

## Supporting Information

### End-on Azido-Bridged 3d-4f Complexes Showing Single-Molecule Magnet Property

Xing-Cai Huang,<sup>†</sup> Chun Zhou,<sup>†</sup> Hai-Yan Wei,<sup>\*,‡</sup> and Xin-Yi Wang<sup>\*,†</sup>

<sup>†</sup>State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, China.

<sup>‡</sup> Jiangsu Key Laboratory of Biofunctional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing, 210097, China.

\*Email: weihaiyan@njnu.edu.cn; wangxy66@nju.edu.cn.

### Experimental Section

All preparations and manipulations were performed under aerobic conditions. The starting material Cu(valpn)·3.5H<sub>2</sub>O and Zn(valpn)·H<sub>2</sub>O was synthesized following a published method.<sup>S1</sup>

**[Cu<sub>2</sub>(valpn)<sub>2</sub>Tb<sub>2</sub>(N<sub>3</sub>)<sub>6</sub>]·2CH<sub>3</sub>OH, 1:** A solution of Cu(valpn)·3.5H<sub>2</sub>O (47 mg, 0.1 mmol) and TbCl<sub>3</sub>·6H<sub>2</sub>O (38 mg, 0.1 mmol) in methanol (5 mL) was layered with a solution of NaN<sub>3</sub> (33 mg, 0.5 mmol) in methanol (7 mL) and left undisturbed. Dark green column shaped crystals suitable for single crystal X-ray diffraction formed after one day. The crystals were filtered off, washed with methanol, and dried in air. Yield: 74 mg, 51%. IR (KBr): 2062 (vs) for ν(N<sub>3</sub><sup>-</sup>); elemental analysis calcd (%) for Cu<sub>2</sub>Tb<sub>2</sub>C<sub>40</sub>H<sub>48</sub>N<sub>22</sub>O<sub>10</sub>: C 33.32, H 3.36, N 21.37; found: C 32.85, H 3.23, N 21.51.

**[Zn<sub>2</sub>(valpn)<sub>2</sub>Tb<sub>2</sub>(N<sub>3</sub>)<sub>6</sub>]·2CH<sub>3</sub>OH, 2:** A solution of Zn(valpn)·H<sub>2</sub>O (43 mg, 0.1 mmol) and TbCl<sub>3</sub>·6H<sub>2</sub>O (38 mg, 0.1 mmol) in 5 mL methanol was added to a solution of *n*Bu<sub>4</sub>NN<sub>3</sub> (285 mg, 1 mmol) in 5 mL methanol and acetonitrile (V(MeOH)/V(MeCN) = 1:1). The resultant yellow solution was left undisturbed. Yellow block-shaped crystals suitable for X-ray diffraction formed after one day. The crystals were filtered off, washed with methanol, and dried in air. Yield: 82 mg, 54%. Elemental analysis for [Zn<sub>2</sub>(valpn)<sub>2</sub>Tb<sub>2</sub>(N<sub>3</sub>)<sub>6</sub>]·2CH<sub>3</sub>OH: calcd. (found) C, 33.23 (33.15); N, 21.26 (20.46); H, 3.61 (3.38%). IR (KBr pellets, cm<sup>-1</sup>): 2071 (vs) for ν(N<sub>3</sub><sup>-</sup>).

**[Cu<sub>2</sub>(valpn)<sub>2</sub>Gd<sub>2</sub>(N<sub>3</sub>)<sub>6</sub>]·2CH<sub>3</sub>OH, 3.** The same procedure was used to synthesize **1** except that TbCl<sub>3</sub>·6H<sub>2</sub>O was used in place of GdCl<sub>3</sub>·6H<sub>2</sub>O. Yield: 76 mg, 53%. Elemental analysis for [Cu<sub>2</sub>(valpn)<sub>2</sub>Gd<sub>2</sub>(N<sub>3</sub>)<sub>6</sub>]·2CH<sub>3</sub>OH: calcd. (found) C, 33.32 (32.77); N, 21.37 (20.46); H, 3.36 (3.32)%. IR (KBr pellets, cm<sup>-1</sup>): 2064 (vs) for v(N<sub>3</sub><sup>-</sup>).

**[Zn<sub>2</sub>(valpn)<sub>2</sub>Gd<sub>2</sub>(N<sub>3</sub>)<sub>6</sub>]·2CH<sub>3</sub>OH, 4.** The same procedure was used to synthesize **2** except that TbCl<sub>3</sub>·6H<sub>2</sub>O was used in place of GdCl<sub>3</sub>·6H<sub>2</sub>O. Yield: 85 mg, 58%. Elemental analysis for [Zn<sub>2</sub>(valpn)<sub>2</sub>Gd<sub>2</sub>(N<sub>3</sub>)<sub>6</sub>]·2CH<sub>3</sub>OH: calcd. (found) C, 33.31 (33.34); N, 21.37 (20.23); H, 3.35 (3.32)%. IR (KBr pellets, cm<sup>-1</sup>): 2074 (vs) for v(N<sub>3</sub><sup>-</sup>).

### Physical Measurements

Elemental analyses were carried out a Vario EL II Elementar. Infrared spectra were obtained on a Bruker Tensor 27 FT-IR spectrometer. Powder X-ray diffraction (PXRD) were recorded at 298 K on a Bruker D8 Advance diffractometer with Cu K $\alpha$  X-ray source (operated at 40kV and 40mA). Magnetic measurements were performed on powdered samples embedded in eicosane with Quantum Design MPMS SQUID or SQUID VSM magnetometers with field up to 7 T. All data were corrected for diamagnetism of the eicosane and the sample holder and of the constituent atoms using Pascal's constants.

### X-ray data collection, structure solution and refinement for 1-4

The X-ray data of **1** to **4** were collected on a Bruker APEX II or a Bruker APEX DUO diffractometer with a CCD area detector (MoK $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ). The APEX II program was used to determine the unit cell parameters and for data collection. The data were integrated using SAINT<sup>S2</sup> and SADABS<sup>S3</sup>. The structures for all four compounds were solved by direct methods and refined by full-matrix least-squares based on F<sup>2</sup> using the SHELXTL program<sup>S4</sup>. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were refined as riding on the corresponding non-hydrogen atoms. Hydrogen atoms of the OH groups of the methanol are located from the difference Fourier maps and refined isotropically. Additional details of the data collections

and structural refinement parameters are provided in Table S2. Selected bond lengths and bond angles are listed in Table S3. CCDC-928330 (**1**), CCDC-928331 (**2**), CCDC-928332 (**3**) and CCDC-928333(**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### DFT Calculation of the Mulliken charges of the coordinated atoms of **1**

The calculations in the present study were carried out using density functional theory with UB3PW91 functional implemented in the Gaussian 09 program package.<sup>S5</sup> The atomic coordinates of the complex were taken from the X-ray structural analysis results described in the manuscript. The CEP-121G Stevens/Basch/Krauss ECP triple split basis set<sup>S6</sup> was used throughout the calculation, along with assigning 5D and 7F keywords for pure d and f functions. First, an initial <sup>8</sup>A electron configuration was generated by an extended Hückel guess, then the occupancies of orbitals were altered to provide the (Cu3d)<sup>9</sup>(Tb4f)<sup>8</sup> electron configuration as an SCF starting point. Then the geometry optimization was carried out using tight convergence criteria and QC option. The population analyses were then carried out to obtain the Mulliken charge.

**Table S1** Reported Azido-Bridged Lanthanides SMMs in the literatures

Compound	Abbrev.	Bridged groups	$U_{\text{eff}}(\text{K})$	$\tau_0(\text{s})$	Hysteresis loop	Ref.
[Cu <sub>2</sub> (valpn) <sub>2</sub> Tb <sub>2</sub> (N <sub>3</sub> ) <sub>6</sub> ]·2CH <sub>3</sub> OH	Cu <sub>2</sub> Tb <sub>2</sub>	Only -N <sub>3</sub>	30.1	1.1×10 <sup>-6</sup>	Yes, up to 2.4K	This work
[Dy <sub>8</sub> (bpt) <sub>8</sub> (μ <sub>4</sub> -O) <sub>2</sub> (μ-O <i>M</i> e) <sub>8</sub> (μ <sub>1,3,3-</sub> N <sub>3</sub> )(μ <sub>1,3</sub> -N <sub>3</sub> )(N <sub>3</sub> ) <sub>2</sub> ]·1H <sub>2</sub> O·9MeOH	Dy <sub>8</sub>	-NN, -O <sub>2</sub> -N <sub>3</sub>	9.83	1.63×10 <sup>-5</sup>	No	2g
[Fe <sub>6</sub> Dy <sub>3</sub> (C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> )(tea) <sub>2</sub> (teaH) <sub>4</sub> (N <sub>3</sub> ) <sub>2</sub> (N <sub>3</sub> ) <sub>6</sub> (NO <sub>3</sub> )] <cdot2etoh< td=""><td>Fe<sub>6</sub>Dy<sub>3</sub></td><td>O,-N<sub>3</sub></td><td>65.1</td><td>1.64×10<sup>-12</sup></td><td>No</td><td>2f</td></cdot2etoh<>	Fe <sub>6</sub> Dy <sub>3</sub>	O,-N <sub>3</sub>	65.1	1.64×10 <sup>-12</sup>	No	2f
[Dy <sub>3</sub> (N <sub>3</sub> )(OH)(H <sub>2</sub> L) <sub>3</sub> (SCN) <sub>3</sub> ]·(SCN)·3CH <sub>3</sub> OH·H <sub>2</sub> O	Dy <sub>3</sub>	-OH, -N <sub>3</sub>	-	-	No	2e
[Dy <sub>4</sub> (L1-2H) <sub>2</sub> (L1-H) <sub>2</sub> (N <sub>3</sub> ) <sub>4</sub> (O)]·14H <sub>2</sub> O	Dy <sub>4</sub>	O, -N <sub>3</sub>	51(low) 91(high)	3.0×10 <sup>-9</sup> 4.5×10 <sup>-7</sup>	No	2d
[Cr <sup>III</sup> Dy <sub>4</sub> (OH) <sub>4</sub> (N <sub>3</sub> ) <sub>4</sub> (mdea) <sub>4</sub> (piv) <sub>4</sub> ]·3CH <sub>2</sub> Cl <sub>2</sub>	Cr <sup>III</sup> <sub>4</sub> Dy <sub>4</sub>	-OH, -N <sub>3</sub>	15	1.9×10 <sup>-10</sup>	No	2c
[Zn <sub>2</sub> Dy <sub>3</sub> (m-salen) <sub>3</sub> (N <sub>3</sub> ) <sub>5</sub> (OH) <sub>2</sub> ]	Zn <sub>2</sub> Dy <sub>3</sub>	-OH, -N <sub>3</sub>	13.4	3.3×10 <sup>-7</sup>	Yes, below 1.8k	2b
[Mn <sup>III</sup> <sub>12</sub> Mn <sup>II</sup> <sub>6</sub> Dy(O) <sub>8</sub> (Cl) <sub>6,5</sub> (N <sub>3</sub> ) <sub>1,5</sub> (HL) <sub>12</sub> (MeOH) <sub>6</sub> ]Cl <sub>3</sub> ·25MeOH	Mn <sub>18</sub> Dy	-O,-Cl,-N <sub>3</sub>	-	-	No	2a

**Table S2** Crystallographic data for **1** to **4**.

complex	<b>1<sub>CuTb</sub></b>	<b>2<sub>ZnTb</sub></b>	<b>3<sub>CuGd</sub></b>	<b>4<sub>ZnGd</sub></b>
Formula	Cu <sub>2</sub> Tb <sub>2</sub> C <sub>40</sub> H <sub>48</sub> N <sub>22</sub> O <sub>10</sub>	Zn <sub>2</sub> Tb <sub>2</sub> C <sub>40</sub> H <sub>48</sub> N <sub>22</sub> O <sub>10</sub>	Cu <sub>2</sub> Gd <sub>2</sub> C <sub>40</sub> H <sub>48</sub> N <sub>22</sub> O <sub>10</sub>	Zn <sub>2</sub> Gd <sub>2</sub> C <sub>40</sub> H <sub>48</sub> N <sub>22</sub> O <sub>10</sub>
Mr [gmol <sup>-1</sup> ]	1441.92	1445.58	1438.58	1442.24
CCDC	928330	928331	928332	928333
Crystal size[mm <sup>3</sup> ]	0.18×0.08×0.08	0.20×0.18×0.12	0.18×0.14×0.14	0.12×0.10×0.08
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	10.6560(3)	10.741(3)	10.630(3)	10.686(9)
<i>b</i> [Å]	10.8760(3)	10.934(3)	10.851(3)	10.824(8)
<i>c</i> [Å]	12.3847(4)	12.238(4)	12.384(3)	12.233(9)
$\alpha$ [°]	74.0420(10)	73.608(5)	74.007(3)	73.706(18)
$\beta$ [°]	84.6710(10)	84.116(5)	84.685(4)	84.235(18)
$\gamma$ [°]	64.2670(10)	63.646(4)	64.286(3)	63.724(16)
<i>V</i> [Å <sup>3</sup> ]	1242.57(6)	1235.1(7)	1236.5(6)	1217.3(16)
<i>Z</i>	1	1	1	1
<i>T</i> , K	173(2)	293(2)	293(2)	173(2)
$\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ]	1.927	1.944	1.932	1.967
$\mu(\text{Mo}-K\alpha)$ [mm <sup>-1</sup> ]	3.735	3.867	3.575	3.743
<i>F</i> (000)	710	712	708	710
$\theta$ range [°]	1.71 – 27.63	1.74 – 27.92	1.71 – 27.70	1.73 – 28.41
Refl. collected / unique	34123/5710	15436 / 5829	16116 / 5751	12524 / 6030
R(int)	0.0323	0.0379	0.0267	0.0653
<i>T</i> <sub>max</sub> / <i>T</i> <sub>min</sub>	0.7543 / 0.5529	0.6540 / 0.5118	0.6345 / 0.5655	0.7539 / 0.6622
Data/restraints/parameters	5710 / 13 / 348	5829 / 0 / 348	5751 / 0 / 348	6030 / 0 / 348
<i>R</i> <sub>1</sub> <sup>a</sup> / <i>wR</i> <sub>2</sub> <sup>b</sup> ( <i>I</i> > 2σ( <i>I</i> ) )	0.0275 / 0.0549	0.0314 / 0.0677	0.0253 / 0.0596	0.0483 / 0.0949
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.0355 / 0.0576	0.0384 / 0.0705	0.0283 / 0.0608	0.0635 / 0.1019
GOF on <i>F</i> <sup>2</sup>	1.036	1.015	1.030	0.976
Max/min [e Å <sup>-3</sup> ]	0.586 / -0.732	0.762 / -0.538	1.013 / -0.448	1.185 / -1.011

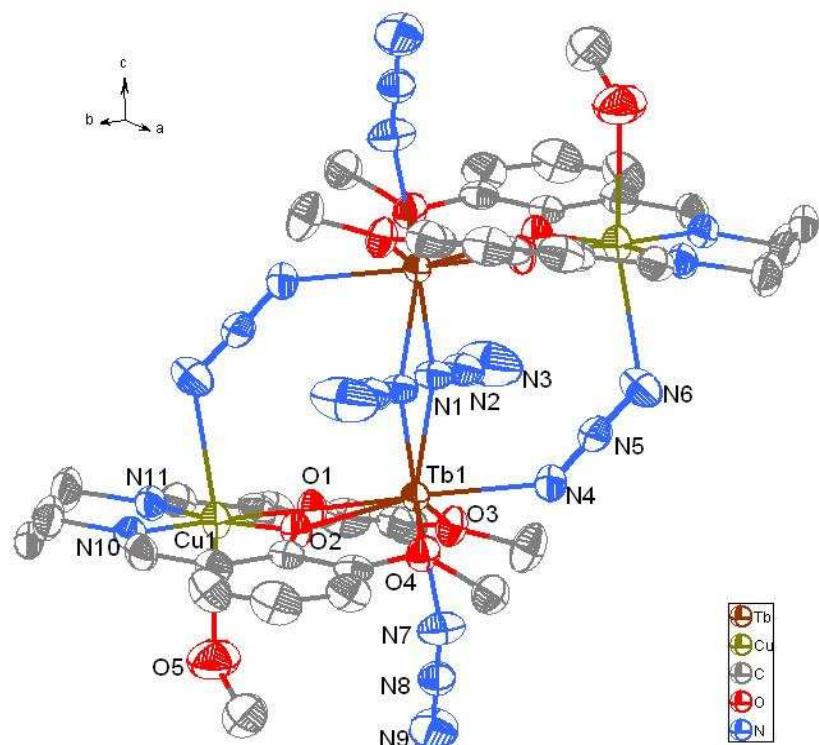
<sup>a</sup>  $R_1 = \sum |F_o| - |F_c| / |\sum F_o|$ . <sup>b</sup>  $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]^2\}^{1/2}$

**Table S3** Selected Bond Lengths (Å) and Angles(°) for **1** to **4**.

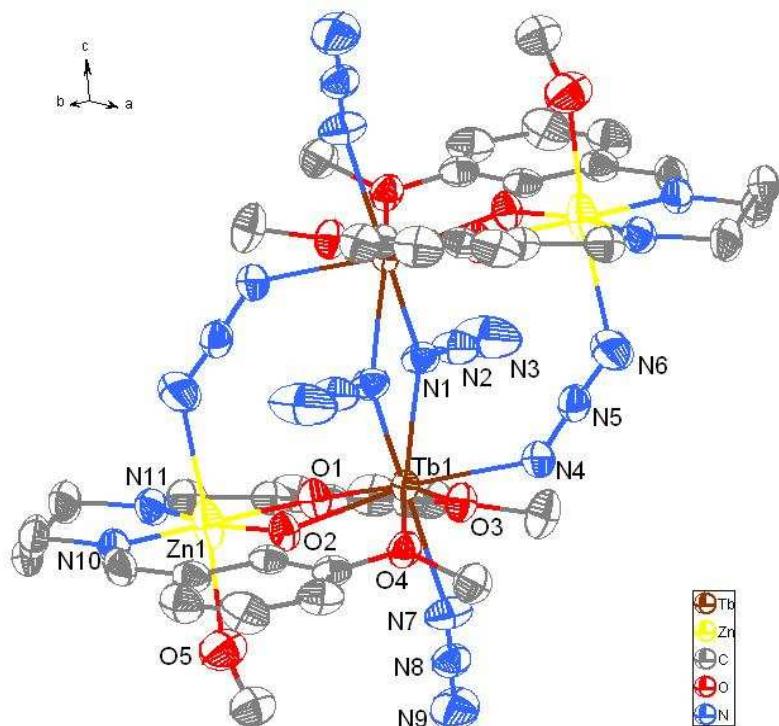
<b>1<sub>CuTb</sub></b>					
Tb1-O1	2.3404(19)	Tb1-N1	2.434(3)	Tb1-O3	2.534(2)
Tb1-O2	2.343(2)	Tb1-N1 <sup>a</sup>	2.456(3)	Tb1-O4	2.546(2)
Tb1-N4	2.366(3)	Tb1-N7	2.398(3)	Cu1-O1	1.966(2)
Cu1-O2	1.967(2)	Cu1-N11	1.991(3)	Cu1-N10	1.993(3)
Tb1-Cu1	3.4880(4)				
O1-Tb1-O2	64.25(7)	O2-Tb1-N7	86.76(9)	N4-Tb1-N1	87.20(10)
O1-Tb1-N4	148.61(9)	N4-Tb1-N7	85.41(11)	N7-Tb1-N1	146.34(10)
O2-Tb1-N4	146.06(9)	O1-Tb1-N1	112.00(8)	O1-Tb1-N1 <sup>a</sup>	83.99(8)
O1-Tb1-N7	90.33(9)	O2-Tb1-N1	81.30(8)	O2-Tb1-N1 <sup>a</sup>	121.65(8)
N4-Tb1-N1 <sup>a</sup>	81.39(10)	O2-Tb1-O3	123.28(7)	N1 <sup>a</sup> -Tb1-O3	73.85(8)
N7-Tb1-N1 <sup>a</sup>	143.84(10)	N4-Tb1-O3	85.06(9)	O1-Tb1-O4	125.90(7)
N1-Tb1-N1 <sup>a</sup>	66.48(10)	N7-Tb1-O3	71.58(9)	O2-Tb1-O4	64.66(7)
O1-Tb1-O3	64.18(7)	N1-Tb1-O3	140.27(8)	N7-Tb1-O4	70.22(9)
N4-Tb1-O4	81.63(9)	O1-Cu1-O2	78.57(8)	O2-Cu1-N10	92.19(10)
N1-Tb1-O4	76.23(8)	O1-Cu1-N11	91.04(10)	N11-Cu1-N10	98.16(11)
N1 <sup>a</sup> -Tb1-O4	139.52(8)	O2-Cu1-N11	169.22(10)	O1-Cu1-Tb1	39.69(6)
O3-Tb1-O4	140.32(7)	O1-Cu1-N10	170.75(10)		
Tb1-N1-Tb1 <sup>a</sup>	113.52(10)	Cu1-O2-Tb1	107.75(8)	Cu1-O1-Tb1	107.86(8)
<b>2<sub>ZnTb</sub></b>					
Tb1-O1	2.305(2)	Tb1-N1 <sup>a</sup>	2.476(3)	Zn1-O1	2.034(3)
Tb1-O2	2.321(2)	Tb1-O3	2.541(2)	Zn1-N10	2.037(3)
Tb1-N7	2.384(3)	Tb1-O4	2.564(3)	Zn1-O5	2.272(3)

Tb1-N4	2.385(3)	Zn1-O2	2.026(2)	Zn1-N6 <sup>a</sup>	2.448(5)
Tb1-N1	2.442(3)	Zn1-N11	2.031(3)	Tb1-Zn1	3.4984(10)
O1-Tb1-O2	66.76(8)	O2-Tb1-N4	144.66(11)	N7-Tb1-N1	146.34(11)
O1-Tb1-N7	92.06(11)	N7-Tb1-N4	85.15(12)	N4-Tb1-N1	85.42(12)
O2-Tb1-N7	88.42(11)	O1-Tb1-N1	112.31(10)	O1-Tb1-N1 <sup>a</sup>	83.37(10)
O1-Tb1-N4	148.05(11)	O2-Tb1-N1	80.94(10)	O2-Tb1-N1 <sup>a</sup>	122.50(10)
N7-Tb1-N1 <sup>a</sup>	142.76(12)	O2-Tb1-O3	125.22(8)	N1 <sup>a</sup> -Tb1-O3	73.22(9)
N4-Tb1-N1 <sup>a</sup>	79.96(11)	N7-Tb1-O3	71.70(11)	O1-Tb1-O4	127.62(8)
N1-Tb1-N1 <sup>a</sup>	66.21(12)	N4-Tb1-O3	85.36(11)	O2-Tb1-O4	63.81(8)
O1-Tb1-O3	63.72(8)	N1-Tb1-O3	139.35(10)	N7-Tb1-O4	70.66(11)
N4-Tb1-O4	81.32(11)	O2-Zn1-N11	168.00(12)	N11-Zn1-N10	100.54(13)
N1-Tb1-O4	75.99(10)	O2-Zn1-O1	77.63(9)	O1-Zn1-N10	168.59(11)
N1 <sup>a</sup> -Tb1-O4	138.79(9)	N11-Zn1-O1	90.59(12)	O2-Zn1-O5	90.86(12)
O3-Tb1-O4	140.90(9)	O2-Zn1-N10	91.14(11)	N11-Zn1-O5	91.81(13)
O1-Zn1-O5	91.85(12)	O2-Zn1-N6 <sup>a</sup>	90.70(12)	O1-Zn1-N6 <sup>a</sup>	93.97(13)
N10-Zn1-O5	90.34(13)	N11-Zn1-N6 <sup>a</sup>	87.82(14)	O5-Zn1-N6 <sup>a</sup>	84.01(14)
O5-Zn1-N6 <sup>a</sup>	174.17(15)				
Zn1-O1-Tb1	107.29(10)	Zn1-O2-Tb1	106.96(10)	Tb1-N1-Tb1 <sup>a</sup>	113.79(12)
<b>3<sub>CuGd</sub></b>					
Gd1-O1	2.346(2)	Gd1-N1	2.458(2)	Gd1-O3	2.530(2)
Gd1-O2	2.3503(19)	Gd1-N1 <sup>a</sup>	2.481(2)	Gd1-O4	2.540(2)
Gd1-N4	2.381(3)	Gd1-N7	2.409(3)	Cu1-O1	1.961(2)
Cu1-O2	1.964(2)	Cu1-N11	1.987(3)	Cu1-N10	1.989(2)
Gd1-Cu1	3.4906(8)				
O1-Gd1-O2	64.08(7)	O2-Gd1-N7	87.61(9)	N4-Gd1-N1	86.96(9)
O1-Gd1-N4	148.82(9)	N4-Gd1-N7	85.06(10)	N7-Gd1-N1	146.00(9)
O2-Gd1-N4	146.27(9)	O1-Gd1-N1	111.57(8)	O1-Gd1-N1 <sup>a</sup>	83.61(8)
O1-Gd1-N7	91.40(9)	O2-Gd1-N1	80.98(8)	O2-Gd1-N1 <sup>a</sup>	121.34(8)
N4-Gd1-N1 <sup>a</sup>	81.15(9)	O2-Gd1-O3	123.13(7)	N1 <sup>a</sup> -Gd1-O3	73.43(7)
N7-Gd1-N1 <sup>a</sup>	143.58(9)	N4-Gd1-O3	85.51(9)	O1-Gd1-O4	125.70(7)
N1-Gd1-N1 <sup>a</sup>	66.71(9)	N7-Gd1-O3	72.00(9)	O2-Gd1-O4	64.50(7)
O1-Gd1-O3	64.06(7)	N1-Gd1-O3	140.12(8)	N4-Gd1-O4	82.07(9)
N7-Gd1-O4	70.24(9)	O1-Cu1-O2	78.80(8)	O2-Cu1-N10	91.99(9)
N1-Gd1-O4	75.94(8)	O1-Cu1-N11	90.84(10)	N11-Cu1-N10	98.35(11)
N1 <sup>a</sup> -Gd1-O4	139.60(7)	O2-Cu1-N11	169.28(9)	O1-Cu1-Gd1	39.76(6)
O3-Gd1-O4	141.04(7)	O1-Cu1-N10	170.78(10)		
Gd1-N1-Gd1 <sup>a</sup>	113.29(9)	Cu1-O2-Gd1	107.68(8)	Cu1-O1-Gd1	107.92(8)
<b>4<sub>ZnGd</sub></b>					
Gd1-O1	2.315(4)	Gd1-N1 <sup>a</sup>	2.490(5)	Zn1-O2	2.028(4)
Gd1-O2	2.327(4)	Gd1-O3	2.529(4)	Zn1-N11	2.030(5)
Gd1-N7	2.391(5)	Gd1-O4	2.553(4)	Zn1-O5	2.242(5)
Gd1-N4	2.407(5)	Zn1-N10	2.024(5)	Zn1-N6 <sup>a</sup>	2.412(6)
Gd1-N1	2.445(4)	Zn1-O1	2.027(4)	Gd1-Zn1	3.505(2)
O1-Gd1-O2	66.48(12)	O2-Gd1-N4	144.98(15)	N7-Gd1-N1	146.34(15)
O1-Gd1-N7	93.41(15)	N7-Gd1-N4	84.98(18)	N4-Gd1-N1	85.59(17)
O2-Gd1-N7	89.06(17)	O1-Gd1-N1	111.03(15)	O1-Gd1-N1 <sup>a</sup>	83.09(14)
O1-Gd1-N4	148.23(16)	O2-Gd1-N1	80.50(15)	O2-Gd1-N1 <sup>a</sup>	122.60(14)
N7-Gd1-N1 <sup>a</sup>	142.37(16)	O2-Gd1-O3	124.50(13)	N1 <sup>a</sup> -Gd1-O3	73.35(13)
N4-Gd1-N1 <sup>a</sup>	79.23(16)	N7-Gd1-O3	71.66(15)	O1-Gd1-O4	127.62(13)
N1-Gd1-N1 <sup>a</sup>	66.27(17)	N4-Gd1-O3	86.07(16)	O2-Gd1-O4	63.76(13)
O1-Gd1-O3	63.54(13)	N1-Gd1-O3	139.61(14)	N7-Gd1-O4	70.77(15)
N4-Gd1-O4	81.76(16)	N10-Zn1-O1	168.69(17)	O1-Zn1-N11	90.52(18)
N1-Gd1-O4	75.93(14)	N10-Zn1-O2	91.08(17)	O2-Zn1-N11	168.03(18)
N1 <sup>a</sup> -Gd1-O4	138.61(13)	O1-Zn1-O2	77.74(14)	N10-Zn1-O5	91.05(19)
O3-Gd1-O4	141.30(13)	N10-Zn1-N11	100.6(2)	O1-Zn1-O5	90.82(18)
O2-Zn1-O5	90.88(17)	N10-Zn1-N6 <sup>a</sup>	84.0(2)	O2-Zn1-N6 <sup>a</sup>	90.56(17)
N11-Zn1-O5	91.65(19)	O1-Zn1-N6 <sup>a</sup>	94.25(19)	N11-Zn1-N6 <sup>a</sup>	87.94(19)
O5-Zn1-N6 <sup>a</sup>	174.9(2)				
Zn1-O1-Gd1	107.48(15)	Zn1-O2-Gd1	107.02(15)	Gd1-N1-Gd1 <sup>a</sup>	113.73(17)

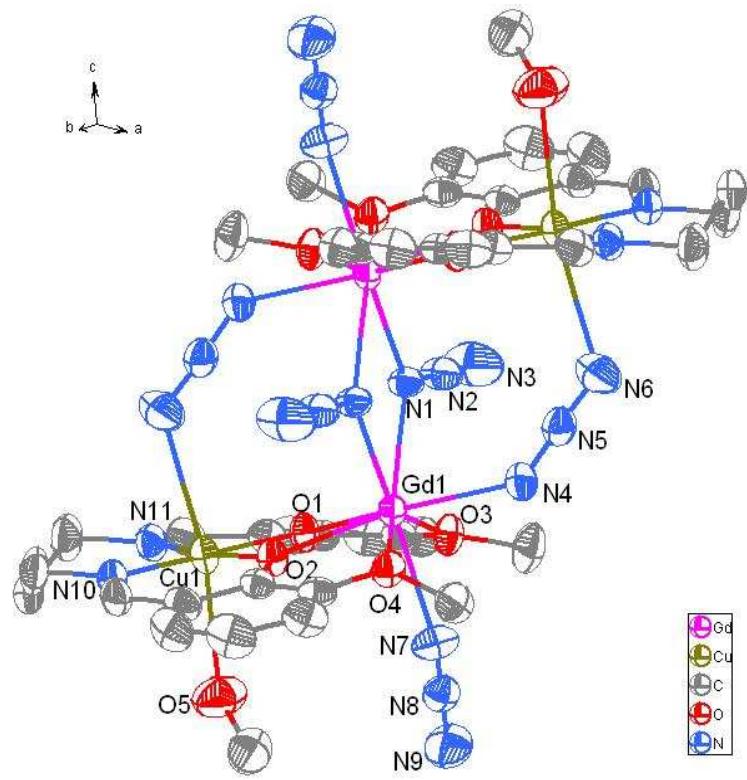
$$\mathbf{a} = \{1-x, 1-y, 1-z\}$$



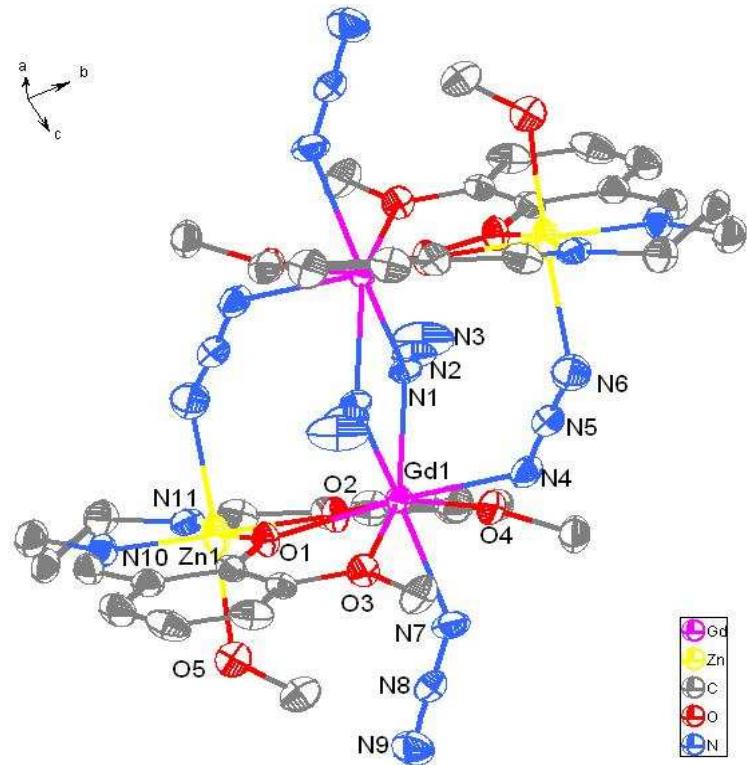
**Figure S1.** The molecular structure of 1. H atoms are not shown for the sake of clarity.



**Figure S2.** The molecular structure of 2. H atoms are not shown for the sake of clarity.

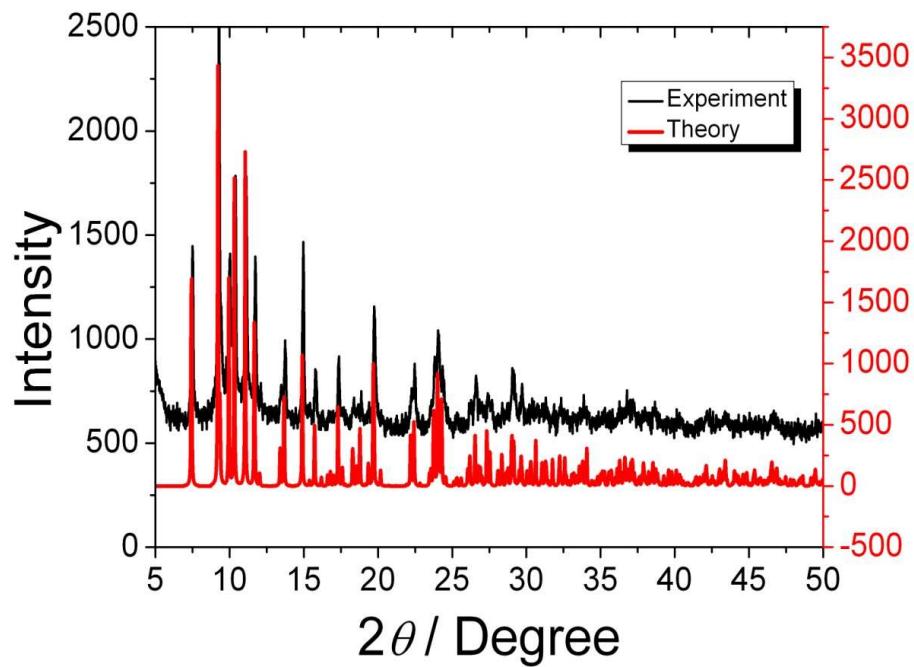


**Figure S3.** The molecular structure of **3**. H atoms are not shown for the sake of clarity.

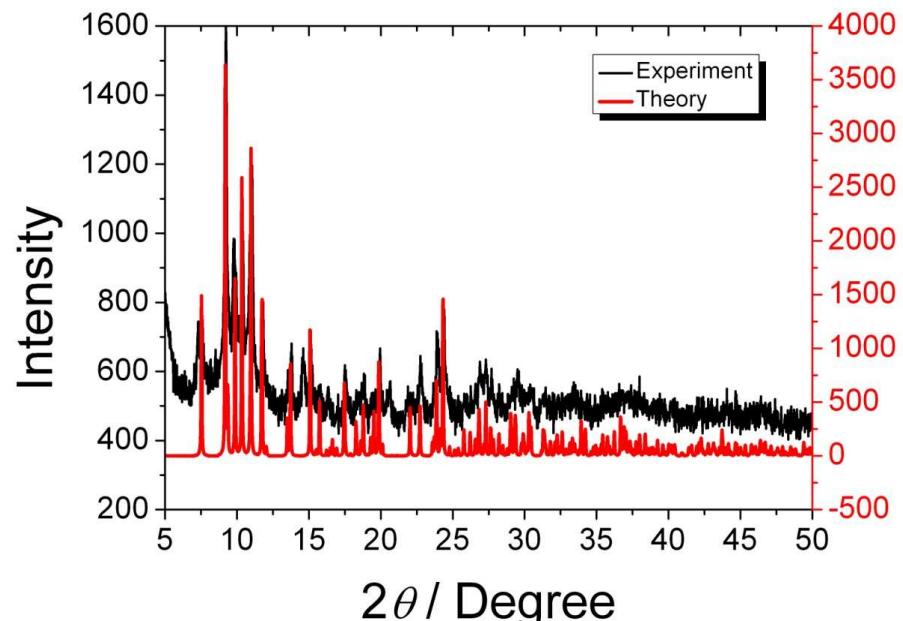


**Figure S4.** The molecular structure of **4**. H atoms are not shown for the sake of clarity.

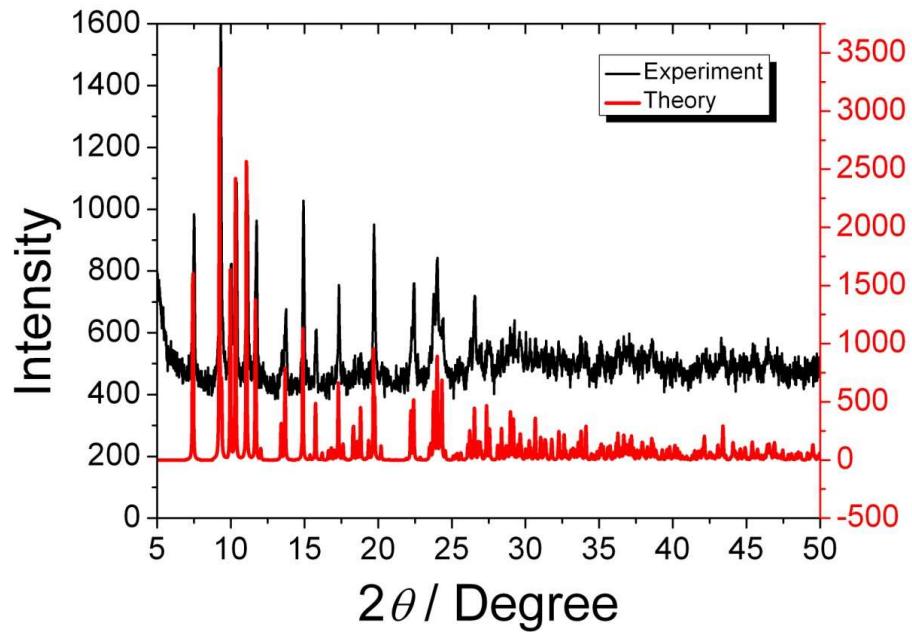
Powder X-ray diffraction (PXRD) spectra of 1 to 4



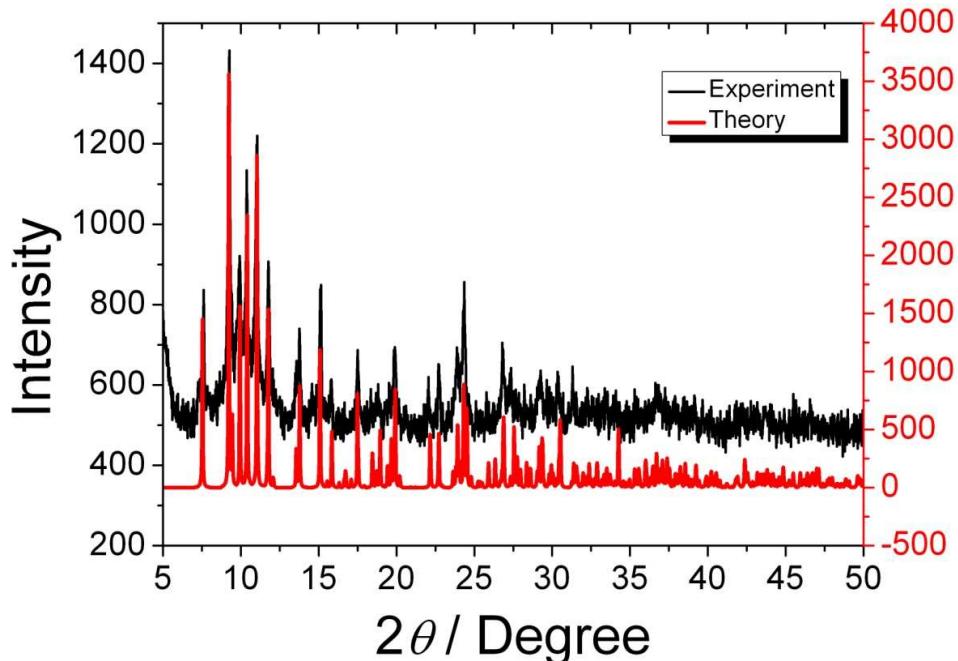
**Figure S5.** X-ray powder diffraction pattern of compound **1** at room temperature, together with the calculated pattern from the single crystal data.



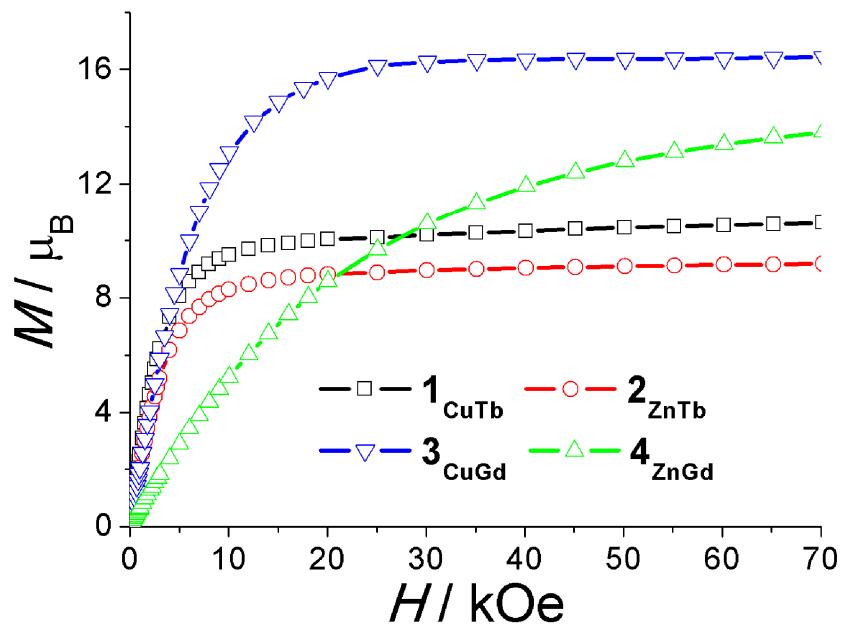
**Figure S6.** X-ray powder diffraction pattern of compound **2** at room temperature, together with the calculated pattern from the single crystal data.



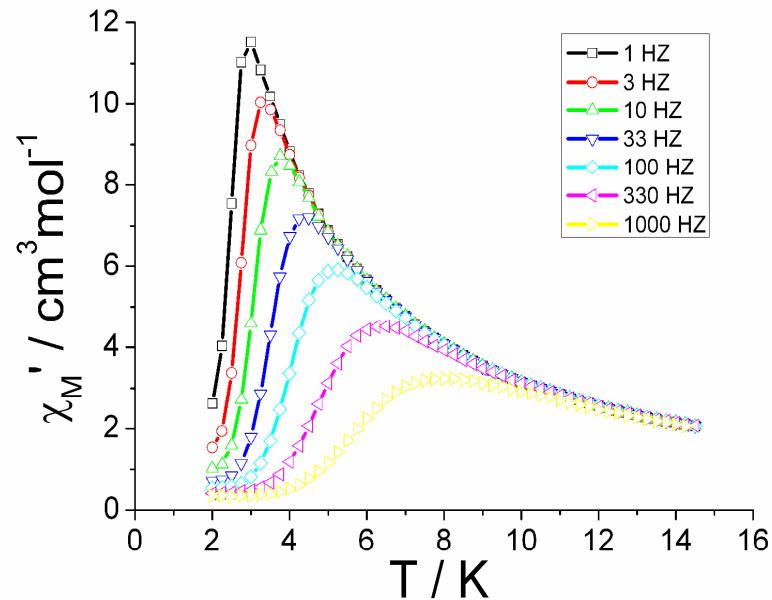
**Figure S7.** X-ray powder diffraction pattern of compound **3** at room temperature, together with the calculated pattern from the single crystal data.



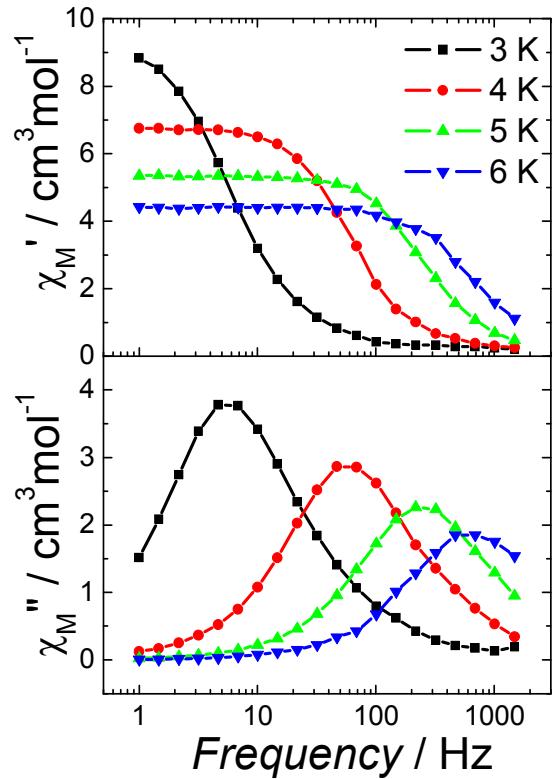
**Figure S8.** X-ray powder diffraction pattern of compound **4** at room temperature, together with the calculated pattern from the single crystal data.



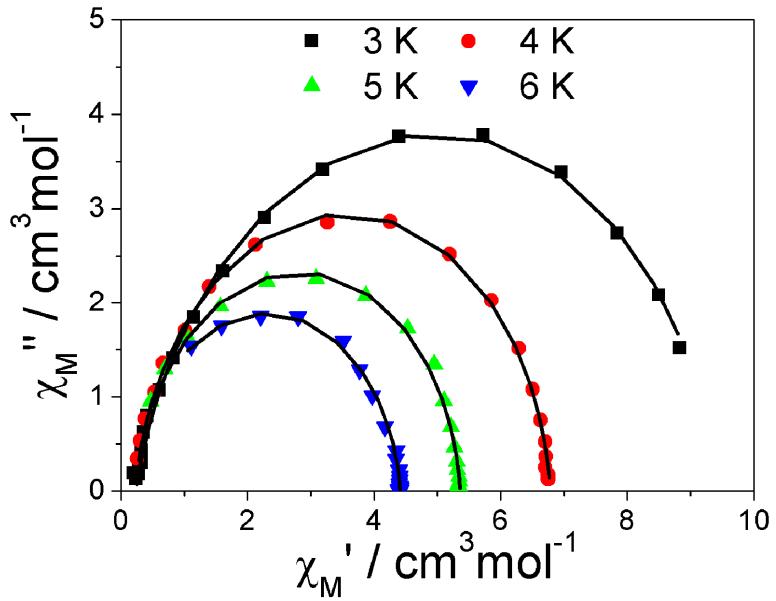
**Figure S9.** Field dependence of the magnetization data for **1-4** at 2.0 K.



**Figure S10.** Temperature dependence of the in-phase *a.c.* susceptibilities for **1** under  $H_{\text{ac}} = 3 \text{ Oe}$  and  $H_{\text{dc}} = 0 \text{ Oe}$ .



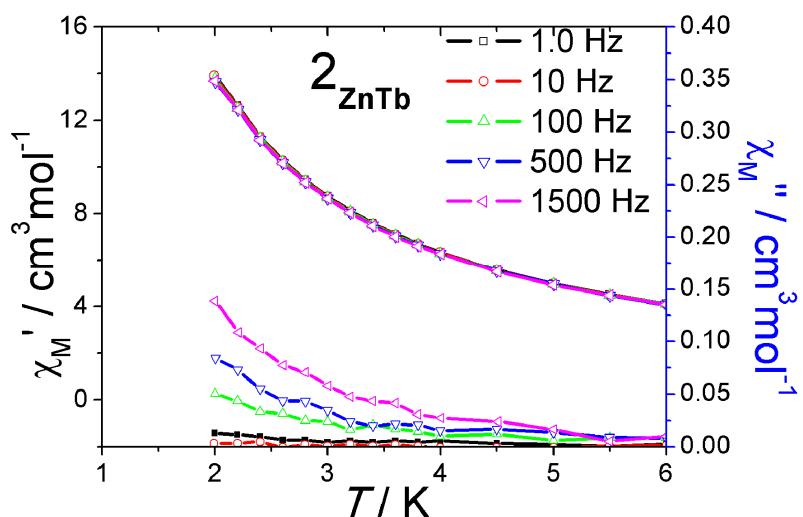
**Figure S11.** Frequency dependence of the ac susceptibilities at zero dc field from 3 to 6 K for **1**.



**Figure S12.** Cole-Cole plots of **1** measured under zero d.c. field from 3 to 6 K. The lines are the best fitting according to the generalized Debye model.

**Table S4** Relaxation Fitting Parameters from the Least-Square Fitting of the Cole-Cole plots of **1** according to the Generalized Debye Model.

Temperature / K	$\chi_s / \text{cm}^3 \text{mol}^{-1} \text{K}$	$\chi_T / \text{cm}^3 \text{mol}^{-1} \text{K}$	$\tau / \text{s}$	$\alpha$
3.0	0.2313	9.39707	0.02671	0.12005
4.0	0.22286	6.77887	0.0026	0.06753
5.0	0.22893	5.35842	6.3E-4	0.06193
6.0	0.12238	4.41159	2.4E-4	0.08256



**Figure S13.** Temperature dependent ac susceptibilities at zero dc field from 2 to 6 K for **2**.

## Reference

- (S1) Pasatoiu, T. D.; Sutter, J. P.; Madalan, A. M.; Fellah, F. Z. C.; Duhayon, C.; Andruh, M. *Inorg. Chem.* **2011**, *50*, 5890.
- (S2) *SAINT* Version 7.68A, Bruker AXS, Inc.; Madison, WI **2009**.
- (S3) Sheldrick, G. M. *SADABS*, Version 2008/1, Bruker AXS, Inc.; Madison, WI **2008**.
- (S4) Sheldrick, G. M. *SHELXTL*, Version 6.14, Bruker AXS, Inc.; Madison, WI **2000-2003**.
- (S5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, J.T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross,

J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, Piskorz, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc., Pittsburgh PA, 2009.

(S6) (a) Stevens, W.; Basch, H.; Krauss, J. *J. Chem. Phys.* **1984**, 81, 6026. (b) Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, 70, 612. (c) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, 98, 5555.