Supporting Information

Photoinduced Large Magnetic Change at Room Temperature and Radical-quenched Spin Glass in a Cyanide-Bridged Mn^{II}–Fe^{III} Compound

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I. Experimental section.

1. Materials

$MnCl_2·5H_2O$ and $K_3[Fe(CN)_6]$ in AR grade were purchased commercially. They were directly used without further purification. Water was deionized and distilled before use. $MQCl·H_2O$ (MQ^+ = *N*-methyl-4,4'-bipyridinium) was synthesized according to the same procedure reported in the literature.[1]

2. Measurements.

IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer using KBr pellets in the range of 4000−450 cm^{-1}. The elemental analyses of C, H and N were measured on an Elementar Vario EL III microanalyzer, and the elemental analyses of Fe and Mn were measured on an ULTIMA 2 ICP Optical Emission Spectrometer. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Desktop MiniFlexII diffractometer using Cu K_α radiation (λ = 1.54056 Å) powered at 30 kV and 15 mA. Dc magnetic susceptibilities were measured on a Quantum Design MPMS−XL superconducting quantum interference device (SQUID) magnetometer. The field/temperature dependence of magnetization was analyzed on a Quantum Design PPMS−9T VSM magnetometer. Besides, an OPOTECK VIBRANT HE 355 LD tunable laser system was used to illuminate samples for photomagnetic susceptibility tests (YAG laser, λ = 320 nm, 4.1 mJ cm^{-2}). Each sample was placed into a gelatin capsule for magnetic determinations. The experimental magnetic data were corrected for the sample holder, the resin, and the diamagnetic contribution calculated from Pascal constants. Photoirradiation (except photomagnetic susceptibility test) was carried out with a PLS-SXE300C 300-W xenon lamp system, wherein an IR filter was applied.

3. Single-crystal X-ray crystallographic study

The single-crystal X-ray diffraction measurement of **1** was performed on a Rigaku SATURN70 CCD diffractometer, using graphite monochromated Mo K_α radiation (λ = 0.71073 Å). Intensity data sets were collected using ω scan techniques, and corrected for *Lp* effects. The primitive structure was solved by the

direct method using the Siemens SHELXTL^{TM} Version 5 package of crystallographic software.[2] Difference Fourier maps based on these atomic positions yielded other non-hydrogen atoms. The final structure was refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The H atoms of C17 were not included, while other H atoms were generated geometrically.

4. Synthesis of [{$Mn^{II}(MQ)_2$}{$Fe^{III}(CN)_6$}]Cl (1)

A 50 mL small beaker was placed in a 250 mL big one, which was filled with distilled water to approximately 0.5 cm above the top of the small beaker. A frozen 2 mL aqueous solution of $MQCl{\cdot}H_2O$ (899 mg, 4 mmol) with $MnCl_2{\cdot}5H_2O$ (432 mg, 2 mmol) were thrown into the bottom of the small beaker, while a frozen 2 mL aqueous solution of $K_3[Fe(CN)_6]$ (659 mg, 2 mmol) was put into the bottom of the big beaker. The big beaker was sealed with a plastic wrap and allowed to stand in the dark at room temperature for one week to yield dark brown cubic crystals. The crystals were filtered, washed with water and ethanol, and finally dried in air for 1 day. Yield: 40% based on $K_3[Fe(CN)_6]$; Anal. Calcd (%) for $C_{28}H_{22}ClFeMnN_{10}$: C, 52.16; H, 3.44; N, 21.72; Fe, 8.66; Mn, 8.52. Found: C, 51.65; H, 3.74; N, 21.68; Fe, 8.92; Mn, 8.69. The phase purity of the as-synthesized crystalline sample was checked *via* PXRD (**Figure S1**).

II. Supporting graphics.

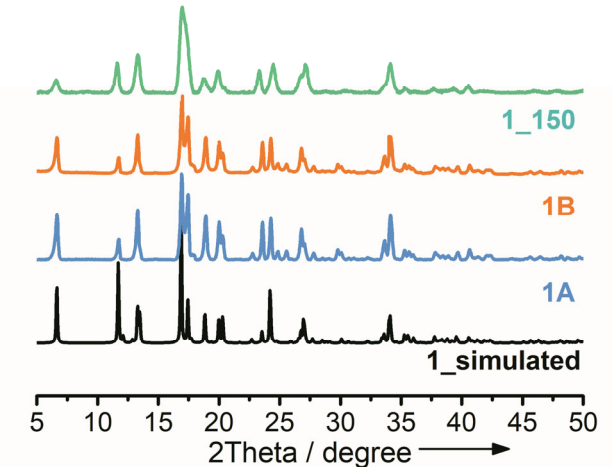

Figure S1. PXRD patterns for **1A, 1B**, **1_150** (**1** annealed at 150 °C for 2 h).

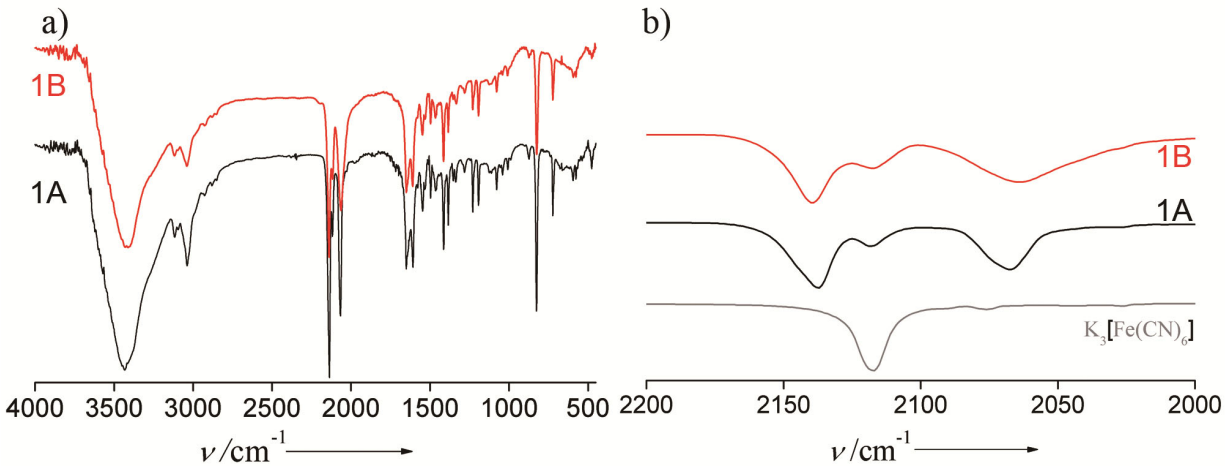

Figure S2. a) IR spectra for **1A** and **1B**. b) IR spectra of the CN groups in **1A**, **1B**, and $K_3[Fe(CN)_6]$.

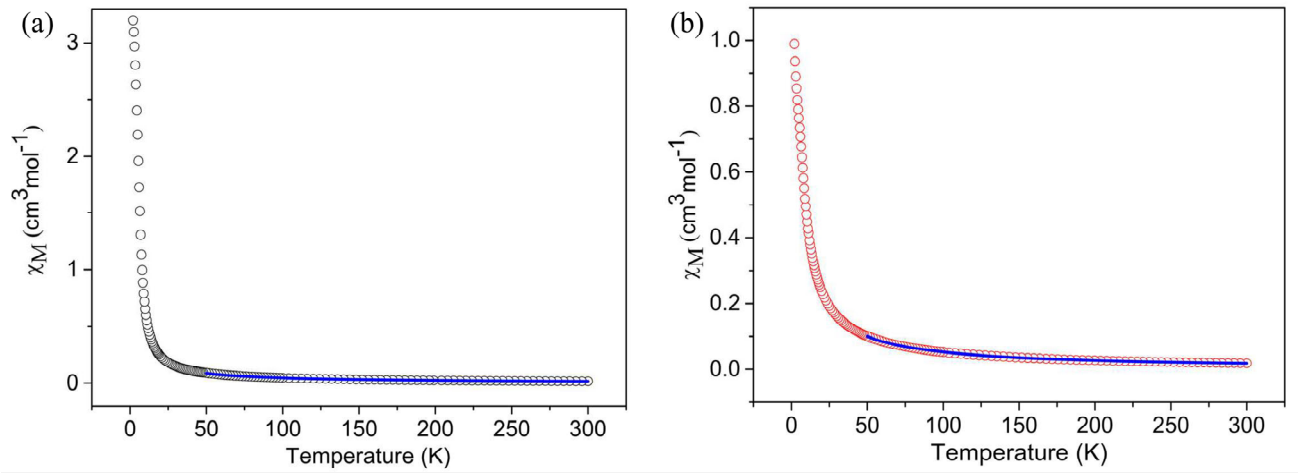

Figure S3. χ_M vs T curves (circles) for **1A** (left) and **1B** (right). The blue solid lines represent the Currie−Weiss law plots.

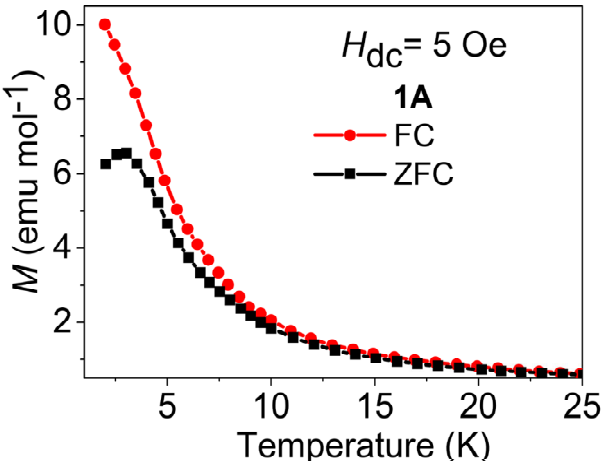

Figure S4. FCM and ZFCM vs T at H = 5 Oe for **1A**.

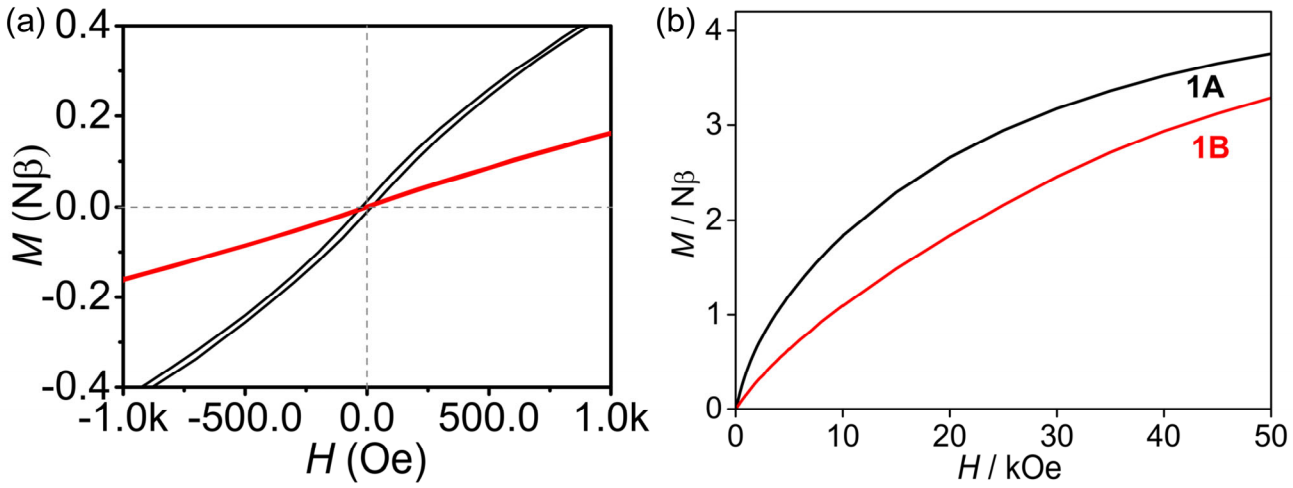

Figure S5. a) the detail in a low field of hysteresis loop of **1A** and **1B** measured at 2.0 K; b) magnetization vs magnetic field at 2 K for **1A** (black) and **1B** (red).

References.

(1) Yang, C.; Wang, M.-S.; Cai, L.-Z.; Jiang, X.-M.; Wu, M.-F.; Guo, G.-C.; Huang, J.-S. *Inorg. Chem. Commun.* **2010**, *31*, 1021.

(2) Siemens, *SHELXTLTM Version 5 Reference Manual*, Siemens Energy & Automation Inc., Madison, Wisconsin, USA, **1994**.