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ORIGINAL ARTICLE

Photo-switchable spin-crossover iron(III) compound based on intermolecular interactions

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Abstract Iron(III) spin-crossover compounds, [Fe(qnal)$_2$]CF$_3$SO$_3$·MeOH (1·MeOH) and [Fe(qnal)$_2$]CF$_3$SO$_3$·acetone (1·acetone) were prepared and their spin transition properties were characterized by magnetic susceptibility measurement, Mössbauer spectroscopy and single crystal analysis. Two iron(III) compounds exhibited abrupt spin transition with thermal hysteresis loop ($T_{1/2}\uparrow = 115$ K and $T_{1/2}\downarrow = 104$ K for 1·MeOH, and $T_{1/2}\uparrow = 133$ K and $T_{1/2}\downarrow = 130$ K for 1·acetone). Single crystal analysis revealed both of the structures in high-spin (HS) and low-spin (LS) states for 1·acetone. The difference of bond length between the HS and LS states for 1·acetone was $\sim$0.10 Å, which was corresponding to that of typical iron(III) SCO compounds. Specially, it showed strong intermolecular interactions by π–π stacking formed between the neighbor complexes leading to 2-D sheet. Both 1·MeOH and 1·acetone exhibited LIESST effect when it was illuminated at 1000 nm. We also confirmed that the introduction of strong intermolecular interactions, such as π–π stacking, can play an important role in LIESST effect.

Keywords Iron(III) · Spin-crossover · LIESST · Intermolecular interaction

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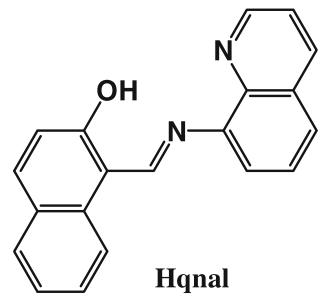
Introduction

It is useful to design the molecules that can exhibit bistability in molecular and materials science because such molecules can be utilized for storage media and switching equipment. Spin-crossover (SCO) compounds showing interconversion between high-spin (HS) and low-spin (LS) states reveal phase-transition phenomenon induced by external stimuli (temperature, pressure, electric field, magnetic field, or light irradiation), which is frequently found in iron(II), iron(III), and cobalt(II) compounds [1]. One of the most extensively studied SCO compounds is the iron(II) complex with the 3d^6 electron configuration [1, 2]. In this case, cooperativity should be considered in the solid state if intermolecular interactions are sufficiently strong. Cooperativity induces abrupt spin transitions and hysteresis loops in SCO compounds, and this is the reason why the role of intermolecular interactions in spin transitions has been extensively studied [3–5]. To date, the design of new SCO compounds with large cooperativity has become one of the main challenging points. It has been theoretically suggested and experimentally confirmed that cooperativity can be increased by designing polymeric structures in which the active sites are linked to each other through chemical bridges [6, 7]. Furthermore, SCO compounds with strong intermolecular interactions, such as π–π

stacking or hydrogen bonding, display abrupt transitions and hysteresis loops [3–8]. Since Gütlich and his coworkers observed photo-induced LS→HS transition of the iron(II) SCO compound, e.g. $[Fe(ptz)_6](BF_4)_2$ in 1984, the phenomenon is called as a light-induced excited spin state trapping (LIESST) [2, 9]. Additionally, it was demonstrated that reverse LIESST is also possible in some cases because the irradiation of light with near infrared region toward the system can pump back the system to the LS state. The discovery of this LIESST effect suggested that the compounds could be used as optical switches, hence a number of iron(II) compounds with LIESST effect were reported until now [1, 2, 10–12].

For iron(II) compounds, it is essential to consider the bond lengths between metal and ligand resulting in the spin transition, with the typical difference of the bond lengths ($\Delta r_{HL} = r_{HS}–r_{LS} \approx 0.2$ Å) [1, 2]. Moreover, the photo-induced HS state shows the same increase of metal–ligand distance around 0.2 Å as the thermally populated HS state. By comparison of this difference, it has been found that the elongated bond length prevents tunneling from photo-induced metastable HS state to LS state at low temperature because the overlap of the wave function on the vibrational state is small. As a result, slow HS→LS relaxation occurs, and LIESST effects can be expected in iron(II) SCO compounds. On the other hand, for iron(III) or cobalt(II) SCO compounds, the bond length difference ($\Delta r_{HL} \approx 0.1$Å) is less than that for iron(II) compounds [13–20]. The relatively small difference enables tunneling from photo-induced metastable HS to LS states even at low temperature because the overlap of the wave function on the vibrational state is large, and the HS→LS relaxation easily occurs. Therefore, the LIESST effects have been found in a number of iron(II) SCO compounds but not in other metal (iron(III) or cobalt(II)) compounds [2].

In order to develop a variety of optically switchable molecular solids, it is necessary to establish some strategies to prevent such rapid relaxation from a metastable state to a ground state. To fulfill this goal, we adopted a well-designed complex with strong intermolecular interactions. It was considered that the cooperativity resulted from the intermolecular interaction increases the activation energy for the relaxation processes, enabling the observation of a long-lived metastable state after illumination [21, 22]. Herein, we describe not only the synthesis of the mononuclear iron(III) compounds, $[Fe(qnal)_2]CF_3SO_3\cdot MeOH$ (1·MeOH) and $[Fe(qnal)_2]CF_3SO_3\cdot$acetone (1·acetone) where qnal is the abbreviations of the deprotonated Hqnal (Hqnal = 1-((8-quinolinylimino)methyl)-2-naphthalenol [23]), but also their magnetic behaviors such as a $S = 5/2$ (HS) ↔ $S = 1/2$ (LS) spin transition with a thermal hysteresis and LIESST effect.



Hqnal

Experimental section

Synthesis

$[Fe(qnal)_2]CF_3SO_3\cdot MeOH$ (1·MeOH) and $[Fe(qnal)_2]CF_3SO_3\cdot$acetone (1·acetone) were prepared as follows: a solution of 8-aminoquinoline (0.28 g, 2 mmol) in methanol (20 ml) and 2-hydroxy-1-naphthaldehyde (0.34 g, 2 mmol) in methanol (10 ml) was stirred for 1 h in order to produce Hqnal. Meanwhile, $FeCl_3$ (0.16 g, 1 mmol) and CF_3SO_3Na (0.52 g, 3 mmol) was dissolved in absolute methanol (5 ml) containing 2,2′-dimethoxy-propane (2 ml) and warmed at 40 °C for 30 min, and was added to the MeOH or acetone solution of Hqnal, respectively. The micro-crystalline black product was collected by suction and dried in vacuum. $[Fe(qnal)_2]CF_3SO_3\cdot MeOH$ (1·MeOH), Anal. Calcd. for $C_{42}H_{30}O_6N_4S_1F_3Fe_1$: C, 60.66; H, 3.64; N, 6.74. Found: C, 60.48; H, 3.71; N, 6.53. $[Fe(qnal)_2]CF_3SO_3\cdot$acetone (1·acetone), Anal. Calcd. For $C_{44}H_{32}O_6N_4S_1F_3Fe_1$: C, 61.62; H, 3.76; N, 6.53. Found: C, 61.72; H, 3.73; N, 6.47.

Susceptibility measurements

The magnetic susceptibilities for 1·MeOH and 1·acetone between 5 K and 300 K were measured with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S) in an external field of 0.5 T. LIESST experiments were carried out using these miconductor laser (1000 nm) coupled through an optical fiber to the cavity of the SQUID magnetometer. The sample was placed on the edge of the optical fiber.

Mössbauer spectroscopy

The Mössbauer spectra (isomer shift vs. metallic iron at room temperature) were measured with a Wissel MVT-1000 Mössbauer spectrometer with a ^{57}Co/Rh source in the transmission mode. All isomer shifts are given relative to α-Fe at room temperature. Measurements at low temperature were performed with a closed-cycle helium refrigerator cryostat (Iwatani Co., Ltd.).

Crystallographic data collection and structural determination

X-ray crystallographic data for 1·MeOH at 80 K ($C_{42}H_{30}O_6N_4S_1F_3Fe_1$): *F.W.* = 831.626, black needle (0.25 × 0.05 × 0.02), triclinic, space group *P-1*, $a = 11.8771(12)$, $b = 13.0317(12)$, $c = 13.3962(11)$ Å, $\alpha = 68.244(2)$, $\beta = 66.410(2)$, $\gamma = 84.898(3)°$, $V = 1760.5(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.569$ g cm^{-3}. The structure was solved by direct methods and expanded using Fourier techniques. The refinements by full matrix least-squares gave an *R* factor of 0.0902 and a weighted *R* factor (R_W) of 0.2312 from 8029 reflections with intensity $I > 2\sigma(I)$ for 515 variables. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Results and discussion

The SCO iron(III) compounds, 1·MeOH and 1·acetone were obtained as single crystals containing the solvent molecule. The single crystal structure of 1·MeOH in LS states was determined at 80 K and it adopted a triclinic *P*-1 space group [24]. The X-ray crystallographic analysis reveals that each of the iron(III) atoms has closed to a octahedral environment with N_4O_2 donor set which are coordinated to four nitrogen atoms and two oxygen atoms from two qnal ligands. The oxygen atoms are situated in *cis* position. The bond lengths of Fe–O(1), Fe–O(2), Fe–N(1), Fe–N(2), Fe–N(3), and Fe–N(4) for 1·MeOH are 1.879(3), 1.868(3), 2.001(3), 1.960(5),1.999(4), and 1.955(5) Å, respectively. These bond lengths are consistent with those of typical LS iron(III) compounds [13–16]. Unfortunately, the crystal structure of HS state for 1·MeOH could not be determined.

The structure in the LS and HS states for 1·acetone was also determined at 120 K and 200 K, respectively. Due to phase transition and solvent molecules contained, *R* values were so high that the crystal structure could not be clearly characterized. However, we could estimate the structure roughly in the HS and LS states, which are similar to those of 1·MeOH. The selected bond lengths of both states are listed in Table S1. The coordination sphere and the molecular packing of $[Fe(qnal)_2]^+$ units in the LS and HS states are similar to each other (Fig. S1 and S2). Comparison of the single crystal structure in the HS and the LS states provides useful information to investigate the structural changes accompanying the spin transition. From these results, it is worthy of note that there is a huge difference of bond lengths between HS and LS states. The average distances of Fe–O and Fe–N are $r_{Fe\text{-}O} = 1.88$ Å, $r_{Fe\text{–}N} = 2.00$ Å in the LS state, and $r_{Fe\text{–}O} = 1.93$ Å, $r_{Fe\text{–}N} = 2.12$ Å in the HS state, respectively. The average differences of the respective distance are $\Delta r_{HL,Fe\text{–}O} = 0.05$ Å and $\Delta r_{HL,Fe\text{–}N} = 0.12$ Å, and these differences lie in the range of $\Delta r_{HL,Fe\text{–}O} = 0.00$–$0.07$ Å and $\Delta r_{HL,Fe\text{–}N} = 0.12$–$0.16$ Å for iron(III) SCO compounds reported so far [13–16]. The differences of bond length for iron(II) SCO compounds are in the range of $\Delta r_{Fe\text{–}N} = 0.18$–$0.27$ Å. The Δr_{HL} value of iron(III) compounds is smaller than that of iron(II) compounds [1, 2]. As regards the intermolecular interaction in the molecular packing of 1·MeOH and 1·acetone, it was found that $[Fe(qnal)_2]^+$ cations formed short contacts (3.5 Å) through quinoline and naphthyl rings, providing an extended 2-D sheet via π–π interactions (Fig. 1b). The molecular packing of 1·MeOH and 1·acetone is very tight and this molecular arrangement suggests that cooperativity arises mainly from the intermolecular π–π interactions between the quinoline and naphthyl rings.

Figure 2a demonstrates the detail magnetic properties of 1·MeOH as function of temperature. The $\chi_m T$ value at 300 K is equal to 3.58 cm^3 K mol^{-1}, which is corresponding to what is expected to the HS state of iron(III) compounds. On cooling, the value of $\chi_m T$ drops abruptly around $T_{1/2}\downarrow = 104$ K, then it is reached to 0.37 cm^3 K mol^{-1} at 70 K. On warming, an abrupt variation of $\chi_m T$ is shown around $T_{1/2}\uparrow = 115$ K. The presence of strong cooperative interactions leads to a considerable abruptness of transition with a hysteresis loop ($\Delta T = 11$ K), but additional thermal cycles did not affect the thermal hysteresis loop. Another important characteristic of 1·MeOH is to exhibit a frozen-in effect. This phenomenon is observed when cooperativity is large and the relaxation rate is quite low. The experimental results reflect that strong cooperative interactions are generated from 1·MeOH.

In order to gain more detail insight of SCO, the Mössbauer spectra were measured for 1·MeOH at 200 K and 78 K (Fig. 2b). At 200 K, a broad singlet with *Q.S.* = 0.31 mm s^{-1} and *I.S.* = 0.22 mm s^{-1} is observed, implying that the iron(III) takes the HS state. A new doublet absorption with wide quadrupole splitting ($\Delta Q = 2.62$ mm s^{-1}; $\delta = 0.07$ mm s^{-1}) appeared at 78 K, corresponding to the LS state. The result of Mössbauer measurement is consistent with the magnetic properties described above.

LIESST experiment was also carried out on powder sample of 1·MeOH to investigate their photo-magnetic properties as depicted in Fig. 2a. It has been reported that a broad energy band (500–1000 nm) of the LS iron(III) compound under the visible region could be ascribed to the spin-allowed ligand to metal charge transfer (LMCT) transition [18–20]. At first 1·MeOH was slowly cooled down from room temperature to 5 K, and then illuminated at 1000 nm for 1 h. It shows rapid magnetic response until it is reached to the limited value ($\chi_m T = 1.98$ cm^3 K mol^{-1}). This suggests that the

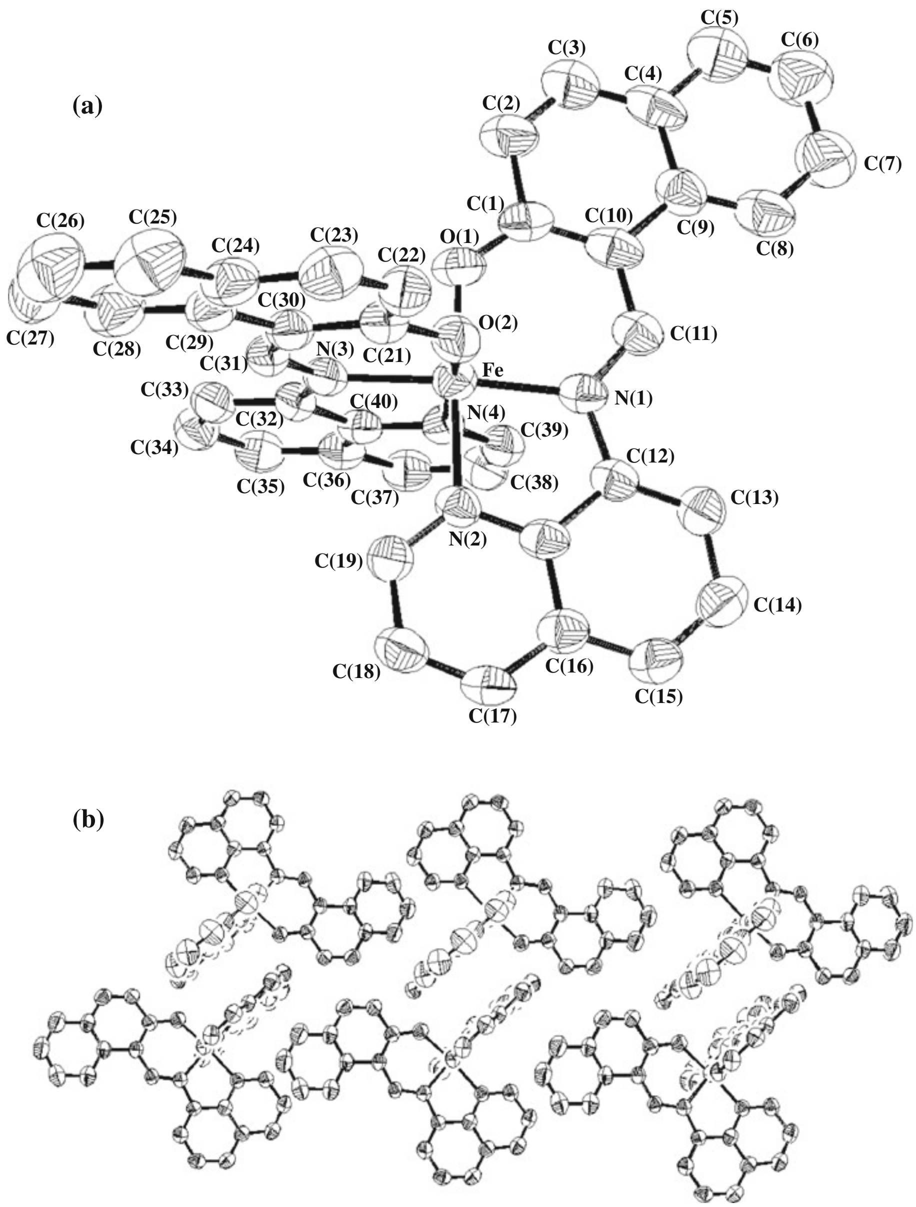


Fig. 1 **a** ORTEP drawing of 1·MeOH at 80 K showing 50% probability displacement ellipsoids. **b** Projection of the crystal structure of 1·MeOH. CF_3SO_3-ions, MeOH molecules, and H atoms are omitted for clarity

irradiation of light converts 52% of the LS fraction into the photo-induced metastable HS state. The χ_mT value remains constant when the temperature is low but decreases on heating. LIESST temperature, T(LIESST) calculated using the extreme of the $\partial\chi_mT/\partial T$ derivative of 1·MeOH is 75 K. The result provides that the metastable state can be maintained for a long time if the sample is retained below 50 K.

The magnetic property of 1·acetone is also shown in Fig. 3a. As expected, the χ_mT value at 300 K is equal to 3.87 cm^3 K mol^{-1}, which is accordance with the HS state in iron(III) compounds. On cooling, the χ_mT value drops abruptly around $T_{1/2}\downarrow = 130$ K, then it is reached to 0.49 cm^3 K mol^{-1} at 70 K. On heating, an abrupt variation of χ_mT is observed around $T_{1/2}\uparrow = 133$ K. The magnetic result shows an abrupt transition with a hysteresis loop ($\Delta T = 3$ K) and the frozen-in effect. Mössbauer spectra of 1·acetone recorded at 200 and 78 K point out a broad singlet peak in the HS state with $Q.S. = 0.43$ mm s^{-1} and $I.S. = 0.21$ mm s^{-1} at 200 K and a new doublet peak in the LS state with wide quadrupole splitting ($\Delta Q = 2.61$ mm s^{-1}; $\delta = 0.08$ mm s^{-1}) at 78 K, respectively. This is consistent with the magnetic properties described above. LIESST experiment was conducted under the same condition for 1·MeOH using powder sample of 1·acetone and its photomagnetic property was depicted in Fig. 3a. The magnetic response of the sample is increased rapidly and finally reaches to the limited value ($\chi_mT = 4.13$ cm^3 K mol^{-1}). This suggests that the LS ground state is completely photoconverted to a metastable HS state after irradiation of sample with light. The T(LIESST) is 58 K.

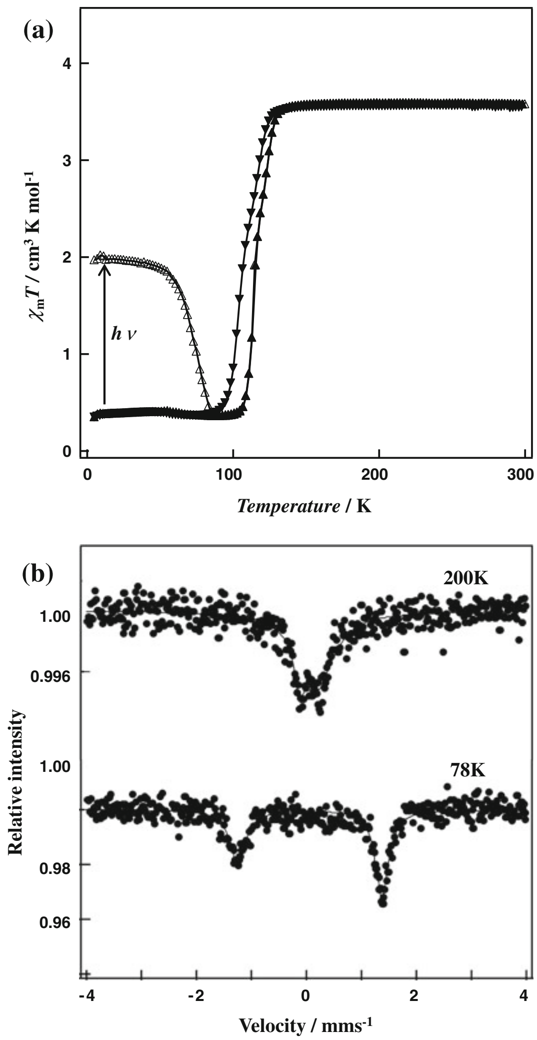


Fig. 2 **a** $\chi_m T$ versus T plots for 1·MeOH. Sample was cooled from 300 to 5 K (*filled inverted triangle*) and then warmed from 5 to 300 K (*filled triangle*) at a rate of 2 K min^{-1}. Sample was warmed at a rate of 2 K min^{-1} after irradiation at 5 K (*open triangle*). **b** ^{57}Fe Mössbauer spectra of 1·MeOH at 200 and 78 K

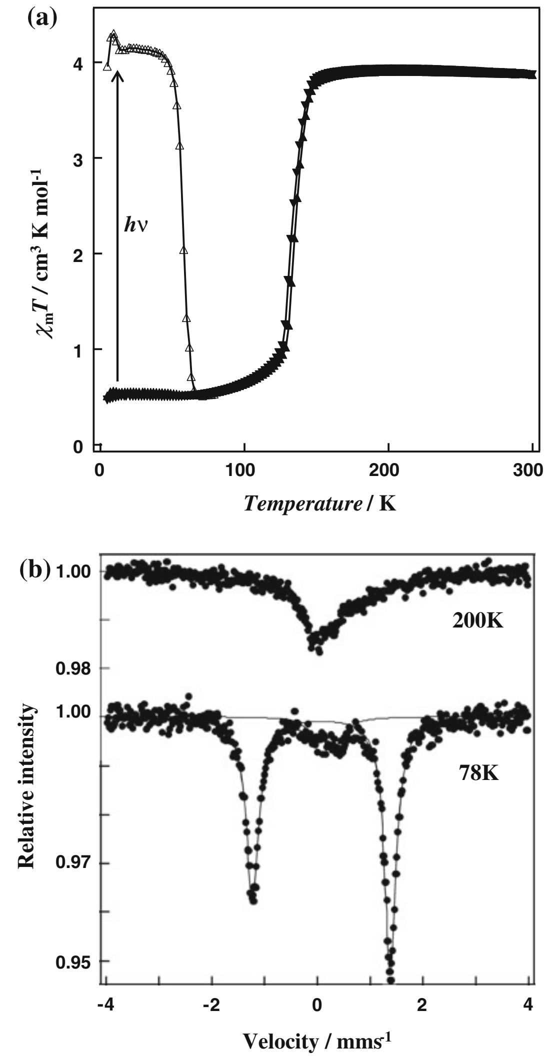


Fig. 3 **a** $\chi_m T$ versus T plots for 1·acetone. Sample was cooled from 300 to 5 K (*filled inverted triangle*) and then warmed from 5 to 300 K (*filled triangle*) at a rate of 2 K min^{-1}. Sample was warmed at a rate of 2 K min^{-1} after irradiation at 5 K (*open triangle*). **b** ^{57}Fe Mössbauer spectra of 1·acetone at 200 and 78 K

The anomalous long-lived metastable state was also considered due to the presence of the strong intermolecular interaction. Owing to the smaller Δr_{HL} value of 1·MeOH and 1·acetone than that of typical iron(II) compounds [1, 2], the LIESST effect should be impossible. However, in spite of small Δr_{HL}, the result of 1·MeOH and 1·acetone shows a larger and wider energy barrier between the HS and LS states. As a rule, it is notable that the single coordinate configuration (SCC) approach may not be applicable to iron(III) SCO compounds with the FeN_4O_2 core in 1·MeOH and 1·acetone [20]. In fact, if the distortion between the HS and LS states is larger, it cannot be approximated by the SCC model. Aside from the stretching mode (Δr_{HL}), it is a reasonable access to investigate the distortion of 1·MeOH and 1·acetone if it is possible to be considered only the bending mode. However, if both stretching and bending modes are considered, the structural changes will be enlarged. Furthermore, the additional bending mode results in a substantial increase in barrier height, and thus effectively slowing down the relaxation process. Accordingly, the LIESST effect could be observed even for iron(III) compound 1·X.

Conclusions

Two iron(III) compounds, $Fe(qnal)_2]CF_3SO_3$·MeOH (1·MeOH) and $[Fe(qnal)_2]CF_3SO_3$·acetone (1·acetone), exhibited abrupt spin transition with thermal hysteresis.

The molecular packing of both compounds formed 2-D sheets by the strong π–π interactions. The difference of bond lengths ($\Delta r_{HL} = 0.1$ Å) was similar to that of other iron(III) SCO compounds while it was considerably smaller than that for iron(II) SCO compounds ($\Delta r_{HL} = 0.2$ Å). Nevertheless, we succeeded in observing the LIESST effect of iron(III) compounds 1·MeOH and 1·acetone. The LIESST effects of 1·MeOH and 1·acetone were observed by excitation at 1000 nm wavelength from the LS state to the photo-induced metastable HS state. Accordingly, herein we have discussed the importance of molecular distortion to produce the LIESST effect of iron(III) SCO compounds. As for the structural changes between the HS and LS states for 1·MeOH and 1·acetone, the degree of distortion was considerably larger than that of normal SCO iron(III) compounds. In general, the effect of the molecular distortion inducing SCO on iron(III) complexes is relatively larger in comparison with other cases due to the presence of qnal ligand with the strong π–π stacking system. It is suggested that the large molecular distortion around metal ions with the bending mode plays an important role in the production of the LIESST effect on iron(III) SCO compounds. It is thought that in case of SCO behavior the cooperativity resulted from the intermolecular interaction induces the structural distortion of the metal complex because of the clear-starching effect among the neighboring molecules. Therefore, it was considered both stretching and bending modes in the reaction coordinate. We believe that our approach, i.e., the introduction of molecular distortion to trap the photo-induced metastable state, can be widely used in the design of other metal complexes with LIESST effect as well as a variety of optically switchable compounds.

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