Switchable Materials

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Photoswitchable Dynamic Magnetic Relaxation in a Well-Isolated {Fe_2Co} Double-Zigzag Chain**

Da-Peng Dong, Tao Liu, Shinji Kanegawa, Soonchul Kang, Osamu Sato,* Cheng He, and Chun-Ying Duan**

The design and synthesis of new molecular compounds whose physical properties can be controlled by external stimuli have recently attracted much attention.[1] Until now, various switchable compounds have been developed.[2–7] An important challenge in this field is controlling the magnetic properties of molecular nanomagnets, that is, single-molecule magnets (SMMs) and single-chain magnets (SCMs).[4–7] Molecular nanomagnets that exhibit slow magnetic relaxation can retain spin information over long time periods at a nanometer scale, and thus have potential applications in high-density information storage, quantum computation, and spintronics.[8] Although several examples of switchable nanomagnets have been reported,[4–7] the number thereof, especially that of SCMs, is very limited. Guest-tuned SCMs with microporous metal–organic frameworks are an important development,[4] and pressure control of nanomagnets has been reported.[5] However, photocontrol of the magnetic properties of SCMs has not yet been disclosed. To observe light-induced SCM behavior, the developed compounds should have both SCM and photoswitching properties. Because simultaneously fulfilling these requirements is difficult, light-induced SCMs have not yet been successfully fabricated.

In this study on developing a phototunable SCM, we designed an Fe_2Co bimetallic one-dimensional system with an N_6 coordination environment around Co ions with the expectation of charge-transfer-induced spin transition between the Fe and Co sites.[9] Furthermore, to prevent through-bond magnetic interactions between chains, we used bulky $[Fe(pzTp)(CN)_3]^-$ (pzTp = tetrakis(pyrazolyl)borate) building blocks to increase the metal–metal distances between neighboring chains and adopted the monodentate 4-styrylpyridine ligand. Note that it has recently been revealed that some of the reported SCMs, including ours, which show slow magnetic relaxation are not actual SCMs but are their antiferromagnetic phases.[10] Hence, we have carefully designed a one-dimensional (1D) system, in which 1D chains are sufficiently separated by bulky ligands. With the above strategy, we synthesized novel switchable complex $\{[Fe(pzTp)(CN)_3]_2Co(4\text{-styrylpyridine})_2\}\cdot 2H_2O\cdot 2CH_3OH$ (**1**), which is composed of well-isolated {Fe_2Co} chains. Complex **1** exhibits thermally induced charge transfer, wherein all Co^{II} ions and half of the Fe^{III} ions are involved in the metal-to-metal charge-transfer (MMCT) process. At low temperatures, Fe^{III} and Fe^{II} are regularly arranged, in contrast to the typical randomly arranged examples.[11,12] Furthermore, when **1** was irradiated, it showed SCM behavior with no antiferromagnetic ordering. This means that **1** is the first example of a photoswitchable SCM.

The target compound was synthesized by a diffusion method in a test tube. A solution of $Bu_4N[Fe(pzTp)(CN)_3]$ and 4-styrylpyridine in methanol was slowly layered over an aqueous solution of $Co(ClO_4)_2\cdot 6H_2O$.[13] Crystallization required several weeks. Single-crystal X-ray diffraction analysis revealed that **1** crystallizes in space group $P\bar{1}$. The crystal structure comprises neutral bimetallic double-zigzag $[Fe(pzTp)(CN)_3]_2Co(4\text{-styrylpyridine})_2$ chains with uncoordinated water and methanol molecules located between them (Figure 1). In the neutral chain, the $[Fe(pzTp)(CN)_3]^-$ unit bridges two Co^{II} ions through two of its three cyanide ligands in the *cis* position, and each Co^{II} ion is coordinated to four nitrogen atoms from the CN^- bridges. Dihedral angles of 38.7° are formed between the planes of the triangular Fe_2Co units owing to the steric effect of the bulky $[Fe(pzTp)(CN)_3]^-$ building blocks. In contrast, in other reported Fe_2Co complexes, four metal ions of the Fe_2Co_2 units are nearly aligned in a plane and the mean planes of the square units are parallel to each other.[14]

The crystal structure contains two unique iron and cobalt centers. Each iron center is located in an octahedral environment with three nitrogen atoms from the pzTp units and three cyanide carbon atoms. The equatorial plane of the cobalt center is occupied by four cyanide nitrogen atoms, and two nitrogen atoms from 4-styrylpyridine occupy its apical positions, providing an N_6 coordination sphere. At 260 K, the $Co{-}N_{equatorial}$ bond lengths are 2.092–2.115 and 2.087–2.112 Å, and the $Co{-}N_{apical}$ distances are 2.150 and 2.162 Å for Co1 and Co2, respectively. The elongated N_6 octahedral environment of cobalt suggests a negative anisotropy constant *D*, which is essential for SCM behavior.[15] However, the apical axis of the neighboring Co^{II} ion shows an angle of 47.0°, which is expected to counteract part of the Co^{II} ion

[*] Dr. D.-P. Dong, Prof. T. Liu, Prof. C. He, Prof. C.-Y. Duan
State Key Laboratory of Fine Chemicals
Dalian University of Technology
2 Linggong Rd., 116024 Dalian (China)
E-mail: liutao@dlut.edu.cn
cyduan@dlut.edu.cn
Dr. S. Kanegawa, Dr. S. Kang, Prof. O. Sato
Institute for Materials Chemistry and Engineering
Kyushu University, 6-1 Kasuga, Fukuoka, 816-8580 (Japan)
E-mail: sato@cm.kyushu-u.ac.jp

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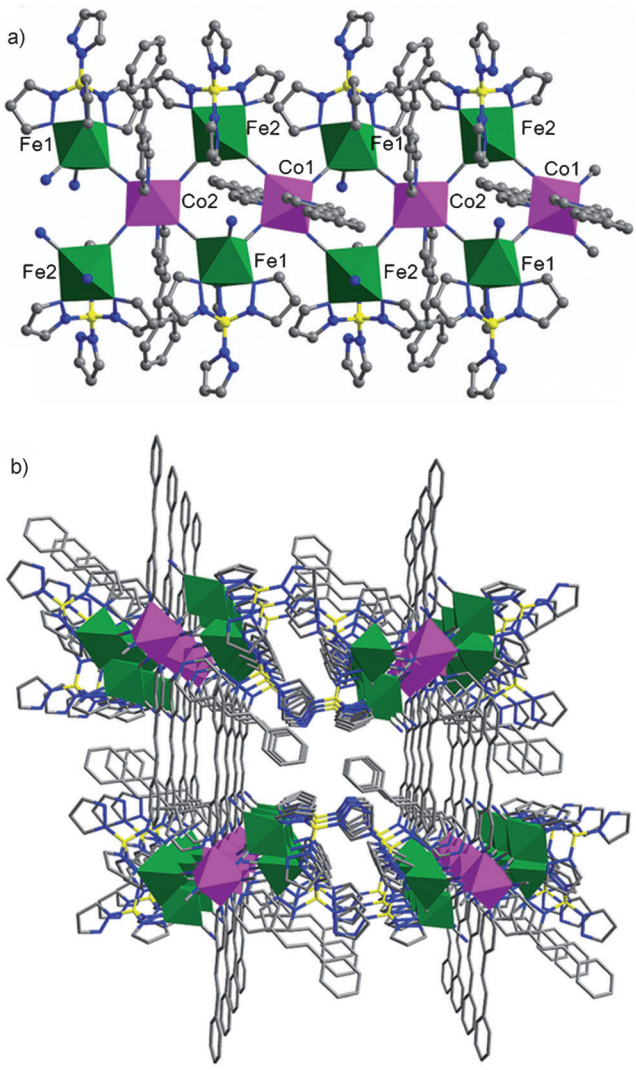

Figure 1. a) Side view of a 1D double-zigzag chain. b) Packing diagram of 1D chains of **1** along the *a* axis. H atoms have been omitted for clarity. Fe green, Co pink, C gray, N blue, B yellow.

anisotropy. The Fe–C bond lengths are 1.905–1.924 and 1.903–1.921 Å, and the Fe–N distances are 1.965–1.973 and 1.961–1.979 Å for Fe1 and Fe2, respectively. The structural parameters indicate that the cobalt centers are Co^{II}_{HS} (HS = high spin) and the iron centers are Fe^{III}_{LS} (LS = low spin), which form $Fe^{III}_{LS}(\mu\text{-CN})Co^{II}_{HS}$ linkages.[9] The shortest interchain metal–metal distance is 11.945 Å. Such a large distance will diminish interchain magnetic interactions, with potential for single-chain magnet behavior without magnetic ordering.

When crystals of **1** were gradually cooled, the Co–N bond lengths decreased by about 0.2 Å. At 140 K, the $Co–N_{equatorial}$ bond lengths were 1.892–1.901 and 1.885–1.886 Å and the $Co–N_{apical}$ bond distances were 1.969 and 1.978 Å for Co1 and Co2, respectively. At 140 K, the Co–N distances were in the range expected for Co^{III}_{LS} (≈1.9 Å).[9] The Fe–C distances were 1.866–1.909 and 1.904–1.925 Å, and the Fe–N bond lengths were 1.981–1.997 and 1.955–1.985 Å for Fe1 and Fe2, respectively. The Fe–C and Fe–N distances for Fe2 were nearly the same as those at 260 K. In contrast, for Fe1, the average Fe–C bond length decreased by about 0.033 Å and the average Fe–N bond distance increased by about 0.020 Å compared with those at 260 K. These temperature-dependent structural variations suggest that intramolecular charge transfer transformed $Fe^{III}_{LS}(\mu\text{-CN})Co^{II}_{HS}$ units into $Fe^{II}_{LS}(\mu\text{-CN})Co^{III}_{LS}$ units and charge transfer occurred between the Fe1 site and all Co^{II} ions.

Additional evidence for regular and complete intramolecular electron transfer was revealed by temperature-dependent IR spectroscopic studies on **1** (Supporting Information Figure S1). At 260 K, three cyanide stretching bands (ν_{CN}) were observed, corresponding to the free ν_{CN} mode of $[Fe^{III}(pzTp)(CN)_3]^-$ (2132 cm^{-1}) and the bridging ν_{CN} absorptions of $Fe^{III}_{LS}(\mu\text{-CN})Co^{II}_{HS}$ linkages (2153 and 2165 cm^{-1}).[9] On cooling, new stretching bands attributed to the free ν_{CN} mode of $[Fe^{II}(pzTp)(CN)_3]^{2-}$ (2071 cm^{-1}) and the bridging ν_{CN} modes of $Fe^{II}_{LS}(\mu\text{-CN})Co^{III}_{LS}$ (2110 cm^{-1}) and $Fe^{III}_{LS}(\mu\text{-CN})Co^{III}_{LS}$ (2178 cm^{-1} and 2201 cm^{-1}) linkages were observed.[9] Moreover, the bands of the $Fe^{III}_{LS}(\mu\text{-CN})Co^{II}_{HS}$ linkages disappeared. These IR results confirmed that all Co^{II} ions and half of the Fe^{III} ions were involved in the regular electron-transfer process. Furthermore, these temperature-induced changes in the IR spectrum of **1** were completely reversible by heating the samples, and this suggests that the MMCT is reversible.

Magnetic measurements were performed to verify charge transfer in **1** (Figure 2a). At room temperature, the χT

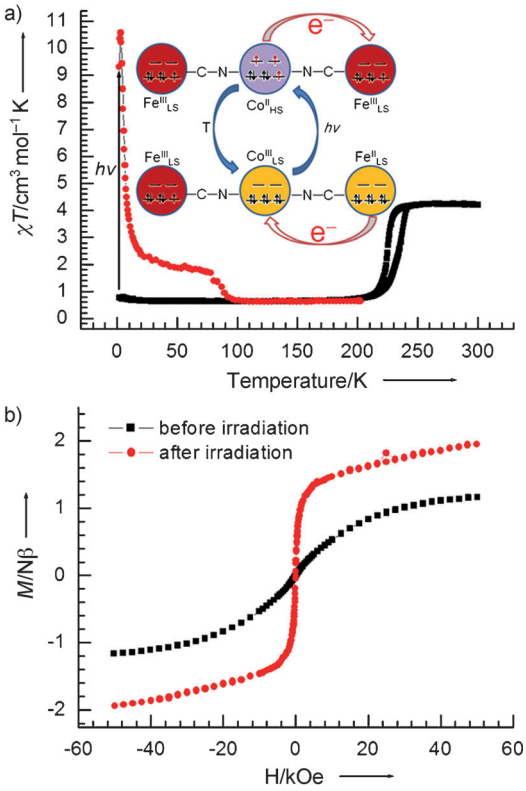

Figure 2. a) Temperature-dependent susceptibility of **1** before (■) and after irradiation (●) in a dc field of 1000 Oe. Inset: scheme of regular electron transfer. HS = high spin; LS = low spin. b) Isothermal magnetization of **1** before (■) and after irradiation (red ●) at 1.8 K.

product was 4.23 $cm^3 mol^{-1} K$ per Fe_2Co unit, corresponding to the presence of one $Co^{II}{}_{HS}$ and two $Fe^{III}{}_{LS}$ with significant orbital contributions.[9] As the temperature decreased, the χT values remained nearly constant between 300 and 250 K. However, a gradual decrease in temperature (0.5 $K min^{-1}$) from 250 to 200 K afforded a steep decrease in χT with $T_{1/2}\downarrow =$ 224 K, which reached 0.65 $cm^3 mol^{-1} K$ at 200 K. In contrast, on heating (0.5 $K min^{-1}$), the χT value increased and returned to the initial value with $T_{1/2}\uparrow = 232$ K, that is, an 8 K-wide thermal hysteresis. This magnetic behavior confirmed a reversible charge-transfer process that involves transformation between the high-temperature (HT) phase with $Fe^{III}{}_{LS}$ ($S = 1/2$) and $Co^{II}{}_{HS}$ ($S = 3/2$) metal ions and the low-temperature (LT) phase with diamagnetic $Fe^{II}{}_{LS}$ ($S = 0$) and $Co^{III}{}_{LS}$ ($S = 0$) centers. According to the change in the χT values and structural parameters, all $Co^{II}{}_{HS}$ ions changed to $Co^{III}{}_{LS}$ ions, whereas half of the $Fe^{III}{}_{LS}$ ions changed to $Fe^{II}{}_{LS}$ ions from the HT phase to the LT phase. Hence, the transformation could be expressed as $\{[Fe^{III}(PzTp)(CN)_3]_2Co^{II}$(4-styrylpyridine)$\}\cdot 2H_2O\cdot 2CH_3OH \rightleftarrows \{[Fe^{II}(PzTp)(CN)_3][Fe^{III}(PzTp)(CN)_3]$-$Co^{III}$(4-styrylpyridine)$\}\cdot 2H_2O\cdot 2CH_3OH$. As the temperature decreased further from 200 K, the χT values remained almost constant, suggesting the behavior of paramagnetic Fe^{III} ions. The field-dependent magnetization at 2 K steeply increased to 1.17 $N\beta$ at 50 kOe, which agrees with the paramagnetic behavior of one $Fe^{III}{}_{LS}$ per $Fe^{II}{}_{LS}Fe^{III}{}_{LS}Co^{III}{}_{LS}$ unit (Figure 2b).

In **1**, the cooperative charge-transfer-induced spin transition occurs concertedly in the sense that the electron is transferred between the cobalt sites and one iron site (Fe1) to form a regular structure in which Fe^{II} is not randomly distributed over the two iron sites (Fe1 and Fe2) at low temperatures. This is in contrast to most charge-transfer complexes, in which charge transfer occurs randomly across all metal sites.[9c,10d,16] The occurrence of regular charge transfer from a fraction of metal ions is very rare.[17] Regular charge transfer has been observed in an Os_2Fe_3 compound, despite its near trigonal molecular symmetry.[17a] Intermolecular π contacts involving the phenanthroline ligand of two of the three iron atoms seem to be the origin of this charge-transfer localization. In **1**, the different behaviors of Fe1 and Fe2 may be attributed to the different types of hydrogen bonds formed between uncoordinated water molecules or methanol molecules and the terminal cyanide nitrogen atoms of Fe1 or Fe2 (Supporting Information Figure S2). Such hydrogen bonds may play an important role in MMCT because they can significantly tune the redox potential, as reported for the non-heme Fe site of superoxide dismutase and quinone molecules.[18] In Fe1, hydrogen bonds are formed between the terminal cyanide nitrogen atoms and oxygen atoms of methanol molecules (O···N 2.80 Å), whereas the hydrogen bonds in Fe2 involve terminal cyanide nitrogen atoms and oxygen atoms of water molecules (O···N 2.91 Å). The electron-donating CH_3 group of methanol molecules may have the following effects on the redox potential of Fe1: shifting the redox potential of $Fe^{III}{}_{LS}$ toward positive potential, destabilizing the $Fe^{III}{}_{LS}$(μ-CN)$Co^{II}{}_{HS}$ pairs, and stabilizing the $Fe^{II}{}_{LS}$(μ-CN)$Co^{III}{}_{LS}$ pairs. This observation underscores the subtle effects of supermolecular crystal packing on charge-transfer phenomenon, which is associated with a significant modification of the coordination sphere of the participating metal ions.

To probe the possibility of photoinduced magnetization, IR spectra were measured after irradiation. Irradiation by a 532 nm laser decreased the IR peaks of the LT phase and generated the spectrum of the HT phase (Supporting Information Figure S3). Hence, irradiation of the LT phase induced a valence-state change from $Fe^{II}{}_{LS}$-$Co^{III}{}_{LS}$ to $Fe^{III}{}_{LS}$-$Co^{II}{}_{HS}$.

On light irradiation ($\lambda = 532$ nm) at 5 K for more than 12 h, a significant increase in χT value was observed because of photoinduced transformation from diamagnetic $Fe^{II}{}_{LS}$(μ-CN)$Co^{III}{}_{LS}$ to metastable paramagnetic $Fe^{III}{}_{LS}$(μ-CN)$Co^{II}{}_{HS}$ units (Figure 2a). The plot obtained for after photoirradiation shows that, on heating, the χT values initially increased steeply to a sharp maximum of 10.5 $cm^3 mol^{-1} K$ at 3.0 K before decreasing gradually and overlapping near 70 K. After irradiation, the spin topology changed from that of isolated Fe^{III} ions to a 1D order. Considering the negative anisotropy constant D of Co^{II}, strong intrachain magnetic interactions transmitted via the cyanide bridge, and weak interchain magnetic interactions because of the large distances between the metal ions of neighboring chains, SCM behavior is expected. At 1.8 K, on increasing the field, the field-dependent magnetization increased steeply to 1.5 $N\beta$ at 5.0 kOe (Supporting Information Figure S3) before increasing gradually and linearly with the applied magnetic field. Further measurements indicate that **1** did not show detectable hysteresis at 1.8 K. In particular, the M versus H curve was smooth and devoid of kinks, and thus rules out the possibility of a three-dimensional antiferromagnetic ordering transition down to 1.8 K.

To investigate the magnetization dynamics, alternating current (ac) magnetic susceptibility was studied as a function of both temperature and frequency. Variable-temperature ac susceptibility measurements revealed a strong frequency dependence of both in-phase (χ') and out-of-phase components (χ''; Figure 3), as was observed in other SCMs. The shift in the peak temperature T_p is given by the parameter $F = (\Delta T_p/T_p)/\Delta(\lg\omega) = 0.28$, which lies in the expected range for an SCM, and thus eliminates the possibility of spin-glass behavior. On the basis of these data, the relaxation times were estimated and fitted to Arrhenius laws, providing a pre-exponential factor of $\tau_0 = 1.5 \times 10^{-10}$ s and a relaxation energy barrier of $\Delta\tau/k_B = 27$ K. The value of τ_0 provides a quantitative estimation of the attempt time of relaxation from the chain bath, and the obtained value is in good agreement with those reported for other SCMs. This analysis demonstrates that the state of **1** after irradiation shows SCM behavior.

The relaxation of the photoinduced metastable state was monitored at different temperatures. The decay of magnetization, normalized to the photoinduced fraction γ (Figure 4), was fitted by a stretched exponential law [Eq. (1)][19]

$$\gamma(t) = \gamma(0)\exp(-t/\tau)^{\beta} \quad (1)$$

where β represents the time-evolving crystal forces acting on a single reference molecule during the decay owing to the different molecular volumes in the high- and low-temperature

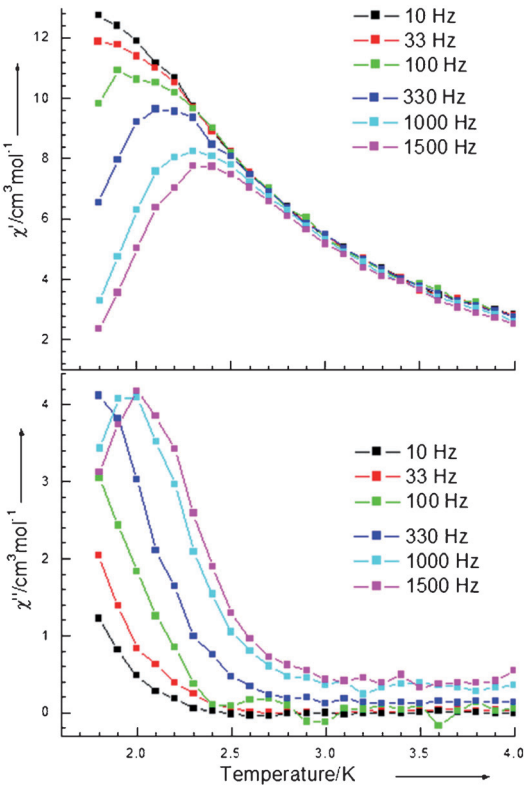

Figure 3. Temperature dependence of the real and imaginary parts of ac susceptibility for **1** after irradiation in zero dc field at varied ac frequency in a 3.5 Oe ac field.

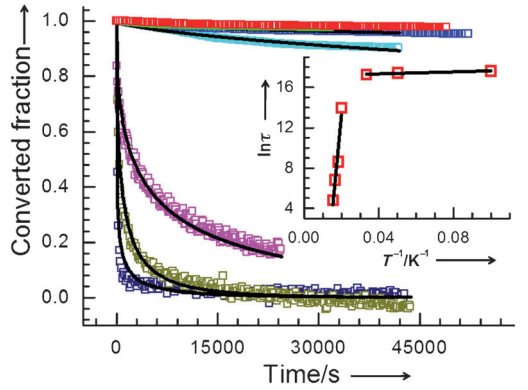

Figure 4. a) Relaxation kinetics of the photoinduced fraction in normalized values ($t=0$, converted fraction = 1) of **1** at 10 K (red □), 20 K (green □), 30 K (blue □), 50 K (turquoise □), 55 K (magenta □), 60 K (olive green □), and 65 K (dark blue □) in the dark. The black solid line is the stretched-exponential fit to Equation (1). Inset: corresponding Arrhenius plot obtained with parameters describing the relaxation kinetics of **1** in the high-temperature range (50–65 K) and low-temperature range (10–30 K).

phases, and τ is the relaxation time of the system at temperature T. Two distinct dependencies of τ on temperature were observed. In the high-temperature range (50–65 K), the relaxation time τ follows an Arrhenius behavior [$\tau(T)=\tau_0\exp(\Delta E/(k_BT)$; Figure 4, inset], where τ_0 and ΔE are the pre-exponential factor and energy barrier, respectively. In our study, an energy barrier ΔE of $1348\pm200\ cm^{-1}$ and a pre-exponential factor τ_0 of 8.4×10^{-12} s were obtained. The activation energy of the thermally induced relaxation is comparable with those of other reported cyanide-bridged {FeCo} complexes.[9,19,20] On the other hand, the low-temperature (10–30 K) behavior of the relaxation time exhibits a very weak dependence on temperature. A best-fitting procedure with the Arrhenius relation gave $\Delta E=3.4\pm0.7\ cm^{-1}$ and $\tau_0=2.8\times10^7$ s, in agreement with temperature-independent tunneling of the system from the metastable $Fe^{III}_{LS}(\mu\text{-}CN)Co^{II}_{HS}$ state to the stable $Fe^{II}_{LS}(\mu\text{-}CN)Co^{III}_{LS}$ state at low temperature.

In summary, by using $[Fe(pzTp)(CN)_3]^-$ as a bulky building block to react with Co^{II} and 4-styrylpyridine, we synthesized a well-isolated cyanide-bridged Fe_2Co double-zigzag chain that shows reversible MMCT on cooling and heating. The charge-transfer-induced spin transition occurs cooperatively between the cobalt sites and one of the two iron sites at about 230 K. By exploiting the light-induced transformation from diamagnetic $Fe^{II}_{LS}(\mu\text{-}CN)Co^{III}_{LS}$ units to paramagnetic $Fe^{III}_{LS}(\mu\text{-}CN)Co^{II}_{HS}$ units, an SCM state could be successfully photoswitched from a paramagnetic state with isolated Fe^{III} ions in the complex. Moreover, 4-styrylpyridine and related stilbene derivatives are known to undergo *cis–trans* photoisomerization on visible-light irradiation both in solution and in the solid state.[21] This structural change can accompany ligand-driven, light-induced spin change, and studies are underway to investigate multistep photoswitchable properties.

Experimental Section

Synthesis of **1**: A 4.0 mL aqueous solution of 0.05 mmol of $Co(ClO_4)_2\cdot6H_2O$ was placed at the bottom of a test tube, and a 10.0 mL methanol solution of 0.1 mmol of $[Bu_4N][Fe(pzTp)(CN)_3]$ and 0.1 mmol 4-styrylpyridine was layered on the solution. Crystallization required several weeks and gave crystals in 65% yield based on $Co(ClO_4)_2\cdot6H_2O$. Elemental analysis calculated for $C_{58}H_{38}B_2CoFe_2N_{24}O_4$: C 51.65, H 4.30, N 24.93; found: C 51.56, H 4.24, N 25.01.

For further information on magnetic properties, measurements, IR, TGA, and XRD, see Supporting Information.

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