Supporting Information

Reversible on–off switching of a single-chain magnet via single-crystal-to-single-crystal transition- and light-induced metal-to-metal electron transfer

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Contents

Table S1. Crystallographic Data for **1·solv**, **1·desolv** and **1·resolv** at 298 K.

	1·solv	**1·desolv**	**1·resolv**
Formula	$C_{50}H_{47}B_2CoFe_2I_2N_{26}O_{2.5}$	$C_{48}H_{38}B_2CoFe_2I_2N_{26}$	$C_{49}H_{44}B_2CoFe_2I_2N_{26}O_2$
Fw	1498.19	1425.09	1475.15
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	13.3825(4)	13.401(4)	13.445(3)
b, Å	13.8767(4)	13.567(5)	13.530(3)
c, Å	17.8617(5)	18.266(6)	17.944(4)
α, °	79.1420(10)	70.833(9)	78.456(6)
β, °	70.1710(10)	78.105(9)	70.117(6)
γ, °	77.3290(10)	75.770(9)	76.611(6)
V, Å^3	3020.78(15)	3011.8(17)	2959.9(10)
Z	1	2	2
ρ_{calc}, g/cm^3	1.647	1.571	1.655
μ/mm^{-1}	1.831	1.829	1.867
F (000)	1488.0	1406.0	1462.0
Reflections collected	65667	45629	57552
Unique reflections (R_{int})	0.0353	0.1805	0.0791
Goodness-of-fit on F^2	1.028	1.024	1.061
R_1 ,[$I>2\sigma(I)$]	0.0428	0.0977	0.0633
wR_2 ,[$I>2\sigma(I)$]	0.0963	0.2152	0.1720

$R_1 = \Sigma\ (|F_o|-|F_c|)/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o{}^2-F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$

Table S2. Crystallographic Data for **1·solv** at 60 K before and after 808- and 532-nm light irradiations.

	1·solv	**1·solv**[808 nm]	**1·solv**[532 nm]
Formula	$C_{50}H_{47}B_2CoFe_2I_2N_{26}O_{2.5}$	$C_{50}H_{47}B_2CoFe_2I_2N_{26}O_{2.5}$	$C_{50}H_{47}B_2CoFe_2I_2N_{26}O_{2.5}$
Fw	1498.19	1498.19	1498.19
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a, Å	13.321(1)	13.365(2)	13.343(1)
b, Å	13.574(0)	13.654(2)	13.538(1)
c, Å	17.762(5)	18.330(3)	17.779(4)
α, °	78.044(3)	78.405(4)	78.010(2)
β, °	70.353(4)	70.864(5)	70.254(2)
γ, °	76.573(3)	75.394(5)	76.594(2)
V, Å^3	2912.8(5)	3032.1(8)	2911.0(4)
Z	1	1	1
ρ_{calc}, g/cm^3	1.708	1.641	1.709
μ/mm^{-1}	1.899	1.824	1.900
F (000)	1488.0	1488.0	1488.0
Reflections collected	17349	44099	43980
Unique reflections (R_{int})	0.0853	0.1066	0.1270
Goodness-of-fit on F^2	1.021	1.013	1.021
R_1 ,[$I > 2\sigma(I)$]	0.0676	0.0777	0.0611
wR_2 ,[$I > 2\sigma(I)$]	0.1603	0.1882	0.1024

$R_1 = \Sigma\,(|F_o|-|F_c|)/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S3. Selected bond distances (Å) and angles (°) for **1·solv** at 298 K.

Bond length (Å)		Bond angle (°)	
Co(1)–N(3)	1.882(3)	N(5)#1–Co(1)–N(7)	89.92(11)
Co(1)–N(3)#1	1.882(3)	N(5)–Co(1)–N(7)#1	89.92(11)
Co(1)–N(5)	1.876(3)	N(5)–Co(1)–N(7)	90.08(11)
Co(1)–N(5)#1	1.876(3)	N(5)#1–Co(1)–N(7)#1	90.08(11)
Co(1)–N(7)	1.940(3)	N(5)–Co(1)–N(3)	89.59(11)
Co(1)–N(7)#1	1.940(3)	N(5)–Co(1)–N(3)#1	90.41(11)
Co(2)–N(2)	1.891(3)	N(5)#1–Co(1)–N(3)#1	89.59(11)
Co(2)–N(2)#2	1.891(3)	N(5)#1–Co(1)–N(3)	90.41(11)
Co(2)–N(6)	1.887(3)	N(3)–Co(1)–N(7)	91.70(11)
Co(2)–N(6)#2	1.887(3)	N(3)–Co(1)–N(7)#1	88.30(11)
Co(2)–N(8)	1.947(3)	N(3)#1–Co(1)–N(7)#1	91.70(11)
Co(2)–N(8)#2	1.947(3)	N(3)#1–Co(1)–N(7)	88.30(11)
Fe(1)–C(1)	1.917(4)	N(6)#2–Co(2)–N(8)	90.13(11)
Fe(1)–C(2)	1.916(4)	N(6)–Co(2)–N(8)#2	90.13(11)
Fe(1)–C(3)	1.912(3)	N(6)–Co(2)–N(8)	89.87(11)
Fe(1)–N(14)	1.969(3)	N(6)#2–Co(2)–N(8)#2	89.87(11)
Fe(1)–N(16)	1.956(3)	N(6)–Co(2)–N(2)	89.36(11)
Fe(1)–N(18)	1.969(3)	N(6)#2–Co(2)–N(2)#2	89.36(11)
Fe(2)–C(4)	1.912(4)	N(6)#2–Co(2)–N(2)	90.64(11)
Fe(2)–C(5)	1.861(3)	N(6)–Co(2)–N(2)#2	90.64(11)
Fe(2)–C(6)	1.866(3)	N(2)–Co(2)–N(8)#2	89.51(11)
Fe(2)–N(22)	2.003(2)	N(2)#2–Co(2)–N(8)#2	90.49(11)
Fe(2)–C(24)	2.014(3)	N(2)–Co(2)–N(8)	90.49(11)
Fe(2)–N(26)	1.991(2)	N(2)#2–Co(2)–N(8)	89.51(11)

#1 1-X, 1-Y, 1-Z; #2 -X, 1-Y, 1-Z

Table S4. Selected bond distances (Å) and angles (°) for **1·desolv** at 298 K.

Bond length (Å)		Bond angle (°)	
Co(1)–N(3)	2.076(10)	N(5)#1–Co(1)–N(7)	92.1(3)
Co(1)–N(3)#1	2.076(10)	N(5)–Co(1)–N(7)	87.9(4)
Co(1)–N(5)	2.072(9)	N(5)#1–Co(1)–N(7)#1	87.9(4)
Co(1)–N(5)#1	2.072(9)	N(5)–Co(1)–N(7)#1	92.1(3)
Co(1)–N(7)	2.127(9)	N(5)–Co(1)–N(3)#1	87.9(4)
Co(1)–N(7)#1	2.127(9)	N(5)–Co(1)–N(3)	92.1(4)
Co(2)–N(2)	2.093(8)	N(5)#1–Co(1)–N(3)#1	92.1(4)
Co(2)–N(2)#2	2.093(8)	N(5)#1–Co(1)–N(3)	87.9(4)
Co(2)–N(6)	2.058(9)	N(3)–Co(1)–N(7)	90.6(4)
Co(2)–N(6)#2	2.058(9)	N(3)–Co(1)–N(7)#1	89.4(4)
Co(2)–N(8)	2.124(8)	N(3)#1–Co(1)–N(7)	89.4(4)
Co(2)–N(8)#2	2.124(8)	N(3)#1–Co(1)–N(7)#1	90.6(4)
Fe(1)–C(1)	1.919(13)	N(2)–Co(2)–N(8)#2	90.4(3)
Fe(1)–C(2)	1.886(10)	N(2)#2–Co(2)–N(8)	90.4(3)
Fe(1)–C(3)	1.884(10)	N(2)–Co(2)–N(8)	89.6(3)
Fe(1)–N(14)	1.958(8)	N(2)#2–Co(2)–N(8)#2	89.6(3)
Fe(1)–N(16)	1.949(8)	N(6)#2–Co(2)–N(2)	89.6(3)
Fe(1)–N(18)	1.974(8)	N(6)#2–Co(2)–N(2)#2	90.4(3)
Fe(2)–C(4)	1.916(13)	N(6)–Co(2)–N(2)#2	89.6(3)
Fe(2)–C(5)	1.882(11)	N(6)–Co(2)–N(2)	90.4(3)
Fe(2)–C(6)	1.898(12)	N(6)–Co(2)–N(8)	89.7(4)
Fe(2)–N(22)	1.972(9)	N(6)#2–Co(2)–N(8)#2	89.7(4)
Fe(2)–C(24)	1.972(8)	N(6)#2–Co(2)–N(8)	90.3(4)
Fe(2)–N(26)	1.961(8)	N(6)–Co(2)–N(8)#2	90.3(4)

#1 1-X, 1-Y, 1-Z; #2 1-X, 2-Y, 1-Z

Table S5. Selected bond distances (Å) and angles (°) for **1·resolv** at 298 K.

Bond length (Å)		Bond angle (°)	
Co(1)–N(3)	1.871(7)	N(5)#1–Co(1)–N(7)	89.7(2)
Co(1)–N(3)#2	1.872(7)	N(5)#3–Co(1)–N(7)#2	89.7(2)
Co(1)–N(5)#1	1.891(6)	N(5)#1–Co(1)–N(7)#2	90.3(2)
Co(1)–N(5)#3	1.891(6)	N(5)#3–Co(1)–N(7)	90.3(2)
Co(1)–N(7)	1.951(6)	N(3)–Co(1)–N(7)	91.1(3)
Co(1)–N(7)#2	1.951(6)	N(3)–Co(1)–N(7)#2	88.9(3)
Co(2)–N(2)	1.887(6)	N(3)#2–Co(1)–N(7)	88.9(3)
Co(2)–N(2)#1	1.887(6)	N(3)#2–Co(1)–N(7)#2	91.1(3)
Co(2)–N(6)	1.873(7)	N(3)–Co(1)–N(5)#1	88.7(3)
Co(2)–N(6)#1	1.874(7)	N(3)#2–Co(1)–N(5)#1	91.3(3)
Co(2)–N(8)	1.953(6)	N(3)#2–Co(1)–N(5)#3	88.7(3)
Co(2)–N(8)#1	1.953(6)	N(3)–Co(1)–N(5)#3	91.3(3)
Fe(1)–C(1)	1.914(9)	N(2)–Co(2)–N(8)	89.0(2)
Fe(1)–C(2)	1.860(7)	N(2)–Co(2)–N(8)#1	91.0(2)
Fe(1)–C(3)	1.854(8)	N(2)#1–Co(2)–N(8)#1	89.0(2)
Fe(1)–N(14)	1.997(6)	N(2)#1–Co(2)–N(8)	91.0(2)
Fe(1)–N(16)	1.981(6)	N(6)#1–Co(2)–N(8)	90.0(3)
Fe(1)–N(18)	2.013(6)	N(6)#1–Co(2)–N(8)#1	90.0(3)
Fe(2)–C(4)	1.932(9)	N(6)–Co(2)–N(8)	90.0(3)
Fe(2)–C(5)	1.907(8)	N(6)–Co(2)–N(8)#1	90.0(3)
Fe(2)–C(6)	1.895(9)	N(6)–Co(2)–N(2)	90.3(3)
Fe(2)–N(22)	1.969(6)	N(6)#1–Co(2)–N(2)#1	90.3(3)
Fe(2)–C(24)	1.950(6)	N(6)#1–Co(2)–N(2)	89.7(3)
Fe(2)–N(26)	1.970(6)	N(6)–Co(2)–N(2)#1	89.7(3)

#1 1-X,1-Y,1-Z; #2 -X,1-Y,1-Z; #3 -1+X,+Y,+Z

Table S6. Selected bond distances (Å) and angles (°) for **1·solv** at 60 K.

Bond length (Å)		Bond angle (°)	
Co(1)–N(3)	1.888(7)	N(3)–Co(1)–N(5)#1	89.7(3)
Co(1)–N(3)#1	1.888(7)	N(3)#1–Co(1)–N(5)#1	90.3(3)
Co(1)–N(5)	1.893(7)	N(3)#1–Co(1)–N(5)	89.7(3)
Co(1)–N(5)#1	1.893(7)	N(3)–Co(1)–N(5)	90.3(3)
Co(1)–N(7)	1.942(7)	N(3)–Co(1)–N(7)#1	90.0(3)
Co(1)–N(7)#1	1.942(7)	N(3)#1–Co(1)–N(7)	90.0(3)
Co(2)–N(2)	1.868(7)	N(3)#1–Co(1)–N(7)#1	90.0(3)
Co(2)–N(2)#2	1.868(7)	N(3)–Co(1)–N(7)	90.0(3)
Co(2)–N(6)#1	1.882(7)	N(5)#1–Co(1)–N(7)	90.3(3)
Co(2)–N(6)#3	1.882(7)	N(5)–Co(1)–N(7)	89.7(3)
Co(2)–N(8)	1.935(7)	N(5)#1–Co(1)–N(7)#1	89.7(3)
Co(2)–N(8)#2	1.935(7)	N(5)–Co(1)–N(7)#1	90.3(3)
Fe(1)–C(1)	1.912(9)	N(6)#3–Co(2)–N(8)	89.1(3)
Fe(1)–C(2)	1.866(9)	N(6)#1–Co(2)–N(8)#2	89.1(3)
Fe(1)–C(3)	1.860(8)	N(6)#3–Co(2)–N(8)#2	90.9(3)
Fe(1)–N(14)	1.999(6)	N(6)#1–Co(2)–N(8)	90.9(3)
Fe(1)–N(16)	2.018(7)	N(2)–Co(2)–N(6)#3	90.1(3)
Fe(1)–N(18)	1.993(6)	N(2)–Co(2)–N(6)#1	89.9(3)
Fe(2)–C(4)	1.931(1)	N(2)#2–Co(2)–N(6)#3	89.9(3)
Fe(2)–C(5)	1.921(9)	N(2)#2–Co(2)–N(6)#1	90.1(3)
Fe(2)–C(6)	1.917(9)	N(2)–Co(2)–N(8)	89.9(3)
Fe(2)–N(22)	1.982(6)	N(2)–Co(2)–N(8)#2	90.1(3)
Fe(2)–N(24)	1.945(7)	N(2)#2–Co(2)–N(8)	90.1(3)
Fe(2)–N(26)	1.973(7)	N(2)#2–Co(2)–N(8)#2	89.9(3)

#1 1-X,1-Y,1-Z; #2 2-X,1-Y,1-Z; #3 1+X,+Y,+Z

Table S7. Selected bond distances (Å) and angles (°) for **1·solv** after 808 nm irradiation at 60 K.

Bond length (Å)	808 nm-irradiated	Bond angle (°)	808 nm-irradiated
Co(1)–N(3)	2.073(8)	N(5)#1–Co(1)–N(7)#1	91.1(4)
Co(1)–N(3)#1	2.073(9)	N(5)–Co(1)–N(7)#1	88.9(4)
Co(1)–N(5)	2.096(1)	N(5)#1–Co(1)–N(7)	88.9(4)
Co(1)–N(5)#1	2.096(1)	N(5)–Co(1)–N(7)	91.1(4)
Co(1)–N(7)	2.129(8)	N(3)#1–Co(1)–N(5)#1	93.2(4)
Co(1)–N(7)#1	2.129(8)	N(3)–Co(1)–N(5)	93.2(4)
Co(2)–N(2)	2.111(12)	N(3)–Co(1)–N(5)#1	86.8(4)
Co(2)–N(2)#2	2.111(12)	N(3)#1–Co(1)–N(5)	86.8(4)
Co(2)–N(6)	2.083(8)	N(3)–Co(1)–N(7)#1	87.1(3)
Co(2)–N(6)#2	2.083(8)	N(3)#1–Co(1)–N(7)	87.1(3)
Co(2)–N(8)	2.130(8)	N(3)#1–Co(1)–N(7)#1	92.9(3)
Co(2)–N(8)#2	2.130(8)	N(3)–Co(1)–N(7)	92.9(3)
Fe(1)–C(1)	1.921(11)	N(2)–Co(2)–N(8)#2	90.1(3)
Fe(1)–C(2)	1.921(14)	N(2)#2–Co(2)–N(8)#2	89.9(3)
Fe(1)–C(3)	1.911(1)	N(2)–Co(2)–N(8)	89.9(3)
Fe(1)–N(14)	1.976(8)	N(2)#2–Co(2)–N(8)	90.1(3)
Fe(1)–N(16)	1.964(11)	N(6)#2–Co(2)–N(2)	88.4(3)
Fe(1)–N(18)	1.998(8)	N(6)–Co(2)–N(2)	91.6(3)
Fe(2)–C(4)	1.940(10)	N(6)#2–Co(2)–N(2)#2	91.6(3)
Fe(2)–C(5)	1.883(12)	N(6)–Co(2)–N(2)#2	88.4(3)
Fe(2)–C(6)	1.907(1)	N(6)#2–Co(2)–N(8)	89.7(3)
Fe(2)–N(22)	1.966(8)	N(6)–Co(2)–N(8)#2	89.7(3)
Fe(2)–C(24)	1.972(7)	N(6)#2–Co(2)–N(8)#2	90.3(3)
Fe(2)–N(26)	1.960(1)	N(6)–Co(2)–N(8)	90.3(3)

#1 2-X,1-Y,1-Z;#2 1-X,1-Y,1-Z

Table S8. Selected bond distances (Å) and angles (°) for **1·solv** after 532 nm irradiation at 60 K.

Bond length (Å)	532 nm-irradiated	Bond angle (°)	532 nm-irradiated
Co(1)–N(3)	1.887(6)	N(5)–Co(1)–N(7)	90.0(3)
Co(1)–N(3)#1	1.887(6)	N(5)#1–Co(1)–N(7)	90.0(3)
Co(1)–N(5)	1.894(7)	N(5)#1–Co(1)–N(7)#1	90.0(3)
Co(1)–N(5)#1	1.894(7)	N(5)–Co(1)–N(7)#1	90.0(3)
Co(1)–N(7)	1.944(6)	N(3)–Co(1)–N(7)#1	90.3(2)
Co(1)–N(7)#1	1.944(6)	N(3)#1–Co(1)–N(7)	90.3(2)
Co(2)–N(2)	1.881(7)	N(3)#1–Co(1)–N(7)#1	89.7(2)
Co(2)–N(2)#2	1.881(7)	N(3)–Co(1)–N(7)	89.7(2)
Co(2)–N(6)	1.885(6)	N(3)#1–Co(1)–N(5)	90.5(3)
Co(2)–N(6)#2	1.885(6)	N(3)#1–Co(1)–N(5)#1	89.5(3)
Co(2)–N(8)	1.932(6)	N(3)–Co(1)–N(5)	89.5(3)
Co(2)–N(8)#2	1.931(6)	N(3)–Co(1)–N(5)#1	90.5(3)
Fe(1)–C(1)	1.906(8)	N(2)#2–Co(2)–N(8)#2	90.1(3)
Fe(1)–C(2)	1.850(8)	N(2)–Co(2)–N(8)	90.1(3)
Fe(1)–C(3)	1.861(8)	N(2)–Co(2)–N(8)#2	89.9(2)
Fe(1)–N(14)	1.979(6)	N(2)#2–Co(2)–N(8)	89.9(2)
Fe(1)–N(16)	2.000(6)	N(2)–Co(2)–N(6)	90.1(3)
Fe(1)–N(18)	2.015(6)	N(2)–Co(2)–N(6)#2	89.9(3)
Fe(2)–C(4)	1.920(8)	N(2)#2–Co(2)–N(6)#2	90.1(3)
Fe(2)–C(5)	1.908(8)	N(2)#2–Co(2)–N(6)	89.9(3)
Fe(2)–C(6)#2	1.918(8)	N(6)–Co(2)–N(8)	88.8(2)
Fe(2)–N(22)	1.937(7)	N(6)–Co(2)–N(8)#2	91.2(2)
Fe(2)–C(24)	1.975(6)	N(6)#2–Co(2)–N(8)	91.2(2)
Fe(2)–N(26)	1.970(6)	N(6)#2–Co(2)–N(8)#2	88.8(2)

#1 1-X,1-Y,1-Z; #2 2-X,1-Y,1-Z

Table S9. Continuous Shape Measure (CShM) analyses of geometries for compounds **1·solv** and **1·desolv** at 298 K by SHAPE 2.0 Software.

Geometry	1·solv				1·desolv			
	Co1	Co2	Fe1	Fe2	Co1	Co2	Fe1	Fe2
Hexagon/D_{6h}	32.557	32.849	32.157	32.340	31.985	32.890	32.438	32.169
Pentagonal pyramid/C_{5v}	29.914	30.041	29.211	29.347	29.624	29.986	29.418	29.017
Octahedron/O_h	0.039	0.023	0.074	0.153	0.059	0.019	0.090	0.131
Trigonal prism/D_{3h}	16.507	16.639	15.599	15.647	16.223	16.678	16.136	15.714
Johnson pentagonal pyramid (J$_2$)/C_{5v}	33.351	33.500	32.784	32.950	33.000	33.400	33.014	32.633

CShM: the continuous shape measurement relative to the ideal octahedron of the M centers, zero value means the ideal octahedron geometries.

Table S10. Hydrogen bond distances (Å) and angles (°) for **1·solv** at 298 K.

D–H···A	d(D–H)/ Å	d(H···A)/ Å	d(D–H···A)/ Å	D–H···A/ °
O1–H1A···N1	0.85	2.15	2.951(12)	156
O2–H18···N4	0.82	2.00	2.809(8)	172

Table S11. ^{57}Fe Mössbauer parameters for **1·solv** at 200 K.

T (K)	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Relative area (%)	Approximation ratio	Fe type
200K	0.23	0.65	50.96	1	Fe$^{II}_{LS}$
	-0.07	0.94	49.04	1	Fe$^{III}_{LS}$

Table S12. Temperature-dependent ^{57}Fe Mössbauer parameters for **1·desolv**.

T (K)	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Relative area (%)	Approximation ratio	Fe type
298K	−0.10	1.04	100	---	Fe$^{III}_{LS}$
80K	0.14	0.54	32.73	1	Fe$^{II}_{LS}$
	-0.01	1.41	67.27	1	Fe$^{III}_{LS}$
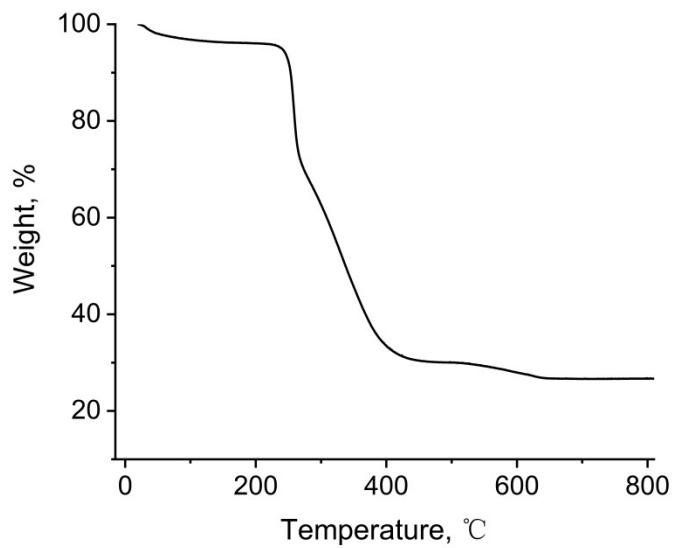
Fig. S1. TGA analyses of **1·solv** in the nitrogen atmosphere at 10 K min^{-1}. The first weight loss below 230 °C (experimental: 5.31% for **1·solv**) should be ascribed to the loss of isolated solvent molecules (expected: 5.48% for **1·solv**).
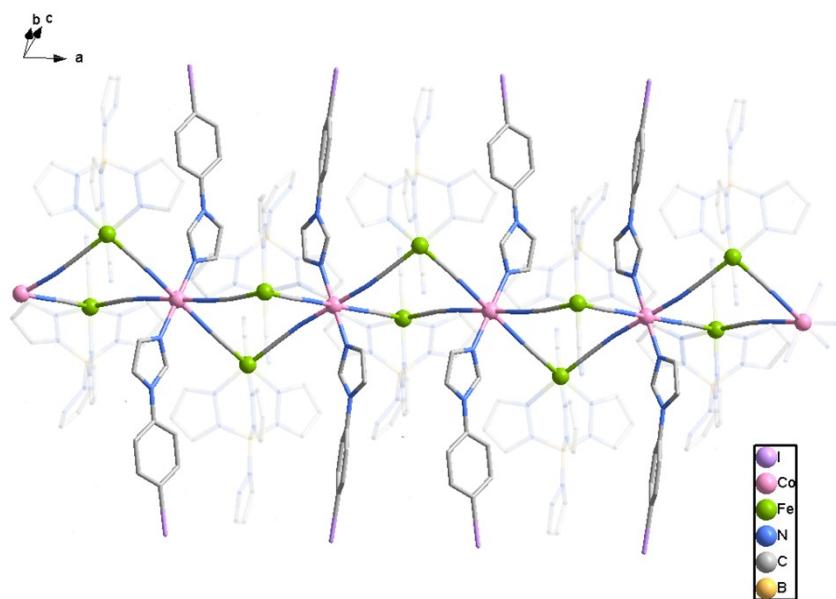
Fig. S2. Schematic structures of the {Fe$_2$Co}-based double zig-zag chains in **1·desolv** at 298 K. H atoms have been omitted for clarity. Color code:Co, pink; Fe, green; B, yellow; C, grey; N, blue; I, purple.

13
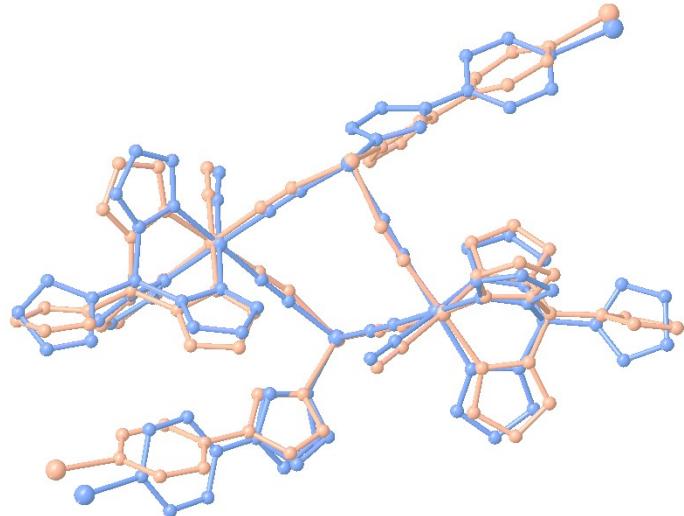
Fig S3. The overlapped molecular structures of **1·solv** (pale blue) and **1·desolv** (pale orange) at 298 K. Hydrogen atoms and solvents are omitted for clarity.
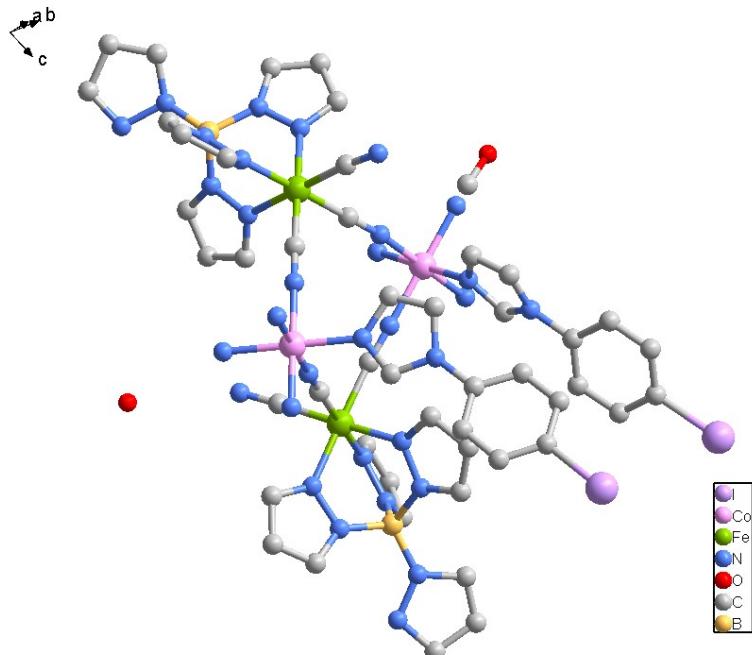
Fig. S4. Crystal structure of **1·resolv** at 298 K. H atoms have been omitted for clarity. Color code: Co, pink; Fe, green; B, yellow; C, grey; N, blue; O, red; I, purple.
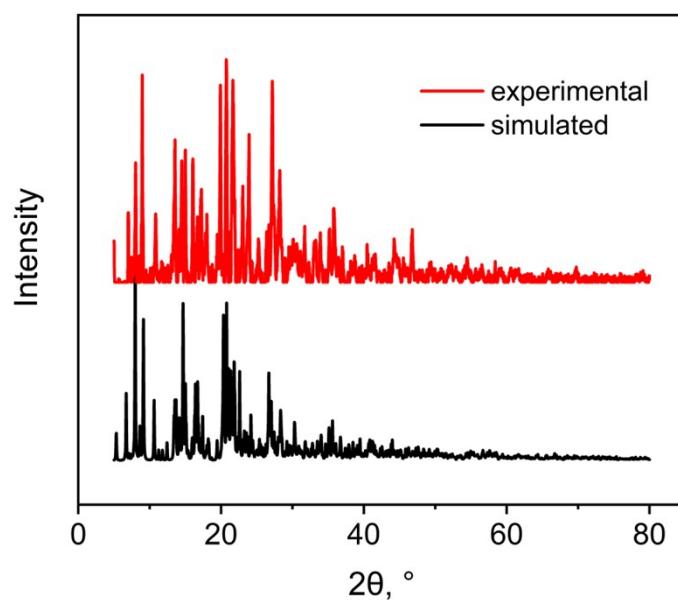
Fig. S5. The simulated and experimental powder X-ray diffraction patterns of **1·solv** at 298 K.
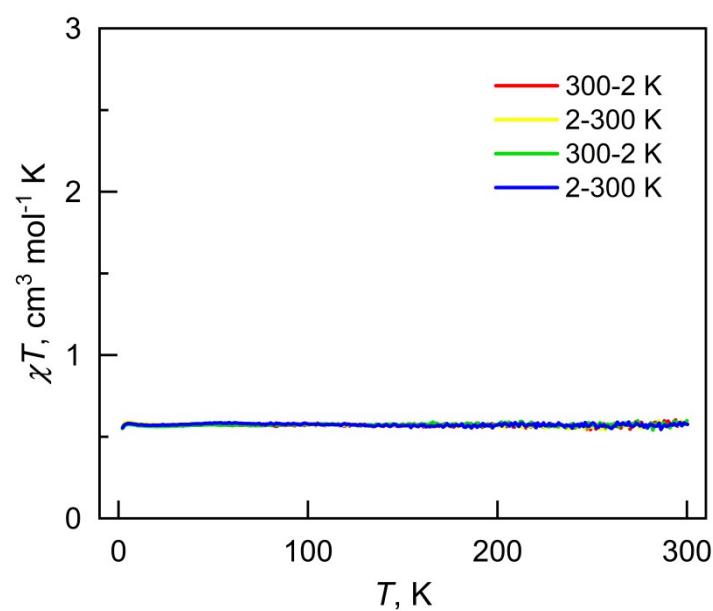
Fig. S6. Plots of χT vs T for **1·solv** between 2 and 300 K.
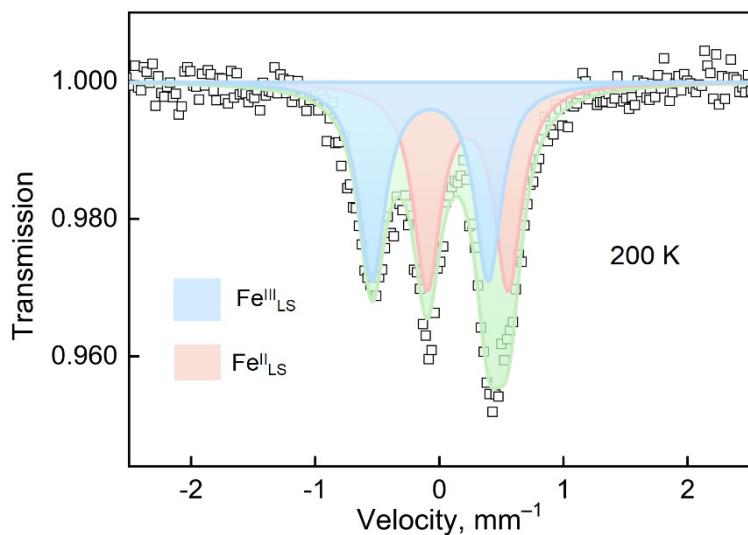
Fig. S7 Temperature dependent ^{57}Fe Mössbauer spectra of **1·solv** at 200 K. All spectra were fitted to Lorentzian profiles by the least-squares method, and the fit quality was controlled by the standard χ^2 and misfit tests (MossWinn program).
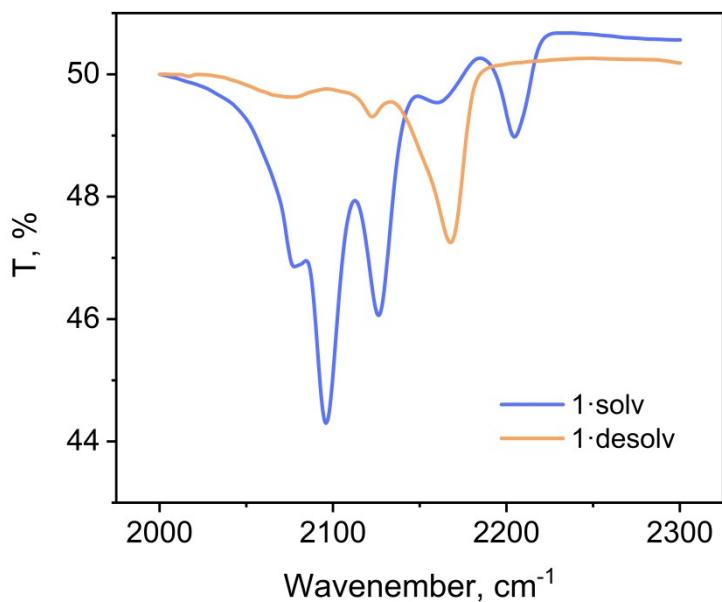
Fig. S8. Infrared spectra for compounds **1·solv** and **1·desolv** at 298 K
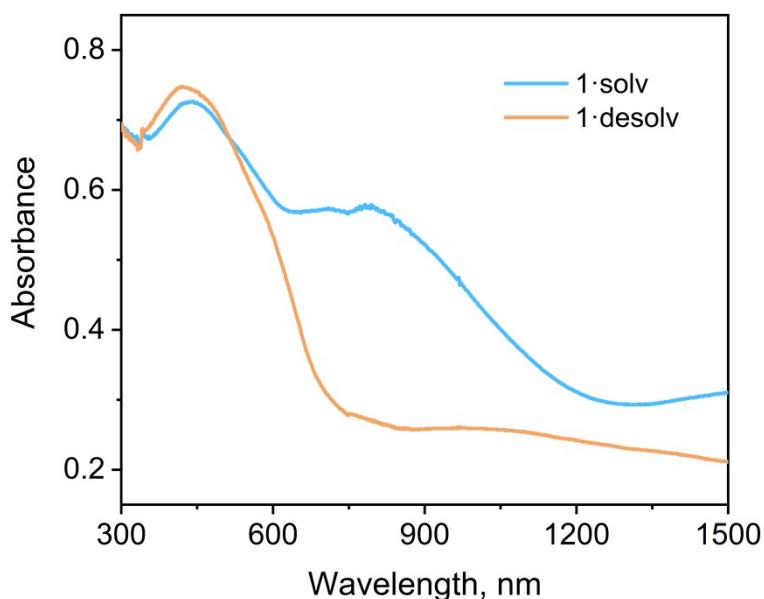
Fig. S9. Solid state UV-vis-NIR spectra for **1·solv** and **1·desolv** at 298 K.
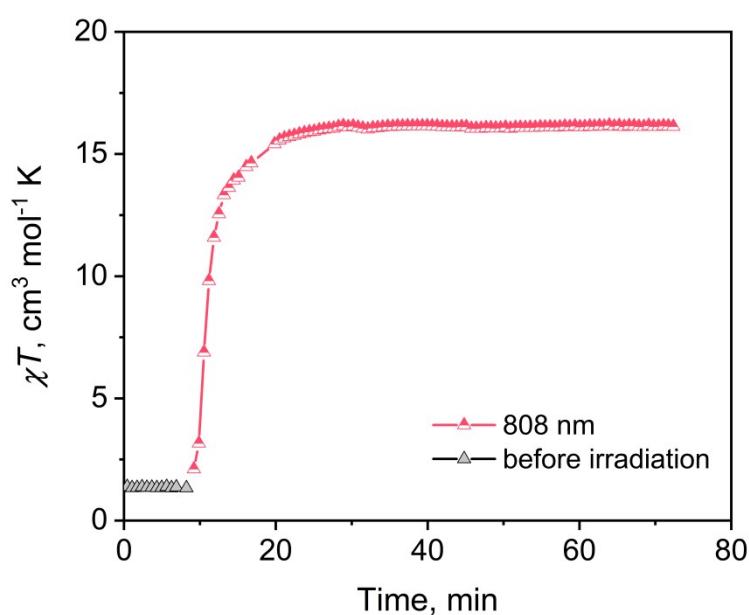
Fig. S10. Plots of χT vs time for **1·solv** irradiated under 808 nm at 10 K.
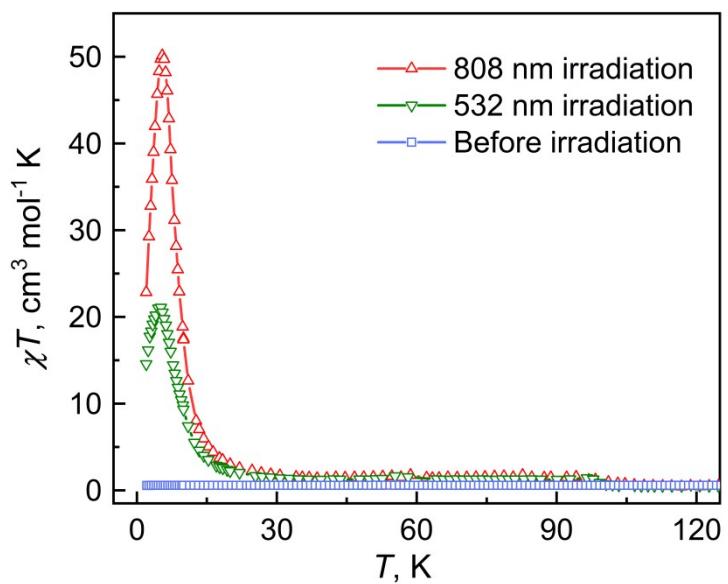
Fig. S11. Temperature-dependent susceptibilities of **1·solv** before and after light irradiation under an 1000 Oe DC field.
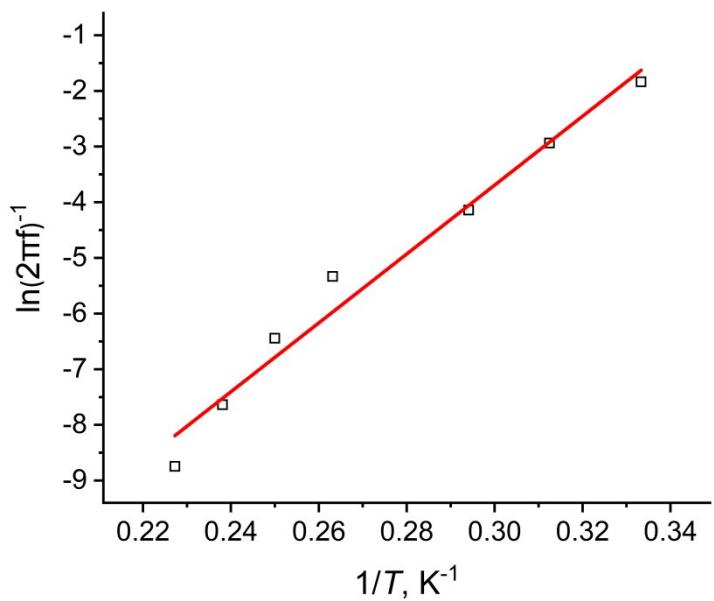
Fig. S12. Arrhenius plots for the magnetic relaxation process of **1·solv** after 808 nm light irradiation based on the peak values of χ''.
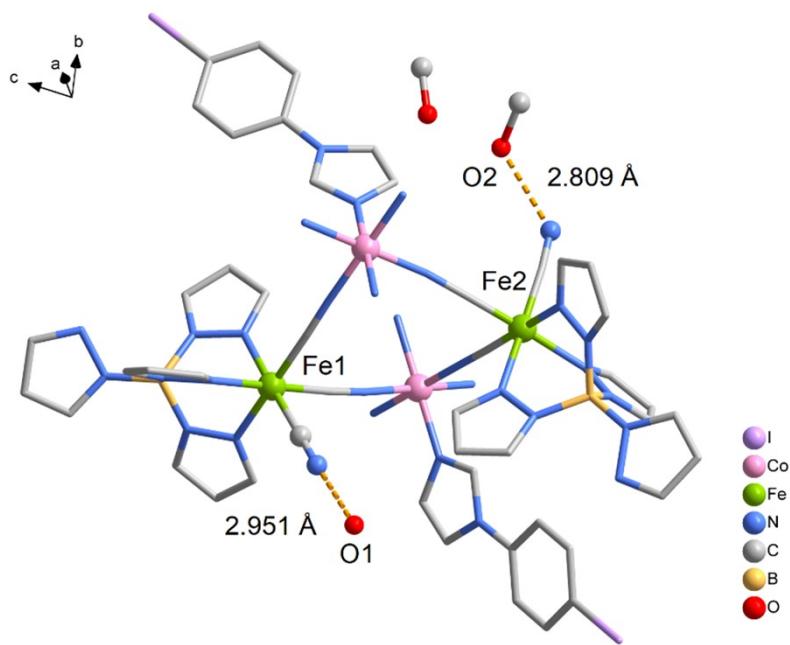
Fig. S13. Hydrogen bonds formed between lattice solvent molecules and terminal cyanide nitrogen atoms for **1·solv**. H atoms have been omitted for clarity. Color code: Co, pink; Fe, green; B, yellow; C, grey; N, blue; O, red; I, purple.
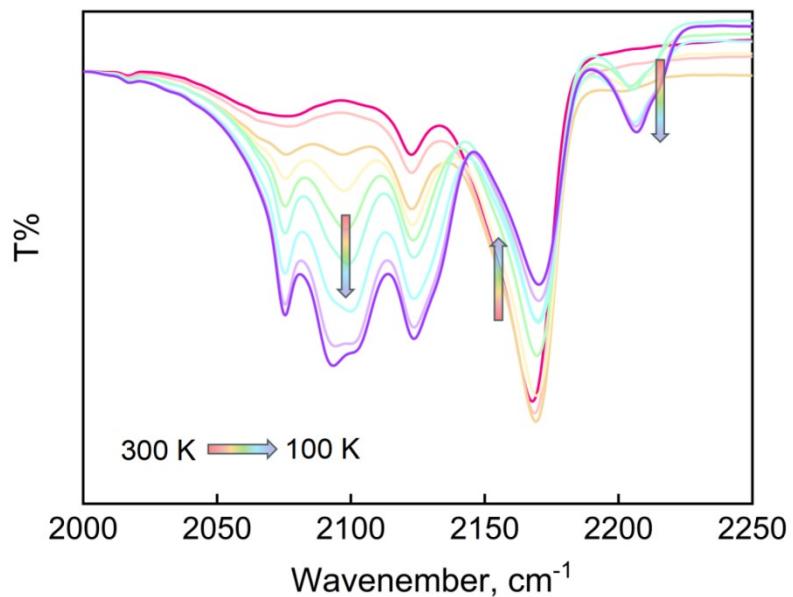

**Fig. S14.** Variable temperature solid state IR spectra of **1·desolv** in cooling mode.
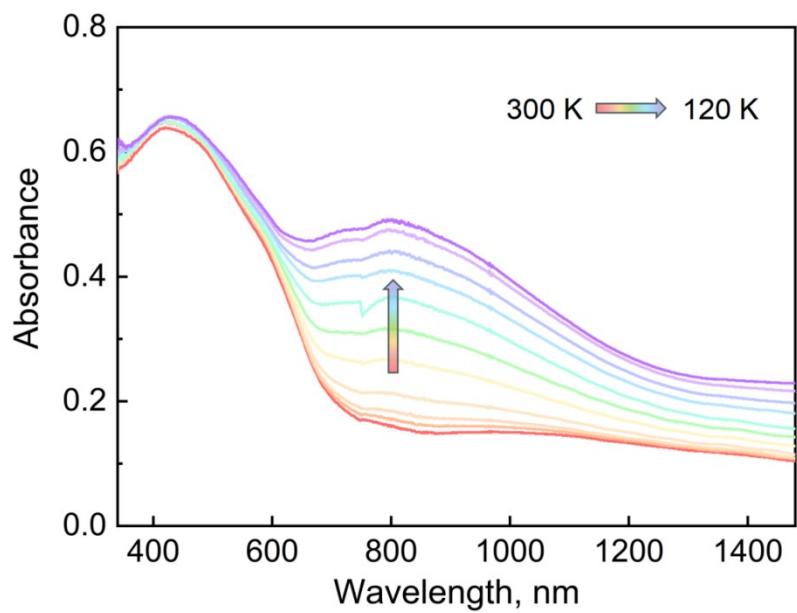
Fig. S15. Variable temperature solid state UV-vis-NIR absorption spectra of **1·desolv** in cooling mode.
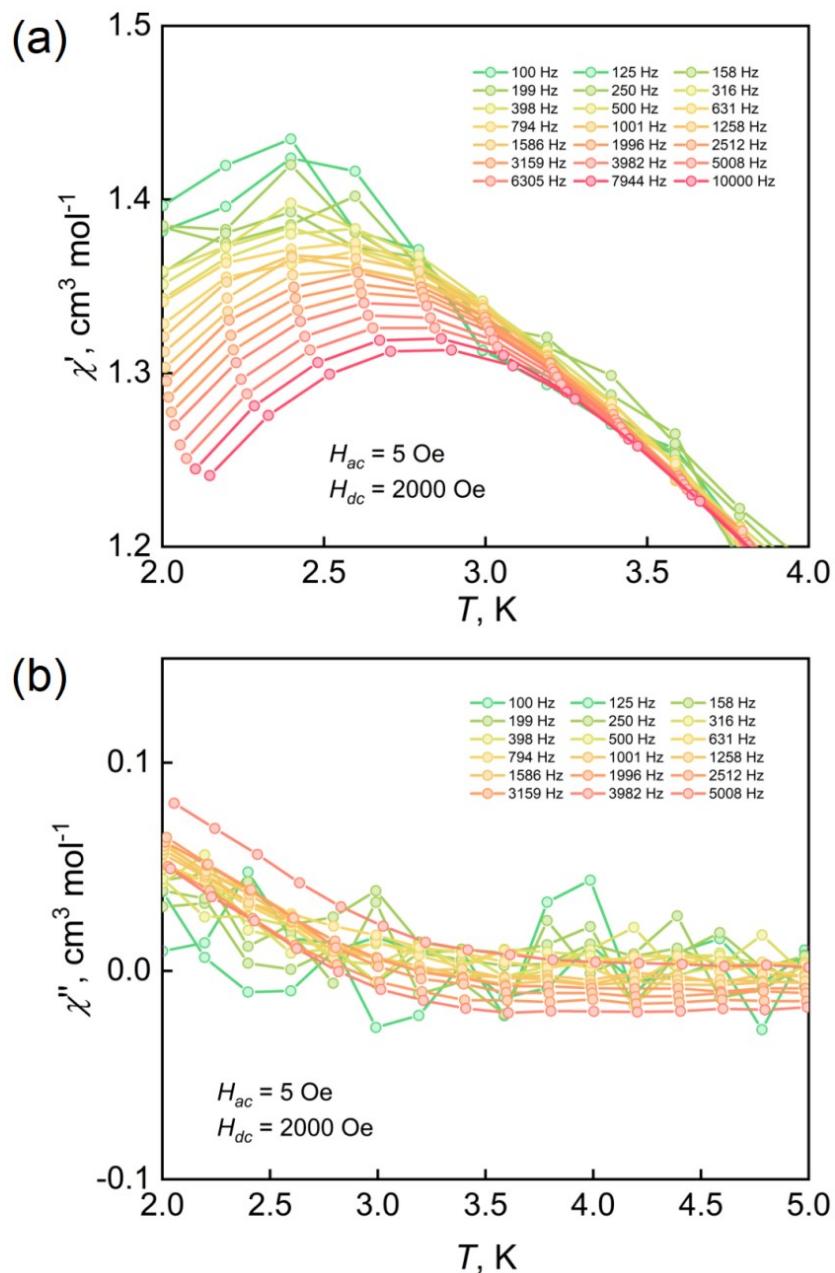
Fig. S16. Temperature dependence of in-phase signals (χ') (a) and out-of-phase signals (χ'') (b) for **1·desolv** under a 5 Oe AC field and 2000 Oe DC field.
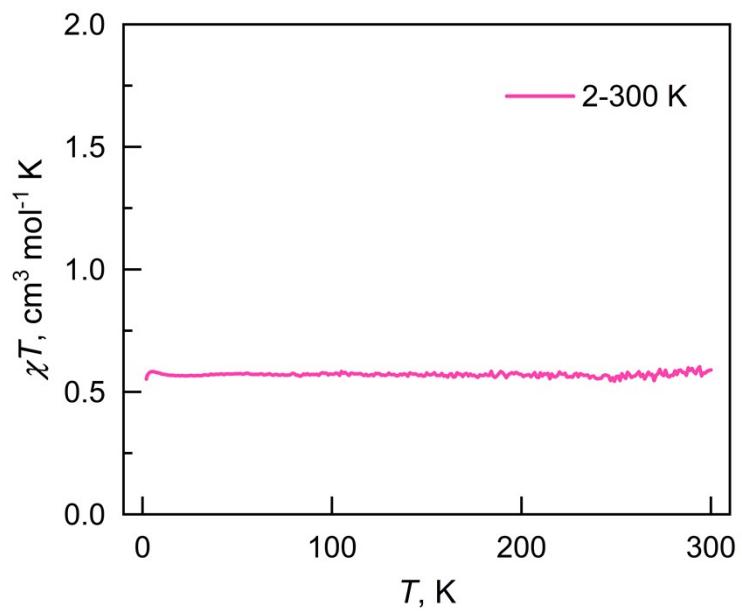
Fig. S17. Plots of χT vs. T for **1·resolv**.