)
E-mail: ktaka@crystal.kobe-u.ac.jp
Dr. T. Sakurai
Center for Supports to Research and Education Activities
Kobe University, 1-1 Rokkodai, Kobe 657-8501 (Japan)
Prof. Dr. H. Ohta
Molecular Photoscience Research Center, Kobe University
1-1 Rokkodai, Kobe 657-8501 (Japan)
Dr. T. Yamamoto, Prof. Dr. Y. Einaga
Department of Chemistry, Keio University
Hiyoshi, Yokohama 223-8522 (Japan)
Prof. Dr. H. Mori
Institute for Solid State Physics, The University of Tokyo
5-1-5 Kashiwanoha, Kashiwa 277-8581 (Japan)

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anion interactions. Furthermore, the photo-induced metastable HS state for **1** could be generated by photo irradiation at low temperature.

The starting Fe^{III} complex, $[Fe(Iqsal)_2](NO_3)\cdot 0.5\,H_2O$,[6] was synthesized by the reaction between $Fe(NO_3)_3\cdot 9\,H_2O$ and HIqsal, which was generated in situ by the condensation between 8-aminoquinoline and 5-iodo-salicylaldehyde.[7] The metathesis reaction between $[Fe(Iqsal)_2](NO_3)\cdot 0.5\,H_2O$ and $(TBA)[Ni(dmit)_2]$[8] (TBA = tetrabutylammonium) in an acetonitrile solution containing 2%v/v H_2O formed compound **1** as stable black platelets. The microanalysis revealed that the composition of **1** is $[Fe(Iqsal)_2][Ni(dmit)_2]\cdot CH_3CN\cdot H_2O$.

The X-ray crystal-structural analysis was performed at 273 K. The crystal structure of **1** is shown in Figure 1 and Figure S1 in the Supporting Information. The crystal belongs to a monoclinic system with the space group $P2_1/c$. The asymmetric unit consists of one $[Fe(Iqsal)_2]$ cation, one $[Ni(dmit)_2]$ anion, one acetonitrile, and one water molecule. The iron atom is coordinated to two tridentate Iqsal anions, giving a distorted octahedral coordination geometry. The bond lengths and angles of the $[Fe(Iqsal)_2]$ cation are in good agreement with those of an $[Fe(qsal)_2]$ cation[5a] in the HS state (Table S2), indicating that the $[Fe(Iqsal)_2]$ cation is in an HS state at 273 K. The quinoline moiety of one of the ligands in the $[Fe(Iqsal)_2]$ cation overlapped the benzene moiety of that in the neighboring $[Fe(Iqsal)_2]$ cation (Figure S3). The mean interplanar distance between the π-ligands is 3.46 Å, indicative of the existence of weak π-stacking interactions. Thus, the $[Fe(Iqsal)_2]$ cations form a one-dimensional array along the a axis by the π-stacking interactions between cations.

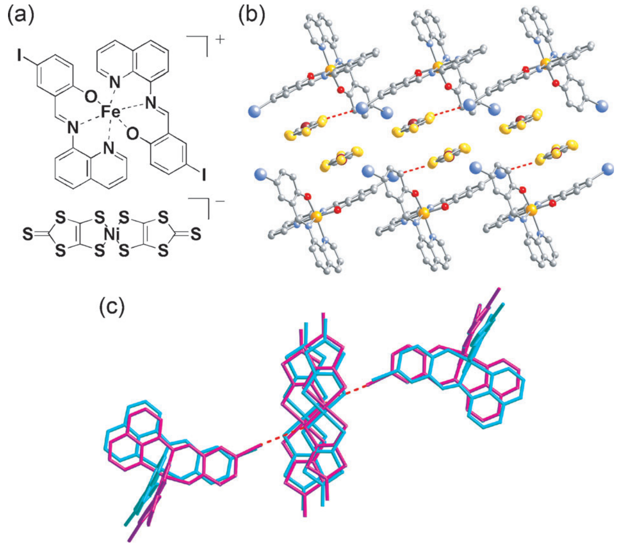

Figure 1. a) Molecular structure of the cation and anion. b) Molecular arrangement of the $[Fe(Iqsal)_2]$ cations and the $[Ni(dmit)_2]$ anions in **1** at 273 K. Hydrogen atoms and solvent molecules are omitted for clarity. The red dashed lines indicate I⋯S short contacts; N blue, O red, S yellow, I blue (larger spheres), Fe yellow (larger spheres), Ni red (larger spheres). c) The superimposed view of the cation–anion arrangement at 130 and 175 K. Cyan and magenta wire frame drawings represent the molecules at 130 and 175 K, respectively. Red dotted lines indicate the halogen bond interactions between the I and S atoms at 175 K.[13]

The $[Ni(dmit)_2]$ anions were arranged alternately in a face-to-face and a side-by-side manner to afford a one-dimensional zigzag molecular array along the *a* axis. However, the mean interplanar distance between the $[Ni(dmit)_2]$ anions in the face-to-face arrangement was 3.71 Å; moreover, no short contacts were found between sulfur atoms in either the face-to-face or side-by-side arrangement. These observations suggest that the spin on the $[Ni(dmit)_2]$ anions may be giving a paramagnetic state. Unfortunately, the EPR spectrum of **1** at room temperature gave only a very weak and broad signal, presumably a result of fast relaxations. Therefore, to confirm this assumption, the transfer integrals between the $[Ni(dmit)_2]$ anions were estimated by extended Hückel molecular orbital calculations.[9] The transfer integrals (at 273 K) for the face-to-face and side-by-side arrangement were 11.4 meV and −2.01 meV, respectively. These values are comparable to that of 10.3 meV reported for paramagnetic $[Ni(dmit)_2]$ salt,[10] whose magnetic behavior was well described by a one-dimensional Heisenberg antiferromagnetic chain model. This indicates that the spin on the $[Ni(dmit)_2]$ anion in **1** results in the paramagnetic state, whereas the non-substituted mother compound[5a] was in a spin-singlet state.

It should be noted that the short contacts between I atoms in the Fe^{III} cation and S atoms in the $[Ni(dmit)_2]$ anion were 3.690 Å, which is less than the sum of van der Waals radii (3.78 Å), and the angle of C29-I2⋯S6 was 164.7(2)° (Figure S2 (shows the atom numbering scheme), Table S3). These structural features clearly indicate that halogen-bond interactions exist between the $[Fe(Iqsal)_2]$ cation and the $[Ni(dmit)_2]$ anion. In addition, the mean interplane distance between the Iqsal ligand and the $[Ni(dmit)_2]$ anion was 3.57 Å, suggesting that weak intermolecular π-stacking interactions between the cation and the anion also exist (Figure S5). As a consequence, the one-dimensional array of the $[Fe(Iqsal)_2]$ cation is linked with two one-dimensional zigzag ones of the $[Ni(dmit)_2]$ anion by the halogen bond and weak π-stacking interactions, giving a three-leg-ladder arrangement.

The magnetic susceptibilities were measured on a polycrystalline sample. The temperature variations of the $\chi_M T$ product for **1** are shown in Figure 2a. The $\chi_M T$ value at 300 K was 4.43 $cm^3\,K\,mol^{-1}$, which is slightly larger than the spin only value for the HS Fe^{III} ion (4.377 $cm^3\,K\,mol^{-1}$). This result suggests the existence of the paramagnetic $[Ni(dmit)_2]$ anion proposed based on the structure. On cooling, the $\chi_M T$ values gradually decreased down to 170 K. By further lowering the temperature, an abrupt decrease in the $\chi_M T$ value was observed ($T_{1/2}\!\downarrow = 150$ K), suggesting that a cooperative SCO transition occurs. Below 135 K, the $\chi_M T$ products gradually decreased again. The $\chi_M T$ value at 10 K was 0.96 $cm^3\,K\,mol^{-1}$, suggesting the existence of an HS fraction. On heating the sample, a reverse transition occurred ($T_{1/2}\!\uparrow = 156$ K), resulting in a thermal hysteresis of approximately 6 K.

The photo-response of magnetic susceptibilities for **1** is depicted in Figure 2b. On illumination with a YAG laser (532 nm) at 5 K, a gradual increase in the magnetization was observed, suggesting that the photo-induced HS state can be

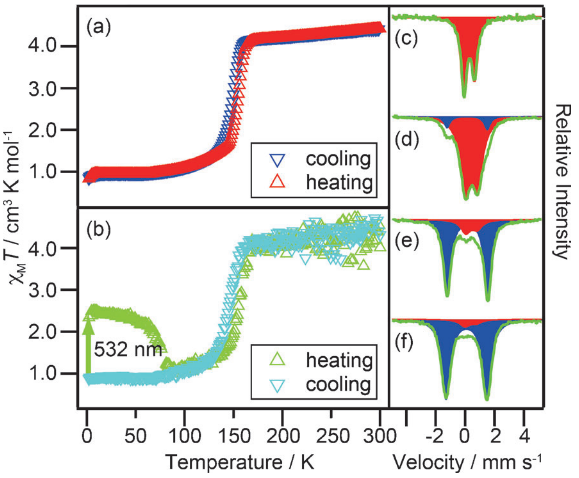

Figure 2. $\chi_M T$ versus T plot for **1** under 0.5 T at a scan speed of 1 K min^{-1} a) in the dark and b) after illumination of 532 nm. Mössbauer spectra at c) 290, d) 173, e) 121, and f) 10.6 K. Green lines are observed spectra. Red areas are fitted HS spectra, blue areas fitted LS spectra.

trapped in **1**. On heating the sample after stopping the photo irradiation, the $\chi_M T$ values relaxed to the original ones at around 80 K. On lowering the temperature, the $\chi_M T$ values corresponded to the original ones before illumination. On the other hand, illumination with a diode laser (1060 nm) resulted in no remarkable magnetic response. These results indicate that the photo-response comes from the light-induced excited spin state trapping (LIESST) effect and is completely reversible.

To determine the spin state of the Fe^{III} cation, variable-temperature Mössbauer spectra were recorded on a ^{57}Fe-enriched sample (Figure 2c–f). The isomer shift (IS) and quadrupole splitting (QS) are listed in Table S6. The spectrum at 290 K demonstrated only single quadrupole asymmetric doublet, which was ascribed to the HS state. On cooling the sample to 173 K, a small shoulder peak appeared. After fitting by two asymmetric doublet components, a new doublet spectrum was assigned to the LS state. Thus the spectrum at 173 K consisted of 10.5 % LS and 89.5 % HS species. This indicates that the gradual decrease in the $\chi_M T$ above 170 K would have originated from an SCO conversion. Further lowering of the temperature below a thermal hysteresis loop resulted in a striking change in the LS doublet spectrum. The spectrum at 121 K consisted of 83.6 % LS doublet and 16.4 % HS doublet. The spectrum at 10.6 K still contains a contribution from the HS species, which was consistent with the magnetic susceptibility measurement.

Let us consider the difference in $\chi_M T$ between magnetic susceptibilities and the Mössbauer spectra. Since the $\chi_M T$ value for the paramagnetic [Ni(dmit)$_2$] salt[10] was 0.33 cm^3 K mol^{-1} at 300 K, the $\chi_M T$ value for the HS state of the [Fe(Iqsal)$_2$] cation for **1** was calculated to be 4.10 cm^3 K mol^{-1} at 300 K. Since the $\chi_M T$ values for the LS state of the [Fe(qsal)$_2$] cation have been reported to be 0.6 cm^3 K mol^{-1},[11] the difference in $\chi_M T$ between 121 K and 173 K from the Mössbauer spectra is calculated to be 2.56 cm^3 K mol^{-1}. On the other hand, the difference in $\chi_M T$ from magnetic susceptibilities is 2.87 cm^3 K mol^{-1}. Thus, the difference in $\chi_M T$ between the Mössbauer spectra and magnetic susceptibilities is 0.31 cm^3 K mol^{-1}, which exactly corresponds to one paramagnetic spin ($S = 1/2$). This suggests that the cooperative magnetic transition originates from simultaneous SCO and SP-like transitions.

To clarify the structural changes below and above the cooperative magnetic transition, crystal-structural analyses were carried out at 175, 130, and 105 K. No changes in the crystal system or space group were observed upon temperature variations (Table S1). The bond lengths and angles around the Fe^{III} cation are listed in Table S2. The changes in the coordination geometries arising from the SCO conversion from HS to LS were evidenced between 130 and 175 K. Meanwhile, no remarkable changes in the distances between the face-to-face π-planes and between sulfur atoms for the [Ni(dmit)$_2$] anions were observed at each temperature. It should be noted that the [Ni(dmit)$_2$] anions in the face-to-face arrangement at 130 K had clearly slipped along the molecular long axis such that the Ni atoms approached each other (Figure 1c and Figure S3). The transfer integrals for the face-to-face arrangement were −138.0 and 28.04 meV at 130 and 175 K, respectively. The transfer integral at 130 K was comparable with those in the reported spin-singlet dimers.[5b,12] Since the magnetic exchange interaction energy is known to be proportional to the square of a transfer integral,[12] the exchange interaction energy at 130 K is found to be about 25-times larger than that at 175 K, indicating that the formation of a spin-singlet dimer from the [Ni(dmit)$_2$] anions takes place. This clearly indicates that the SP-like magnetic transition on the [Ni(dmit)$_2$] anion coincides with the cooperative SCO transition on the [Fe(Iqsal)$_2$] cation.

The additional structural information on the intermolecular arrangement between the cation and the anion provides insight into the mechanism of this synergistic spin transition. The I2···S6 distances were 3.634(3) and 3.796(3) Å at 175 and 130 K, respectively (Figure S2, Table S3). This indicates that the halogen-bond interactions disappeared from 175 K to 130 K. On the other hand, the mean distances between the Iqsal and [Ni(dmit)$_2$] molecules were 3.53 and 3.50 Å at 175 and 130 K, respectively, suggesting no remarkable changes in the overlaps between the cation and the anion. These observations along with the dramatic structural change arising from the spin-singlet formation of the [Ni(dmit)$_2$] dimer suggest that the halogen-bond interactions between the cation and the anion compete with the π-stacking interactions between the face-to-face [Ni(dmit)$_2$] anions. The entropy gain derived from spin degeneracies and elastic contributions including the halogen-bond interactions favors the high-temperature phase. However, since the π-stacking interactions between the [Ni(dmit)$_2$] anions would dominate the halogen-bond interactions in the ground state, the rearrangement from the halogen bonded to the π-dimer-formed structures would trigger the synergistic spin transition. From another point of view, the halogen-bond interactions should stabilize the paramagnetic arrangement of the [Ni(dmit)$_2$] anion.

In conclusion, we have successfully synthesized and characterized a novel phototunable d–π hybrid SCO compound **1** into which the halogen-bond interaction between the cation and the anion was introduced. The competition between the halogen bond interactions and π-stacking interactions plays a significant role in the synergistic spin transition between the SCO and SP-like singlet formation. The use of an intermolecular interaction between a cation and an anion opens the way to a wide variety of molecular designs towards multifunctional molecular hybrid systems. If much stronger intermolecular interactions than π-stacking interactions could be introduced into an SCO hybrid system, it would be possible to manipulate electronic properties directly by external stimuli. Further investigations of the photo responses for **1** and the application of **1** to a mixed-valence conducting system are now in progress.

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