Reversible Light-Induced Spin State Switching in a Dinuclear Fe(II) Spin Crossover Complex

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Table S1. Crystallographic Data for $[Fe_2L_5(NCS)_4]\cdot 2DMF\cdot 2H_2O$ at 292 and 90 K

Temperature, K	**292**	**90**
formula	$C_{300}H_{266}Fe_8N_{104}O_{13}S_{16}$	$C_{75}H_{68}Fe_2N_{26}O_4S_4$
Fw	6495.91	1637.49
crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	12.5490(15)	12.3484(10)
b, Å	21.076(3)	20.7584(16)
c, Å	30.415(4)	30.015(2)
V, Å^3	8044.3(17)	7693.9(11)
Z	1	4
D_c, g/cm^3	1.341	1.414
μ(Mo K_α), mm^{-1}	0.528	0.554
θ_{min}, θ_{max} , °	2.004, 25.026	2.035, 27.394
no. total reflns.	48489	46847
no. uniq. reflns (R_{int})	14185 (0.0825)	16849 (0.0616)
no. params	973	1047
$R1$,$wR2$ [I≥2σ(I)]	0.0666, 0.1601	0.0966, 0.1086
$R1$,$wR2$ (all data)	0.1178, 0.1816	0.0583, 0.1207
GOF	1.082	1.026
CCDC	1506797	1506798

Table S2. Selected bond distances (Å) and angles (°) for $[Fe_2L_5(NCS)_4]\cdot 2DMF\cdot 2H_2O$ at 292 K

Bond distances (Å)			
Fe(1)-N(1)	2.094(8)	Fe(1)-N(2)	2.122(7)
Fe(1)-N(5)	2.138(7)	Fe(1)-N(21)	2.184(7)
Fe(1)-N(13)	2.191(6)	Fe(1)-N(9)	2.224(6)
Fe(2)-N(3)	2.104(7)	Fe(2)-N(4)	2.110(9)
Fe(2)-N(14)	2.158(6)	Fe(2)-N(17)	2.179(7)
Fe(2)-N(10)	2.206(7)	Fe(2)-N(22)	2.210(7)
Bond angles (°)			
N(1)-Fe(1)-N(2)	95.0(3)	N(1)-Fe(1)-N(5)	97.2(3)
N(2)-Fe(1)-N(5)	89.6(3)	N(1)-Fe(1)-N(21)	90.3(3)
N(2)-Fe(1)-N(21)	88.1(3)	N(5)-Fe(1)-N(21)	172.3(3)
N(1)-Fe(1)-N(13)	88.9(3)	N(2)-Fe(1)-N(13)	175.9(3)
N(5)-Fe(1)-N(13)	88.7(3)	N(21)-Fe(1)-N(13)	93.1(3)
N(1)-Fe(1)-N(9)	174.3(3)	N(2)-Fe(1)-N(9)	89.6(3)
N(5)-Fe(1)-N(9)	86.3(3)	N(21)-Fe(1)-N(9)	86.4(2)
N(13)-Fe(1)-N(9)	86.6(2)	N(3)-Fe(2)-N(4)	92.7(3)
N(3)-Fe(2)-N(14)	176.4(2)	N(4)-Fe(2)-N(14)	89.1(3)
N(3)-Fe(2)-N(17)	95.4(3)	N(4)-Fe(2)-N(17)	92.0(3)
N(14)-Fe(2)-N(17)	87.6(3)	N(3)-Fe(2)-N(10)	91.6(3)
N(4)-Fe(2)-N(10)	175.7(3)	N(14)-Fe(2)-N(10)	86.6(2)
N(17)-Fe(2)-N(10)	87.4(3)	N(3)-Fe(2)-N(22)	87.3(3)
N(4)-Fe(2)-N(22)	91.1(3)	N(14)-Fe(2)-N(22)	89.5(3)
N(17)-Fe(2)-N(22)	175.7(3)	N(10)-Fe(2)-N(22)	89.2(3)
Σ_{Fe1}	31.4	Σ_{Fe2}	26.1

Table S3. Selected bond distances (Å) and angles (°) for $[Fe_2L_5(NCS)_4]\cdot 2DMF\cdot 2H_2O$ at 90 K

Bond distances (Å)			
Fe(1)-N(1)	1.971(5)	Fe(1)-N(9)	1.992(4)
Fe(1)-N(2)	1.968(5)	Fe(1)-N(13)	2.005(4)
Fe(1)-N(5)	1.998(4)	Fe(1)-N(21)	1.968(4)
Fe(2)-N(3)	1.979(5)	Fe(2)-N(14)	2.006(5)
Fe(2)-N(4)	1.967(5)	Fe(2)-N(17)	2.006(5)
Fe(2)-N(10)	1.996(4)	Fe(2)-N(22)	1.992(4)
Bond angles (°)			
N(2)-Fe(1)-N(21)	89.46(19)	N(2)-Fe(1)-N(1)	89.71(19)
N(21)-Fe(1)-N(1)	178.54(18)	N(2)-Fe(1)-N(9)	89.46(17)
N(21)-Fe(1)-N(9)	91.42(18)	N(1)-Fe(1)-N(9)	87.37(19)
N(2)-Fe(1)-N(5)	90.70(18)	N(21)-Fe(1)-N(5)	88.66(18)
N(1)-Fe(1)-N(5)	92.56(19)	N(9)-Fe(1)-N(5)	179.8(2)
N(2)-Fe(1)-N(13)	178.7(2)	N(21)-Fe(1)-N(13)	89.25(18)
N(1)-Fe(1)-N(13)	91.58(18)	N(9)-Fe(1)-N(13)	90.24(17)
N(5)-Fe(1)-N(13)	89.60(16)	N(4)-Fe(2)-N(3)	90.13(19)
N(4)-Fe(2)-N(22)	89.79(18)	N(3)-Fe(2)-N(22)	179.6(2)
N(4)-Fe(2)-N(10)	89.57(19)	N(3)-Fe(2)-N(10)	88.22(19)
N(22)-Fe(2)-N(10)	92.18(17)	N(4)-Fe(2)-N(14)	177.97(18)
N(3)-Fe(2)-N(14)	90.81(18)	N(22)-Fe(2)-N(14)	89.28(17)
N(10)-Fe(2)-N(14)	88.67(17)	N(4)-Fe(2)-N(17)	93.02(19)
N(3)-Fe(2)-N(17)	89.00(18)	N(22)-Fe(2)-N(17)	90.61(17)
N(10)-Fe(2)-N(17)	176.20(19)	N(14)-Fe(2)-N(17)	88.78(18)
Σ_{Fe1}	12.99	Σ_{Fe2}	13.44

Table S4. Intramolecular and intermolecular H–bonds in 1 at 292 K

Type	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry codes
Inter	O1W–H1WA…N6	0.8500	2.2300	2.951(16)	142.00	
Inter	O1W–H1WB…N18	0.8500	2.1900	3.030(16)	169.00	
Inter	C7–H7…O2	0.9300	2.3500	3.17(2)	146.00	
Inter	C19–H19…O1	0.9300	2.2600	3.172(13)	165.00	1_655
Inter	C20–H20…S1	0.9300	2.8600	3.788(9)	173.00	4_645
Inter	C21–H21…O1	0.9300	2.3300	3.239(16)	167.00	1_655
Inter	C27–H27…O1W	0.9300	2.5700	3.473(16)	164.00	3_565
Inter	C33–H33…S3	0.9300	2.7200	3.647(9)	174.00	4_655
Intra	C37–H37…N16	0.9300	2.1600	2.828(8)	128.00	
Intra	C50–H50…N20	0.9300	2.3200	2.960(9)	126.00	
Intra	C63–H63…N24	0.9300	2.1900	2.87(3)	129.00	
Inter	C66–H66…S3	0.9300	2.7700	3.620(15)	152.00	3_566
Intra	C71–H71C…O1	0.9600	2.3000	2.71(2)	105.00	
Intra	C75–H75C…O2	0.9600	2.2200	2.62(3)	104.00	

Symmetry codes: [4655] = 1-x,1/2+y,1/2-z; [4645] = 1-x,-1/2+y,1/2-z; [1655] = 1+x,y,z; [3566] = 1/2+x,3/2-y,1-z; [3565] = 1/2+x,3/2-y,-z.

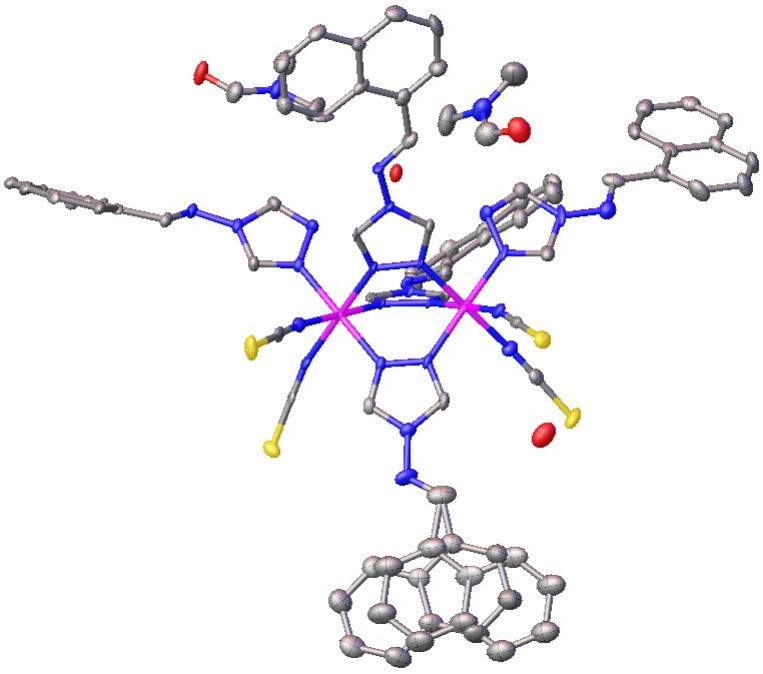
Table S5. Intramolecular and intermolecular H–bonds in 1 at 90 K

Type	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry codes
Inter	O2W–H2WA…S4	0.8400	2.7200	3.550(6)	169.00	
Inter	O1W–H1WA…N18	0.8700	2.1200	2.880(6)	146.00	
Inter	O1W–H1WB…N6	0.8700	2.0600	2.925(6)	171.00	
Inter	O2W–H2WB…S3	0.8900	2.5400	3.425(6)	172.00	
Intra	C16–H16…N8	0.9500	2.3400	2.972(8)	123.00	
Inter	C19–H19…O2W	0.9500	2.2900	3.224(8)	167.00	
Inter	C20–H20…O2W	0.9500	2.5300	3.455(9)	166.00	
Inter	C26–H26…S1	0.9500	2.8200	3.632(4)	144.00	3_565
Inter	C27–H27…S2	0.9500	2.7300	3.651(5)	163.00	3_565
Intra	C29–H29…N12	0.9500	2.1100	2.819(7)	130.00	
Inter	C31–H31…S4	0.9500	2.8200	3.770(6)	179.00	4_755
Inter	C32–H32…O1	0.9500	2.1900	3.122(6)	166.00	1_655
Inter	C33–H33…O1	0.9500	2.2900	3.235(7)	170.00	1_655
Inter	C39–H39…O1W	0.9500	2.5000	3.410(8)	161.00	3_566
Inter	C44–H44…O2	0.9500	2.2700	3.083(8)	143.00	
Inter	C46–H46…O2	0.9500	2.5500	3.490(9)	170.00	
Inter	C55–H55…O2	0.9500	2.5600	3.506(9)	171.00	
Inter	C58–H58···S1	0.9500	2.6100	3.554(6)	173.00	4_745
Intra	C68–H68···N24	0.9500	2.2000	2.847(7)	125.00	
Intra	C71–H71A···O1	0.9800	2.3900	2.778(8)	103.00	
Inter	C72–H72B···O1W	0.9800	2.5400	3.507(8)	169.00	
Intra	C74–H74A···O2	0.9800	2.3900	2.791(9)	104.00	

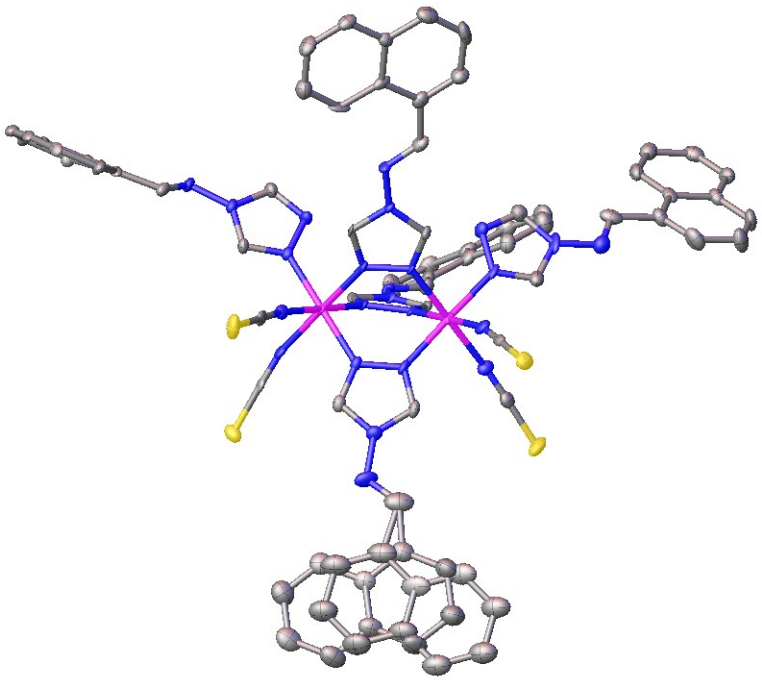
Symmetry codes: [1655] = 1+x,y,z; [4755] = 2-x,1/2+y,1/2-z; [4745] = 2-x,-1/2+y,1/2-z; [3565] = 1/2+x,3/2-y,-z; [3566.00] = 1/2+x,3/2-y,1-z.

Table S6. Intermolecular π - π stacking in 1 at 292 K and 90 K

T(K)	Moiety 1	Moiety 2	d (Å)
292	N9–N10–C20–N11–C19	C48–C49–C54–C55–C56–C57	3.739(4)
90	N13–N14–C32–N15–C31	C8–C9–C10–C11–C12–C17	3.631(3)



(a)



(b)

Fig. S1 ORTEP view of the crystal structure for **1** at 90 K with the 50% probability thermal ellipsoid. One naphthalene entity was disordered over two positions. (a) Hydrogen atoms are omitted for clarity. (b) H atoms, H_2O, and DMF molecules have been omitted for clarity.

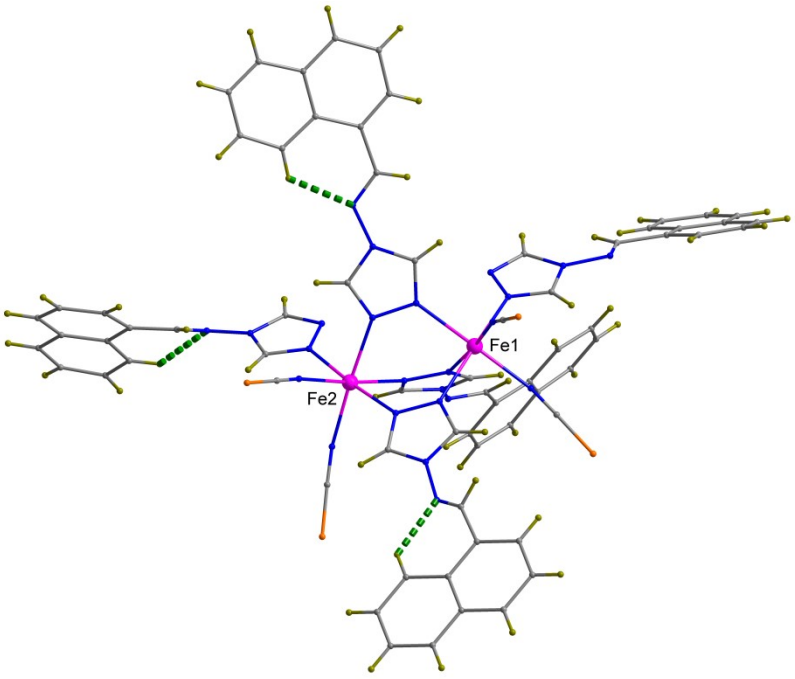


Fig. S2 Intramolecular C–H···N hydrogen bonds (green dashed lines)) in **1** at 292 K.

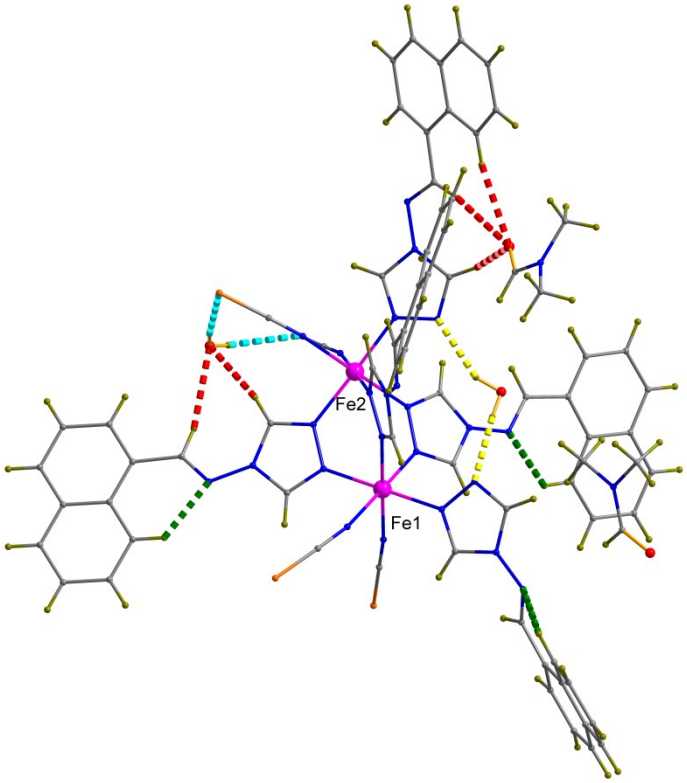


Fig. S3 Interactions of a single molecule with two H_2O and one DMF molecules via intermolecular hydrogen bonds at 90 K.

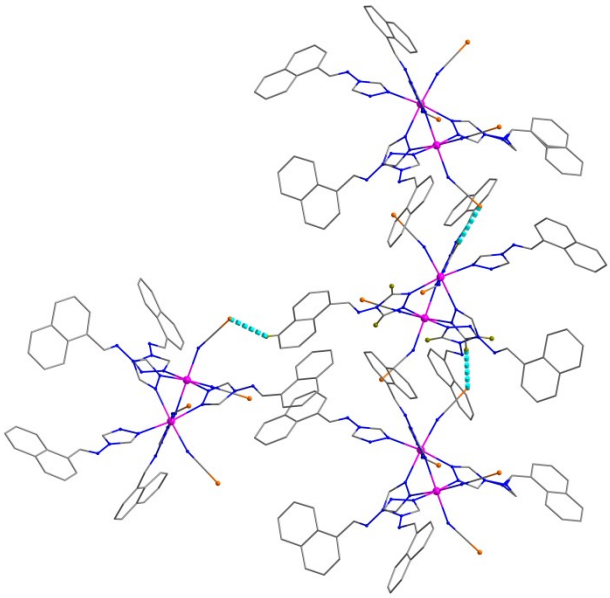


Fig. S4 One molecule connecting adjacent three molecules via three C–H···S (turquoise dashed lines) hydrogen bonds at 292 K.

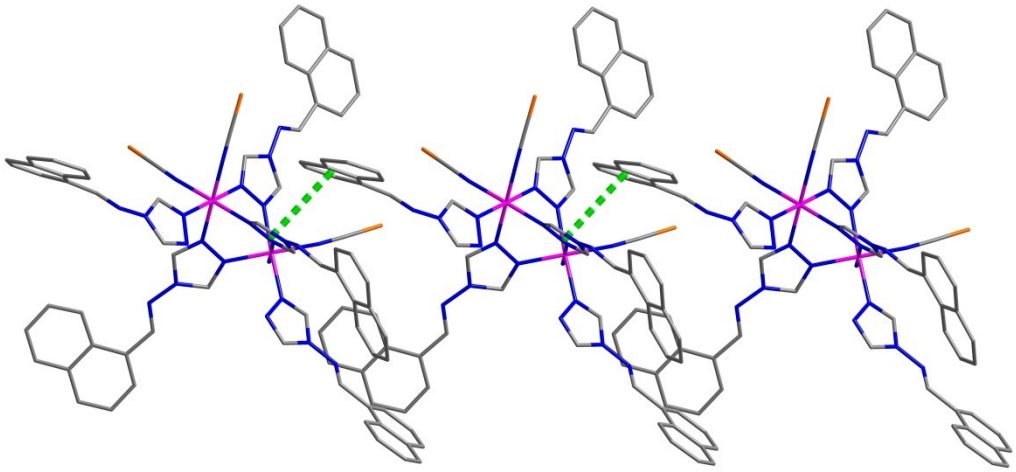


Fig. S5 Only one π–π stacking interaction between triazole and naphthyl group of adjacent molecules.

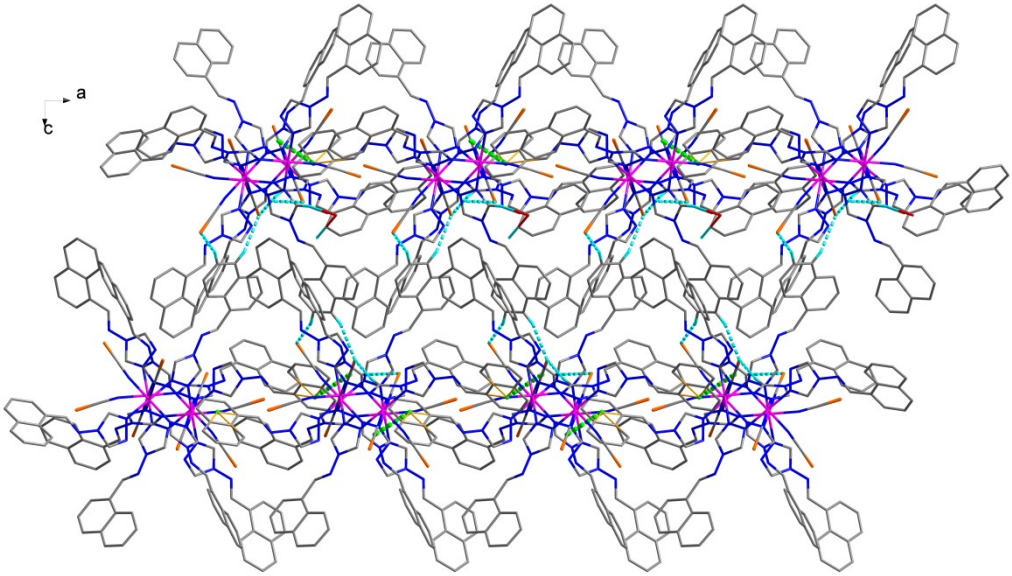


Fig. S6 Three-dimensional supramolecular network including π–π stacking interactions and C–H···S hydrogen bonds along the b-direction.

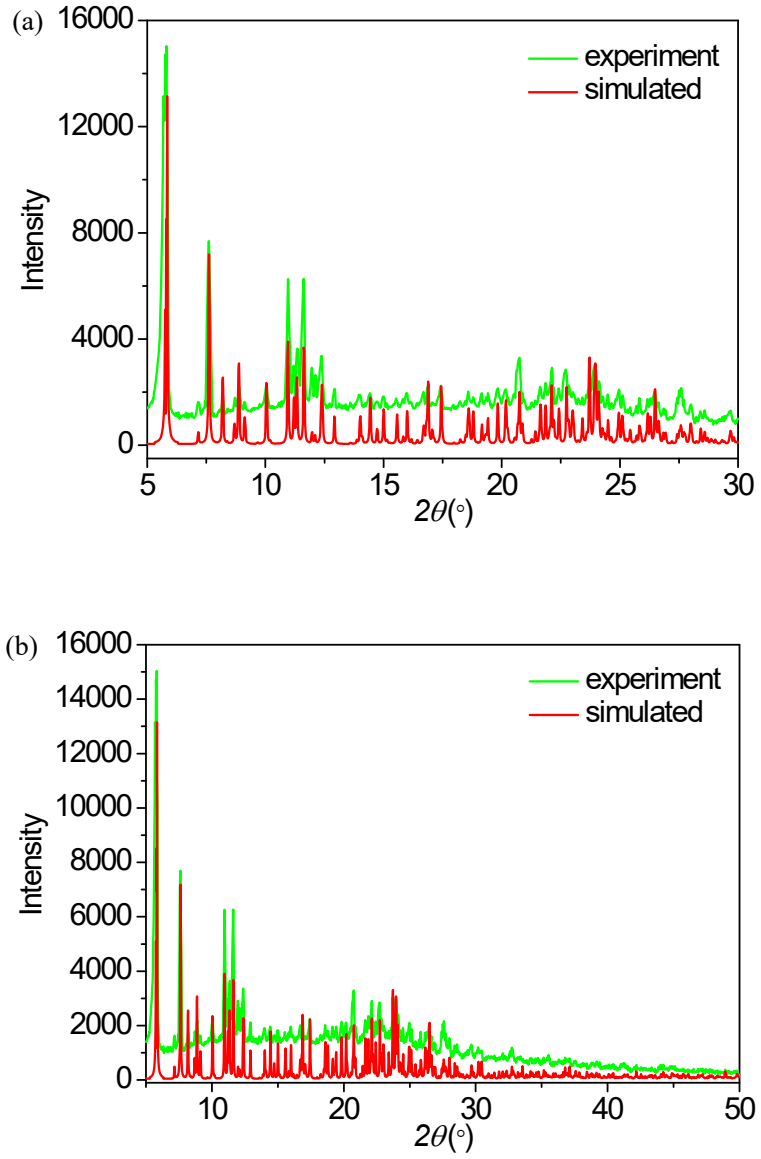


Fig. S7 Powder X-ray diffraction (PXRD) patterns of experiment (top) at room temperature and simulated (down) from the crystal structure at 292 K in the range of 5-30° (a) and 5-50° (b).

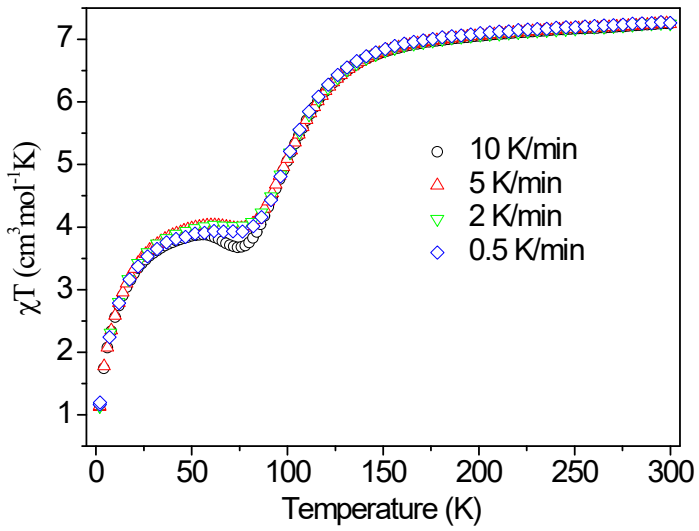


Fig. S8 Thermal evolutions of the χT product after TIESST effect of **1** with several heating rates.

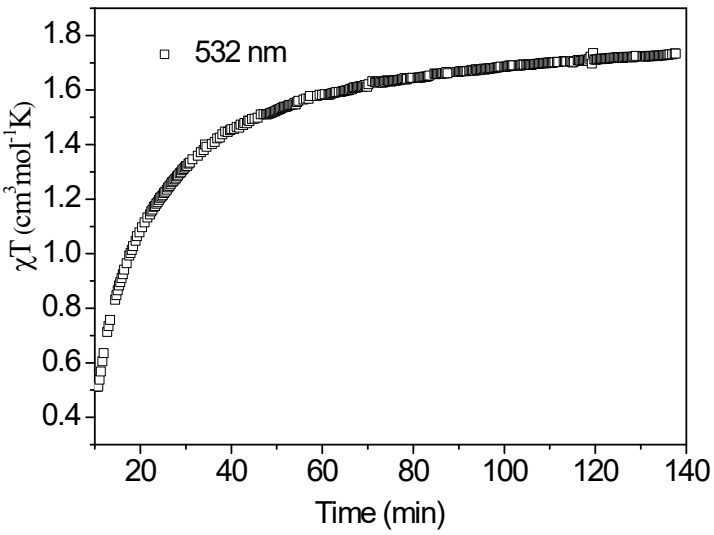


Fig. S9 Plot of χT vs time under 532-nm light irradiation at 10 K. The nominal laser power is 10 mW/cm^2.

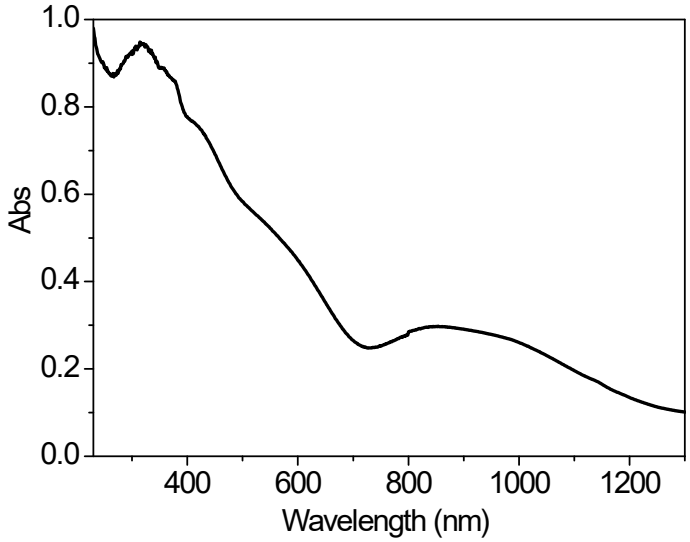


Fig. S10 UV−vis absorption spectrum of **1** at room temperature in the solid state.

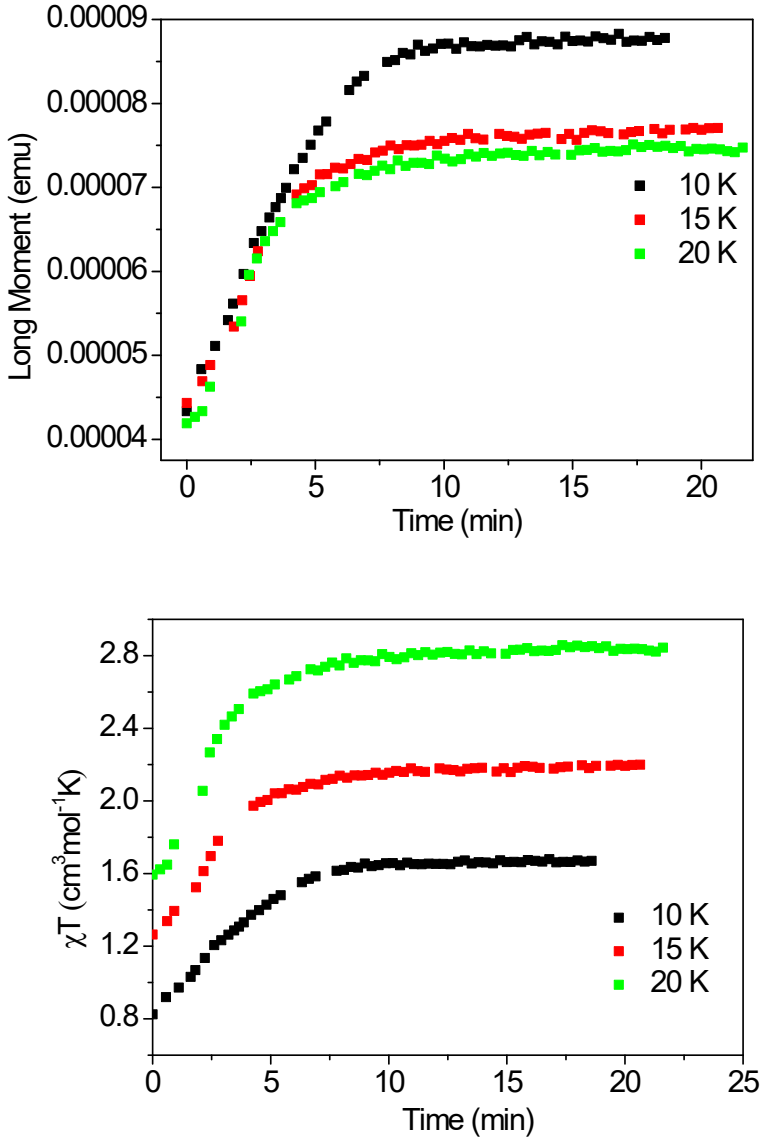


Fig. S11 Excitation curves at 10 K, 15 K and 20 K for irradiation at 532 nm with the nominal light intensity of 13 mW/cm^2. The mass of the samples is 0.60 mg.

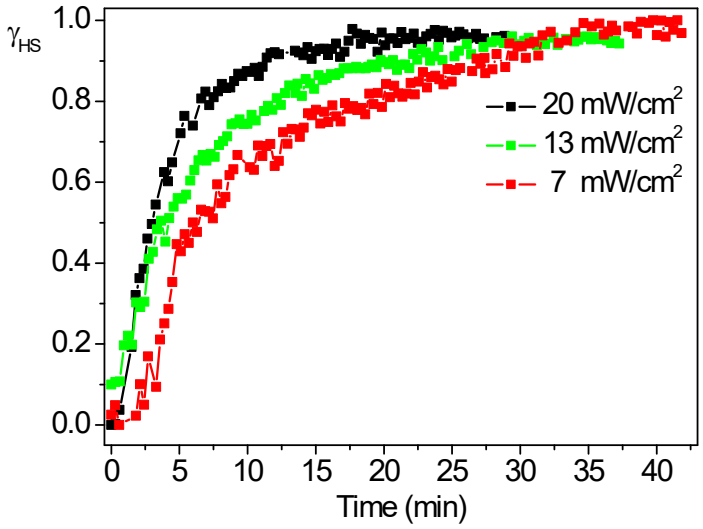


Fig. S12 Excitation curves at 10 K for irradiation at 532 nm with the nominal light intensities varying from 7 to 20 mW/cm^2. The mass of the samples is 0.86 mg.

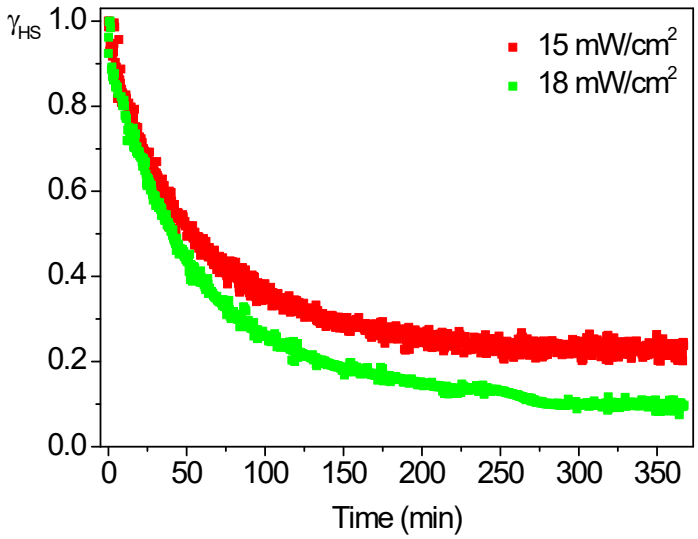


Fig. S13 Excitation curves at 10 K for irradiation at 808 nm with the nominal light intensities of 15 and 18 mW/cm^2.