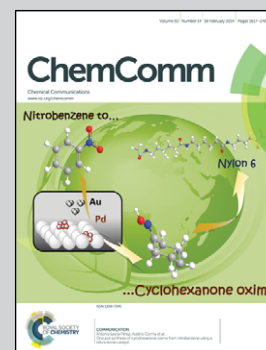


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Selective on/off switching at room temperature of a magnetic bistable $\{Fe_2Co_2\}$ complex with single crystal-to-single crystal transformation *via* intramolecular electron transfer

A cyano-bridged $\{Fe_2Co_2\}$ complex shows reversible single crystal-to-single crystal transformation between diamagnetic and paramagnetic states switched specifically by losing and absorbing methanol at room temperature in the solid state. The solvent loss form presents temperature- and pressure-induced intramolecular electron transfer behaviour.

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Selective on/off switching at room temperature of a magnetic bistable $\{\text{Fe}_2\text{Co}_2\}$ complex with single crystal-to-single crystal transformation *via* intramolecular electron transfer†

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A cyano-bridged $\{\text{Fe}_2\text{Co}_2\}$ complex shows reversible single crystal-to-single crystal transformation between diamagnetic and paramagnetic states switched specifically by losing and absorbing methanol at room temperature in the solid state. And the solvent loss form presents temperature- and pressure-induced intramolecular electron transfer behaviour.

Since the three-dimensional Co/Fe Prussian blue analogue, $\text{K}_{0.2}\text{Co}_{1.4}[\text{Fe}(\text{CN})_6] \cdot 6.9\text{H}_2\text{O}$,¹ was found to exhibit reversible electron-transfer in the linkage of $\text{Fe}^{\text{II}}-\text{C}\equiv\text{N}-\text{Co}^{\text{III}}$ induced by light irradiation, many efforts have been devoted to prepare zero-dimensional cyano-bridged bimetallic molecules with such bistability induced by external stimuli such as temperature and/or light in recent years.^{2–8} These small molecules show tunable optical and magnetic behavior for the reversible conversion between diamagnetic $\text{Co}^{\text{III}}/\text{Fe}^{\text{II}}(\text{W}^{\text{IV}})$ and paramagnetic $\text{Co}^{\text{II}}/\text{Fe}^{\text{III}}(\text{W}^{\text{V}})$ species as a function of temperature,^{2a,b,d,3,4,5,c,6–8} light^{2c,3,4,c,5a,b,6,7} or solvent,^{2b,4c,6} which make them have promising applications in information processing, high-density data storage, molecular switches, sensors, electronic devices, spintronics, *etc.*⁹

Compared with the numerous spin crossover (SCO) compounds¹⁰ bearing spin transition behavior due to the change of the electron configuration of the transition metal's d atomic orbitals, the reported

cyano-bridged bimetallic clusters with reversible CTIST behavior are very limited.^{2–8} It is still a challenge for chemists to design and obtain such bistable materials with desirable properties. With the efforts of several groups towards determining the structure–property relationships of cyano-bridged $\{(\text{Tp}^{\text{R}})_2\text{Fe}_2(\mu\text{-CN})_4\text{Co}_2\text{L}_4\}$ squares,^{3b,4a,b,5a,6a} it can be concluded that the capping ligands on the Fe and Co centers are crucial for the transition temperature of CTIST, and the CTIST phenomenon for this kind of complexes can only be fulfilled when the ancillary ligands on the two metal centers match well to tune the metal centers' redox potentials with an appropriate difference value. For the $\{(\text{Tp}^{\text{R}})_2\text{Fe}_2(\mu\text{-CN})_4\text{Co}_2(\text{bpy}^{\text{R}})_4\}$ series, it is clear that the higher transition temperature of CTIST is observed with the stronger electron donation of the modifying groups of bpy on the Co centers.^{3b,4b,6a} Based on this knowledge and the advantage of easy ligand-modification on this system, the $\{\text{Fe}_2(\mu\text{-CN})_4\text{Co}_2\}$ square can be treated as a structural archetype to readily design new CTIST compounds with novel properties.

By an elaborate choice of ancillary ligands, we designed and synthesized a new $\{\text{Fe}_2\text{Co}_2\}$ square complex, $\{[(\text{Tp})\text{Fe}(\text{CN})_3]_2[\text{Co}(4,4'\text{-bc bpy})_2]_2\}(\text{ClO}_4)_2 \cdot 2\text{MeOH}$ (**1·2MeOH**, Tp = hydrotris(pyrazolyl)borate, 4,4'-bc bpy = 4,4'-bis(ethoxycarbonyl)-2,2'-bipyridine), which exhibited reversible CTIST behavior around room temperature upon desorption–absorption of methanol molecules in a reversible single crystal-to-single crystal (SC–SC) transformation manner in the solid state. Interestingly, this process is specific to methanol and not responsive to other alcohols, ammonia, other protic or aprotic solvents, as well as dilute acids and bases, *etc.* We also found that the solvent loss form, **1**, showed an incomplete intramolecular charge transfer process with the decrease of temperature, furthermore, which can be finished by application of external hydrostatic pressure to give a complete low spin state.

Treatment of 4,4'-bc bpy with cobalt perchlorate hexahydrate in MeOH, followed by $(\text{Bu}_4\text{N})[(\text{Tp})\text{Fe}(\text{CN})_3]$, affords dark-green crystals of $\{[(\text{Tp})\text{Fe}(\text{CN})_3]_2[\text{Co}(4,4'\text{-bc bpy})_2]_2\}(\text{ClO}_4)_2 \cdot 2\text{MeOH}$ (**1·2MeOH**) within several days. The X-ray structure shown in Fig. 1 exhibits a $\{\text{Fe}_2\text{Co}_2\}$ core similar to the reported analogues^{3b,4b,6a} as expected. The crystallographic data (**1·2MeOH**) reveal that the Co–N bond lengths vary from 1.877(2) to 1.936(2) Å, implying that the complex is in a low spin state

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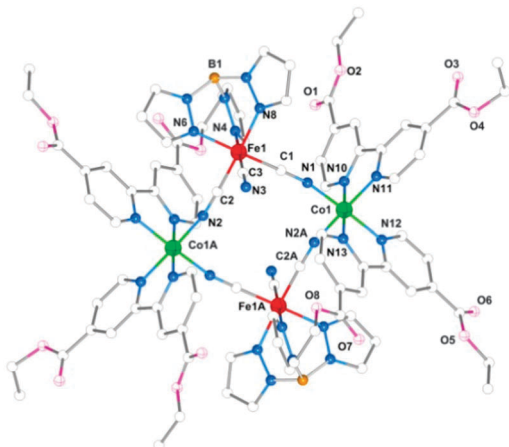


Fig. 1 Crystal structure of complex **1·2MeOH**. Hydrogen atoms, solvents and anions are omitted for clarity. $A = x, 1 - y, 1 - z$.

with the $\text{Fe}^{\text{II}}(\mu\text{-CN})\text{Co}^{\text{III}}$ linkage. This is consistent with the green color of this compound and the typical vibrations of cyanide groups (2110, 2089, and 2065 cm^{-1} , Fig. S1, ESI[†]) in infrared spectra for cyano-bridged $\{\text{Fe}_2\text{Co}_2\}^{\text{III}}$ squares.^{2a,b,3b,4a,b,5a,6a}

When the green crystals are exposed to an ambient atmosphere at room temperature, the green color turns red soon to give $\{[(\text{Tp})\text{Fe}(\text{CN})_3]_2[\text{Co}(4,4'\text{-bcppy})_2]_2\}(\text{ClO}_4)_2$ (**1**). According to the related literatures,²⁻⁷ the red color of cyano-bridged $\{\text{Fe}_2\text{Co}_2\}$ complexes indicates that the molecules are in a high spin state with the $\text{Fe}^{\text{III}}(\mu\text{-CN})\text{Co}^{\text{II}}$ linkage, which is confirmed by the $\nu_{\text{C}\equiv\text{N}}$ stretching absorptions (2168 and 2122 cm^{-1} , Fig. S1, ESI[†]) of **1**. Further evidence was obtained by collecting the X-ray diffraction data (**1**_{273K}) for the resulting red crystal at 273 K. The crystallographic data demonstrate that the Co–N bond lengths vary from 2.049(11) to 2.138(9) (average 2.098) Å, confirming the high spin state in the red crystals of **1**.²⁻⁷ The PXRD spectra were recorded for **1** to check the crystallinity of the bulk sample, and the results verified the uniformity of the sample with good crystallization (Fig. S2, ESI[†]).

Interestingly, the transition process is reversible in a single crystal-to-single crystal (SC–SC) transformation manner. It has been shown above about the change from the original as-synthesized green form to the red form. To check the reverse way, the red crystals of **1** were soaked in methanol, and we found that the color changed to green immediately. The FT-IR spectra confirm that the new green product is the same as the original as-synthesized sample. One of the resulting green crystals was chosen to collect X-ray diffraction data (**1·2MeOH**). The solved structure is exactly the same as that of the original **1·2MeOH** (Fig. S3 and Table S1, ESI[†]), although the quality of the crystal is not as good as the original one. The process of loss and recombination of methanol molecules for the crystalline solid was repeated over 20 times, and showed no discernable change. This behavior demonstrates that this compound is a molecular memory material.

The structure of **1·2MeOH** indicates that there are hydrogen bonds ($\text{O}_{\text{MeOH}} \cdots \text{N}_{\text{CN}} = 2.872(2)$ Å) between the lattice methanol molecules and the nitrogen atoms of the terminal cyanide groups (Fig. S4, ESI[†]). Therefore, the reason for methanol molecules in the lattice controlling the transition is ascribable to the

electron-withdrawing effect of these H-bonds which induced a positive shift of the reduction potentials of iron centers.^{2b} And the chosen capping ligands on iron and cobalt centers in this $\{\text{Fe}_2\text{Co}_2\}$ square match well to make the CTIST process fall into the room temperature range. This implies that other hydrogen bonding donor molecules may play the same role to influence the charge transfer behavior. However, when we tried to substitute methanol with other alcohols, the red crystals remained unchanged. Other protic or aprotic solvents (such as water, ammonia, acetic acid, ethyl acetate, CH_2Cl_2 , MeCN, THF, DMF, DMSO, etc.) were also tested, but the results were all negative. Moreover, when we treated the red sample with dilute acids (such as 3 M HCl) or bases (such as 2 M NaOH), it was able to retain the color for several hours without any obvious change, but it was destroyed slowly when more concentrated acids (such as 6 M HCl) or bases (such as 4 M NaOH) were used. This specificity to methanol of **1** can be attributed to (i) the template effect of methanol in the original structure which will form a cavity with the loss of the lattice methanol that is just good for methanol to prevent other bigger protic or aprotic solvent molecules to access the $\{\text{Fe}_2\text{Co}_2\}$ core; and (ii) the ethoxycarbonyl groups in the structure forming a hydrophobic protecting shell around the $\{\text{Fe}_2\text{Co}_2\}$ core being an encumbrance to any hydrophilic species.

Magnetic susceptibility measurements in an applied dc field of 0.1 T were performed on **1·2MeOH** and **1** in the temperature range of 2–300 K and 2–323 K, respectively (Fig. S5, ESI[†]). Magnetic data for the former confirmed that **1·2MeOH** is diamagnetic with the configuration of $\{\text{Fe}_2^{\text{II}}\text{Co}_2^{\text{III}}\}$ in the whole temperature range measured and shows no CTIST. For **1**, the $\chi_{\text{M}}T$ value at 300 K is 6.18 $\text{cm}^3 \text{K mol}^{-1}$ (per Fe_2Co_2), which agrees well with the high-spin $\{\text{Fe}_{2\text{LS}}^{\text{III}}\text{Co}_{2\text{HS}}^{\text{II}}\}$ configuration. Upon cooling, $\chi_{\text{M}}T$ values for **1** decrease and show an incomplete spin transition curve to give a plateau platform below ca. 120 K with a $\chi_{\text{M}}T$ value of 2.66 $\text{cm}^3 \text{K mol}^{-1}$, suggesting that ca. 43% of the $\{\text{Fe}_2\text{Co}_2\}$ molecules are still in the high-spin state. The abrupt drop in the $\chi_{\text{M}}T$ value below 10 K might be due to the orbital contribution of the metal ions and/or the antiferromagnetic interactions in the complex.

Variable-temperature FT-IR spectra of **1** were recorded in the temperature range of 80–298 K to confirm the intramolecular charge-transfer behavior (Fig. S5, inset, ESI[†]). As expected, the $\nu_{\text{C}\equiv\text{N}}$ stretching absorptions increase at ca. 2110, 2089, and 2065 cm^{-1} (for $\text{Fe}^{\text{II}}(\mu\text{-CN})\text{Co}^{\text{III}}$ linkage) and decrease at ca. 2168, and 2122 cm^{-1} (for $\text{Fe}^{\text{III}}(\mu\text{-CN})\text{Co}^{\text{II}}$ linkage) with a decrease of temperature. Below 100 K, the spectra show no change with a portion of the high-spin state $\text{Fe}^{\text{III}}(\mu\text{-CN})\text{Co}^{\text{II}}$ signal, which demonstrates the incompleteness of transition and is consistent with the magnetic results.

The ⁵⁷Fe Mössbauer spectrum of **1** at 100 K exhibited two resolved quadrupole doublets with the parameters (relative to metallic iron) of $\delta = 0.0116 \text{ mm s}^{-1}$, $\Delta E_{\text{Q}} = 1.290 \text{ mm s}^{-1}$ and $\delta = 0.146 \text{ mm s}^{-1}$, $\Delta E_{\text{Q}} = 0.429 \text{ mm s}^{-1}$, characteristic of $\text{Fe}_{\text{LS}}^{\text{III}}$ and $\text{Fe}_{\text{LS}}^{\text{II}}$ species, respectively (Fig. S6, ESI[†]). The peak area ratio of the two doublets gives the ratio of $\text{Fe}_{\text{LS}}^{\text{III}}/\text{Fe}_{\text{LS}}^{\text{II}} = 0.47/0.53$, close to the results obtained from magnetic data, which confirm the incomplete electron transfer process from $\{\text{Fe}_{2\text{LS}}^{\text{III}}\text{Co}_{2\text{HS}}^{\text{II}}\}$ to $\{\text{Fe}_{2\text{LS}}^{\text{II}}\text{Co}_{2\text{HS}}^{\text{III}}\}$ in **1** at 100 K.

For the red crystals of **1**, X-ray measurements were performed at 273 K, then cooled down slowly to 100 K, and a new set of diffraction

data was collected at 100 K ($1_{100\text{K}}$). Although the terminal ethyl groups are seriously disordered, the backbone in the structure is well refined. The Co–N bond lengths vary from 1.968(10) to 2.037(7) Å with an average of 2.009(9) Å, which lies in the middle of the range of the bond lengths for low-spin Co(III) and high-spin Co(II) ions (Table S2, ESI†). This kind of phenomenon has been found and characterized well in some incomplete or two-step SCO compounds¹¹ and the CTIST complex.^{2b} We tentatively assigned the incomplete state to either a mixture of $\{\text{Fe}_{\text{LS2}}^{\text{III}}\text{Co}_{\text{HS2}}^{\text{II}}\}$ and $\{\text{Fe}_{\text{LS2}}^{\text{II}}\text{Co}_{\text{LS2}}^{\text{III}}\}$ or the positional disorder of $\text{Co}_{\text{LS}}^{\text{III}}$ and $\text{Co}_{\text{HS}}^{\text{II}}$ ions in $\{[\text{Fe}_{\text{LS}}^{\text{II}}\text{Co}_{\text{LS}}^{\text{III}}]_x[\text{Fe}_{\text{LS}}^{\text{III}}\text{Co}_{\text{HS}}^{\text{II}}]_{1-x}\}$ generated by electron transfer. The reason for the incomplete transition is likely due to the seriously disordered ethoxycarbonyl groups in the structure which may block the electron transfer for part of the clusters or the $\{\text{Fe}^{\text{III}}\text{–CN–Co}^{\text{II}}\}$ pairs in the solid.

As verified by some examples, application of pressure can shorten the metal–donor-atom distances of SCO complexes and increase the ligand field strength at the metal center.¹² It is therefore expected that application of pressure favors the low-spin state of $\{\text{Fe}^{\text{II}}(\mu\text{-CN})\text{Co}^{\text{III}}\}$. We propose that hydrostatic pressure will work well to induce the intramolecular electron transfer from a high-spin state $\{\text{Fe}^{\text{III}}(\mu\text{-CN})\text{Co}^{\text{II}}\}$ to a low-spin state $\{\text{Fe}^{\text{II}}(\mu\text{-CN})\text{Co}^{\text{III}}\}$ in $\{\text{Fe}^{\text{III}}(\mu\text{-CN})\text{Co}^{\text{II}}\}_n$ clusters. As expected, the $\chi_{\text{M}}T$ value of **1** goes to almost zero when the applied pressure increases to 8.35 kbar at *ca.* 130 K (Fig. 2). And the $\chi_{\text{M}}T$ values are smaller with higher pressure imposed on complex **1** in the whole temperature range measured, which demonstrates that application of pressure can indeed stimulate charge transfer through the $\text{Fe}^{\text{III}}(\mu\text{-CN})\text{Co}^{\text{II}}$ linkage in the $\{\text{Fe}_2(\mu\text{-CN})_4\text{Co}_2\}$ cluster. Plots of $\chi_{\text{M}}T$ values *versus* external pressures at different temperatures are shown in Fig. S7 (ESI†), which shows good linear dependence, especially for the data over 200 K.

In conclusion, we have designed and prepared a new $\{\text{Fe}_2(\mu\text{-CN})_4\text{Co}_2\}$ complex. The charge-transfer-induced spin transition (CTIST) behaviour of this complex can be controlled specifically upon desorption–absorption of methanol molecules in the solid state with distinct colour change in a reversible SC–SC transformation manner at room temperature. The solvent loss form of this complex displays an incomplete thermal-induced intramolecular electron transfer process, which can be finished by

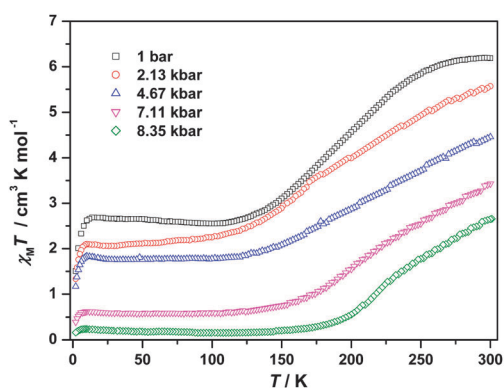


Fig. 2 $\chi_{\text{M}}T$ vs. T plots of complex **1** under different hydrostatic pressures ($H = 5000$ Oe).

application of external hydrostatic pressure to reach a complete low spin state. This is the first example to fulfil the pressure-induced CTIST on an isolated cyano-bridged bimetallic $\{\text{FeCo}\}$ cluster. The strategy to explore a new functional material based on the $\{\text{Fe}_2(\mu\text{-CN})_4\text{Co}_2\}$ framework with specific functional modification will open up a way for constructing novel multifunctional bistable materials with CTIST behaviour for practical applications.

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