

Supporting Information

**Thermo- and photo-induced electron transfer in a series of [Fe₂Co₂]
capsules**

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Experimental section

Materials and physical measurements. $[\text{NBu}_4][(\text{Tp}^*)\text{Fe}(\text{CN})_3]$ and $[\text{Ph}_3\text{PMe}][(\text{Tp}^{\text{Me}})\text{Fe}(\text{CN})_3]$ were prepared according to the literature.¹ All other reagents were of commercial grade and used without further purification.

Variable temperature infrared (FT-IR) spectra were recorded in the range of 600 - 4000 cm^{-1} on a Bruker Tensor II spectrophotometer equipped with liquid nitrogen cooled and evacuated Specac Golden Gate low temperature ATR accessories. Thermogravimetric analysis (TGA) data were collected on a METTLER TOLEDO TGA2 instrument, under an insert argon atmosphere between 30 - 500 °C, at a heating rate of 3 °C/min using freshly filtered crystals. Elemental analyses (C, H, N) were measured by a vario EL cube CHNOS Elemental Analyzer Elementar Analysensysteme GmbH. The PXRD measurements were recorded at room temperature on a Rigaku Smartlab X-ray diffractometer using Cu $K\alpha$ radiation (45 kV, 200 mA) between 5 and 50° (2 θ). The simulated patterns are calculated from the single crystal data at 260 K.

Synthesis of $\{[(\text{Tp}^*)\text{Fe}(\text{CN})_3\text{Co}(\text{bpy}^{\text{C}=\text{N}(\text{CH}_2)_5\text{N}=\text{C}})]_2[\text{ClO}_4]_2\} \cdot 8\text{DMF}$ (**1**). An ethanolic solution (4 mL) of 1, 5-pentanediamine (5.1 mg, 0.05 mmol) and 4-formyl-4'-methyl-2,2'-bipyridine (19.8 mg, 0.1 mmol) was refluxed for 8 h then concentrated to dryness. The remaining solid was dissolved in methanol (5 mL) and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (18.3 mg, 0.05 mmol), followed by $[\text{NBu}_4][(\text{Tp}^*)\text{Fe}(\text{CN})_3]$ (33.6 mg, 0.05 mmol), were subsequently added. The mixture was stirred for 3 h, filtered, and the filtrate evacuated to dryness. The residue was extracted into DMF (4 mL), layered with Et_2O , and allowed to stand at room temperature for 5 d. The red crystals were isolated via suction filtration and dried (in air) at room temperature for 5 min. Yield: 14.2 mg (10.6%). FT-IR (cm^{-1} ; 273 K): $\nu = 2532$ (m, ν_{BH}), 2154 (s, ν_{CN}), 2136 (w, ν_{CN}). Anal. Calcd $\text{C}_{118}\text{H}_{160}\text{B}_2\text{Cl}_2\text{Co}_2\text{Fe}_2\text{N}_{38}\text{O}_{16}$: C, 52.67; H, 5.95; N, 19.79. Found: C, 52.63; H, 5.98; N, 19.67.

Synthesis of $\{[(\text{Tp}^{\text{Me}})\text{Fe}(\text{CN})_3\text{Co}(\text{bpy}^{\text{C}=\text{N}(\text{CH}_2)_9\text{N}=\text{C}})]_2[\text{ClO}_4]_2\} \cdot 5\text{MeCN}$ (**2**). An ethanolic solution (4 mL) of 1,9-diaminononane (7.9 mg, 0.05 mmol) and 4-formyl-4'-methyl-2,2'-bipyridine (19.8 mg, 0.1 mmol) was refluxed for 8 h and then concentrated to dryness. The remaining solid was dissolved into methanol (5 mL) and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (18.3 mg, 0.05 mmol) followed by $[\text{Ph}_3\text{PMe}][(\text{Tp}^{\text{Me}})\text{Fe}(\text{CN})_3]$ (33.8 mg, 0.05 mmol), were subsequently added. The mixture was stirred for 3 h, filtered, and the filtrate evacuated to dryness. The residue was extracted into acetonitrile (5 mL), layered with Et_2O , and allowed to stand at room temperature for ca. 4-5 d. The red crystals were isolated via suction filtration and dried (in air) at room temperature for 3 min. Yield: 15.6 mg (13.4%). FT-IR (cm^{-1} ; 293 K): $\nu = 2510$ (m, ν_{BH}), 2158 (s, ν_{CN}), 2133 (w, ν_{CN}). Anal. Calcd $\text{C}_{106}\text{H}_{121}\text{B}_2\text{Cl}_2\text{Co}_2\text{Fe}_2\text{N}_{35}\text{O}_8$: C, 54.47; H, 5.18; N, 20.98. Found: C, 54.38; H, 5.30; N, 20.92.

Synthesis of $\{[(\text{Tp}^*)\text{Fe}(\text{CN})_3\text{Co}(\text{bpy}^{\text{C}=\text{N}(\text{CH}_2)_{11}\text{N}=\text{C}})]_2[\text{ClO}_4]_2\} \cdot 5\text{MeCN}$ (**3**). An ethanolic solution (4 mL) of 1,11-diaminoundecane (9.3 mg, 0.05 mmol) and 4-formyl-4'-methyl-2,2'-bipyridine (19.8 mg, 0.1 mmol) was refluxed for 8 h and then concentrated to dryness. The residue was extracted into acetonitrile (3 mL), solid $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (18.3 mg, 0.05 mmol) added, and a MeCN (2 mL) solution of $[\text{NBu}_4][(\text{Tp}^*)\text{Fe}(\text{CN})_3]$ (33.6 mg, 0.05 mmol) added. After stirring for 2 h at 50 °C, the red solution was allowed to cool to room temperature then layered with Et_2O , and allowed to stand for 10 d. The red crystals were isolated via suction filtration and dried (in air) at room temperature for 2 min. Yield: 13.5 mg (10.9 %). FT-IR (cm^{-1} ; 253 K): $\nu = 2531$ (m, ν_{BH}), 2154 (s, ν_{CN}), 2127 (w, ν_{CN}). Anal. Calcd $\text{C}_{116}\text{H}_{140}\text{B}_2\text{Cl}_2\text{Co}_2\text{Fe}_2\text{N}_{36}\text{O}_8$: C, 55.93; H, 5.62; N, 20.25. Found: C, 55.84; H, 5.82; N, 20.17.

Caution: Although no such issues happened during the present work, perchlorate salts are potentially explosive and should be handled in small quantities with great care.

X-ray crystallographic data. The single crystal data for **1** – **3** at were collected on a Bruker D8 VENTURE diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 100 K and 260 K. Lorentz/polarization corrections were applied during data reduction and the structures were solved via direct

methods (SHELXS-2014). Refinements were performed by full-matrix least squares (SHELXL-2014) on F^2 and empirical absorption corrections (SADABS) were applied.² Anisotropic thermal parameters were used for the non-hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. CCDC-2014191 (1-100 K), 2014192 (1-260 K), 2014188 (2-100 K), 2014189 (2-260 K), 2014190 (3-100 K) and 2014193 (3-260 K) contain the crystallographic data that may be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Magnetic measurements. Magnetic susceptibility data were collected on a Quantum Design SQUID MPMS3 magnetometer under a static 1 kOe dc field and at temperatures ranging between 2 - 300 K. Single crystals of **1** – **3** were filtered from the mother liquor and dried in air momentarily before insertion into the magnetometer sample chamber. For the photomagnetic experiments, irradiation was performed on the fresh samples cooled to 10 K and light from an infrared diode laser [20 mW, 808 nm; MDL-III-808 nm-19060627, Changchun New Industries Optoelectronics Technology Co., Ltd (CNI)] was guided via a flexible optical fiber (5 m length; CNI Fiber) into the magnetometer. Sample temperatures were corrected for light-induced heating effect (avg. +4 K for the red light), which was referenced to the data collected in the absence of light. Magnetic data were corrected for the diamagnetism of the sample holder and sample using Pascal's constants.³

Table S1. Selected bond lengths [\AA] and angles [deg] for **1** at 100 and 260 K.

	100 K	260 K
Fe1-C1	1.900(6)	1.917(4)
Fe1-C2	1.900(6)	1.922(4)
Fe1-C3	1.908(6)	1.924(5)
Fe1-N4	2.005(5)	1.998(4)
Fe1-N6	2.037(5)	2.001(3)
Fe1-N8	2.013(4)	2.012(3)
Fe-C(average)	1.903	1.921
Co1-N1	1.986(5)	2.073(4)
Co1-N11	2.028(5)	2.133(3)
Co1-N10	2.016(6)	2.126(4)
Co1-N2A	1.968(5)	2.103(4)
Co1-N14A	2.019(5)	2.121(3)
Co1-N15A	2.040(5)	2.153(3)
Co-N(average)	2.009	2.118
C1-Fe1-N8	92.9(2)	92.0(2)
C1-Fe1-N6	177.0(2)	177.4(2)
C1-Fe1-N4	92.9(2)	93.2(2)
C1-Fe1-C3	86.9(2)	86.3(2)
C1-Fe1-C2	86.4(2)	85.3(2)
N1-Co1-N14A	89.1(2)	169.1(1)
N1-Co1-N15A	86.3(2)	94.2(1)
N1-Co1-N11	92.6(2)	90.7(1)
N1-Co1-N2A	94.2(2)	96.0(1)
N1-Co1-N10	170.2(2)	92.2(1)
Fe1-C1-N1	174.6(4)	175.8(4)

Fe1-C2-N2	174.7(5)	175.1(4)
Co1-N1-C1	173.0(4)	179.4(4)
Co1A-N2-C2	179.0(5)	173.3(3)

Symmetry transformations used to generate equivalent atoms: A 1-x, 1-y, 1-z.

Table S2. Selected bond lengths [\AA] and angles [deg] for **2** at 100 and 260 K.

	100 K	260 K
Fe1-C1	1.894(7)	1.915(5)
Fe1-C2	1.889(6)	1.921(5)
Fe1-C3	1.923(7)	1.914(7)
Fe1-N4	2.007(6)	1.997(5)
Fe1-N6	2.017(5)	2.009(4)
Fe1-N8	2.007(5)	2.004(4)
Fe-C(average)	1.902	1.917
Co1-N1	1.995(6)	2.076(4)
Co1-N11	2.029(6)	2.119(5)
Co1-N10	2.038(6)	2.128(4)
Co1-N2A	1.988(5)	2.080(4)
Co1-N14	2.050(6)	2.145(4)
Co1-N15	2.048(5)	2.136(4)
Co-N(average)	2.025	2.114
C1-Fe1-N8	93.5(2)	92.7(2)
C1-Fe1-N6	176.3(2)	176.0(2)
C1-Fe1-N4	93.2(2)	92.7(2)
C1-Fe1-C3	85.4(3)	84.9(2)
C1-Fe1-C2	87.0(2)	86.8(2)
N1-Co1-N2A	93.3(2)	93.6(2)
N2A-Co1-N14	86.0(2)	86.1(2)
N2A-Co1-N15	88.5(2)	89.2(2)
N2A-Co1-N11	91.6(2)	92.2(2)
N2A-Co1-N10	171.4(2)	168.7(2)
Fe1-C1-N1	175.3(5)	176.7(4)
Fe1-C2-N2	177.8(6)	177.3(5)
Co1-N1-C1	173.5(5)	173.2(4)
Co1A-N2-C2	170.6(5)	172.4(4)

Symmetry transformations used to generate equivalent atoms: A 1/2-x, 3/2-y, 1-z.

Table S3. Selected bond lengths [\AA] and angles [deg] for **3** at 100 and 260 K.

	100 K	260 K
Fe1-C1	1.895(5)	1.910(3)
Fe1-C2	1.915(5)	1.940(3)
Fe1-C3	1.930(5)	1.929(4)
Fe1-N4	1.999(4)	1.987(3)
Fe1-N6	2.042(4)	2.020(3)

Fe1-N8	2.006(4)	1.994(3)
Fe-C(average)	1.912	1.926
Co1-N1	2.019(4)	2.077(3)
Co1-N11	2.077(4)	2.128(3)
Co1-N10	2.100(4)	2.146(3)
Co1-N2A	2.058(4)	2.134(3)
Co1-N14A	2.096(5)	2.157(3)
Co1-N15A	2.084(5)	2.131(3)
Co-N(average)	2.072	2.129
C1-Fe1-N4	93.3(2)	93.1(1)
C1-Fe1-N6	174.8(2)	174.6(1)
C1-Fe1-N8	94.3(2)	93.9(1)
C1-Fe1-C2	87.0(2)	86.7(1)
C1-Fe1-C3	85.8(2)	85.4(1)
N1-Co1-N14A	92.6(2)	169.2(1)
N1-Co1-N15A	93.6(2)	93.1(1)
N1-Co1-N11	93.1(2)	95.3(1)
N1-Co1-N2A	92.7(2)	92.9(1)
N1-Co1-N10	171.2(2)	93.4(1)
Fe1-C1-N1	174.8(4)	176.2(3)
Fe1-C2-N2	179.0(4)	177.4(3)
Co1-N1-C1	168.7(4)	168.7(3)
Co1A-N2-C2	164.7(4)	166.0(3)

Symmetry transformations used to generate equivalent atoms: A 1-x, 1-y, 1-z.

Table S4. Selected bond lengths [Å] and angles (°) for $\{[(\text{Tp}^*)\text{Fe}(\text{CN})_3\text{Co}(\text{bpy}^{\text{C}=\text{N}(\text{CH}_2)_5\text{N}=\text{C}}\text{bpy})]_2[\text{PF}_6]_2\} \cdot 6\text{DMF} (\mathbf{R1})$.^{1b}

Temperature / K	100	260
Co1-N1 [Å]	1.891(2)	2.072(3)
Co1-N11 [Å]	1.924(3)	2.135(3)
Co1-N10 [Å]	1.924(3)	2.123(3)
Co1-N2A [Å]	1.910(3)	2.112(4)
Co1-N14(A) [Å]	1.926(3)	2.121(4)
Co1-N15(A) [Å]	1.947(3)	2.112(4)
Co-N _{ave.} [Å]	1.92(3)	2.11(1)
Fe1-C1-N1 [°]	174.3(3)	176.8(4)
Fe1-C2-N2 [°]	173.4(3)	176.2(4)
Co1-N1-C1 [°]	178.3(2)	179.3(4)
Co1A-N2-C2 [°]	176.1(2)	175.9(3)
$\Sigma_{\text{Co}}^{\text{a}}$ [°]	44.84(1)	72.50(1)
CShM _{Co} ^b	0.349	1.157

^a Σ_{Co} : the sum of $|90-\alpha|$ for the 12 *cis*-N-Co-N angles around the cobalt atom; ^b CShM_{Co}: the continuous shape measurement relative to ideal octahedron of the Co centre.

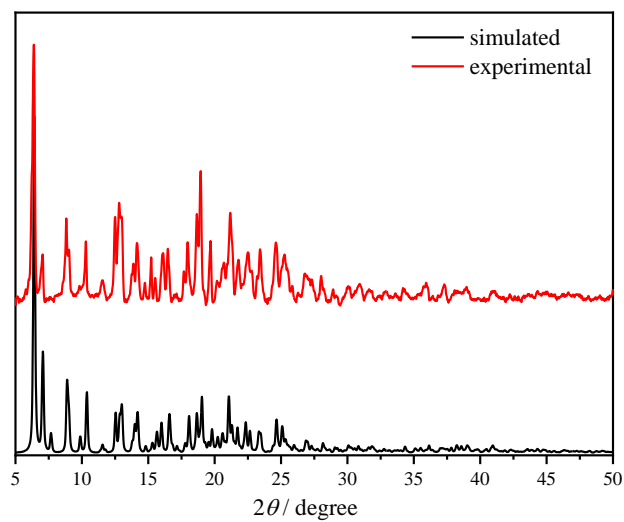


Fig. S1 Powder X-ray diffraction data for **2**. The simulated patterns are calculated from the single crystal data at 260 K.

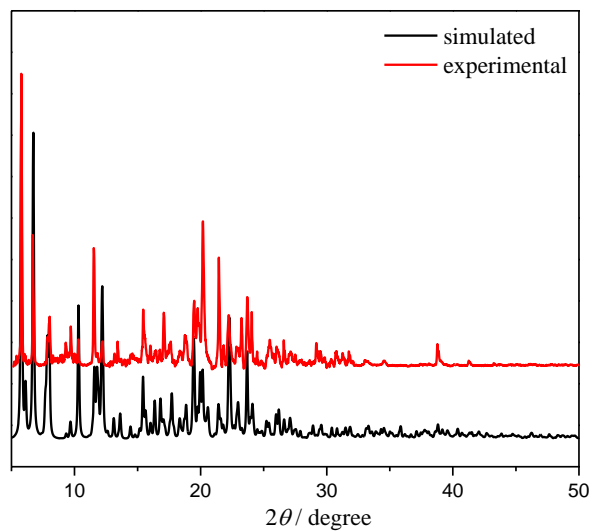


Fig. S2 Powder X-ray diffraction data for **3**. The simulated patterns are calculated from the single crystal data at 260 K.

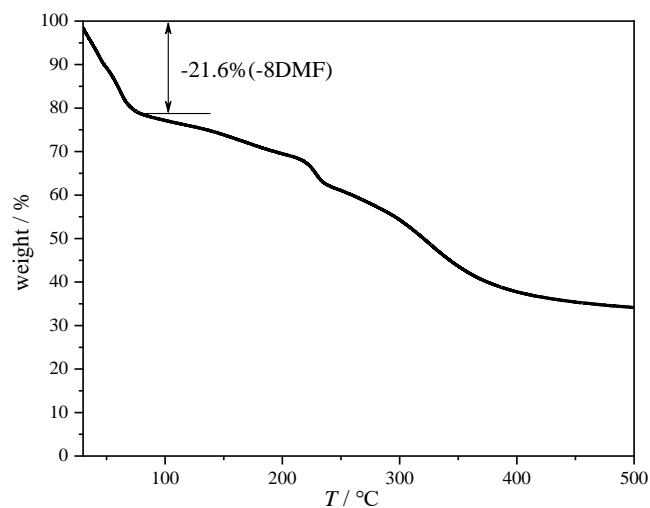


Fig. S3 TGA plot for 1.

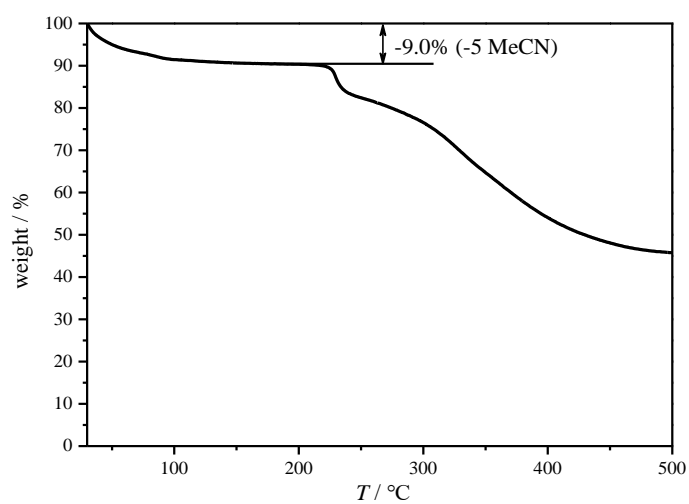


Fig. S4 TGA plot for 2.

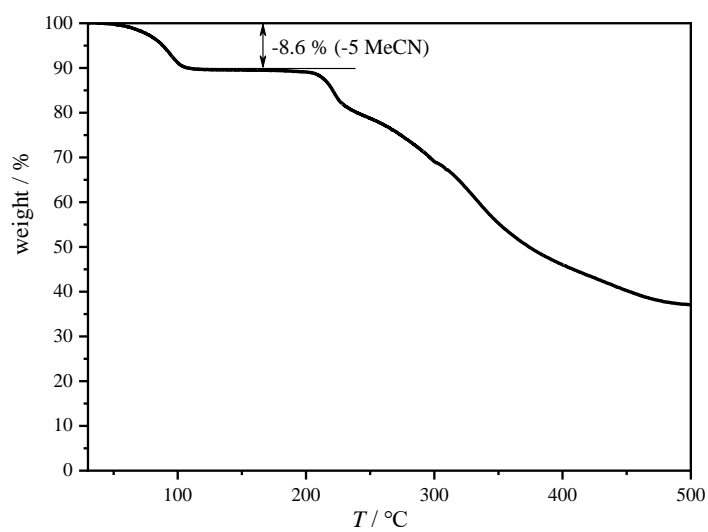


Fig. S5 TGA plot for 3.

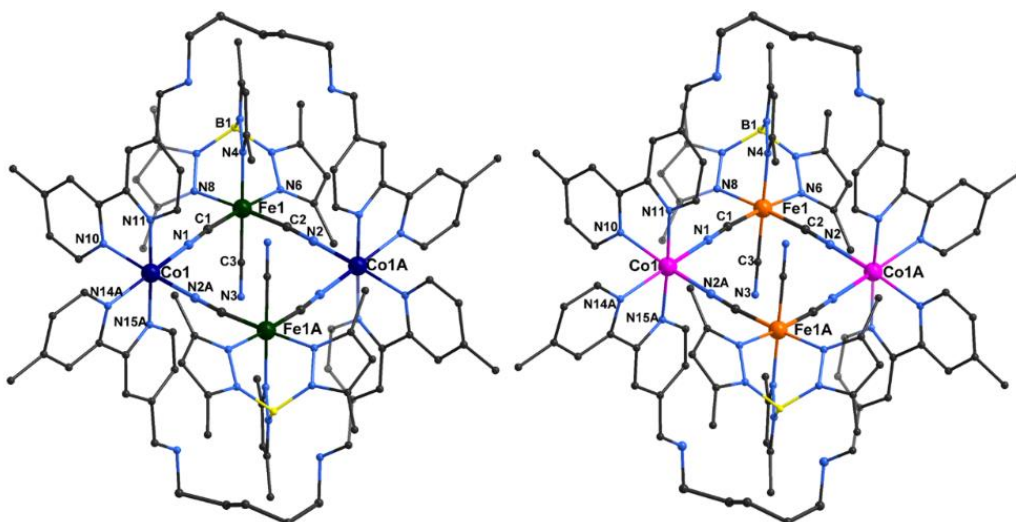


Fig. S6 The cationic $[\text{Fe}_2\text{Co}_2]$ square in **1** at 100 K (left) and 260 K (right). All the hydrogen atoms, counterions and lattice solvents are omitted for clarity.

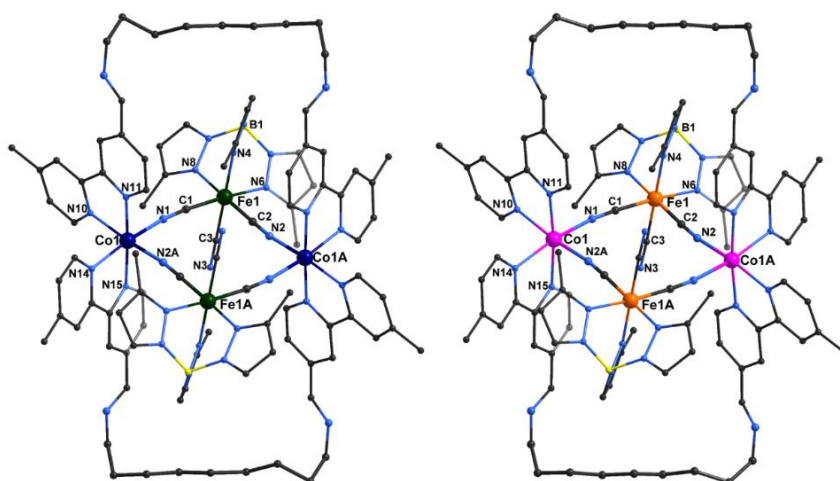


Fig. S7 The cationic $[\text{Fe}_2\text{Co}_2]$ square in **2** at 100 K (left) and 260 K (right). All the hydrogen atoms, counterions and lattice solvents are omitted for clarity.

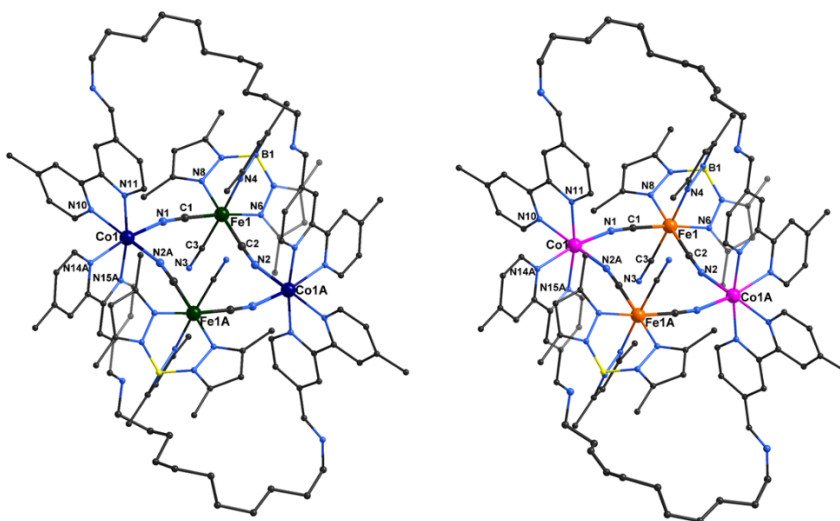


Fig. S8 The cationic $[\text{Fe}_2\text{Co}_2]$ square in **3** at 100 K (left) and 260 K (right). All the hydrogen atoms, counterions and lattice solvents are omitted for clarity.

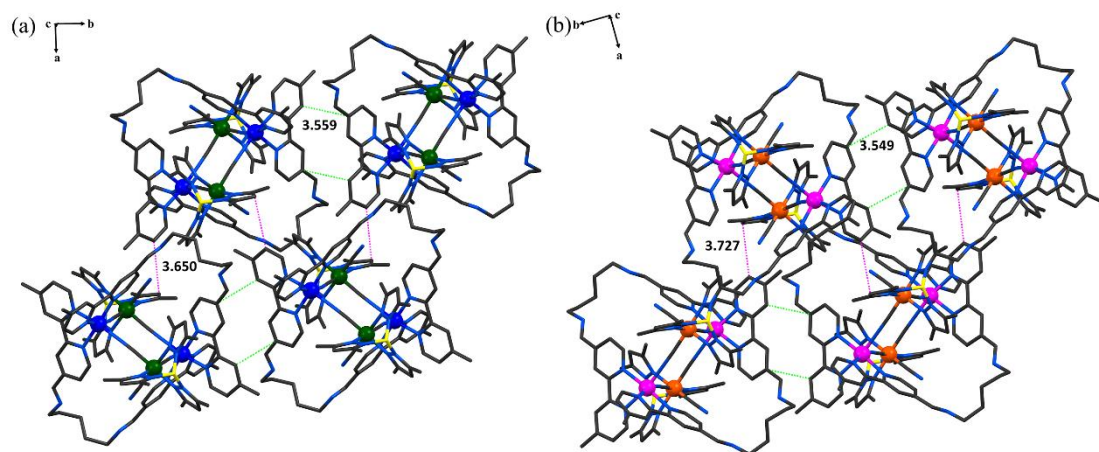


Fig. S9 Packing diagrams for **1** at 100 K (a) and 260 K (b) showing the inter-cluster interactions involving the edge-to-edge $\pi\cdots\pi$ interactions for adjacent bpy - bpy (3.559 Å at 100 K; 3.549 Å at 260 K) and bpy - Tp* ligands (3.650 Å at 100 K; 3.727 Å at 260 K). Hydrogen atoms, counter anions and lattice solvents are omitted for clarity.

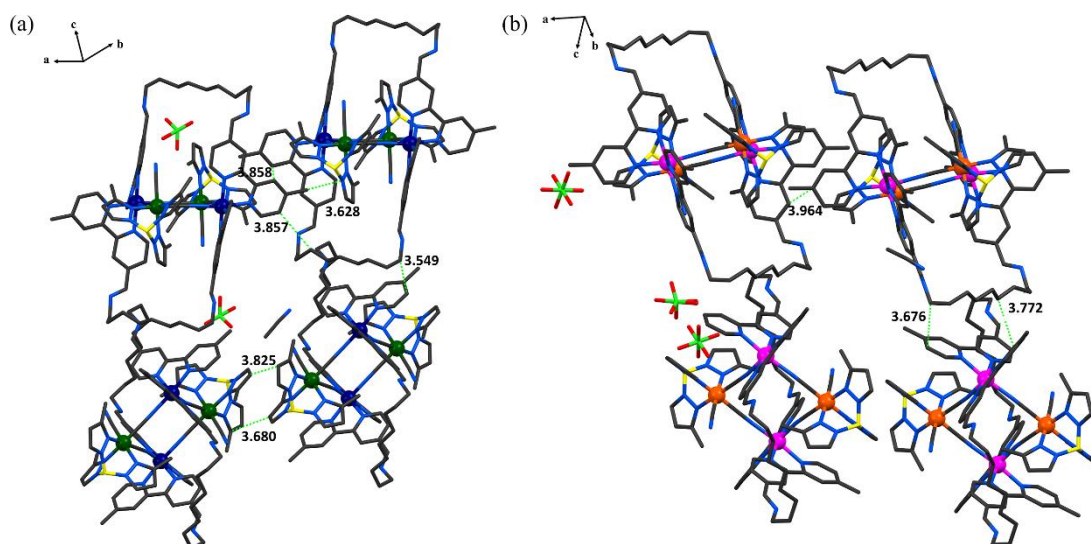


Fig. S10 Packing diagrams for **2** at 100 K (a) and 260 K (b) showing the inter-cluster interactions involving the edge-to-edge $\pi\cdots\pi$ interactions for adjacent bpy - bpy (3.858 Å at 100 K; 3.964 Å at 260 K) and Tp^{Me} - Tp^{Me} ligands (3.825 and 3.680 Å at 100 K), and C-H $\cdots\pi$ interactions (3.628, 3.857 and 3.549 Å at 100 K; 3.676 and 3.772 Å at 260 K). Hydrogen atoms, counter anions and lattice solvents are omitted for clarity.

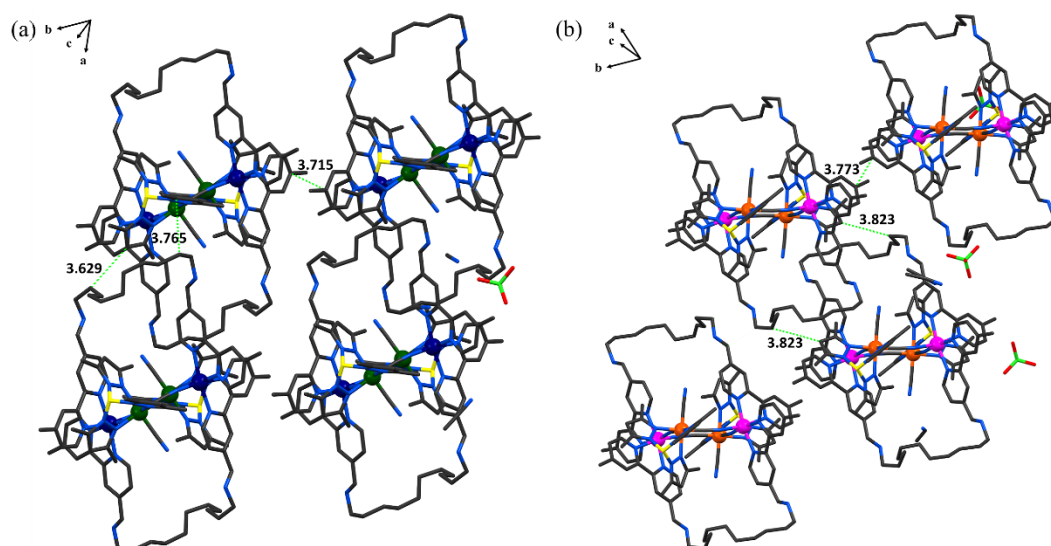


Fig. S11 Packing diagrams for **3** at 100 K (a) and 260 K (b) showing the inter-cluster interactions involving the edge-to-edge $\pi \cdots \pi$ interactions for adjacent bpy - bpy ligands (3.715 Å at 100 K; 3.773 Å at 260 K) and C-H $\cdots\pi$ interactions (3.765 and 3.629 Å at 100 K; 3.823 Å at 260 K). Hydrogen atoms, counter anions and lattice solvents are omitted for clarity.

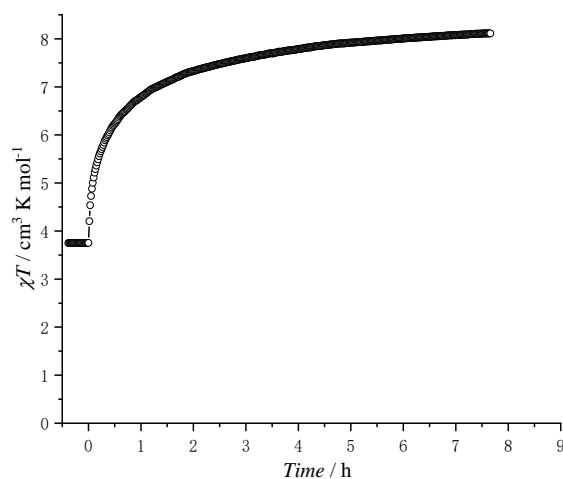


Fig. S12 Time evolution of the χT products of **1** under light irradiation (808 nm, 20 mW) at 10 K and 10 kOe dc field.

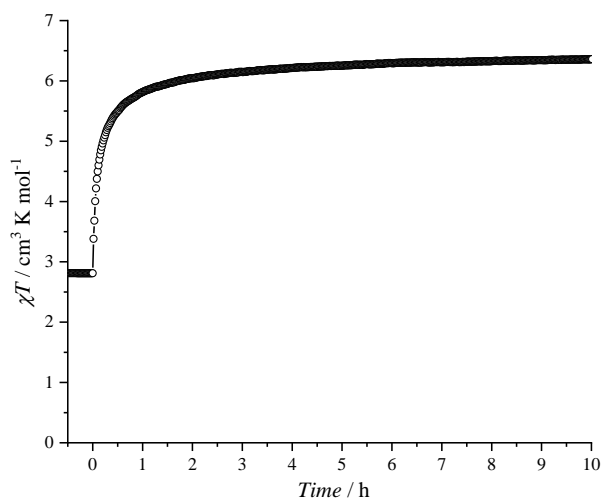


Fig. S13 Time evolution of the χT products of **2** under light irradiation (808 nm, 20 mW) at 10 K and 10 kOe dc field.

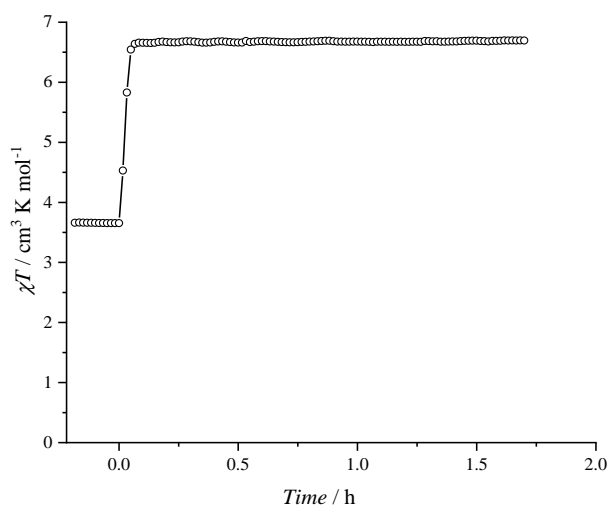


Fig. S14 Time evolution of the χT products of **3** under light irradiation (808 nm, 20 mW) at 10 K and 10 kOe dc field.

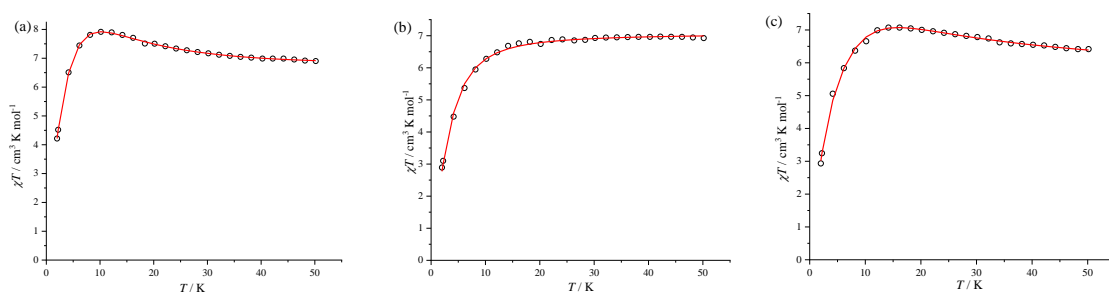


Fig. S15 Photo-irradiated magnetic susceptibility data for **1** (a), **2** (b) and **3** (c) at 2 - 50 K. Solid lines represent the fit to the data.

References

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