Supplementary Information for

Interchain Interactions Raised Photo-Induced [LS]→[HS*] Transition Temperature up to 78 K in Cyanide-Bridged [$Fe^{III}_2Co^{II}$] Chain

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Experimental Section

Materials. All chemical reagents were commercially available and used without further purification. The building block, Li[Fe(bipy)$(CN)_4$] (bipy = 2,2′-bipyridine), were synthesized according to the literature method.[1]

Synthesis. Compound **1-papy** was synthesized by a diffusion method in a test tube. A mixture of methanol/water (1:3, *v*/*v*, 3 mL) was gently layered on the top of a solution of $Co(ClO_4)_2 \cdot 6H_2O$ (0.0050 mmol) in water (1.0 mL), and then a 1.0 mL methanol solution of Li[Fe(bipy)$(CN)_4]\cdot H_2O$ (0.010 mmol) and 4-[(1*E*)-2-phenyldiazenyl]-pyridine (papy) (0.010 mmol) was added as the third layer. After a few weeks, dark-red flake crystals were obtained. Yield: 43% based on $Co(ClO_4)_2 \cdot 6H_2O$. Anal. Calcd (%) for $C_{100}H_{74}Co_2Fe_4N_{36}O_3$: C 55.37, H 3.44, N 23.25; found: C 55.53, H 3.57, N 23.37. Compound **1-pepy** was synthesized by the similar method. Yield: 56% based on $Co(ClO_4)_2 \cdot 6H_2O$. Anal. Calcd (%) for $C_{110}H_{78}Co_2Fe_4N_{28}O_3$: C 60.57, H 3.60, N 17.98; found: C 60.73, H 3.54, N 18.09.

^{57}Fe Mössbauer spectra. ^{57}Fe Mössbauer spectra were measured with transmission geometry on WSS-10 spectrometer controlled by Wissoft 2003 software. Samples were set in a plastic container and sealed with parafilm. The sample was placed on a copper mount inside the JANIS CCS-800 cryostat system with a helium atmosphere. The temperature was controlled by Cryo-con Model 22C Cryogenic Temperature Controller ranging from 10 K to 300 K. Deconvolution of Mössbauer spectra was carried by least-square fitting using Lorentzian functions (Mosswinn software). The isomer shifts δ and quadrupole splitting ΔE_Q were calibrated in relation to α-Fe at 298 K.

Structure Determination and Refinement. The single-crystal XRD data were collected on a Bruker D8 VENTURE diffractometer equipped with a CMOS detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). APEX-III program was used to determine the unit-cell parameters. The data were integrated with the SAINT program and were corrected for the Lorentz factor and polarization effects. Multi-scan absorption corrections were applied using SADABS. The molecular

structures were solved by direct methods and refined by the full-matrix least squares on F^2 using SHELXTL program (version 2014/7). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of organic ligands were located geometrically and fixed isotropic thermal parameters. Crystal data and the final refinement parameters of the studied compounds were shown in Table S1-S6. The X-ray crystallographic coordinates for structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition nos. CCDC-2247067, for **1-papy** at 110 K; -2247068, for **1-papy** at 290 K; -2247069, for **1-papy** at 78 K; -2247070, for **1-papy** after irradiation at 78 K; and -2247071, for **1-pepy** at 110 K; -2247073, for **1-pepy** at 300 K; -2247074, for **1-pepy** at 50 K; -2247075, for **1-pepy** after irradiation at 50 K. These data can be obtained free of charge from CCDC *via* http://www.ccdc.cam.ac.uk/data_request/cif.

UV-vis-NIR Spectra Measurements. Solid-state UV-vis-NIR absorption spectra were recorded by a UV spectrophotometer (HITACHI-UH4150) equipped with a liquid helium type cryostat (Janis ST-500). The sample was set in a silica glass groove. For the UV-vis-NIR absorption spectra of **1-papy** under irradiation, the sample was continuously irradiated with harmonic of Nd: YAG lasers at 78 K via a flexible optical fiber guided laser diode.

Magnetic and Photomagnetic Studies. Magnetic measurements were performed on a Quantum Design SQUID (MPMS XL-7) magnetometer with the polycrystalline samples. Data were corrected for the diamagnetic contribution calculated from Pascal's constants.[2] Photomagnetic measurements were equipped with a flexible optical fiber guided laser diode pumped Nd: YAG lasers. The polycrystalline sample were attached to a commercial adhesive tape and placed on the edge of the optical fiber. The photo-irradiation of the sample was carried out by 808-nm laser setting temperature to 10 K and 78 K for **1-papy** and by 808-nm laser setting temperature to 10 K for **1-pepy**, respectively. The temperature-dependent magnetization was measured both before and after irradiation in the temperature range from 2 to 150 K. The difference in the

magnetization before and after irradiation was extracted by subtracting the magnetization value before irradiation from that after irradiation.

Crystallographic data for the LT and HT phases

Table S1. Table of crystallographic parameters for **1**-**papy** and **1**-**pepy**.

	1-papy$^{110\ K}$	**1-papy$^{290\ K}$**	**1-pepy$^{110\ K}$**	**1-pepy$^{300\ K}$**
CCDC	2247067	2247068	2247071	2247073
Formula	$C_{100}H_{74}Co_2Fe_4N_{36}O_3$	$C_{100}H_{74}Co_2Fe_4N_{36}O_3$	$C_{110}H_{78}Co_2Fe_4N_{28}O_3$	$C_{110}H_{78}Co_2Fe_4N_{28}O_3$
Fw	2169.14	2169.14	2181.23	2181.23
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.5731(7)	13.863(3)	13.4529(14)	13.8579(12)
b (Å)	14.3430(7)	14.431(3)	14.6385(17)	14.8053(12)
c (Å)	15.6188(7)	15.991(3)	15.8026(18)	16.0832(14)
α (°)	113.6750(10)	114.141(5)	111.867(4)	112.412(2)
β (°)	109.519(2)	110.063(5)	109.080(4)	109.571(2)
γ (°)	99.1830(10)	98.012(5)	100.127(4)	99.235(2)
V (Å^3)	2468.0(2)	2591.9(9)	2567.5(5)	2712.4(4)
Z	1	1	1	1
ρ_{calc} (g/cm^3)	1.455	1.386	1.404	1.329
μ (mm^{-1})	0.971	0.925	0.932	0.882
θ_{min}, θ_{max} (°)	4.506 to 49.998	4.392 to 49.998	4.878 to 54.99	3.738 to 50.054
Reflns. (all data)	19158	18665	95194	69836
Reflns [$I \geq 2\sigma(I)$]	8670	9015	11762	9573
R_{int}	0.1237	0.0698	0.0419	0.0506
R_1,wR_2 [$I \geq 2\sigma(I)$]	0.0671, 0.1702	0.0663, 0.1251	0.0384, 0.1070	0.0635, 0.1935
R_1,wR_2 (all data)	0.1023, 0.1836	0.1301, 0.1417	0.0471, 0.1142	0.0820, 0.2123
GOF	1.054	1.058	1.033	1.061

$R_1 = \Sigma(|F_0|-|F_C|)/\Sigma|F_0|$; $wR_2 = [\Sigma w(|F_0|-|F_C|)^2/\Sigma wF_0^2]^{1/2}$.

Table S2. Selected bond lengths (Å) for compound **1-papy** at 110 K and 290 K.

1-papy$^{110\ K}$		**1-papy$^{290\ K}$**	
Co1–N1	1.900(4)	Co1–N1	2.091(4)
Co1–N1^{1}	1.900(4)	Co1–N1^{1}	2.091(4)
Co1–N5^{2}	1.890(5)	Co1–N5^{2}	2.098(4)
Co1–N5^{3}	1.890(5)	Co1–N5^{3}	2.098(4)
Co1–N13	1.977(4)	Co1–N13	2.164(4)
Co1–N13^{1}	1.977(4)	Co1–N13^{1}	2.164(4)
Co2–N16	1.973(4)	Co2–N16^{3}	2.166(4)
Co2–N16^{3}	1.973(4)	Co2–N16	2.166(4)
Co2–N2	1.891(5)	Co2–N2	2.112(4)
Co2–N2^{3}	1.891(5)	Co2–N2^{3}	2.112(4)
Co2–N6^{3}	1.886(4)	Co2–N6^{3}	2.063(4)
Co2–N6	1.886(4)	Co2–N6	2.063(4)
Fe2–N12	1.983(5)	Fe2–N12	1.991(3)
Fe2–N11	1.994(4)	Fe2–N11	1.986(4)
Fe2–C7	1.943(6)	Fe2–C7	1.960(6)
Fe2–C6	1.893(5)	Fe2–C6	1.890(5)
Fe2–C5	1.877(6)	Fe2–C5	1.917(5)
Fe2–C8	1.933(6)	Fe2–C8	1.955(6)
Fe1–N10	1.971(4)	Fe1–N10	1.978(4)
Fe1–N9	1.984(4)	Fe1–N9	1.968(4)
Fe1–C2	1.881(6)	Fe1–C2	1.913(5)
Fe1–C3	1.950(6)	Fe1–C3	1.940(5)
Fe1–C1	1.892(5)	Fe1–C1	1.890(5)
Fe1–C4	1.947(6)	Fe1–C4	1.946(5)

Symmetry transformations used to generate equivalent atoms:

^{1}-X,1-Y,1-Z; ^{2}-1+X,+Y,+Z; ^{3}1-X,1-Y,1-Z (**1-papy**$^{110\ K}$)

^{1}-X,1-Y,1-Z; ^{2}-1+X,+Y,+Z; ^{3}1-X,1-Y,1-Z; ^{4}1-X,2-Y,2-Z (**1-papy**$^{290\ K}$)

Table S3. Selected bond lengths (Å) for compound **1-pepy** at 110 K and 300 K.

1-pepy$^{110\ K}$		**1-pepy$^{300\ K}$**	
Co1–N1^{1}	1.8881(18)	Co1–N1^{2}	2.088(4)
Co1–N1	1.8881(18)	Co1–N1	2.088(4)
Co1–N5^{2}	1.8946(18)	Co1–N5^{3}	2.099(4)
Co1–N5^{3}	1.8946(18)	Co1–N5^{1}	2.099(4)
Co1–N13^{1}	1.9628(18)	Co1–N13^{2}	2.145(4)
Co1–N13	1.9628(18)	Co1–N13	2.145(4)
Co2–N2	1.9154(19)	Co2–N2^{1}	2.112(4)
Co2–N2^{3}	1.9154(19)	Co2–N2	2.112(4)
Co2–N14^{3}	1.9819(19)	Co2–N6^{1}	2.072(4)
Co2–N14	1.9818(19)	Co2–N6	2.072(4)
Co2–N6^{3}	1.8917(18)	Co2–N14	2.166(4)
Co2–N6	1.8917(18)	Co2–N14^{1}	2.166(4)
Fe2–C6	1.884(2)	Fe1–C2	1.915(4)
Fe2–C5	1.904(2)	Fe1–C3	1.953(5)
Fe2–C7	1.948(2)	Fe1–C1	1.903(4)
Fe2–C8	1.949(2)	Fe1–C4	1.945(5)
Fe2–N12	1.9862(19)	Fe1–N9	1.979(4)
Fe2–N11	1.9833(18)	Fe1–N10	1.975(4)
Fe1–C1	1.882(2)	Fe2–C5	1.917(4)
Fe1–C2	1.891(2)	Fe2–C6	1.900(4)
Fe1–C4	1.944(2)	Fe2–C8	1.947(5)
Fe1–C3	1.951(2)	Fe2–C7	1.937(5)
Fe1–N9	1.9892(19)	Fe2–N11	1.977(3)
Fe1–N10	1.983(2)	Fe2–N12	1.984(3)

Symmetry transformations used to generate equivalent atoms:

^{1}-X,-Y,-Z; ^{2}-1+X,+Y,+Z; ^{3}1-X,-Y,-Z (**1-pepy**$^{110\ K}$)

^{1}1-X,2-Y,1-Z; ^{2}-X,2-Y,1-Z; ^{3}-1+X,+Y,+Z (**1-pepy**$^{300\ K}$)

Table S4. Selected angles (°) for compound **1-papy** at 110 K and 290 K.

1-papy$^{110\ K}$		**1-papy$^{290\ K}$**	
N1–Co1–N1^{1}	180.0(2)	N1–Co1–N1^{1}	180.0
N1–Co1–N13	89.27(16)	N1^{1}–Co1–N5^{2}	88.56(14)
N1–Co1–N13^{1}	90.73(16)	N1^{1}–Co1–N5^{3}	91.44(14)
N1^{1}–Co1–N13^{1}	89.27(16)	N1–Co1–N5^{2}	91.44(14)
N1^{1}–Co1–N13	90.73(16)	N1–Co1–N5^{3}	88.56(14)
N5^{2}–Co1–N1^{1}	90.91(18)	N1–Co1–N13^{1}	90.93(15)
N5^{2}–Co1–N1	89.09(17)	N1^{1}–Co1–N13	90.93(15)
N5^{3}–Co1–N1	90.91(18)	N1–Co1–N13	89.07(15)
N5^{3}–Co1–N1^{1}	89.09(17)	N1^{1}–Co1–N13^{1}	89.07(15)
N5^{3}–Co1–N5^{2}	180.0	N5^{2}–Co1–N5^{3}	180.0
N5^{2}–Co1–N13^{1}	88.66(18)	N5^{3}–Co1–N13^{1}	88.99(15)
N5^{2}–Co1–N13	91.34(18)	N5^{3}–Co1–N13	91.00(15)
N5^{3}–Co1–N13	88.66(18)	N5^{2}–Co1–N13	89.00(15)
N5^{3}–Co1–N13^{1}	91.34(18)	N5^{2}–Co1–N13^{1}	91.01(15)
N13^{1}–Co1–N13	180.0(3)	N13^{1}–Co1–N13	180.0
N16^{3}–Co2–N16	180.0	N16–Co2–N16^{2}	180.0
N2–Co2–N16^{3}	92.51(17)	N2–Co2–N16	86.20(15)
N2^{3}–Co2–N16^{3}	87.49(17)	N2–Co2–N16^{2}	93.79(15)
N2^{3}–Co2–N16	92.51(17)	N2^{2}–Co2–N16^{2}	86.21(15)
N2–Co2–N16	87.49(17)	N2^{2}–Co2–N16	93.80(15)
N2^{3}–Co2–N2	180.0	N2^{2}–Co2–N2	180.0
N6^{3}–Co2–N16^{3}	89.87(17)	N6^{2}–Co2–N16	90.31(16)
N6–Co2–N16^{3}	90.13(17)	N6^{2}–Co2–N16^{2}	89.69(16)
N6–Co2–N16	89.87(17)	N6–Co2–N16	89.69(16)
N6^{3}–Co2–N16	90.13(17)	N6–Co2–N16^{2}	90.31(16)
N6–Co2–N2	89.11(17)	N6^{2}–Co2–N2	91.26(14)
N6^{3}–Co2–N2	90.89(18)	N6–Co2–N2	88.75(14)
N6–Co2–N2^{3}	90.89(18)	N6–Co2–N2^{2}	91.25(14)
N6^{3}–Co2–N2^{3}	89.12(17)	N6^{2}–Co2–N2^{2}	88.74(14)
N6^{3}–Co2–N6	180.00(11)	N6–Co2–N6^{2}	180.0
Σ_{Co1}	11.92	Σ_{Co1}	13.5
Σ_{Co2}	14.12	Σ_{Co2}	21.44
N12–Fe2–N11	81.06(17)	N11–Fe2–N12	81.20(15)
C7–Fe2–N12	91.9(2)	C7–Fe2–N12	90.78(18)
C7–Fe2–N11	93.21(18)	C7–Fe2–N11	92.88(17)
C6–Fe2–N12	94.17(19)	C6–Fe2–N12	95.93(17)
C6–Fe2–N11	174.66(19)	C6–Fe2–N11	176.64(17)
C6–Fe2–C7	89.3(2)	C6–Fe2–C7	88.91(19)
C6–Fe2–C8	88.8(2)	C6–Fe2–C5	84.91(18)
C5–Fe2–N12	177.03(18)	C6–Fe2–C8	88.4(2)
C5–Fe2–N11	96.09(19)	C5–Fe2–N12	178.93(17)
C5–Fe2–C7	89.1(2)	C5–Fe2–N11	97.94(17)
C5–Fe2–C6	88.6(2)	C5–Fe2–C7	89.9(2)
C5–Fe2–C8	87.5(2)	C5–Fe2–C8	88.3(2)
C8–Fe2–N12	91.6(2)	C8–Fe2–N12	91.11(19)
C8–Fe2–N11	88.90(18)	C8–Fe2–N11	89.93(18)
C8–Fe2–C7	176.1(2)	C8–Fe2–C7	176.8(2)
N10–Fe1–N9	81.51(18)	N9–Fe1–N10	81.43(17)
C2–Fe1–N10	177.4(2)	C2–Fe1–N10	179.08(17)
C2–Fe1–N9	96.78(19)	C2–Fe1–N9	97.69(18)
C2–Fe1–C3	90.4(2)	C2–Fe1–C3	91.7(2)
C2–Fe1–C1	86.2(2)	C2–Fe1–C4	90.73(19)
C2–Fe1–C4	91.1(2)	C3–Fe1–N10	88.05(19)
C3–Fe1–N10	87.6(2)	C3–Fe1–N9	89.79(18)
C3–Fe1–N9	89.27(19)	C3–Fe1–C4	177.6(2)
C1–Fe1–N10	95.50(19)	C1–Fe1–N10	97.08(18)

C1–Fe1–N9	176.93(19)	C1–Fe1–N9	178.33(18)
C1–Fe1–C3	89.9(2)	C1–Fe1–C2	83.80(18)
C1–Fe1–C4	91.4(2)	C1–Fe1–C3	89.40(19)
C4–Fe1–N10	90.8(2)	C1–Fe1–C4	91.22(19)
C4–Fe1–N9	89.38(19)	C4–Fe1–N10	89.54(18)
C4–Fe1–C3	178.1(2)	C4–Fe1–N9	89.52(17)
C1–N1–Co1	168.2(4)	C1–N1–Co1	166.1(4)
C2–N2–Co2	163.4(4)	C2–N2–Co2	159.7(4)
C5–N5–Co1[4]	174.5(4)	C5–N5–Co1[4]	177.6(4)
C6–N6–Co2	172.8(4)	C6–N6–Co2	175.0(4)
N2–C2–Fe1	175.2(4)	N2–C2–Fe1	177.3(4)
N7–C7–Fe2	176.4(5)	N7–C7–Fe2	178.3(5)
N6–C6–Fe2	179.0(5)	N6–C6–Fe2	179.0(5)
N3–C3–Fe1	176.6(5)	N3–C3–Fe1	175.3(5)
N5–C5–Fe2	177.3(4)	N5–C5–Fe2	177.8(4)
N8–C8–Fe2	177.4(6)	N8–C8–Fe2	179.4(5)
N1–C1–Fe1	176.3(5)	N1–C1–Fe1	177.3(4)
N4–C4–Fe1	177.6(5)	N4–C4–Fe1	176.8(5)

Symmetry transformations used to generate equivalent atoms:

[1]-X,1-Y,1-Z; [2]-1+X,+Y,+Z; [3]1-X,1-Y,1-Z; [4]1+X,+Y,+Z (**1**-**papy**$^{110\ K}$)

[1]-X,1-Y,1-Z; [2]1-X,1-Y,1-Z; [3]-1+X,+Y,+Z; [4]1+X,+Y,+Z (**1**-**papy**$^{290\ K}$)

Table S5. Selected angles (°) for compound **1-pepy** at 110 K and 300 K.

1-pepy$^{110\ K}$		**1-pepy$^{300\ K}$**	
N1^{1}–Co1–N1	180.0	N13^{2}–Co1–N13	180.0
N1–Co1–N5^{2}	91.19(8)	N5^{3}–Co1–N13^{2}	89.58(15)
N1–Co1–N5^{3}	88.81(8)	N5^{1}–Co1–N13^{2}	90.42(15)
N1^{1}–Co1–N5^{2}	88.80(8)	N5^{1}–Co1–N13	89.58(15)
N1^{1}–Co1–N5^{3}	91.20(8)	N5^{3}–Co1–N13	90.42(15)
N1–Co1–N13^{1}	90.55(8)	N5^{1}–Co1–N5^{3}	180.0
N1–Co1–N13	89.45(8)	N1–Co1–N13^{2}	91.13(15)
N1^{1}–Co1–N13	90.55(8)	N1^{2}–Co1–N13^{2}	88.87(15)
N1^{1}–Co1–N13^{1}	89.45(8)	N1–Co1–N13	88.87(15)
N5^{2}–Co1–N5^{3}	180.00(16)	N1^{2}–Co1–N13	91.13(15)
N5^{3}–Co1–N13	90.60(8)	N1–Co1–N5^{1}	91.28(15)
N5^{2}–Co1–N13	89.40(8)	N1^{2}–Co1–N5^{3}	91.28(15)
N5^{2}–Co1–N13^{1}	90.60(8)	N1^{2}–Co1–N5^{1}	88.72(15)
N5^{3}–Co1–N13^{1}	89.40(8)	N1–Co1–N5^{3}	88.72(15)
N13^{1}–Co1–N13	180.00(12)	N1^{2}–Co1–N1	180.0
N2–Co2–N2^{2}	180.0	N14–Co2–N14^{1}	180.0
N2–Co2–N14	86.81(8)	N6^{1}–Co2–N14	90.27(15)
N2^{2}–Co2–N14	93.19(8)	N6^{1}–Co2–N14^{1}	89.73(15)
N2^{2}–Co2–N14^{2}	86.81(8)	N6–Co2–N14^{1}	90.27(15)
N2–Co2–N14^{2}	93.19(8)	N6–Co2–N14	89.73(15)
N14–Co2–N14^{2}	180.0	N6^{1}–Co2–N6	180.0
N6–Co2–N2^{2}	90.87(8)	N6^{1}–Co2–N2^{1}	89.14(14)
N6–Co2–N2	89.13(8)	N6–Co2–N2^{1}	90.87(14)
N6^{2}–Co2–N2^{2}	89.13(8)	N6^{1}–Co2–N2	90.86(14)
N6^{2}–Co2–N2	90.87(8)	N6–Co2–N2	89.13(14)
N6^{2}–Co2–N14^{2}	90.05(8)	N2^{1}–Co2–N14^{1}	85.53(14)
N6–Co2–N14	90.05(8)	N2–Co2–N14^{1}	94.47(14)
N6^{2}–Co2–N14	89.95(8)	N2^{1}–Co2–N14	94.47(14)
N6–Co2–N14^{2}	89.95(8)	N2–Co2–N14	85.53(14)
N6–Co2–N6^{2}	180.00(9)	N2^{1}–Co2–N2	180.0
Σ_{Co1}	9.38	Σ_{Co1}	11.32
Σ_{Co2}	16.44	Σ_{Co2}	22.42
C6–Fe2–C5	87.35(9)	N10–Fe1–N9	81.03(17)
C6–Fe2–C7	90.14(9)	C2–Fe1–N9	97.55(17)
C6–Fe2–C8	89.04(10)	C2–Fe1–N10	178.52(17)
C6–Fe2–N12	94.46(8)	C2–Fe1–C3	92.41(19)
C6–Fe2–N11	175.22(8)	C2–Fe1–C4	90.08(19)
C5–Fe2–C7	88.82(9)	C3–Fe1–N9	90.59(18)
C5–Fe2–C8	87.13(10)	C3–Fe1–N10	88.03(18)
C5–Fe2–N12	178.05(8)	C1–Fe1–N9	178.53(17)
C5–Fe2–N11	96.90(8)	C1–Fe1–N10	97.51(17)
C7–Fe2–C8	175.90(10)	C1–Fe1–C2	83.91(18)
C7–Fe2–N12	90.44(9)	C1–Fe1–C3	89.15(19)
C7–Fe2–N11	92.12(9)	C1–Fe1–C4	90.36(18)
C8–Fe2–N12	93.63(9)	C4–Fe1–N9	89.84(17)
C8–Fe2–N11	89.00(9)	C4–Fe1–N10	89.49(18)
N11–Fe2–N12	81.32(8)	C4–Fe1–C3	177.39(19)
C1–Fe1–C2	85.82(9)	N11–Fe2–N12	81.09(15)
C1–Fe1–C4	90.78(9)	C5–Fe2–N12	178.72(17)
C1–Fe1–C3	89.27(9)	C5–Fe2–N11	98.07(16)
C1–Fe1–N10	96.07(9)	C5–Fe2–C8	88.3(2)
C1–Fe1–N9	177.25(9)	C5–Fe2–C7	88.56(19)
C2–Fe1–C4	89.86(9)	C6–Fe2–N12	95.87(16)
C2–Fe1–C3	92.78(9)	C6–Fe2–N11	176.57(16)
C2–Fe1–N10	178.11(8)	C6–Fe2–C5	85.00(18)
C2–Fe1–N9	96.93(8)	C6–Fe2–C8	88.68(19)

C4–Fe1–C3	177.36(10)	C6–Fe2–C7	89.28(19)
C4–Fe1–N10	90.32(9)	C8–Fe2–N12	92.66(19)
C4–Fe1–N9	89.46(9)	C8–Fe2–N11	89.87(18)
C3–Fe1–N10	87.05(9)	C7–Fe2–N12	90.51(18)
C3–Fe1–N9	90.36(9)	C7–Fe2–N11	92.33(18)
N10–Fe1–N9	81.19(8)	C7–Fe2–C8	176.4(2)
N1–C1–Fe1	176.3(2)	N1–C1–Fe1	176.1(4)
N2–C2–Fe1	177.52(19)	N3–C3–Fe1	175.1(5)
N4–C4–Fe1	178.4(2)	N2–C2–Fe1	177.6(4)
N3–C3–Fe1	175.3(2)	N4–C4–Fe1	177.0(5)
N6–C6–Fe2	178.4(2)	N5–C5–Fe2	177.6(4)
N5–C5–Fe2	178.07(19)	N6–C6–Fe2	179.0(4)
N7–C7–Fe2	178.9(2)	N7–C7–Fe2	179.6(5)
N8–C8–Fe2	176.1(2)	N8–C8–Fe2	179.8(7)
C1–N1–Co1	170.82(19)	C1–N1–Co1	170.1(4)
C5–N5–Co1[4]	176.17(18)	C5–N5–Co1[4]	177.1(4)
C2–N2–Co2	158.49(18)	C2–N2–Co2	158.6(4)
C6–N6–Co2	175.64(18)	C6–N6–Co2	175.5(4)

Symmetry transformations used to generate equivalent atoms:

[1]-X,-Y,-Z; [2]-1+X,+Y,+Z; [3]1-X,-Y,-Z; [4]-X,1-Y,-Z (**1**-**pepy**$^{110\ K}$)

[1]1-X,2-Y,1-Z; [2]-X,2-Y,1-Z; [3]-1+X,+Y,+Z; [4]1+X,+Y,+Z (**1**-**pepy**$^{300\ K}$)

Crystallographic data for the LS and photo-excited HS* phases

Table S6. Table of crystallographic parameters for **1-papy** and **1-pepy** before and after 808-nm laser irradiation at 78 and 50 K, respectively.

	1-papy$^{78\ K}$	**1-papy**$^{808\ nm}$	**1-pepy**$^{50\ K}$	**1-pepy**$^{808\ nm}$
CCDC	2247069	2247070	2247074	2247075
Formula	$C_{100}H_{74}Co_2Fe_4N_{36}O_3$	$C_{100}H_{74}Co_2Fe_4N_{36}O_3$	$C_{110}H_{78}Co_2Fe_4N_{28}O_3$	$C_{110}H_{78}Co_2Fe_4N_{28}O_3$
Fw	2169.14	2169.14	2181.23	2181.23
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.6276(15)	13.8374(13)	13.4126(4)	13.6686(11)
b (Å)	14.3424(16)	14.4192(14)	14.6128(6)	14.8739(12)
c (Å)	15.6194(18)	15.8950(15)	15.7476(6)	16.0438(13)
α (°)	113.678(3)	114.184(3)	112.0100(10)	112.159(2)
β (°)	109.594(3)	110.012(3)	109.1130(10)	110.128(3)
γ (°)	99.000(3)	98.189(3)	99.9300(10)	100.153(3)
V (Å^3)	2479.5(5)	2566.4(4)	2545.68(16)	2654.9(4)
Z	1	1	1	1
ρ_{calc} (g/cm^3)	1.449	1.400	1.416	1.358
μ (mm^{-1})	0.967	0.934	0.940	0.902
θ_{min}, θ_{max} (°)	4.49 to 50	4.85 to 49.994	3.808 to 49.994	4.458 to 50
Reflns. (all data)	49747	55575	62891	112256
Reflns [$I \geq 2\sigma(I)$]	8413	8890	8924	9122
R_{int}	0.0940	0.0864	0.0580	0.0968
R_1,wR_2 [$I \geq 2\sigma(I)$]	0.0810, 0.2253	0.0749, 0.2098	0.0452, 0.1230	0.0656, 01752
R_1,wR_2 (all data)	0.1099, 0.2488	0.1024, 0.2335	0.0527, 0.1276	0.0831, 0.1876
GOF	1.116	1.119	1.144	1.138

$R_1 = \Sigma(||F_0|-|F_C||)/\Sigma|F_0|$; $wR_2 = [\Sigma w(|F_0|-|F_C|)^2/\Sigma wF_0^2]^{1/2}$.

Table S7. Selected bond lengths (Å) for compound **1-papy** before and after 808-nm laser irradiation at 78 K.

1-papy$^{78\ K}$		**1-papy$^{808\ nm}$**	
Co1–N1	1.897(5)	Co1–N1	2.093(4)
Co1–N1^{1}	1.897(5)	Co1–N1^{1}	2.093(4)
Co1–N5^{2}	1.916(6)	Co1–N5^{2}	2.102(5)
Co1–N5^{3}	1.916(6)	Co1–N5^{3}	2.102(5)
Co1–N13	1.983(5)	Co1–N13^{1}	2.155(4)
Co1–N13^{1}	1.983(5)	Co1–N13	2.155(4)
Co2–N16	1.973(5)	Co2–N16^{3}	2.148(4)
Co2–N16^{3}	1.973(5)	Co2–N16	2.148(4)
Co2–N2	1.906(6)	Co2–N2^{3}	2.114(5)
Co2–N2^{3}	1.906(6)	Co2–N2	2.114(5)
Co2–N6^{3}	1.889(5)	Co2–N6^{3}	2.065(4)
Co2–N6	1.889(5)	Co2–N6	2.065(4)
Fe2–N12	1.997(5)	Fe2–N12	1.992(5)
Fe2–N11	1.992(5)	Fe2–N11	1.983(4)
Fe2–C7	1.943(6)	Fe2–C7	1.960(5)
Fe2–C6	1.879(6)	Fe2–C6	1.904(5)
Fe2–C5	1.899(7)	Fe2–C5	1.917(6)
Fe2–C8	1.939(6)	Fe2–C8	1.945(6)
Fe1–N10	1.975(5)	Fe1–N10	1.976(5)
Fe1–N9	1.979(5)	Fe1–N9	1.974(4)
Fe1–C2	1.900(7)	Fe1–C2	1.914(6)
Fe1–C3	1.940(6)	Fe1–C3	1.953(6)
Fe1–C1	1.893(6)	Fe1–C1	1.912(5)
Fe1–C4	1.955(6)	Fe1–C4	1.957(6)

Symmetry transformations used to generate equivalent atoms:

^{1}-X,1-Y,1-Z; ^{2}-1+X,+Y,+Z; ^{3}1-X,1-Y,1-Z (**1-papy**$^{78\ K}$)

^{1}-X,1-Y,1-Z; ^{2}-1+X,+Y,+Z; ^{3}1-X,1-Y,1-Z (**1-papy**$^{808\ nm}$)

Table S8. Selected bond lengths (Å) for compound **1-pepy** before and after 808-nm laser irradiation at 50 K.

1-pepy$^{50\ K}$		**1-pepy$^{808\ nm}$**	
Co1–N1[1]	1.881(3)	Co1–N1	2.090(4)
Co1–N1	1.881(3)	Co1–N1[1]	2.090(4)
Co1–N5[2]	1.894(3)	Co1–N5[2]	2.103(3)
Co1–N5[3]	1.894(3)	Co1–N5[3]	2.103(3)
Co1–N13[1]	1.963(3)	Co1–N13	2.142(3)
Co1–N13	1.963(3)	Co1–N13[1]	2.142(3)
Co2–N2	1.904(3)	Co2–N2	2.131(3)
Co2–N2[2]	1.904(3)	Co2–N2[3]	2.131(3)
Co2–N14[2]	1.976(3)	Co2–N14	2.162(3)
Co2–N14	1.976(3)	Co2–N14[3]	2.162(3)
Co2–N6	1.882(3)	Co2–N6	2.061(4)
Co2–N6[2]	1.882(3)	Co2–N6[3]	2.062(4)
Fe2–C6	1.880(3)	Fe2–C6	1.891(5)
Fe2–C5	1.905(3)	Fe2–C5	1.911(4)
Fe2–C7	1.950(3)	Fe2–C7	1.952(4)
Fe2–C8	1.954(3)	Fe2–C8	1.957(5)
Fe2–N12	1.983(3)	Fe2–N12	1.987(3)
Fe1–N10	1.983(3)	Fe1–N10	1.984(3)
Fe1–N9	1.988(3)	Fe1–N9	1.979(4)
Fe2–N11	1.981(3)	Fe2–N11	1.981(4)
Fe1–C1	1.875(3)	Fe1–C1	1.911(5)
Fe1–C2	1.887(3)	Fe1–C2	1.915(4)
Fe1–C4	1.943(3)	Fe1–C4	1.959(4)
Fe1–C3	1.953(3)	Fe1–C3	1.962(4)

Symmetry transformations used to generate equivalent atoms:

[1]-X,-Y,-Z; [2]1-X,-Y,-Z; [3]-1+X,+Y,+Z (**1-pepy**$^{50\ K}$)

[1]-X,-Y,-Z; [2]-1+X,+Y,+Z; [3]1-X,-Y,-Z (**1-pepy**$^{808\ nm}$)

Table S9. Selected angles (°) for compound **1-papy** before and after 808-nm laser irradiation at 78 K.

1-papy$^{78\ K}$		**1-papy $^{808\ nm}$**	
N1–Co1–N1^{1}	180.0(3)	N1–Co1–N1^{1}	180.0
N1^{1}–Co1–N5^{2}	90.9(2)	N1^{1}–Co1–N5^{2}	91.51(17)
N1–Co1–N5^{2}	89.1(2)	N1–Co1–N5^{2}	88.49(17)
N1^{1}–Co1–N5^{3}	89.1(2)	N1^{1}–Co1–N5^{3}	88.49(17)
N1–Co1–N5^{3}	90.9(2)	N1–Co1–N5^{3}	91.51(17)
N1^{1}–Co1–N13	90.63(19)	N1–Co1–N13^{1}	90.37(16)
N1–Co1–N13	89.37(19)	N1^{1}–Co1–N13^{1}	89.63(16)
N1–Co1–N13^{1}	90.63(19)	N1–Co1–N13	89.63(16)
N1^{1}–Co1–N13^{1}	89.37(19)	N1^{1}–Co1–N13	90.37(16)
N5^{3}–Co1–N5^{2}	180.0	N5^{3}–Co1–N5^{2}	180.0
N5^{2}–Co1–N13^{1}	89.0(2)	N5^{2}–Co1–N13^{1}	88.41(18)
N5^{3}–Co1–N13^{1}	91.0(2)	N5^{2}–Co1–N13	91.59(18)
N5^{3}–Co1–N13	89.0(2)	N5^{3}–Co1–N13	88.41(18)
N5^{2}–Co1–N13	91.0(2)	N5^{3}–Co1–N13^{1}	91.59(18)
N13–Co1–N13^{1}	180.0	N13^{1}–Co1–N13	180.0(3)
N16^{3}–Co2–N16	180.0	N16–Co2–N16^{3}	180.0
N2^{3}–Co2–N16^{3}	87.8(2)	N2–Co2–N16	86.96(17)
N2–Co2–N16^{3}	92.2(2)	N2–Co2–N16^{3}	93.04(17)
N2^{3}–Co2–N16	92.2(2)	N2^{3}–Co2–N16^{3}	86.96(17)
N2–Co2–N16	87.8(2)	N2^{3}–Co2–N16	93.04(17)
N2–Co2–N2^{3}	180.0	N2^{3}–Co2–N2	180.0
N6^{3}–Co2–N16^{3}	89.92(19)	N6^{3}–Co2–N16	90.30(17)
N6–Co2–N16^{3}	90.08(19)	N6–Co2–N16	89.70(17)
N6^{3}–Co2–N16	90.08(19)	N6^{3}–Co2–N16^{3}	89.70(17)
N6–Co2–N16	89.92(19)	N6–Co2–N16^{3}	90.30(17)
N6^{3}–Co2–N2^{3}	89.4(2)	N6^{3}–Co2–N2	91.28(17)
N6–Co2–N2^{3}	90.6(2)	N6^{3}–Co2–N2^{3}	88.72(17)
N6–Co2–N2	89.4(2)	N6–Co2–N2^{3}	91.28(17)
N6^{3}–Co2–N2	90.6(2)	N6–Co2–N2	88.72(17)
N6–Co2–N6^{3}	180.0(3)	N6–Co2–N6^{3}	180.0(2)
Σ_{Co1}	10.12	Σ_{Co1}	13.88
Σ_{Co2}	11.52	Σ_{Co2}	18.48
N11–Fe2–N12	80.8(2)	N11–Fe2–N12	81.02(18)
C7–Fe2–N12	91.6(2)	C7–Fe2–N12	92.0(2)
C7–Fe2–N11	93.6(2)	C7–Fe2–N11	94.07(18)
C6–Fe2–N12	94.3(2)	C6–Fe2–N12	95.9(2)
C6–Fe2–N11	174.6(2)	C6–Fe2–N11	176.5(2)
C6–Fe2–C7	88.9(2)	C6–Fe2–C7	87.6(2)
C6–Fe2–C5	88.3(2)	C6–Fe2–C5	84.5(2)
C6–Fe2–C8	88.6(2)	C6–Fe2–C8	88.3(2)
C5–Fe2–N12	177.1(2)	C5–Fe2–N12	178.17(19)
C5–Fe2–N11	96.5(2)	C5–Fe2–N11	98.5(2)
C5–Fe2–C7	89.6(3)	C5–Fe2–C7	89.8(2)
C5–Fe2–C8	87.0(3)	C5–Fe2–C8	87.3(2)
C8–Fe2–N12	91.8(2)	C8–Fe2–N12	90.9(2)
C8–Fe2–N11	89.1(2)	C8–Fe2–N11	90.11(19)
C8–Fe2–C7	175.9(2)	C8–Fe2–C7	175.3(2)
N10–Fe1–N9	81.9(2)	N9–Fe1–N10	82.05(19)
C2–Fe1–N10	177.7(2)	C2–Fe1–N10	179.0(2)
C2–Fe1–N9	96.7(2)	C2–Fe1–N9	97.6(2)
C2–Fe1–C3	90.2(2)	C2–Fe1–C3	90.8(2)
C2–Fe1–C4	91.2(2)	C2–Fe1–C4	91.9(2)
C3–Fe1–N10	88.0(2)	C3–Fe1–N10	88.2(2)
C3–Fe1–N9	89.3(2)	C3–Fe1–N9	89.50(19)

C3–Fe1–C4	178.1(2)	C3–Fe1–C4	177.3(2)
C1–Fe1–N10	95.4(2)	C1–Fe1–N10	97.2(2)
C1–Fe1–N9	177.3(2)	C1–Fe1–N9	179.1(2)
C1–Fe1–C2	85.9(2)	C1–Fe1–C2	83.2(2)
C1–Fe1–C3	90.1(2)	C1–Fe1–C3	90.0(2)
C1–Fe1–C4	91.3(2)	C1–Fe1–C4	90.7(2)
C4–Fe1–N10	90.7(2)	C4–Fe1–N10	89.0(2)
C4–Fe1–N9	89.2(2)	C4–Fe1–N9	89.81(18)
Σ_{Fe2}	35.5	Σ_{Fe2}	42.96
Σ_{Fe1}	31.3	Σ_{Fe1}	36.44
C1–N1–Co1	168.1(4)	C1–N1–Co1	165.3(4)
C2–N2–Co2	162.5(4)	C2–N2–Co2	159.4(4)
C5–N5–Co1[4]	173.6(5)	C5–N5–Co1[4]	176.2(5)
C6–N6–Co2	172.8(5)	C6–N6–Co2	170.5(4)
N2–C2–Fe1	175.4(5)	N2–C2–Fe1	176.3(4)
N7–C7–Fe2	177.4(5)	N7–C7–Fe2	176.1(4)
N6–C6–Fe2	179.3(5)	N6–C6–Fe2	179.0(5)
N3–C3–Fe1	177.1(5)	N3–C3–Fe1	177.0(5)
N5–C5–Fe2	177.5(5)	N5–C5–Fe2	176.7(5)
N8–C8–Fe2	178.5(6)	N8–C8–Fe2	179.1(7)
N1–C1–Fe1	176.1(5)	N1–C1–Fe1	176.3(4)
N4–C4–Fe1	178.1(5)	N4–C4–Fe1	177.2(5)

Symmetry transformations used to generate equivalent atoms:

[1]-X,1-Y,1-Z; [2]-1+X,+Y,+Z; [3]1-X,1-Y,1-Z; [4]1+X,+Y,+Z (**1**-**papy**$^{78\ K}$)

[1]-X,1-Y,1-Z; [2]-1+X,+Y,+Z; [3]1-X,1-Y,1-Z; [4]1+X,+Y,+Z (**1**-**papy**$^{808\ nm}$)

Table S10. Selected angles (°) for compound **1-pepy** before and after 808-nm laser irradiation at 50 K.

1-pepy$^{50\ K}$		**1-pepy**$^{808\ nm}$	
N1^{1}–Co1–N1	180.00(13)	N1–Co1–N1^{1}	180.0
N1–Co1–N5^{2}	91.35(11)	N1–Co1–N5^{2}	92.18(13)
N1–Co1–N5^{3}	88.65(11)	N1^{1}–Co1–N5^{2}	87.82(13)
N1^{1}–Co1–N5^{2}	88.65(11)	N1–Co1–N5^{3}	87.82(13)
N1^{1}–Co1–N5^{3}	91.35(11)	N1^{1}–Co1–N5^{3}	92.18(13)
N1^{1}–Co1–N13	90.40(10)	N1^{1}–Co1–N13	90.87(13)
N1^{1}–Co1–N13^{1}	89.60(10)	N1–Co1–N13	89.13(13)
N1–Co1–N13	89.60(10)	N1–Co1–N13^{1}	90.87(13)
N1–Co1–N13^{1}	90.40(10)	N1^{1}–Co1–N13^{1}	89.13(13)
N5^{2}–Co1–N5^{3}	180.0(2)	N5^{2}–Co1–N5^{3}	180.0(3)
N5^{2}–Co1–N13	89.56(11)	N5^{2}–Co1–N13	90.16(13)
N5^{3}–Co1–N13	90.44(11)	N5^{3}–Co1–N13^{1}	90.16(13)
N5^{3}–Co1–N13^{1}	89.56(11)	N5^{2}–Co1–N13^{1}	89.84(13)
N5^{2}–Co1–N13^{1}	90.44(11)	N5^{3}–Co1–N13	89.84(13)
N13–Co1–N13^{1}	180.0	N13–Co1–N13^{1}	180.0
N2–Co2–N2^{2}	180.0	N2^{2}–Co2–N2	180.0
N2^{2}–Co2–N14^{2}	86.72(11)	N2^{2}–Co2–N14	95.26(13)
N2^{2}–Co2–N14	93.28(11)	N2–Co2–N14^{2}	95.26(13)
N2–Co2–N14^{2}	93.28(11)	N2^{2}–Co2–N14^{2}	84.74(13)
N2–Co2–N14	86.72(11)	N2–Co2–N14	84.74(13)
N14^{2}–Co2–N14	180.0	N14^{2}–Co2–N14	180.0(2)
N6–Co2–N2	89.07(10)	N6–Co2–N2	88.21(14)
N6^{2}–Co2–N2	90.93(10)	N6^{2}–Co2–N2	91.79(14)
N6^{2}–Co2–N2^{2}	89.07(10)	N6–Co2–N2^{2}	91.79(14)
N6–Co2–N2^{2}	90.93(10)	N6^{2}–Co2–N2^{2}	88.21(14)
N6^{2}–Co2–N14	90.11(11)	N6^{2}–Co2–N14	90.46(14)
N6–Co2–N14	89.89(11)	N6–Co2–N14	89.54(14)
N6–Co2–N14^{2}	90.11(11)	N6^{2}–Co2–N14^{2}	89.54(14)
N6^{2}–Co2–N14^{2}	89.89(11)	N6–Co2–N14^{2}	90.46(14)
N6^{2}–Co2–N6	180.0	N6–Co2–N6^{2}	180.0
Σ_{Co1}	8.76	Σ_{Co1}	12.84
Σ_{Co2}	17.28	Σ_{Co2}	30.04
C6–Fe2–C5	86.94(12)	C6–Fe2–C5	83.72(17)
C6–Fe2–C7	90.12(13)	C6–Fe2–C7	89.09(17)
C6–Fe2–C8	88.91(13)	C6–Fe2–C8	88.96(18)
C6–Fe2–N12	94.79(12)	C6–Fe2–N12	96.25(16)
C6–Fe2–N11	175.40(12)	C6–Fe2–N11	176.79(15)
C5–Fe2–C7	88.70(13)	C5–Fe2–C7	87.95(16)
C5–Fe2–C8	87.08(13)	C5–Fe2–C8	88.56(16)
C5–Fe2–N12	178.18(11)	C5–Fe2–N12	178.55(15)
C5–Fe2–N11	97.03(12)	C5–Fe2–N11	98.85(16)
C7–Fe2–C8	175.72(13)	C7–Fe2–C8	176.17(16)
C7–Fe2–N12	90.73(12)	C7–Fe2–N12	90.60(15)
C7–Fe2–N11	92.29(12)	C7–Fe2–N11	92.90(16)
C8–Fe2–N12	93.50(12)	C8–Fe2–N12	92.89(15)
C8–Fe2–N11	88.97(12)	C8–Fe2–N11	89.20(16)
N11–Fe2–N12	81.26(11)	N11–Fe2–N12	81.22(15)
C1–Fe1–C2	85.83(12)	C1–Fe1–C2	82.10(17)
C1–Fe1–C4	90.82(13)	C1–Fe1–C4	90.58(17)
C1–Fe1–C3	89.41(13)	C1–Fe1–C3	88.37(17)
C1–Fe1–N10	95.93(12)	C1–Fe1–N10	98.20(16)
C1–Fe1–N9	177.09(12)	C1–Fe1–N9	179.30(15)
C2–Fe1–C4	89.99(13)	C2–Fe1–C4	90.99(16)
C2–Fe1–C3	92.74(13)	C2–Fe1–C3	93.57(16)

C2–Fe1–N10	178.21(12)	C2–Fe1–N10	178.99(15)
C2–Fe1–N9	97.06(12)	C2–Fe1–N9	98.15(16)
C4–Fe1–C3	177.26(13)	C4–Fe1–C3	175.14(17)
C4–Fe1–N10	90.26(12)	C4–Fe1–N10	88.04(15)
C4–Fe1–N9	89.43(12)	C4–Fe1–N9	90.07(16)
C3–Fe1–N10	87.00(12)	C3–Fe1–N10	87.41(15)
C3–Fe1–N9	90.21(12)	C3–Fe1–N9	90.96(16)
N10–Fe1–N9	81.17(11)	N9–Fe1–N10	81.55(15)
Σ_{Fe2}	36.6	Σ_{Fe2}	42.79
Σ_{Fe1}	34.19	Σ_{Fe1}	45.05
N1–C1–Fe1	176.2(3)	N1–C1–Fe1	175.8(3)
N2–C2–Fe1	177.2(3)	N2–C2–Fe1	177.8(4)
N6–C6–Fe2	178.4(3)	N4–C4–Fe1	175.0(3)
N5–C5–Fe2	177.8(3)	N3–C3–Fe1	175.3(4)
N7–C7–Fe2	177.9(3)	N6–C6–Fe2	179.4(4)
N8–C8–Fe2	175.3(3)	N5–C5–Fe2	176.3(4)
N4–C4–Fe1	177.8(3)	N7–C7–Fe2	177.2(4)
N3–C3–Fe1	174.7(3)	N8–C8–Fe2	178.5(4)
C1–N1–Co1	169.9(3)	C1–N1–Co1	169.3(3)
C5–N5–Co1[4]	175.9(2)	C5–N5–Co1[4]	174.9(3)
C2–N2–Co2	158.1(2)	C2–N2–Co2	156.8(3)
C6–N6–Co2	175.6(2)	C6–N6–Co2	177.0(3)

Symmetry transformations used to generate equivalent atoms:

[1]-X,-Y,-Z; [2]1-X,-Y,-Z; [3]-1+X,+Y,+Z; [4]1+X,+Y,+Z (**1**-**pepy**$^{50\ K}$)

[1]-X,-Y,-Z; [2]1-X,-Y,-Z; [3]-1+X,+Y,+Z; [4]1+X,+Y,+Z (**1**-**pepy**$^{808\ nm}$)

Table S11. Selected average coordination bond lengths, interchain contact distances around the Co sites, distortion parameters, and cell volume before and after irradiation at 78 and 50 K for **1-papy and 1-pepy, respectively**.

	1-papy$^{78\ K}$	**1-papy**$^{808\ nm}$	**1-pepy**$^{50\ K}$	**1-pepy**$^{808\ nm}$
Av. Co–N_{CN} (Å)	1.902(5)	2.094(4)	1.890(3)	2.096(4)
Av. Co–N_L (Å)	1.978(5)	2.152(4)	1.969(3)	2.152(3)
Σ_{Co1} (°) [a]	10.12	13.88	8.76	12.84
Σ_{Co2} (°)	11.52	18.48	17.28	30.04
Θ_{co1} (°)[a]	20.67	20.85	20.85	21.71
Θ_{co2} (°)	25.19	30.36	33.56	49.07
$\pi_L\cdots\pi_L$ (Å)[b]	3.726(4)	3.688(4)	3.776(1)	3.766(1)
Its dihedral angles (°)[c]	165.46	166.07	161.72	159.29
$\pi_{bipy}\cdots\pi_{bipy}$ (Å)[b]	3.838(4)	3.771(4)	3.8872(1)	3.8266(3)
Its dihedral angles (°)[c]	180.0	180.0	161.72	180.0
Cell volume (Å^3)[d]	2479.5(5)	2566.4(4)	2545.68(16)	2654.9(4)

[a] Distortion parameters of $\Sigma = (\sum_{i=1}^{12}|90-\alpha_i|$ and $\Theta = (\sum_{j=1}^{24}|60-\theta_j|)$ are the sums of twelve *cis*-N–Co–N angles (α_i) and twenty-four unique N–Co–N angles (θ_j) measured on the projection of two triangular faces of the octahedron along their common pseudo-threefold axis, respectively. [b] The interchain $\pi_L\cdots\pi_L$ and $\pi_{bipy}\cdots\pi_{bipy}$ distances are calculated by the distances between centers of the corresponding aromatic rings. [c] The dihedral angles of the interacting aromatic rings. [d] The numbers of molecules in the unit cell are 2 for **1-papy** and **1-pepy**.

Schemes of interchain $\pi\cdots\pi$ stacks

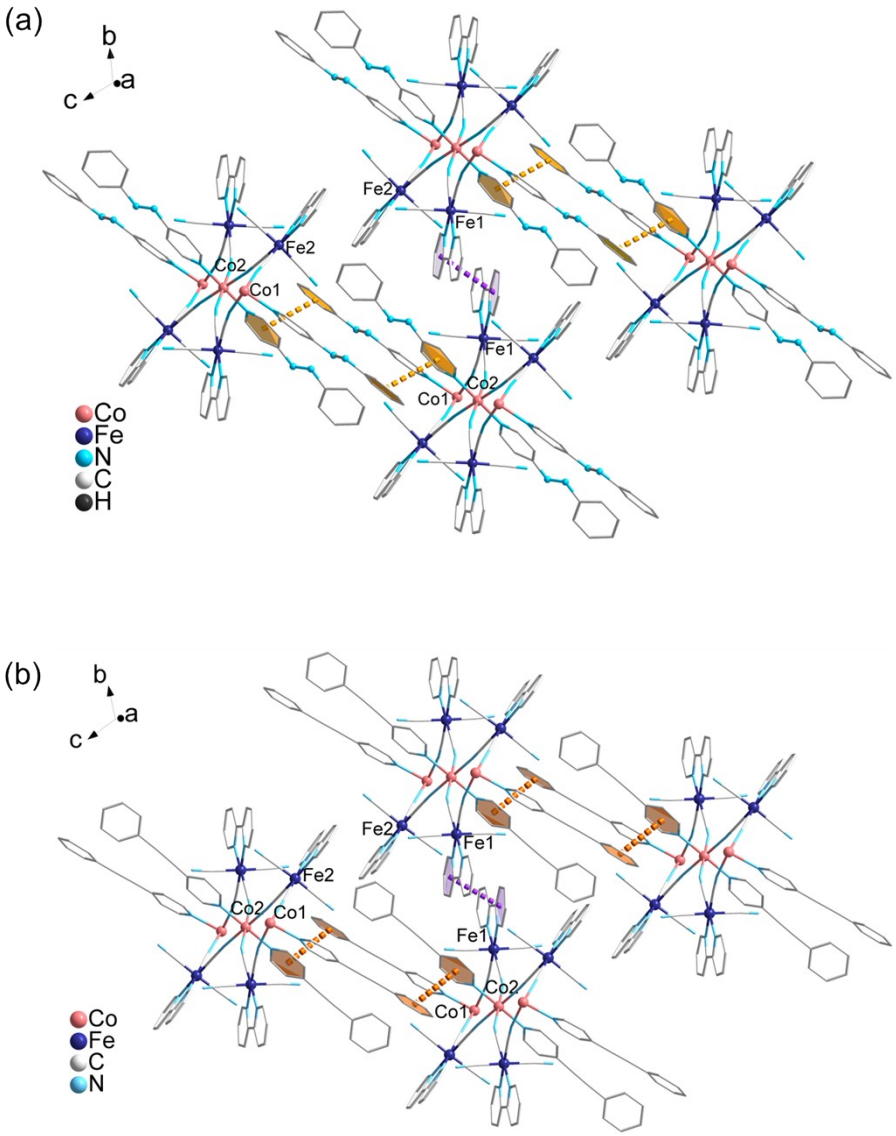


Figure S1. Interchain $\pi\cdots\pi$ interactions for **1-papy** (a) and **1-pepy** (b). Orange-dash: interchain $\pi_L\cdots\pi_L$ contacts of the phenyl and pyridyl rings coordinating to Co1 and Co2 ions, respectively. Purple-dash: interchain $\pi_{bipy}\cdots\pi_{bipy}$ contacts of the bipyridine rings coordinating to Fe1 ions.

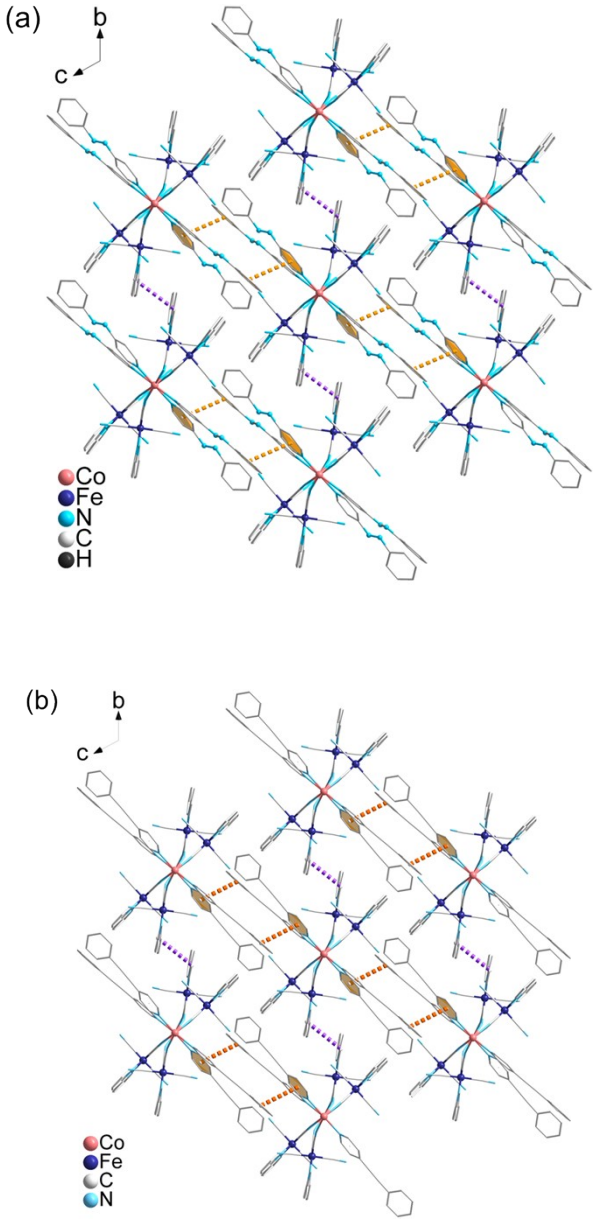
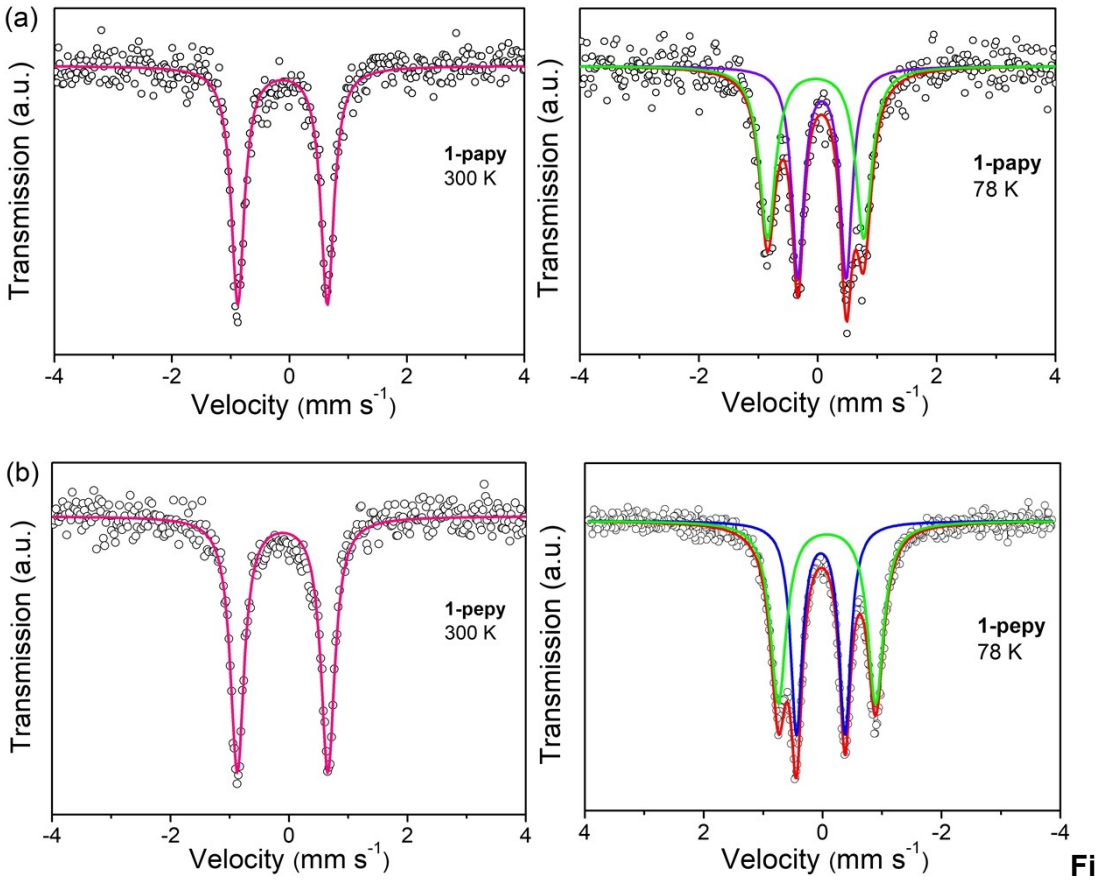


Figure S2. View of packing diagrams with the $\pi\cdots\pi$ interaction network in the neighbouring chains for (a) **1**-**papy** and (b) **1**-**pepy** along the crystallographic *a*-axis.

^{57}Fe Mössbauer spectra for LT and HT phases



Fi gure S3. ^{57}Fe Mössbauer spectra of **1-papy** (a) and **1-pepy** (b) collected at 300 and 78 K.

UV-vis-NIR absorption spectra

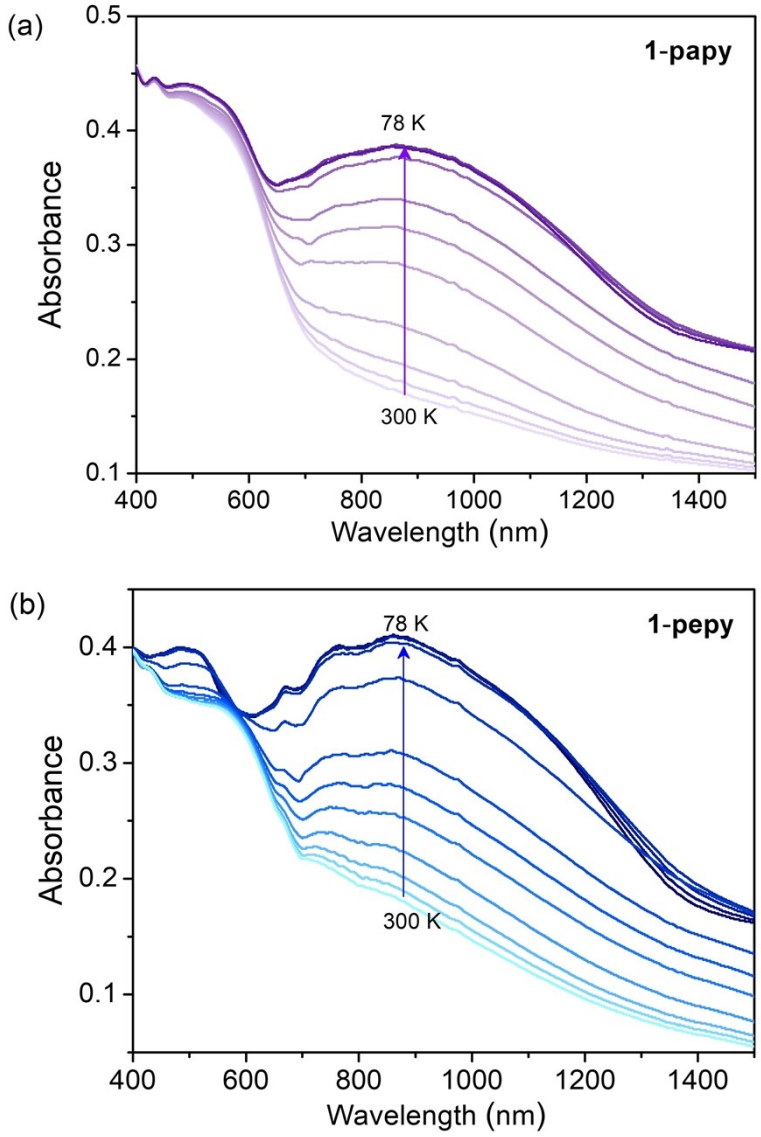


Figure S4. Variable temperature solid-state UV-vis-NIR absorption spectra from 300 K to 78 K for **1**-**papy** (a) and **1**-**pepy** (b).

Single-chain magnetic properties for the photo-excited HS* phases

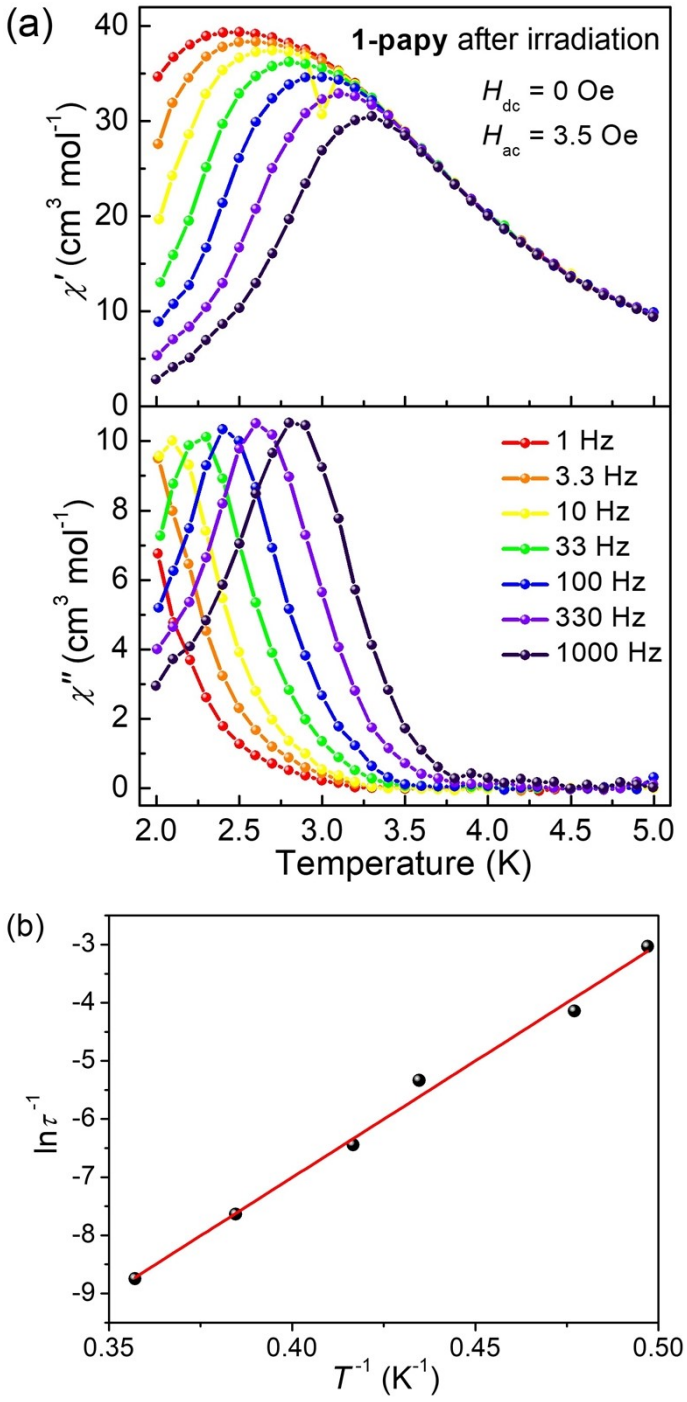


Figure S5. (a) Temperature dependence of the in-phase χ' and out-of-phase χ'' components of ac magnetic susceptibility under a 3.5 Oe oscillating field for the photo-induced HS* phase after 808-nm irradiation at 78 K of **1**-**papy**. (b) Arrhenius plots for the magnetic relaxation process for the photo-induced HS* phase after 946-nm irradiation at 78 K of **1**-**papy**.

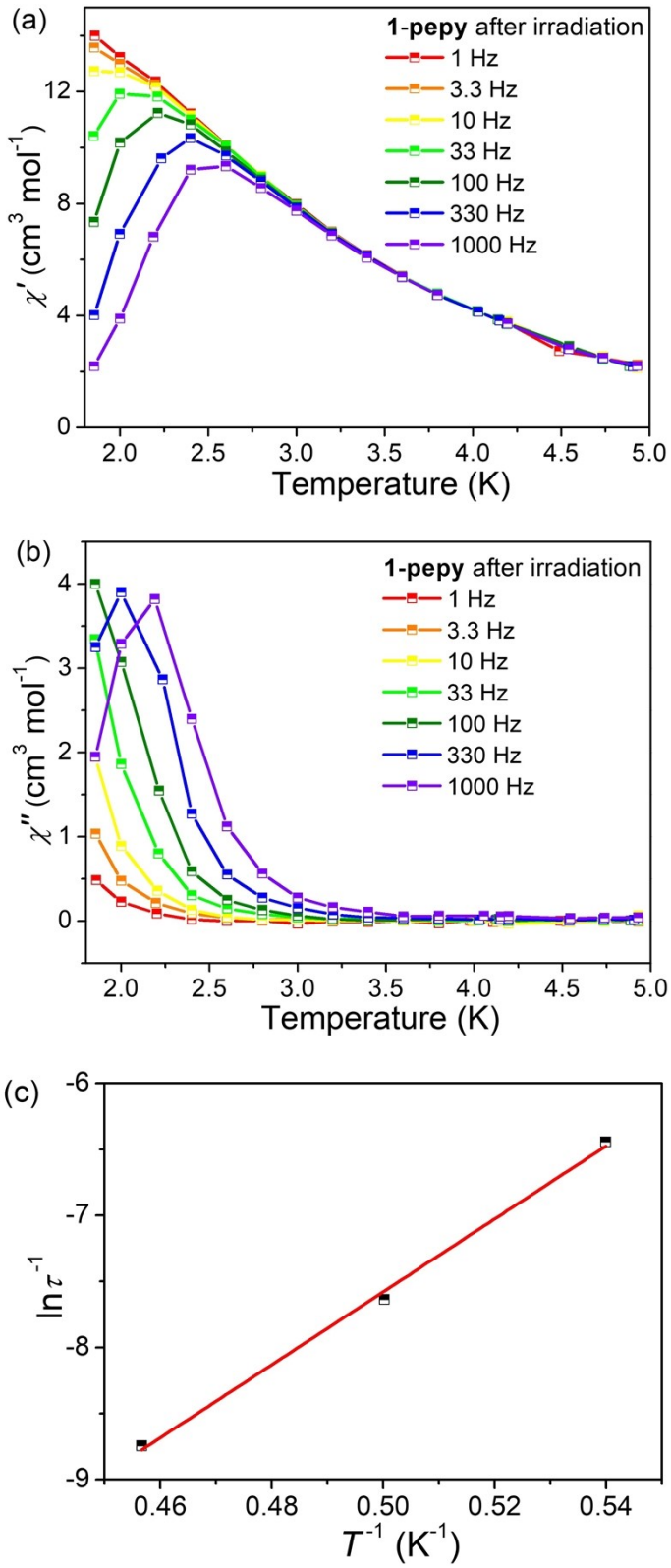


Figure S6. Temperature dependence of the in-phase χ' (a) and out-of-phase χ'' (b) components of ac magnetic susceptibility under a 3.5 Oe oscillating field for the photo-induced HS* phase after irradiation of **1-pepy**. (c) Arrhenius plots for the magnetic relaxation process in the photo-generated HS* phases after irradiation at 10 K.

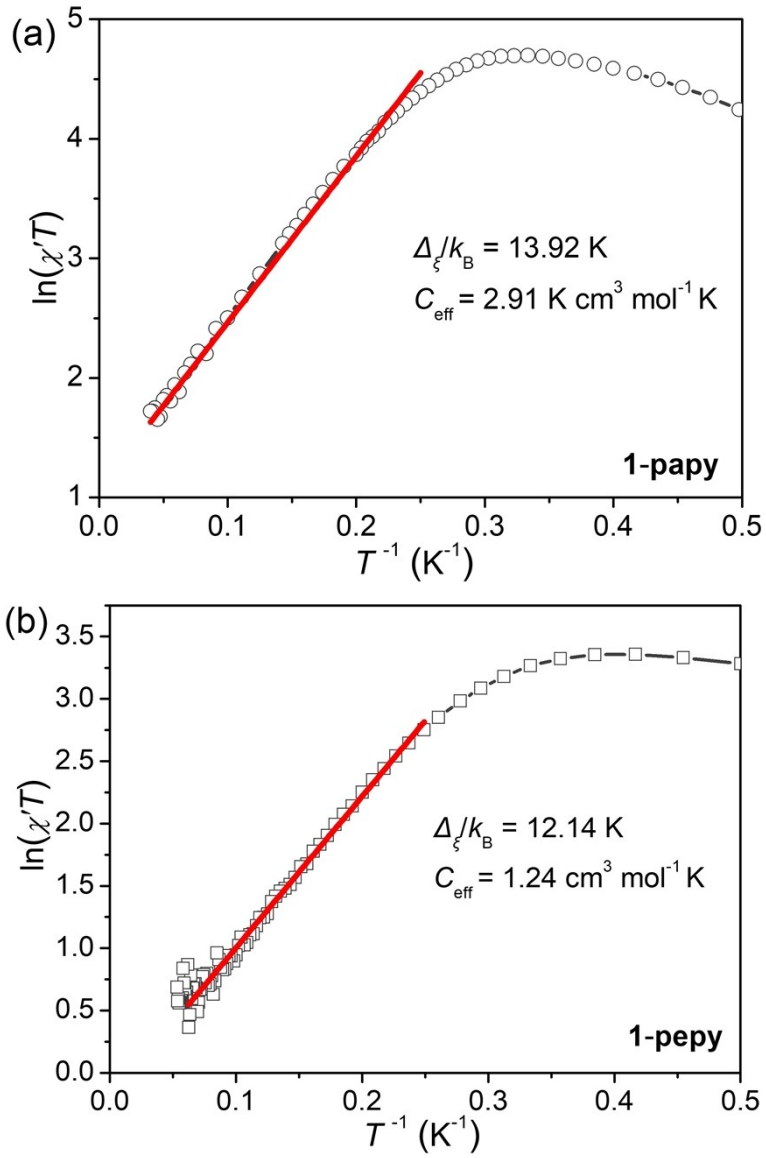


Figure S7. Plots of ln($\chi'T$) versus T^{-1} for the photo--induced HS* chains after irradiation under 808 nm laser. The red solid lines represent fitting with the equation $\chi'T/C_{eff}$ = exp(Δ_ξ/k_BT) between 4 and 25 K for **1-papy** and between 4 and 15 K for **1-pepy**.

Reference:

[1] R. Lescouëzec, F. Lloret, M. Julve, J. Vaissermann, M. Verdaguer, R. Llusar, S. Uriel, *Inorg. Chem.* **2001**, *40*, 2065-2072.

[2] G. A. Bain, J. F. Berry, *J. Chem. Edu.* **2008**, *85*, 532.