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Spin Crossover

A Spin-Crossover Cluster of Iron(II) Exhibiting a Mixed-Spin Structure and Synergy between Spin Transition and Magnetic Interaction**

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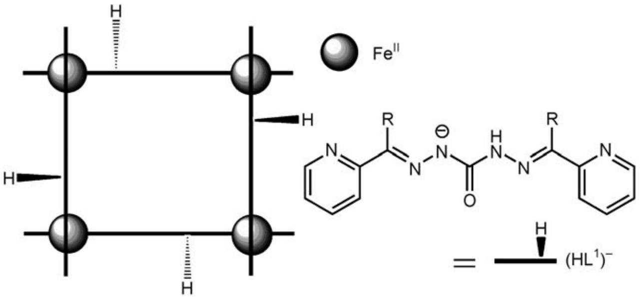
The development of advanced materials whose physical properties can be switched by external perturbations, such as temperature, light, and pressure, has recently been attracting much attention.[1–4] Toward this end, molecules that exhibit bistability, meaning that they can exist in two different electronic states,[5] are being actively investigated. Typical examples of molecular species that exhibit such bistability are spin-crossover (SCO) compounds, which can switch between a high-spin (HS) and a low-spin (LS) state.[6] Since the first observation of a spin-crossover compound in 1931,[7] many interesting spin-transition compounds have been synthesized.[8–12] These exhibit large hysteresis loops,[13] room-temperature hysteresis,[14] and photoinduced phase transitions.[15] Most SCO compounds consist of monomeric units. Spin crossover in binuclear systems is rare and interesting, because both the spin state and the magnetic coupling in polynuclear systems can be switched by the external stimuli of temperature, pressure, or light.[16] In 1992, Real et al. reported pioneering work on a two-step dinuclear spin-crossover compound.[17] This work has attracted much attention from the groups of Real and Gütlich,[18] Murray and Brooker,[19] Kaizaki,[20] and others.[21] To date, this singular switchable behavior and these phenomena have not been extended to clusters with higher nuclearity.

The construction of clusters that allow the SCO centers to communicate through covalent bonds is an important strategy to explore and enhance cooperativity. In binuclear systems,[22] interactions tending to favor pair states consisting of identical spin states (HS–HS or LS–LS) are usually referred to as "cooperative" or "ferromagnetic-like", while those tending to favor pair states composed of different spin states (HS–LS or LS–HS) are usually called "anticooperative" or "antiferromagnetic-like";[23] in particular, the synergy between electronic, magnetic, and elastic interactions (ferromagnetic- or antiferromagnetic-like) in a cluster may lead to unusual behavior of the spin transition. For example, it was proposed that antiferromagnetic-like interactions between Fe^{II} ions play an important role in the induction of spin transition in the dinuclear Fe^{II} compound [Fe$_2^{II}$(bt)$_2$(NCS)$_4$(bpym)] (bt = 2,2′-bithiazoline, bpym = 2,2′bipyrimidine).[24] Just recently, Grunert et al. reported the elegant confirmation of an unusual [HS–LS] pair structure associated with half SCO.[25] To our knowledge, however, no examples exhibiting SCO arising from this type of synergy are clusters with more than two spin-crossover sites. Oshio and co-workers reported an interesting two-step spin transition in a cyano-bridged square iron(II) compound, in which two spin-crossover sites are separated by the diamagnetic subunit [Fe(bpy)$_2$(CN)$_2$] (bpy = 2,2′-bipyridine) at the crossing site of the square, and the actual number of possible spin-crossover sites is two.[26] Recently, Lehn, Gütlich, and co-workers reported [2 × 2] grid compounds that show successive spin transitions, but the transition is very gradual, and molecular bistability must still be improved.[27] Herein, we report an (Fe^{II})$_4$ oxo-bridged cluster that undergoes abrupt thermally induced and complete photoinduced spin transition. In particular, the spin transition occurs on the same side of the Fe^{II} square, and consequently the mixed-spin alignment adopts a *cis*-(LS-LS-HS-HS) rather than *trans*-(LS-HS-LS-HS) geometric configuration, different from the typical checkerboard pattern structure.[28] It is of note that the ligand H$_2$L^1 (Scheme 1) is well predetermined for the tetranuclear square,[29] as the bridging oxygen atom facilitates effective magnetic coupling



Scheme 1. Schematic representation of the self-assembly of the tetranuclear square.

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between SCO sites. The spin transition was observed to be synergistically coupled to magnetic superexchange interactions. Light-induced excited spin state trapping (LIESST) experiments revealed the complete photoinduced spin transition and the synergy between the LIESST effect and the intramolecular antiferromagnetic interaction.

The reaction between the ligand H_2L^1 (Scheme 1) and the corresponding ferrous salt without adding any base in air and at room temperature gave the self-assembly compounds $[Fe_4(HL^1)_4](BF_4)_4{\cdot}(H_2O)_2{\cdot}CH_3OH$ ($\mathbf{1}(BF_4)_4$) and $[Fe_4(HL^1)_4](PF_6)_4{\cdot}(H_2O)_2{\cdot}CH_3OH$ ($\mathbf{2}(PF_6)_4$). Their compositions were identified with ESI mass spectrometry and elemental analysis (Figure S1 in the Supporting Information). The X-ray crystal structure of compound $\mathbf{1}(BF_4)_4$ at 123 K, which is representative for both compounds, is shown in Figure 1.

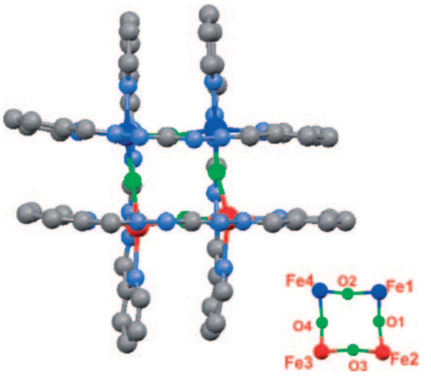

Figure 1. Molecular structure of $\mathbf{1}^{4+}$ at 123 K. Average Fe–O and Fe–N bond lengths [Å] at 123 K: 2.032 and 1.976 (Fe1, LS), 2.093 and 2.119 (Fe2, HS), 2.129 and 2.152 (Fe3, HS), 2.045 and 1.993 (Fe4, LS); at 283 K: 2.132 and 2.160 (Fe1, HS), 2.102 and 2.153 (Fe2, HS), 2.114 and 2.139 (Fe3, HS), 2.113 and 2.151 (Fe4, HS). Inset: Fe_4O_4 core structure. Blue LS, red HS.

X-ray crystallographic analysis at both high and low temperature revealed that the asymmetric unit contains a tetranuclear cationic cluster of $\mathbf{1}^{4+}$.[30] With decreasing temperature, the chiral space group $P2_12_12_1$ is unchanged and the cell dimensions decrease slightly. Investigation of the other crystals in the same batch revealed that the compound is composed of a racemic mixture of opposite handedness. As shown in Figure 1, the cation is composed of four iron ions and four partially deprotonated ligands; each pseudooctahedral iron atom is positioned at a corner of the square. Each ligand loses one proton upon coordination to Fe^{II}, which is evidenced by the bond distances in the ligand skeleton. (Tables S2 and S3 in the Supporting Information). Each metal center is surrounded by two sets of N_2O tridentate units from different ligands. Neighboring iron ions are bridged by the single oxygen atoms of the ligand "edges" with M···M separations of approximately 3.8 Å and M-O-M angles of about 130°, facilitating the antiferromagnetic superexchange pathway.[31] On the other hand, since the coordination bond lengths around the Fe^{II} centers differ for low-spin (LS) and high-spin (HS) states ($\Delta d = 0.14$–0.24 Å),[32] LS and HS states can be identified by the metal–ligand bond length. In fact, at 123 K, the average Fe–N coordination bond lengths involving two of the Fe^{II} ions (Fe1 and Fe4) along one side of the square are 1.976 and 1.993 Å, which fall into the range characteristic of LS Fe^{II} ions. For Fe2 and Fe3, the average Fe–N bond lengths are 2.119 and 2.152 Å, respectively, typical for HS Fe^{II} ions. Upon heating to 283 K, all the Fe^{II} ions form longer bonds to the ligands [$d(\text{Fe–N}) = 2.139$–2.160 Å, $d(\text{Fe–O}) = 2.102$–2.160 Å], characteristic of the HS state for all the Fe^{II} centers. The bond angles around the Fe^{II} ions also distinguish between HS and LS; LS Fe^{II} ions tend to form larger angles than HS ones. At 123 K, the average *cis*-(N-Fe-N) angle of LS Fe1 and Fe4 is 78.71°, while for HS Fe2 and Fe4, the average *cis*-(N-Fe-N) angle is decreased to 74.65°. X-ray analysis shows that two of the four spin-crossover sites undergo thermally induced spin transitions. Hence, the magnetic interaction and spin transition coexist or compete in the cluster. It should be noted that in the case of tetranuclear mixed-spin species $(Fe^{II}_{hs})_2(Fe^{II}_{ls})_2$, two possible spin geometries may exist, namely, HS species exist either on the same side (a *cis* structure) or on the diagonal (*trans* geometry) of the square. In our case, $\mathbf{1}(BF_4)_4$ is the *cis* isomer concerning the intracluster spin alignment.

Magnetic susceptibility measurements for $\mathbf{1}(BF_4)_4$ were performed in the temperature range 5–300 K (Figure 2). The product of molar susceptibility and temperature ($\chi_M T$) at room temperature is approximately 11.72 emu mol^{-1} K, which is somewhat lower than the value corresponding to four HS Fe^{II} ions ($\chi_M T = 4 \times 3$ emu mol^{-1} K), and the smooth decrease of $\chi_M T$ in the high-temperature range is indicative of antiferromagnetic coupling in the square. As the temperature was decreased to 200 K, $\chi_M T$ decreased quite suddenly and reached a new plateau value of 6.2 emu mol^{-1} K at 125 K, which is close to the value expected for two HS and two LS Fe^{II} centers in a square. The slightly sloping plateau has a width of approximately 90 K. No hysteresis loop was observed in the temperature-dependent susceptibility measurements.

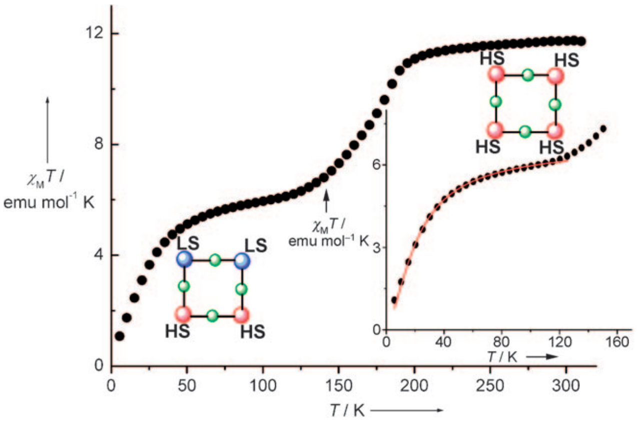

Figure 2. $\chi_M T$ versus T for $\mathbf{1}(BF_4)_4$. Inset: Expansion of the data below 150 K. The red line represents the best theoretical fit (see the Supporting Information) to the experimental data below 120 K.

On further lowering the temperature, the $\chi_M T$ value progressively decreases to a value of 1.08 emu mol^{-1} K at 5 K. In the low-temperature range (below 120 K), the experimental data obeys the Curie–Weiss law. The negative value of θ (-22.84 K) indicates antiferromagnetic exchange coupling between the two HS Fe^{II} centers mediated by the μ_2-O bridge. In other words, the residual two HS iron(II) ions in the Fe_4 square do not exhibit any spin transition. Although the analysis as to why the last two Fe^{II} ions do not undergo SCO is beyond the scope of the present work, theoretical calculations are underway to investigate the balance between cooperative and anticooperative interactions in the system. To interpret the magnetic data quantitatively, we used the calculated expression of the magnetic susceptibility $\chi_M{}^D$ for the remaining pair of local spins in the Fe_4 tetramer.[33] For temperatures below 120 K, the experimental data was fit to the theoretical expressions using a nonlinear least-squares fitting method. The best fit was found with a coupling parameter J of $-4.5\ \mathrm{cm}^{-1}$ and g factor of 2.13 with $R = \Sigma(\chi_M T_{\mathrm{obsd}} - \chi_M T_{\mathrm{calcd}})^2/\Sigma(\chi_M T_{\mathrm{obsd}})^2 = 1.6\times10^{-4}$, which corresponds to an excellent agreement between experimental and calculated values.

The magnetic susceptibility of compound $\mathbf{2}(PF_6)_4$ was measured for comparison and gave different results. No spin transition was observed within the whole temperature range. Antiferromagnetic coupling dominated between the four HS Fe^{II} ions (Figure S5 in the Supporting Information).

Selected ^{57}Fe Mössbauer spectra of $\mathbf{1}(BF_4)_4$ were recorded as a function of temperature between 300 and 8 K (Figure S6 in the Supporting Information). At 300 K, the Mössbauer spectrum exhibits a wide quadrupole doublet with a quadrupole splitting (QS) of 2.74 and an isomer shift (IS) of $0.78\ \mathrm{mm\,s^{-1}}$, showing a typical HS state and the presence of only [HS-HS-HS-HS] species. On cooling to 180 K, a narrow quadrupole doublet appears and gains in intensity at the expense of the original HS doublet. The peak with QS = 1.52, IS = $0.10\ \mathrm{mm\,s^{-1}}$, and area fraction of 33.6 % can be assigned to LS Fe^{II} in an [LS_2-HS_2] cluster arising from the thermally induced spin transition. The original doublet signal corresponding to the HS state in the [HS-HS-HS-HS] species becomes slightly wider, with QS = 2.80, IS = $0.91\ \mathrm{mm\,s^{-1}}$, and an area fraction of 66.4 %. Unfortunately, it is difficult to distinguish between HS Fe^{II} in [HS-HS-HS-HS] species and the [LS-LS-HS-HS] hybrid using standard Mössbauer spectra, because the coordination sphere remains the same around the Fe^{II} ions.[25] With a further decrease of the temperature, the original HS doublet arising from this [HS-HS-HS-HS] cluster continues to lose intensity in favor of the new doublets with equal area fraction arising from LS Fe^{II} and HS Fe^{II} in the hybrid [LS-LS-HS-HS] cluster. At 150 K, the HS and LS states are detected in nearly equal populations (51.3:48.7 %), which gives unambiguous evidence of spin crossover. Below 120 K in the antiferromagnetic coupling region, the LS and HS molar fractions are almost equal, with an area fraction ratio of 1:1. The Mössbauer measurements together with the X-ray structural analysis suggest the complete transition of the two neighboring Fe^{II} ions below 120 K.

Laser irradiation ($\lambda = 785$ nm, 80 mW) was available to investigate photoeffects on compound $\mathbf{1}(BF_4)_4$. After irradiation at 5 K for 30 min, the temperature dependence of $\chi_m T$ in the warming mode was recorded. The magnetic behavior arises from the synergy between the LIESST effect and intramolecular antiferromagnetic interaction at the four HS Fe^{II} ions, of which two are in a photoinduced metastable HS state. Before irradiation, two neighboring HS Fe^{II} ions interact antiferromagnetically and hence yield an $S = 0$ ground spin state. Irradiation of this type of compound at low temperature will actually result in the population of a local HS state of Fe^{II} ions. The antiferromagnetic coupling between the four neighboring HS Fe^{II} centers within the tetranuclear cluster gives rise to a new $S = 0$ ground spin state. So, both before and after irradiation, the compound has a diamagnetic $S = 0$ ground spin state. This result does not mean that the LIESST effect does not occur for compound $\mathbf{1}(BF_4)_4$.[24] As seen in Figure 3 a, with increasing temperature the low-lying magnetic spin states $S = 1$–8, located at higher energy just above the ground state, are progressively populated, and $\chi_m T$ increases. The temperature dependence of $\chi_m T$ above 60 K corresponds to the relaxation of two metastable HS states to LS states. The relaxation temperature of the LIESST effect is defined as T(LIESST) at ca. 77 K. Compound $\mathbf{1}(BF_4)_4$ displays photoswitching magnetism below 77 K. Irradiation at $\lambda = 532$ nm had the same effect on compound $\mathbf{1}(BF_4)_4$.

The magnetic behavior of compound $\mathbf{1}(BF_4)_4$ after two LS Fe^{II} ions are trapped in the local HS states should be very close to that of compound $\mathbf{2}(PF_6)_4$ (antiferromagnetic interaction between HS ions), as the bridging network in $\mathbf{1}(BF_4)_4$ is identical to that in $\mathbf{2}(PF_6)_4$ and the coupling parameter (J) is essentially equal. Figure 3 b confirms this point, which suggests that the conversion yield of the LIESST effect at low temperature is nearly quantitative.

In conclusion, the combined analyses of single crystal X-ray diffraction, magnetic studies, and Mössbauer data unambiguously confirmed the existence of pure [LS_2-HS_2] entities in the tetranuclear half-SCO compound. The spin alignment in the [LS_2-HS_2] entities gave a *cis* structure, that is, [LS-LS-HS-HS]. Because Fe^{II} spin-crossover sites were bridged by single oxygen atoms, synergy between magnetic interaction and spin transition was observed. LIESST revealed a form of synergy between the light-induced excited spin state trapping and magnetic interaction. Further work will investigate the nature of the SCO phenomenon in clusters and theoretically probe the relationship between the magnetic interaction and spin crossover in this system.[34,35]

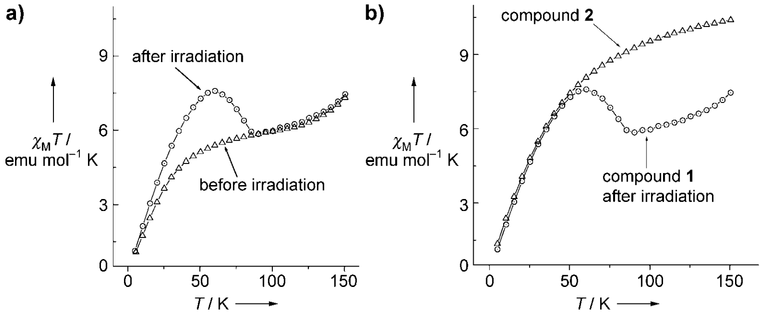

Figure 3. a) The photomagnetism of $\mathbf{1}(BF_4)_4$; △: $\chi_M T$ per cluster before irradiation; ○: $\chi_M T$ upon warming after irradiation at $\lambda = 785$ nm at 5 K for 30 min. b) Comparison of $\chi_M T$ versus T for $\mathbf{2}(PF_6)_4$ and $\mathbf{1}(BF_4)_4$ after irradiation.

Experimental Section

1(BF_4)$_4$: $Fe(BF_4)_2{\cdot}6H_2O$ (0.2 mmol, 0.0675 g) was added to a well-stirred suspension of H_2L^1 (0.2 mmol, 0.0841 g) in methanol (30 mL) without any added base in air. The mixture was stirred for another 10 min to form a dark red solution. Dark red single crystals suitable for X-ray diffraction were isolated by slow evaporation of the solution in air for two weeks (0.0145 mg, 12.6%) IR (KBr pellet): $\tilde{\nu}=$ 521.27(w), 533.22(w), 608.91(w), 703.41(m), 794.05(m), 1039.93(m), 1084.28(s), 1326.30(m), 1364.87(m), 1457.44(m), 1540.36(m), 1569.78(s). Elemental analysis (%) calcd for $C_{101}H_{84}B_4F_{16}Fe_4N_{24}O_7$: H 3.65, C 52.37, N 14.51; found: H 3.62, C 51.91, N 14.54.

See the Supporting Information for preparation of **2**(PF_6)$_4$, Mössbauer spectra, and photomagnetism measurements.

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[30] Crystallographic data for compound **1**(BF_4)$_4$ at $T=283$ K: $C_{101}H_{84}B_4F_{16}Fe_4N_{24}O_7$, $M_r=2316.45$, dimensions: $0.20\times0.15\times0.10$ mm^3, orthorhombic, space group $P2_12_12_1$, $a=15.146(3)$, $b=25.943(5)$, $c=27.130(5)$ Å, $V=10660(4)$ Å^3, $Z=4$, $\rho_{\text{calcd}}=1.438$ g cm^{-3}, $\mu=0.627$ mm^{-1}, 69762 reflections collected, 18683 independent reflections [17074 $I>2\sigma(I)$]. The final R values were $R=0.1053$, $wR_2=0.2622$ for $I>2\sigma(I)$. $R=0.1133$, $wR_2=0.2697$ for all data. Flack parameter: 0.00(2). Crystallographic data for compound **1**(BF_4)$_4$ at 123 K: orthorhombic, space group $P2_12_12_1$, $a=15.048(3)$, $b=25.582(5)$, $c=26.638(5)$ Å, $V=10255(4)$ Å^3, $Z=4$, $\rho_{\text{calcd}}=1.495$ g cm^{-3}, $\mu=0.652$ mm^{-1}, 68110 reflections collected, 18029 independent reflections [17280 $I>2\sigma(I)$]. The final R value were $R=0.0885$, $wR_2=0.2213$ for $I>2\sigma(I)$. $R=0.0918$, $wR_2=0.2241$ for all data. Flack parameter: 0.04(2). The structures were solved by direct methods and refined with full-matrix least-squares procedures using the program SHELXS-97 (G. M. Sheldrick, 1997, SHELXS-97 and SHELXL-97, University of Göttingen, Germany) . CCDC-700719 and 700720 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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