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Bistable Materials

Reversible Electron Transfer in a Linear {Fe_2Co} Trinuclear Complex Induced by Thermal Treatment and Photoirraditaion**

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Bistable materials possess two close-lying states, which can be reversibly interchanged by external stimuli such as temperature, light, pressure, and guest molecules.[1] These materials offer attractive opportunities for the realization of energy-efficient, switchable, molecule-based data storage in electronic devices.[2] A current topic for research in this field is the preparation of switchable multifunctional molecules in which more than two properties coexist or interact synergistically.[3] An important multifunctional compound shows a significant change in both magnetic properties and charge distribution (polarization) at the molecular level. Tunable magnetic molecules, such as spin-crossover complexes, are important for magnetic recording devices.[4] Furthermore, switchable polarity is an essential feature for regulating nonlinear optical and ferroelectric properties.[5] In particular, the study of electronic ferroelectricity, in which an electronic charge order without inversion symmetry is responsible for the electric polarization, has recently attracted significant attention.[6,7] Thus, it is important to design new compounds in which the spin state and charge distribution can be reversibly controlled by external stimuli. To this end, the development of compounds that consist of paramagnetic donors and acceptors is attracting considerable interest because lattice distortion and charge-transfer processes in such compounds involve not only concomitant spin-state changes but also changes in their dielectric properties.[8,9] Significant changes in the magnetic susceptibility and the dielectric constant were observed near the neutral–ionic phase transition temperature of charge-transfer complexes.[8] Furthermore, dimerization of the donor and the acceptor induces the formation of a polar structure from a nonpolar structure because of the breaking of the inversion center as a result of molecular charge transfer. Moreover, it has been reported that a dinuclear cobalt complex with a dioxolene bridging ligand exhibits charge transfer between the bridging ligand (donor/acceptor) and cobalt (acceptor/donor) induced by a temperature change and light irradiation.[9] This transfer is accompanied by magnetization change and the formation of a polar structure in the cluster, which is a molecular-level representation of the interconversion of both magnetization and electric polarization similar to that in the aforementioned charge-transfer complex. With a rational design, various discrete multinuclear complexes have been synthesized by using different building blocks such as cyanometallates.[10] However, until now, only the cobalt-dioxolene system has been reported to show such magnetization changes and polar–nonpolar transformation through charge transfer in response to both thermal and optical stimuli. Therefore, the preparation of new compounds with such properties remains a challenge.

In this work, we aimed at synthesizing linear bimetallic trinuclear clusters with centrosymmetrical structures that are capable of charge transfer between the metal in the center and a metal ion on the edge. The charge-transfer process was expected to induce a change in magnetization because of the change in spin multiplicity.[11] Furthermore, charge transfer in a cluster with an inversion center also induces the formation of a polar structure from a nonpolar one.

To synthesize such a centrosymmetric bimetallic trinuclear cluster, we choose $[FeTp(CN)_3]^-$ (Tp = hydrotris(pyrazolyl)borate) as the building block to treat with $[Co(Meim)_4]^{2+}$ (Meim = *N*-methylimidazole). One cyanide bridge of the $[FeTp(CN)_3]^-$ unit is thought to coordinate with the Co^{II} ion, which tunes the redox potential required for charge transfer. Moreover, the terminal cyanide ligands are thought to form potential hydrogen-bonding interactions with noncoordinated solvent molecules, stabilizing the bistable state through intermolecular cooperative interactions. In fact, we recently synthesized an Fe_2Co trinuclear cluster $\{[FeTp(CN)_3]_2Co(Meim)_4\}\cdot 6\,H_2O$ (**1**), in which the cobalt ion is sandwiched between two iron building blocks (Scheme 1). Compound **1** exhibited thermally induced, reversible electron transfer with a thermal hysteresis and photoinduced electron transfer by excitation of the charge-transfer band.

Single-crystal X-ray diffraction (XRD) analysis revealed that **1** crystallizes in a $P\bar{1}$ space group. The crystal structure comprises neutral $\{[FeTp(CN)_3]_2Co(Meim)_4\}$ trinuclear clusters (Figure 1 a) with noncoordinated water molecules located between the clusters (Figure 1 b). Within the neutral trinu-

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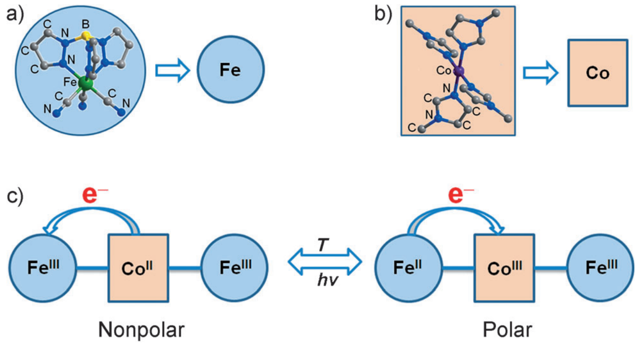

Scheme 1. a) Structure of the $[Fe(Tp)(CN)_3]^-$ building block. b) Structure of the $[Co(N\text{-methylimidazole})_4]^{2+}$ building block. c) Arrangement of iron and cobalt building blocks in **1** and electron-transfer-induced polar–nonpolar transformation of the molecule.

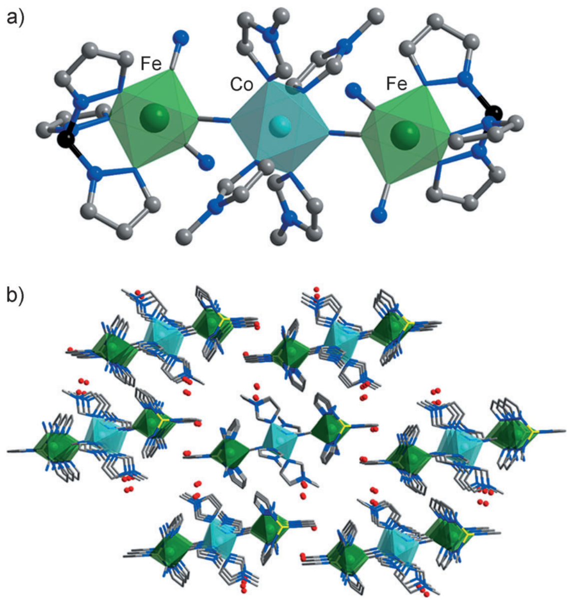

Figure 1. a) Side view of the linear trinuclear arrangement of **1** at 240 K and 150 K. b) Packing diagram of **1** along the *a* axis at 240 K and 150 K. H atoms have been omitted for clarity. Fe green, Co teal, C gray, N blue, B yellow, O red.

clear cluster, three nitrogen atoms from Tp and three cyanide carbon atoms are coordinated to each iron center. Each cobalt center was located in the N_6 octahedral environment with four nitrogen atoms from the Meim ligands in the equatorial plane and two nitrogen atoms from the cyanide bridge of monodentate $[FeTp(CN)_3]^-$ at the apical position. The crystal structure comprised one unique iron center and one unique cobalt center. Three metal ions were in a linear array with a Fe1–Co1–Fe1 (symmetry codes $1-x$, $1-y$, $1-z$) angle of 180.0°. Moreover, hydrogen bonds were formed between noncoordinated water molecules (O···O distance 2.76–2.92 Å) and between terminal cyanide nitrogen atoms and noncoordinated water molecules (O···N distance 2.75–2.94 Å) (Figure S1), providing strong intermolecular cooperative interactions that are needed to stabilize the bistable state.

At 240 K, the Co^{II} ion was located in an elongated N_6 octahedral environment with four short equatorial $Co-N_{Meim}$ distances of 2.121–2.133 Å and two longer apical $Co-N_{cyanide}$ distances of 2.154 Å. The Fe–C bond lengths were 1.924–1.932 Å, and the Fe–N bond lengths were 1.977–1.983 Å. Such structural characteristics indicated that the cobalt centers were Co^{II}_{HS} (HS = high spin) ions whereas the iron centers were Fe^{III}_{LS} (LS = low spin) ions, forming Fe^{III}_{LS}-(μ-CN)Co^{II}_{HS} linkages.[12] However, when crystals of **1** were slowly cooled from 240 to 150 K, the $Co-N_{Meim}$ bond lengths decreased to 1.966–1.967 Å and the $Co-N_{cyanide}$ bond lengths decreased to 1.915 Å, forming a compressed octahedral coordination sphere. The $Co-N_{cyanide}$ bond lengths are in the expected range for Co^{III}_{LS} ions (ca. 1.9 Å).[12] The Fe–C bond lengths were 1.897–1.927 Å, and the Fe–N bond lengths were 1.994–1.996 Å. These temperature-dependent structural variations observed in the crystals of **1** suggested that intramolecular charge transfer converted Co^{II} into Co^{III} ions and parts of Fe^{III} into Fe^{II} ions on the basis of charge balance, and charge transfer occurred randomly on the two iron sites.

Additional evidence for intramolecular electron transfer and spin transition was found in temperature-dependent infrared (IR) spectroscopy studies of **1** (Figure S2). At 290 K, we observed three ν_{CN} absorptions attributed to the free ν_{CN} absorption of $[Fe^{III}Tp(CN)_3]^-$ (2120 and 2141 cm^{-1}) and the bridging ν_{CN} absorption of Fe^{III}_{LS}(μ-CN)Co^{II}_{HS} linkages (2150 cm^{-1}). As the temperature decreased, new ν_{CN} stretches were observed at 2044, 2061, 2085, and 2172 cm^{-1}, which were attributed to free ν_{CN} absorption of $[Fe^{II}Tp(CN)_3]^{2-}$ and the bridging ν_{CN} absorptions of Fe^{II}_{LS}(μ-CN)Co^{III}_{LS} and Fe^{III}_{LS}-(μ-CN)Co^{III}_{LS} linkages.[12] Moreover, these temperature-induced changes in the IR spectra of **1** were completely reversible upon warming the samples, which is consistent with the induction of reversible metal-to-metal charge transfer (MMCT).

^{57}Fe Mössbauer spectra were recorded at 300 K and 6.0 K to characterize the electric states of the Fe centers in **1** (Figure S3). In the high-temperature (HT) phase at 300 K, one quadrupole doublet was observed with Mössbauer parameters of δ (isomer shift) = −0.01 and ΔE_Q (quadrupole splitting) = 0.86 $mm\,s^{-1}$, which is characteristic of LS Fe^{III} species. As the temperature was cooled to 6.0 K, an additional doublet with $\delta = 0.21$ and $\Delta E_Q = 0.41$ $mm\,s^{-1}$, corresponding to the LS Fe^{II} species, was observed. The peak area ratio of the Fe^{II} to Fe^{III} species is 0.51/0.49 at 6.0 K, suggesting complete charge transfer from the HT to the low-temperature (LT) phase.

Magnetic susceptibility measurements were performed to verify the MMCT transition in **1**. At room temperature, the χT value was 4.10 $cm^3\,mol^{-1}\,K$ per Fe_2Co unit, corresponding to the presence of one Co^{II}_{HS} and two Fe^{III}_{LS} ions with significant orbital contribution.[12] The χT values remained nearly constant between 300 and 240 K (Figure 2). However, slowly decreasing the temperature (0.5 $K\,min^{-1}$) from 240 to 160 K afforded a decrease in the χT values, reaching 0.70 $cm^3\,mol^{-1}\,K$ at 170 K. In contrast, upon heating (0.5 $K\,min^{-1}$), the χT values increased and returned to the initial values with a small thermal hysteresis loop. Such a magnetic feature confirmed a reversible charge-transfer

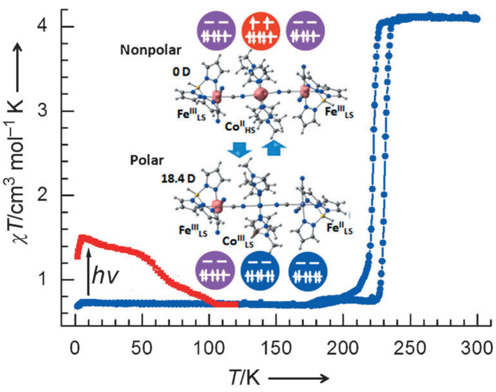

Figure 2. Temperature-dependent magnetic susceptibilities of **1** before light irradiation (●) and after light irradiation (■) in χT vs. T. Inset: α–β SCF densities of **1** in the HT and LT phases, and polar–nonpolar transformation of the molecule. HS = high spin and LS = low spin.

process that involved transformation from the HT phase with $\mathrm{Fe^{III}}_{\mathrm{LS}}$ ($S=1/2$) and $\mathrm{Co^{II}}_{\mathrm{HS}}$ ($S=3/2$) ions into the LT phase with diamagnetic $\mathrm{Fe^{II}}_{\mathrm{LS}}$ ($S=0$) and $\mathrm{Co^{III}}_{\mathrm{LS}}$ ($S=0$) centers. According to the χT values and ^{57}Fe Mössbauer spectra results, all $\mathrm{Co^{II}}_{\mathrm{HS}}$ changed to $\mathrm{Co^{III}}_{\mathrm{LS}}$ ions because of the transformation from the HT phase to the LT phase. Therefore, the transformation could be expressed by $\{[\mathrm{Fe^{III}Tp(CN)_3}]_2\mathrm{Co^{II}(Meim)_4}\}\cdot 6\,\mathrm{H_2O} \rightleftarrows \{[\mathrm{Fe^{III}Tp(CN)_3}][\mathrm{Fe^{II}Tp(CN)_3}]\mathrm{Co^{III}(Meim)_4}\}\cdot 6\,\mathrm{H_2O}$. As the temperature further decreased from 160 K, the χT values remained nearly constant down to 2.0 K, indicating the paramagnetic behavior of the isolated $\mathrm{Fe^{III}}$ ions. Field-dependent magnetization at 1.8 K steeply increased to 1.17 $N\beta$ at 50 kOe, which agrees with the paramagnetic behavior of one $\mathrm{Fe^{III}}_{\mathrm{LS}}$ ion per $\mathrm{Fe^{II}}_{\mathrm{LS}}\mathrm{Fe^{III}}_{\mathrm{LS}}\mathrm{Co^{III}}_{\mathrm{LS}}$ unit (Figure S4). Because of intermolecular cooperative interactions, the system exhibited bistability with respect to temperature. The phase transition is an entropy-driven process, as revealed in similar charge-transfer systems.[13] The $[\mathrm{FeTp(CN)_3}]^-$ unit plays an important role in not only tuning the redox potential required for charge transfer but also forming hydrogen-bonding interactions with non-coordinated solvents and cooperative intermolecular interactions.

In **1**, ligand-based absorption bands were observed in the UV region and a relatively broad absorption band was observed at 438 nm with a small shoulder at 520 nm (Figure S5). The absorption band at 438 nm in **1** can be assigned to the LMCT and MLCT bands in the Fe and Co chromophores. The shoulder band at 520 nm can be assigned as the $\mathrm{Fe^{II}} \rightarrow \mathrm{Co^{III}}$ intervalence charge-transfer band, as reported in related complexes.[14] This absorption is weak at room temperature, because most of the components have a $\mathrm{Fe^{III}}_{\mathrm{LS}}$-CN-$\mathrm{Co^{II}}_{\mathrm{HS}}$-NC-$\mathrm{Fe^{III}}_{\mathrm{LS}}$ state. At low temperature, **1** is in the $\mathrm{Fe^{II}}_{\mathrm{LS}}$-CN-$\mathrm{Co^{III}}_{\mathrm{LS}}$-NC-$\mathrm{Fe^{III}}_{\mathrm{LS}}$ state. Irradiation with a 532 nm laser corresponds to the excitation of the $\mathrm{Fe^{II}} \rightarrow \mathrm{Co^{III}}$ intervalence charge-transfer band.

We investigated the photo-effect of the LT phase of **1** to determine the possibility of photoinduced electron transfer and spin transition at the Co site. Under light irradiation with a laser-diode-pumped Nd:YAG laser ($\lambda = 532$ nm, 30 mW cm^{-2}, 24 h) at 5 K, the χT values rapidly increased and reached a maximum of 1.5 cm^3 mol^{-1} K after 24 h, thus suggesting that $\mathrm{Fe^{III}}_{\mathrm{LS}}$(μ-CN)$\mathrm{Co^{II}}_{\mathrm{HS}}$ pairs are photogenerated. Photoinduced magnetization relaxed to the initial value on thermal treatment up to 90 K (Figure 2), indicating that magnetization could be increased by light irradiation and recovered with a thermal treatment. IR spectra support the occurrence of the charge transfer. Irradiation by a 532-nm laser decreased the IR peaks of the LT phase and generated the spectra of the HT phase (Figure S6). This result is consistent with the fact that the irradiation of the LT phase induced a valence-state change from the $\mathrm{Fe^{II}}_{\mathrm{LS}}$-$\mathrm{Co^{III}}_{\mathrm{LS}}$ state to the $\mathrm{Fe^{III}}_{\mathrm{LS}}$-$\mathrm{Co^{II}}_{\mathrm{HS}}$ state.

The LT phase of **1** crystallizes in a nonpolar $P\bar{1}$ space group, and charge transfer occurred randomly on the two iron sites. However, for each molecule in the transformation from the HT to LT phase, one electron transferred from $\mathrm{Co^{II}}$ to one of the $\mathrm{Fe^{III}}$ ions, and the centrosymmetric nonpolar molecule in the HT phase became the asymmetric polar molecule in the LT phase.[15] Upon heating, one electron was transferred from $\mathrm{Co^{III}}$ to $\mathrm{Fe^{II}}$ ions, and the polar molecule returned to its nonpolar state, demonstrating switchable polarity. To estimate changes in electronic structures, we carried out DFT calculations in the doublet spin state (the LT phase) and the sextet spin state (the HT phase) using the X-ray crystal structures of **1** (Table S1). Calculated spin densities of metal centers are $\mathrm{Fe^{III}}_{\mathrm{LS}}$(1.0), $\mathrm{Co^{III}}_{\mathrm{LS}}$(0.0), and $\mathrm{Fe^{II}}_{\mathrm{LS}}$(0.0) in the doublet spin state and $\mathrm{Fe^{III}}_{\mathrm{LS}}$(1.1), $\mathrm{Co^{II}}_{\mathrm{HS}}$(2.8), and $\mathrm{Fe^{III}}_{\mathrm{LS}}$(1.1) in the sextet spin state at the B3LYP/6-311G* level of theory. However, calculated Mulliken charges of the metal centers are not influenced by the valence state. In the DFT calculations, the LT phase has a permanent electric dipole moment of 18.4 D, whereas the HT phase has no dipole moment (Figure 2). Therefore, the interconversion between the two spin states induces polar–nonpolar transformation of **1**. These computational results are completely consistent with the experimental observations. Note that, in contrast with ionic cobalt–dioxolene system,[9] the molecules in **1** are neutral. For ionic molecules, the dipole moment depends on both charge distribution within the molecule and the position of counterions. To design and synthesize such a molecule with switchable polarity, the intermolecular interactions and crystal-packing effect should be considered, which are relatively difficult to control. However, for neutral molecules, dipole moment depends on charge distribution within the molecule. It is easier to control the polarity by choosing different building blocks to control the intramolecular linkage and charge distribution.

In conclusion, we obtained a linear trinulear $\mathrm{Fe_2Co}$ compound showing reversible, thermally and photoinduced electron transfer. Accompanying the electron transfer, the $\mathrm{Fe_2Co}$ complex showed reversible polar–nonpolar transformation as a result of breaking of the inversion center induced by charge transfer between Fe and Co ions. Furthermore, a significant change in the magnetic properties was observed as a result of electron transfer and spin transition at the Co site. For the future, it might be interesting to direct the electron transfer in the solid state by an external electric field.[7]

Experimental Section

Synthesis of **1**: A solution of $Bu_4N[(Tp)Fe(CN)_3]$[16] (0.1 mmol) in 6.0 mL methanol was placed at the bottom in one side of an H-shaped tube, and 6.0 mL of an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ (0.05 mmol) and *N*-methylimidazole (0.1 mmol) was introduced into the other side. Then, 6.0 mL of methanol was layered over the solutions on both sides to provide a diffusion pathway. Crystallization required several weeks and gave crystals in 60 % yield on the basis of $Co(NO_3)_2{\cdot}6H_2O$. Elemental analysis, calculated for $C_{40}H_{56}N_{26}O_6B_2CoFe_2$: C 40.40, H 4.75, N 30.62; found: C 40.74, H 4.57, N 30.95.

For further information about magnetic properties, measurements, IR, and XRD results, as well as computational methods, see the Supporting Information.

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