Electronic Supplementary Information (ESI)

Reversible single-crystal-to-single-crystal transition in Gd(III) metal-organic frameworks induced by heat and solvents with a significant magnetocaloric effect

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Materials and instrumentations

All chemical reagents were obtained from commercial sources and used without further purification. The powder X-ray diffraction (PXRD) patterns were recorded by Rigaku MiniFlex 600. The simulated PXRD patterns of single-crystal data were obtained using the Mercury software, which are freely available on the Internet at http://www.iucr.org. Thermogravimetric analysis (TGA) was performed under a N_2 flow at a heating rate of 10 ^{o}C min^{-1} from 25 to 1000 ^{o}C on a NETZSCH STA2500 thermal analyzer. IR spectra in the range of 4000–400 cm^{-1} were collected with KBr particles on a Bruker Alpha FT-IR spectrometer. Elemental analysis (C, H, and N) was performed on a vario EL cube elemental analyzer. Magnetic data were collected by a Quantum Design MPMS-XL-7 SQUID magnetometer. Diamagnetic corrections were estimated by employing Pascal constants and background corrections by experimental measurement on sample holders. DC magnetic susceptibilities were measured in temperature range of 2-300 K under a 0.1 T dc field. The plots of M vs H for **JXUST-41** and **JXUST-41a** were recorded at 2 K under the fields between 0 and 7 T. While for **JXUST-40** and **JXUST-40a**, M vs H plots were measured at the temperature range of 2-10 K under the field of 0-7 T. AC susceptibilities were performed at 2-12 K (2-7 K, 0.25 K per step; 7-12 K, 1 K per step) under a 2 kOe dc filed and 3 Oe oscillating ac filed.

Crystallographic studies for JXUST-40, JXUST-40a, JXUST-40b, JXUST-41, JXUST-41a and JXUST-41b

Single crystal X-ray diffraction data of **JXUST-40**, **JXUST-40a**, **JXUST-40b**, **JXUST-41**, **JXUST-41a** and **JXUST-41b** were recorded on a Bruker D8 QUEST diffractometer Mo-Kα radiation (λ = 0.71073 Å) by ω scan mode. SAINT program was used for diffraction profile integration.[S1] The SHELXT program of SHELXTL software package was used to solve the structure directly, and the full matrix least square method was used to refine the structure.[S2] The non-hydrogen atoms were situated in successive difference Fourier syntheses and refined by anisotropic thermal parameters on F^2. Theoretically, the hydrogen atoms of BTDI^{4-} ligands are formed on specific atoms, and isotropic refinement was carried out by a fixed thermal factor. The

program SQUEEZE,[S3] a part of the PLATON package of crystallographic software, was used to calculate the solvent-accessible area and remove their contributions to the overall intensity data. A solvent mask during SQUEEZE process are six water molecules for **JXUST-40a** and **JXUST-41a** based on elemental analysis and TGA. The crystal structures have been deposited at the Cambridge Crystallographic Data Center (CCDC) and allocated the deposition numbers: 230884 (**JXUST-40** at 273 K), 230885 (**JXUST-40a** at 293 K), 230886 (**JXUST-40b** at 273 K), 230887 (**JXUST-41** at 273 K), 230888 (**JXUST-41** at 293 K), 230889 (**JXUST-41b** at 273 K). A summary of the crystallographic data and refinement parameters is given in Tables S1 and S2.

References

S1 *SAINT*, *Version 6.02a*, Bruker AXS Inc, Madison, WI, 2002.

S2 G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Adv.,* 2015, ***A71***, 3-8.

S3 A. L. Spek, Acta Crystallogr. Sect. D-Biol. Crystallogr. 2009, ***65***, 148−155

Table S1. Crystal data and structure refinements for **JXUST-40**, **JXUST-40a** and **JXUST-40b**

Compound	**JXUST-40**	**JXUST-40a**	**JXUST-40b**
formula	$C_{78}H_{52}N_{10}O_{28}S_3Gd_4$	$C_{66}H_{44}N_6O_{34}S_3Gd_4$	$C_{78}H_{52}N_{10}O_{28}S_3Gd_4$
*M*r	2302.47	2190.25	2302.47
T (K)	273(2)	293(2)	273(2)
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.9770(6)	11.0108(10)	10.9670(6)
b (Å)	11.9536(7)	11.1168(10)	11.1536(7)
c (Å)	15.8824(10)	15.8231(14)	15.9824(10)
α (º)	73.776(2)	104.973(3)	73.676(2)
β (º)	70.816(2)	109.460(3)	71.786(2)
γ (º)	86.974(2)	90.221(3)	86.984(2)
V (Å^3)	1888.20(19)	1755.6(3)	1780.85(19)
Z	1	1	1
F(000)	1118	1058	1118
D_{calc} (g cm^{-3})	2.025	2.072	2.147
μ (mm^{-1})	3.645	3.919	3.865
Collected reflections	23531	19408	22729
Unique reflections	6575	6112	6234
R_{int}	0.0538	0.0685	0.0514
R_1^a/wR_2^b [$I>2\sigma(I)$]	0.0375/0.0646	0.0634/0.1454	0.0343/0.0616
R_1^a/wR_2^b (all data)	0.0618/0.0735	0.1044/0.1612	0.0568/0.0691
GOF on F^2	1.036	1.065	1.025

$^aR_1 = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$. $^bwR_2 = [\Sigma w(|F_0|^2 - |F_C|^2)^2/(\Sigma w|F_0|^2)^2]^{1/2}$.

Table S2. Crystal data and structure refinements for **JXUST-41**, **JXUST-41a** and **JXUST-41b**

Compound	**JXUST-41**	**JXUST-41a**	**JXUST-41b**
formula	$C_{78}H_{52}N_{10}O_{28}S_3Dy_4$	$C_{66}H_{44}N_6O_{34}S_3Dy_4$	$C_{78}H_{52}N_{10}O_{28}S_3Dy_4$
*M*r	2323.47	2211.28	2323.47
T (K)	273(2)	293(2)	273(2)
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	10. 9183(5)	10.9980 (12)	10.9883(5)
b (Å)	12.0025(6)	11.1805(13)	12.5025(6)
c (Å)	15.8371(6)	15.8136(17)	15.4371(6)
α (º)	73.454(10)	104.902(4)	73.354(10)
β (º)	70.816(10)	109.430(3)	70.616(10)
γ (º)	86.911(10)	90.228(4)	86.511(10)
V (Å^3)	1877.18(15)	1763.5(3)	1915.34(15)
Z	1	1	1
F(000)	1126	1066	1126
D_{calc} (g cm^{-3})	2.055	2.082	2.014
μ (mm^{-1})	4.114	4.378	4.032
Collected reflections	23053	18642	23480
Unique reflections	6546	6110	6703
R_{int}	0.0265	0.0615	0.0269
R_1^a/wR_2^b [$I>2\sigma(I)$]	0.0244/0.0491	0.0657/0.1406	0.0293/0.0685
R_1^a/wR_2^b (all data)	0.0307/0.0511	0.1014/0.1619	0.0358/0.0711
GOF on F^2	1.067	1.052	1.091

$^aR_1 = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$. $^bwR_2 = [\Sigma w(|F_0|^2 - |F_C|^2)^2/(\Sigma w|F_0|^2)^2]^{1/2}$.

Table S3. Selected bond lengths (Å) and angles (°) for **JXUST-40**[a]

Gd1—O1	2.299(5)	Gd2—O13	2.340(5)
Gd1—O5^{i}	2.263(11)	Gd2—O6A^{ii}	2.230(19)
Gd1—O7^{ii}	2.450(4)	Gd2—O2^{iii}	2.304(4)
Gd1—O8^{ii}	2.422(4)	Gd2—O3	2.454(4)
Gd1—O11	2.434(14)	Gd2—O4	2.373(4)
Gd1—O12	2.367(5)	Gd2—O6^{ii}	2.350(18)
Gd1—O14	2.412(6)	O5^{i}—Gd1—O14	84.5(7)
O1—Gd1—O7^{ii}	77.40(17)	O8^{ii}—Gd1—O7^{ii}	53.26(15)
O1—Gd1—O8^{ii}	103.87(17)	O8^{ii}—Gd1—O11	116.7(4)
O1—Gd1—O11	98.9(5)	O11—Gd1—O7^{ii}	76.4(5)
O1—Gd1—O12	158.3(2)	O12—Gd1—O7^{ii}	118.24(16)
O1—Gd1—O14	84.1(2)	O12—Gd1—O8^{ii}	77.84(16)
O5^{i}—Gd1—O1	87.2(5)	O12—Gd1—O11	99.5(6)
O5^{i}—Gd1—O7^{ii}	147.2(6)	O12—Gd1—O14	74.8(2)
O5^{i}—Gd1—O8^{ii}	159.5(5)	O14—Gd1—O7^{ii}	121.7(2)
O5^{i}—Gd1—O11	77.7(8)	O14—Gd1—O8^{ii}	79.58(19)
O5^{i}—Gd1—O12	85.6(5)	O14—Gd1—O11	161.7(5)
O6^{ii}—Gd2—O4	114.5(5)	O2^{iii}—Gd2—O3	145.10(16)
O13—Gd2—O3	80.65(17)	O2^{iii}—Gd2—O4	158.69(16)
O13—Gd2—O4	105.17(18)	O2^{iii}—Gd2—O6^{ii}	85.2(5)
O13—Gd2—O6^{ii}	104.1(5)	O2^{iii}—Gd2—O13	75.75(17)
O4—Gd2—O3	53.45(15)	O6^{ii}—Gd2—O3	76.0(5)

[a]Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*-1, *y*, *z*+1; (iii) *x*-1, *y*, *z*; (iv) *x*+1, *y*, *z*-1.

Table S4. Selected bond lengths (Å) and angles (°) for **JXUST-40a**[b]

Gd1—O1	2.38(3)	Gd1—O10^{i}	2.371(9)
Gd1—O1W	2.277(8)	Gd1—O11^{ii}	2.276(8)
Gd1—O5	2.264(10)	Gd2—O2W	2.309(8)
Gd1—O9^{i}	2.498(9)	Gd2—O7^{ii}	2.455(8)
Gd2—O3	2.59(4)	Gd2—O8^{ii}	2.410(10)
Gd2—O4	2.48(2)	Gd2—O12^{iii}	2.241(8)
Gd2—O6^{i}	2.234(8)	O1W—Gd1—O1	78.4(7)
O1W—Gd1—O9^{i}	79.2(4)	O1—Gd1—O9^{i}	111.8(8)
O1W—Gd1—O10^{i}	107.4(4)	O5—Gd1—O1	170.1(8)
O5—Gd1—O9^{i}	73.7(3)	O5—Gd1—O1W	95.0(4)
O5—Gd1—O10^{i}	113.8(3)	O5—Gd1—O11^{ii}	88.1(3)
O10^{i}—Gd1—O1	75.5(8)	O10^{i}—Gd1—O9^{i}	52.3(3)
O11^{ii}—Gd1—O1	83.3(8)	O11^{ii}—Gd1—O9^{i}	149.0(3)
O11^{ii}—Gd1—O1W	77.6(4)	O11^{ii}—Gd1—O10^{i}	156.5(3)
O2W—Gd2—O3	123.5(8)	O2W—Gd2—O7^{ii}	118.7(4)
O2W—Gd2—O4	74.6(6)	O2W—Gd2—O8^{ii}	77.0(4)
O4—Gd2—O3	51.7(9)	O6^{i}—Gd2—O4	87.3(6)
O6^{i}—Gd2—O2W	82.1(4)	O6^{i}—Gd2—O7^{ii}	152.1(4)
O6^{i}—Gd2—O8^{ii}	154.4(4)	O7^{ii}—Gd2—O3	76.7(9)
O6^{i}—Gd2—O12^{iii}	90.7(3)	O7^{ii}—Gd2—O4	115.0(6)
O8^{ii}—Gd2—O3	72.2(9)	O12^{iii}—Gd2—O3	152.2(9)
O8^{ii}—Gd2—O4	73.1(6)	O12^{iii}—Gd2—O4	152.3(6)
O8^{ii}—Gd2—O7^{ii}	53.5(3)	O12^{iii}—Gd2—O7^{ii}	77.1(3)
O12^{iii}—Gd2—O2W	77.8(4)	O12^{iii}—Gd2—O8^{ii}	99.0(4)

[b]Symmetry codes: (i) x, y, z+1; (ii) x+1, y, z+1; (iii) x+1, y, z+2.

Table S5. Selected bond lengths (Å) and angles (°) for **JXUST-40b**[c]

Gd1—O8^{ii}	2.416(4)	Gd1—O14	2.260(6)
Gd1—O11	2.114(5)	Gd2—O2^{iii}	2.307(4)
Gd1—O12	2.390(5)	Gd2—O3	2.438(4)
O8^{ii}—Gd1—O7^{ii}	52.18(15)	O14—Gd1—O5^{i}	78.8(2)
O11—Gd1—O5^{i}	79.2(2)	O14—Gd1—O7^{ii}	122.2(2)
O11—Gd1—O7^{ii}	79.21(19)	O14—Gd1—O8^{ii}	81.7(2)
O11—Gd1—O8^{ii}	119.11(18)	O14—Gd1—O12	74.4(2)
O11—Gd1—O14	157.9(2)	O2^{iii}—Gd2—O4	158.57(16)
O12—Gd1—O7^{ii}	117.56(16)	O2^{iii}—Gd2—O6^{ii}	83.55(15)
O12—Gd1—O8^{ii}	76.88(17)	O2^{iii}—Gd2—O9^{iv}	86.25(15)
O10^{iii}—Gd2—O6^{ii}	90.19(17)	O4—Gd2—O3	53.65(15)
O10^{iii}—Gd2—O9^{iv}	86.64(16)	O6^{ii}—Gd2—O3	74.38(15)
O10^{iii}—Gd2—O13	154.57(18)	O6^{ii}—Gd2—O4	116.90(16)
O13—Gd2—O2^{iii}	75.52(18)	O6^{ii}—Gd2—O9^{iv}	169.65(14)
O13—Gd2—O3	81.75(18)	O9^{iv}—Gd2—O3	115.48(15)
O13—Gd2—O4	105.58(19)	O9^{iv}—Gd2—O4	73.05(15)
O13—Gd2—O6^{ii}	98.76(19)	O10^{iii}—Gd2—O2^{iii}	81.97(16)
O13—Gd2—O9^{iv}	80.31(18)	O10^{iii}—Gd2—O3	123.65(17)

[c]Symmetry codes: (i) x, y, z+1;(ii) x-1, y, z+1;(iii) x-1, y, z;(iv) -x, -y+1, -z+1;

Table S6. Selected bond lengths (Å) and angles (°) for **JXUST-41**[d]

Dy1—O2^{i}	2.269(3)	Dy1—O17	2.312(19)
Dy1—O6^{ii}	2.275(3)	Dy2—O5	2.268(3)
Dy1—O7	2.434(3)	Dy2—O14	2.380(4)
Dy1—O8	2.341(3)	Dy1—O13	2.317(3)
Dy1—O11^{iii}	2.17(2)	O2^{i}—Dy1—O6^{ii}	84.76(10)
O11^{iii}—Dy1—O7	127.6(5)	O2^{i}—Dy1—O7	74.58(10)
O11^{iii}—Dy1—O8	91.6(6)	O2^{i}—Dy1—O8	114.72(11)
O11^{iii}—Dy1—O13	152.4(5)	O2^{i}—Dy1—O13	100.99(12)
O11^{iii}—Dy1—O17	7.8(10)	O2^{i}—Dy1—O17	85.7(5)
O13—Dy1—O7	80.00(12)	O6^{ii}—Dy1—O7	144.54(11)
O13—Dy1—O8	106.23(12)	O6^{ii}—Dy1—O8	158.92(10)
O17—Dy1—O7	120.0(5)	O6^{ii}—Dy1—O13	75.99(12)
O17—Dy1—O8	87.5(5)	O6^{ii}—Dy1—O17	86.0(5)
O17—Dy1—O13	160.0(5)	O8—Dy1—O7	54.28(10)
O5—Dy2—O14	85.25(14)	O11^{iii}—Dy1—O2^{i}	90.0(6)
O11^{iii}—Dy1—O6^{ii}	79.9(6)		

[d]Symmetry codes: (i) x+1, y, z-1; (ii) x+1, y, z; (iii) -x+2, -y, -z+1.

Table S7. Selected bond lengths (Å) and angles (°) for **JXUST-41a**[e]

Dy1—O2	2.255(9)	Dy1—O5^{i}	2.257(10)
Dy1—O2W	2.340(15)	Dy1—O7^{ii}	2.498(11)
Dy2—O1	2.193(10)	Dy1—O8^{ii}	2.356(10)
Dy2—O1W	2.222(9)	Dy1—O9	2.33(3)
Dy2—O3^{iv}	2.431(10)	Dy1—O13^{iii}	2.26(2)
Dy2—O4^{iv}	2.408(10)	O2—Dy1—O2W	95.0(5)
Dy2—O6^{i}	2.217(9)	O2—Dy1—O5^{i}	87.6(4)
Dy2—O11	2.48(3)	O2—Dy1—O7^{ii}	73.3(4)
O2—Dy1—O9	87.7(7)	O2—Dy1—O8^{ii}	113.5(4)
O2—Dy1—O13^{iii}	171.0(6)	O2W—Dy1—O7^{ii}	78.3(5)
O5^{i}—Dy1—O2W	77.9(5)	O2W—Dy1—O8^{ii}	107.4(4)
O5^{i}—Dy1—O9	85.7(7)	O5^{i}—Dy1—O7^{ii}	147.9(4)
O8^{ii}—Dy1—O7^{ii}	52.9(4)	O5^{i}—Dy1—O8^{ii}	157.1(4)
O9—Dy1—O2W	163.2(7)	O9—Dy1—O7^{ii}	118.2(7)
O13^{iii}—Dy1—O2W	89.4(6)	O9—Dy1—O8^{ii}	86.5(7)
O13^{iii}—Dy1—O9	85.9(8)	O13^{iii}—Dy1—O5^{i}	85.6(6)
O1—Dy2—O1W	72.5(4)	O13^{iii}—Dy1—O7^{ii}	115.3(6)
O1—Dy2—O3^{iv}	153.7(4)	O13^{iii}—Dy1—O8^{ii}	72.4(6)
O1—Dy2—O4^{iv}	152.2(4)	O1W—Dy2—O3^{iv}	124.6(5)
O1—Dy2—O6^{i}	89.6(4)	O1W—Dy2—O4^{iv}	83.5(4)
O1—Dy2—O11	82.1(7)	O1W—Dy2—O11	153.0(7)
O4^{iv}—Dy2—O3^{iv}	53.7(4)	O3^{iv}—Dy2—O11	76.5(7)
O4^{iv}—Dy2—O11	123.4(7)	O6^{i}—Dy2—O3^{iv}	76.7(4)
O6^{i}—Dy2—O1W	77.5(5)	O6^{i}—Dy2—O4^{iv}	98.7(4)
O6^{i}—Dy2—O11	93.6(7)		

[e]Symmetry codes: (i) x+1, y, z+1; (ii) x, y, z+1; (iii) x-1, y-1, z; (iv) x+1, y, z.

Table S8. Selected bond lengths(Å) and angles(°) for **JXUST-41b**[f]

Gd1—O8^{i}	2.269(4)	Gd2—O1^{iii}	2.307(4)
Gd1—O12^{ii}	2.432(4)	Gd2—O4	2.438(4)
Gd1—O9	1.948(17)	Gd2—O6	2.398(4)
Gd1—O5	2.389(4)	Gd2—O10^{ii}	2.309(4)
Gd1—O3	2.304(5)	Gd2—O11	2.182(4)
Gd1—O13	2.261(6)	O8^{i}—Gd1—O12^{ii}	150.56(16)
O8^{i}—Gd1—O3	84.62(16)	O8^{i}—Gd1—O5	86.34(16)
O9—Gd1—O8^{i}	79.0(6)	O5—Gd1—O12^{ii}	117.52(16)
O9—Gd1—O12^{ii}	77.5(6)	O3—Gd1—O12^{ii}	77.29(16)
O9—Gd1—O5	107.4(5)	O3—Gd1—O5	159.96(18)
O9—Gd1—O3	88.4(5)	O9—Gd1—O13	157.6(6)
O13—Gd1—O8^{i}	78.9(2)	O13—Gd1—O5	74.4(2)
O13—Gd1—O12^{ii}	122.2(2)	O13—Gd1—O3	86.3(2)
O1^{iii}—Gd2—O4	145.46(15)	O6—Gd2—O4	53.53(14)
O1^{iii}—Gd2—O6	158.58(15)	O10^{ii}—Gd2—O4	74.43(14)
O1^{iii}—Gd2—O10^{ii}	83.58(14)	O10^{ii}—Gd2—O6	116.87(15)
O11—Gd2—O1^{iii}	75.63(17)	O11—Gd2—O6	105.49(18)
O11—Gd2—O4	81.69(17)	O11—Gd2—O10^{ii}	98.73(18)

[f]Symmetry codes: (i) x+1, y, z-1; (ii) x+1, y, z; (iii) x-1, y+1, z.

Table S9. SHAPE analysis of the Gd^{III} ions in **JXUST-40**

Ions	Label	Shape	Symmetry	Distortion (τ)
Gd1	HP-7	Heptagon	D_{7h}	29.478
	HPY-7	Hexagonal pyramid	C_{6v}	19.495
	PBPY-7	Pentagonal bipyramid	D_{5h}	5.023
	COC-7	Capped octahedron	C_{3v}	2.510
	CTPR-7	**Capped trigonal prism**	$\boldsymbol{C_{2v}}$	**1.858**
	JPBPY-7	Johnson pentagonal bipyramid J13	D_{5h}	8.322
	JETPY-7	Johnson elongated triangular pyramid J7	C_{3v}	16.540
Gd2	HP-7	Heptagon	D_{7h}	33.217
	HPY-7	Hexagonal pyramid	C_{6v}	19.430
	PBPY-7	Pentagonal bipyramid	D_{5h}	6.190
	COC-7	**Capped octahedron**	$\boldsymbol{C_{3v}}$	**1.988**
	CTPR-7	**Capped trigonal prism**	$\boldsymbol{C_{2v}}$	**1.794**
	JPBPY-7	Johnson pentagonal bipyramid J13	D_{5h}	9.400
	JETPY-7	Johnson elongated triangular pyramid J7	C_{3v}	18.228

Table S10. SHAPE analysis of the Gd^{III} ions in **JXUST-40a**

ions	label	Shape	symmetry	distortion(τ)
Gd1	HP-7	Heptagon	D_{7h}	31.882
	HPY-7	Hexagonal pyramid	C_{6v}	20.265
	PBPY-7	Pentagonal bipyramid	D_{5h}	6.091
	COC-7	Capped octahedron	C_{3v}	2.508
	CTPR-7	**Capped trigonal prism**	$\boldsymbol{C_{2v}}$	**1.501**
	JPBPY-7	Johnson pentagonal bipyramid J13	D_{5h}	9.392
	JETPY-7	Johnson elongated triangular pyramid J7	C_{3v}	17.531
Gd2	OP-8	Octagon	D_{8h}	33.514
	HPY-8	Heptagonal pyramid	C_{7v}	21.895
	HBPY-8	Hexagonal bipyramid	D_{6h}	15.247
	CU-8	Cube	O_h	10.301
	SAPR-8	**Square antiprism**	$\boldsymbol{D_{4d}}$	**2.340**
	TDD-8	Triangular dodecahedron	D_{2d}	3.084
	JGBF-8	Johnson gyrobifastigium J26	D_{2d}	14.003
	JETBPY-8	Johnson elongated triangular bipyramid J14	D_{3h}	28.586

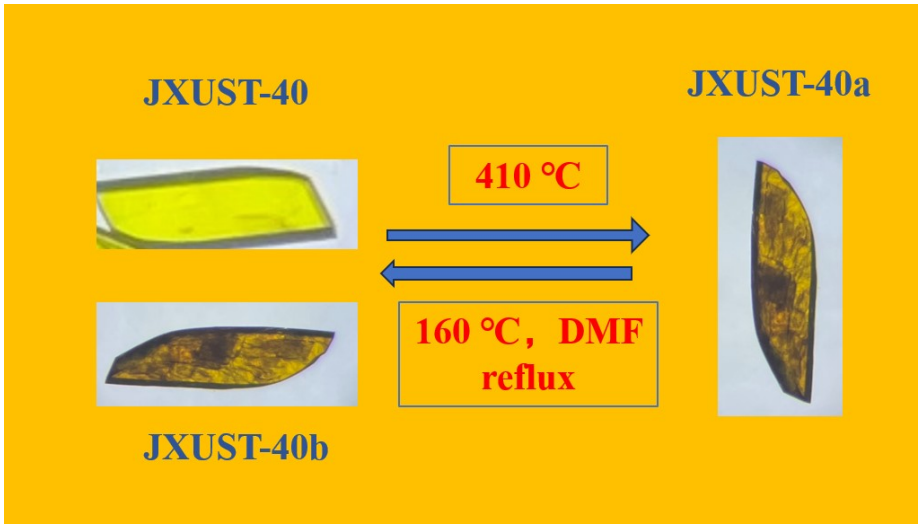


Fig. S1 Schematic diagram of the reversible transformation of **JXUST-40**, **JXUST-40a** and **JXUST-40b**

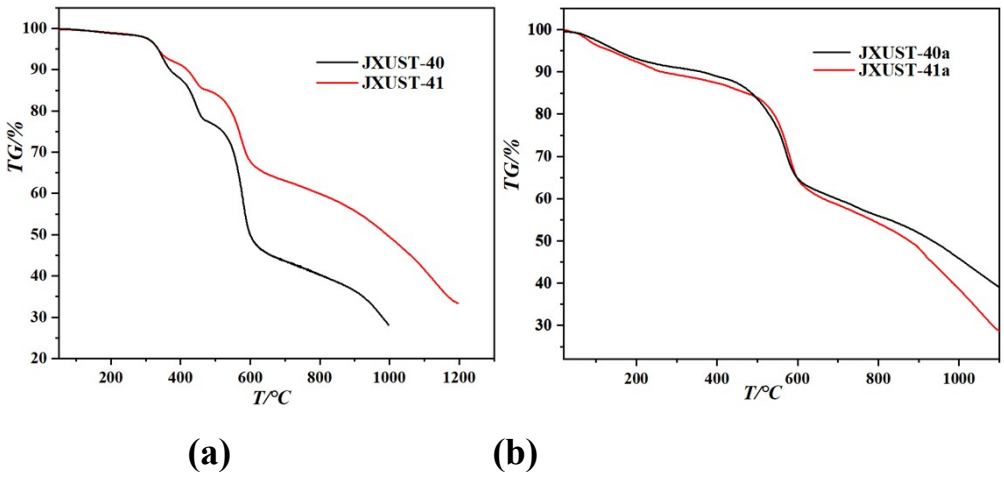
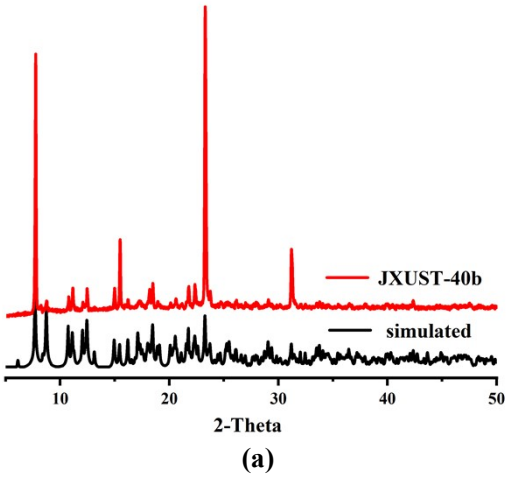
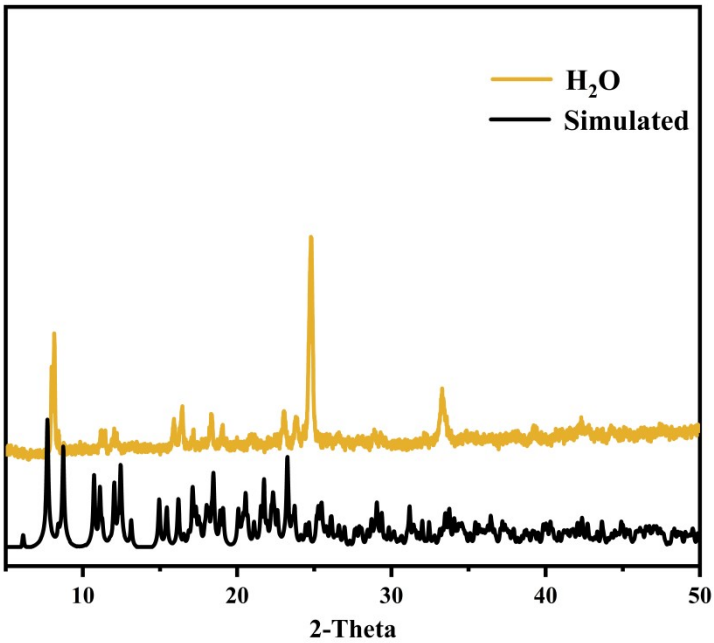


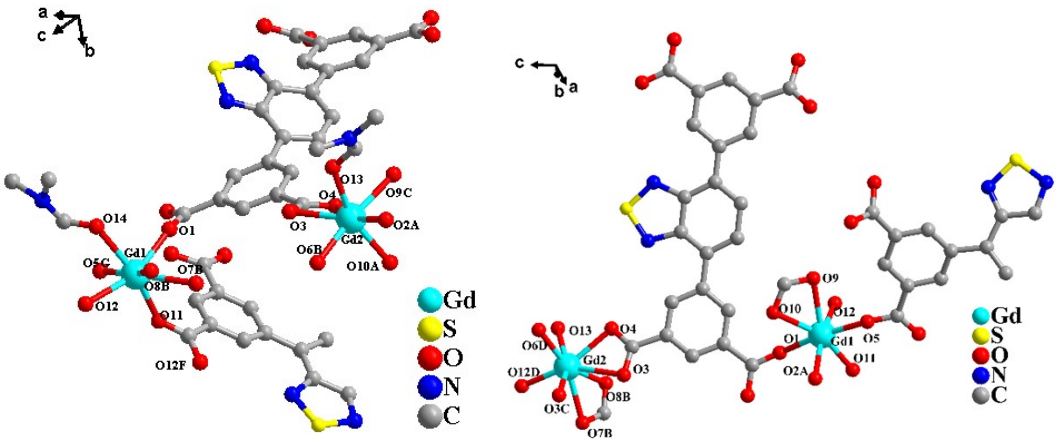
Fig. S2 (a) The TGA curves for **JXUST-40** and **JXUST-41**; (b) The TGA curves for **JXUST-40a** and **JXUST-41a**.





(b)

Fig. S3 (a) The simulated and experimental PXRD patterns of **JXUST-40b**; (b) the simulated and experimental PXRD patterns of **JXUST-40** soaked in aqueous solution for 24 h.



(a) **(b)**

Fig. S4 (a) Ball-and-stick view of the coordination environments of Gd^{III} in **JXUST-40** (symmetry codes: A: *x*, *y*, *z*+1; B: *x*-1, *y*, *z*+1; C: -*x*, -*y*+1, -*z*+2; D: *x*-1, *y*, *z*); (b) Ball-and-stick view of the coordination environments of Gd^{III} in **JXUST-40a** (symmetry codes: A: -*x*+1, -*y*+1, -*z*+2; B: -*x*+1, -*y*+1, -*z*+3; C: *x*, *y*, *z*+1; D: *x*+1, *y*, *z*+1).

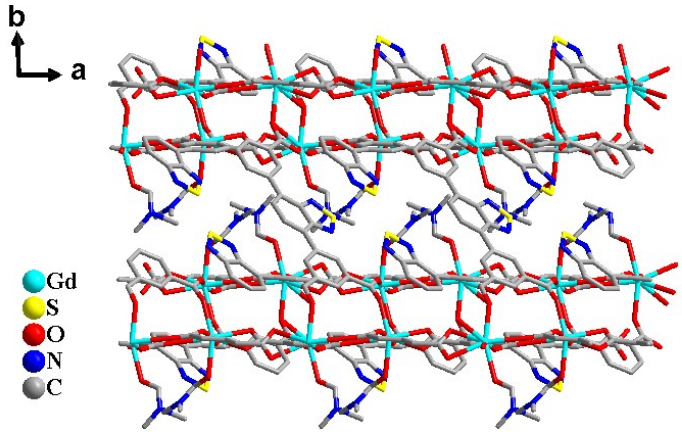


Fig. S5 View of the 3D structure of **JXUST-40** along the *c* axis.

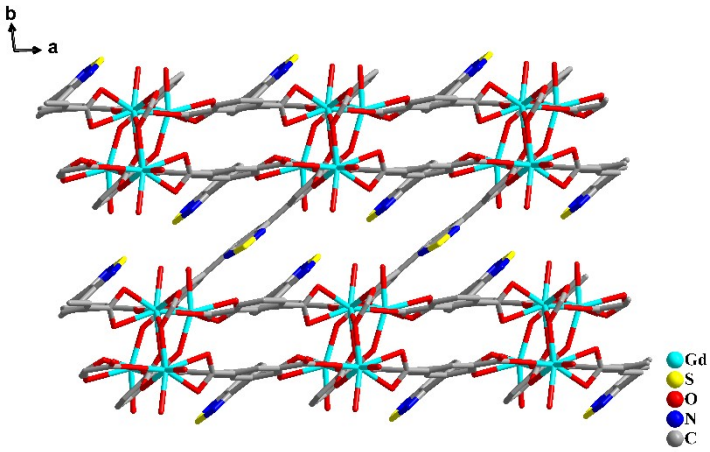
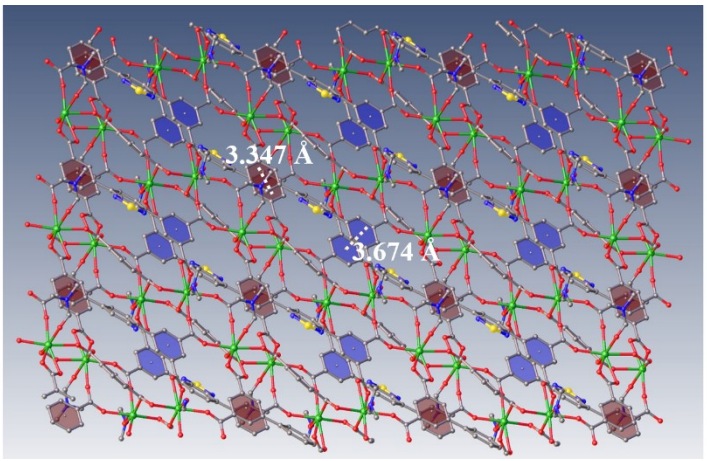
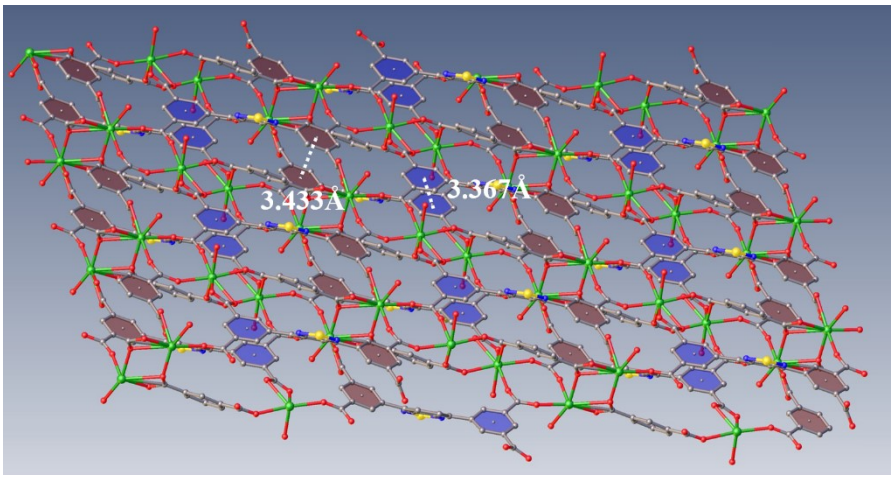


Fig. S6 View of the 3D structure of **JXUST-40a** along the *c* axis



(a)



(b)

Fig. S7 The π···π stacking structures of (a) **JXUST-40** and (b) **JXUST-40a**.

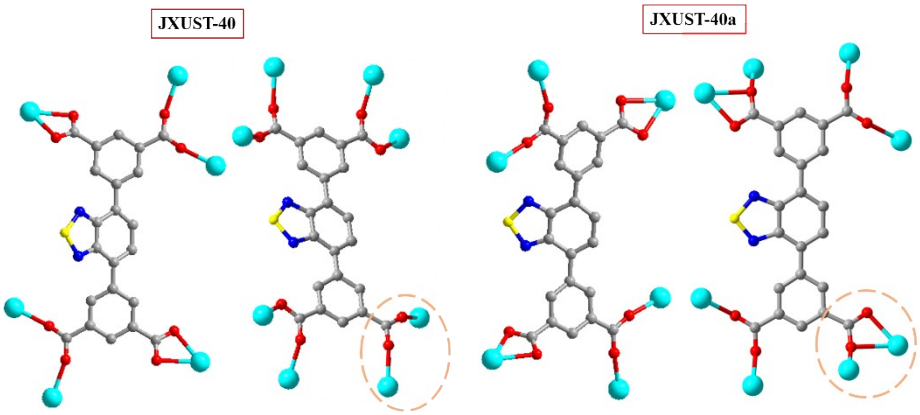


Fig. S8 The coordination modes of $BTDI^{4-}$ ligands in **JXUST-40** and **JXUST-40a**.

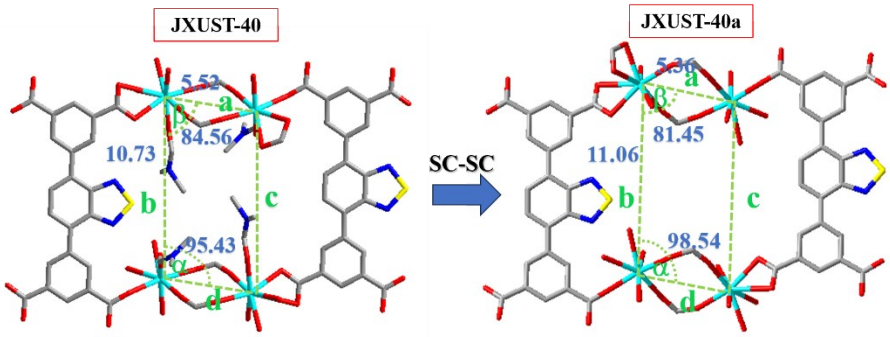


Fig. S9 Variation in bond lengths and angles of the edges of a parallelogram for **JXUST-40** and **JXUST-40a**.

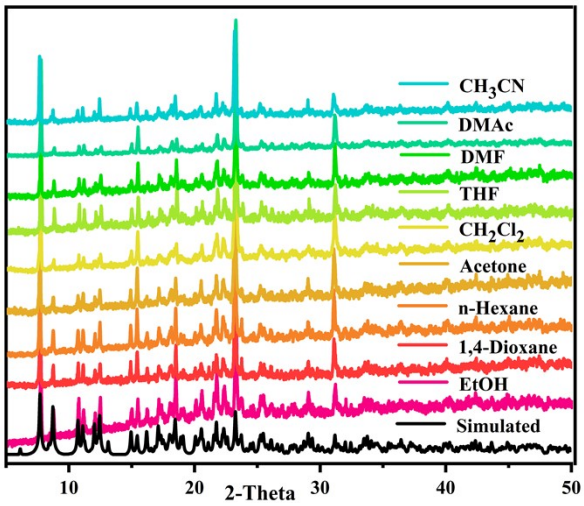


Fig. S10 The experimental PXRD patterns of **JXUST-40** soaked in common solvents.

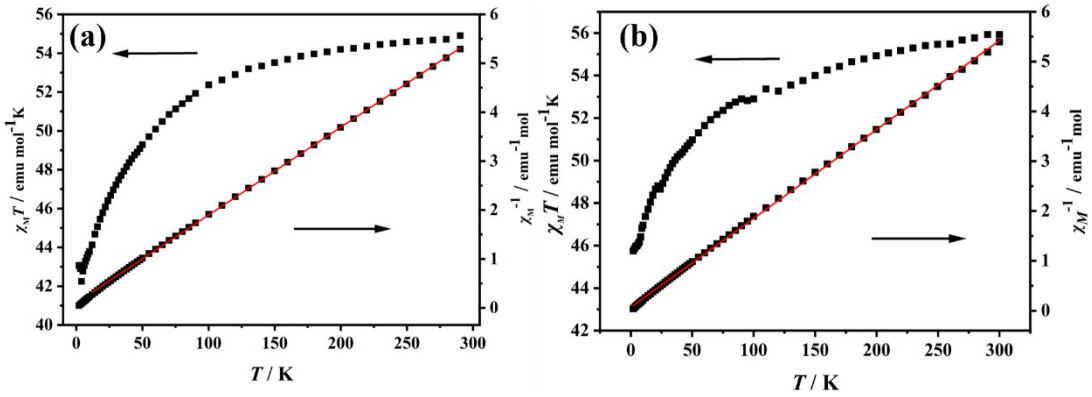


Fig. S11 Temperature dependencies of the magnetic susceptibility product ($\chi_M T$) at 2−300 K with a dc field of 1 kOe for (a) **JXUST-41** and (b) **JXUST-41a**.

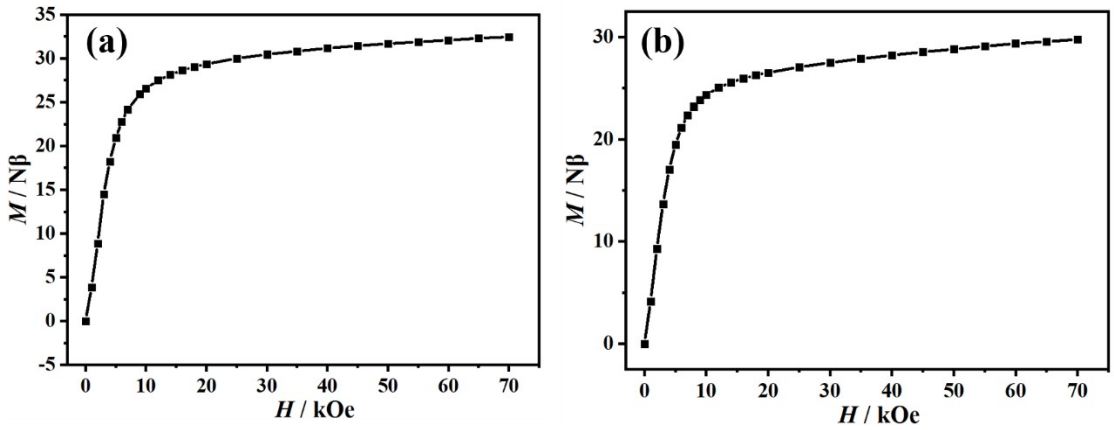


Fig. S12 The *M*−*H* plots at 2 K for (a) **JXUST-41** and (b) **JXUST-41a**.

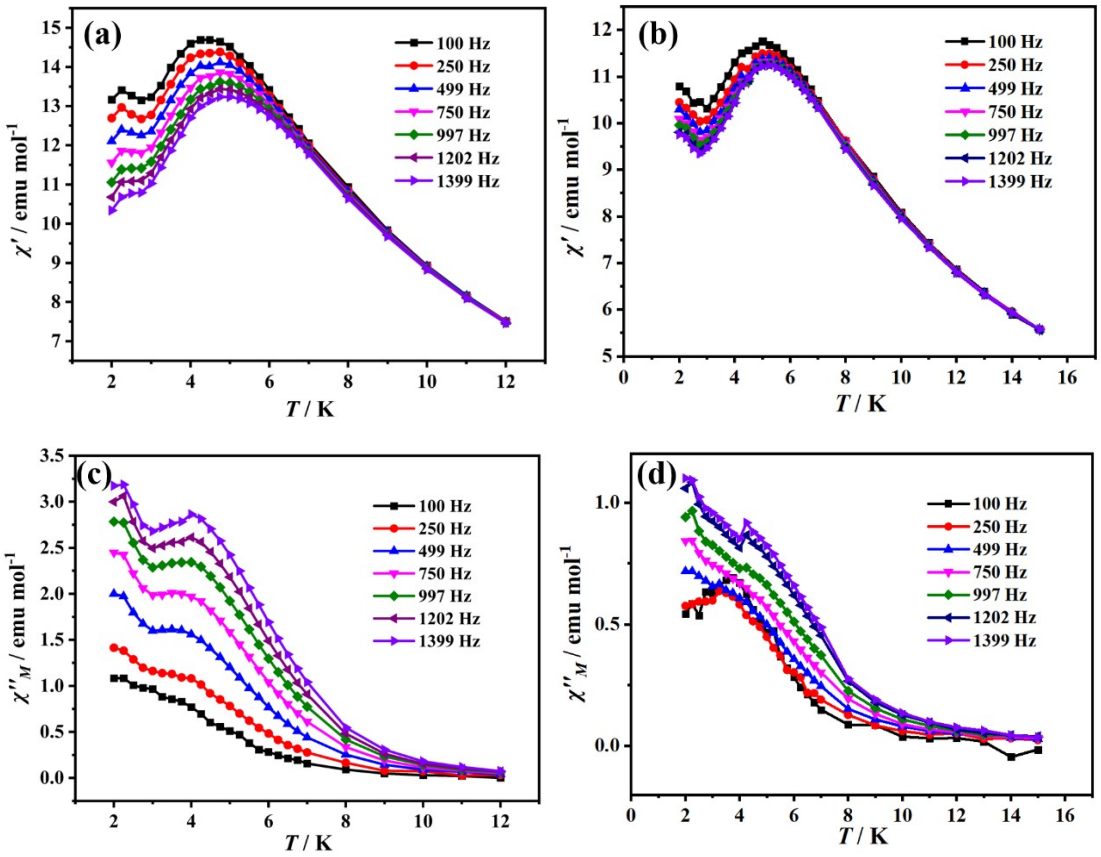


Fig. S13 Temperature dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibilities measured at varying frequencies under 2 kOe dc field for (a, c) **JXUST-41** and (b, d) **JXUST-41a**.