Supporting Information

Construction of Multifunctional Materials Based on Tb^{3+} and Croconic Acid Directed by K^+ Cation: Synthesis, Structures Fluorescent, Magnetic and Ferroelectric Behaviors

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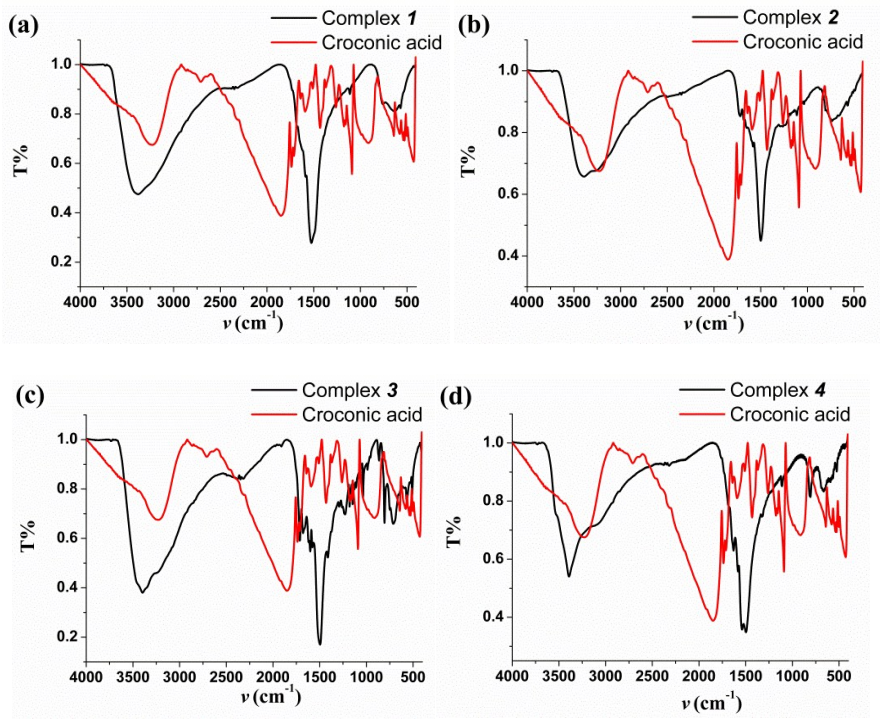


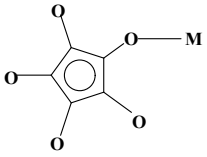
Fig. S1 IR curves of **1** (a), **2** (b), **3** (c), **4** (d) and the croconic acid ligand.

Table S1 The main FT-IR vibrations of the ligand and complexes **1-4** (cm^{-1})

Vibration Fashion	Ligand	**1**	**2**	**3**	**4**
υ_{O-H}	3236 s, br	3381 s, br	3395 s, br	3397 s, br	3392 s
$\upsilon_{C=O}$	1850 s, br	1525 s	1500 s	1496 s	1540 and 1497 s, sh
$\upsilon_{C=C}$	1450 m, 1512 w, 1598 w	covered	covered	covered	covered
υ_{C-O}	1100 m	1113 w	1113 w	1111 w	1111 w

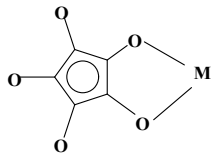
S (strong), m (medium), w (weak), br (broad), sh (shoulder).

Monodentate ligand



I

Bidentate ligand



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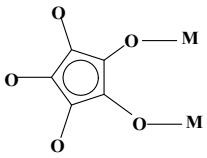

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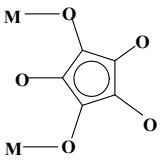

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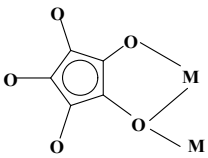
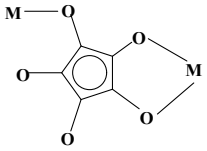


V

Tridentate ligand



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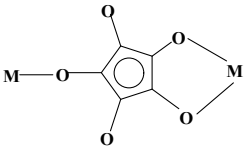

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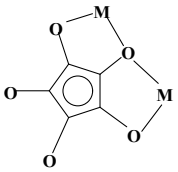

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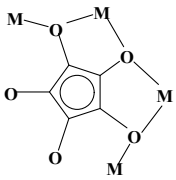

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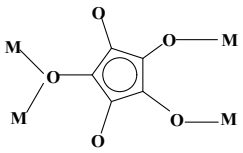

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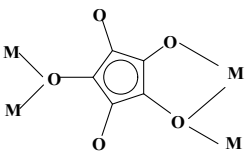

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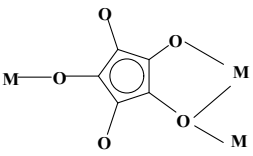
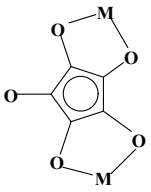


XII

Tetradentate ligand



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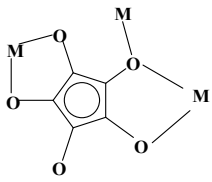

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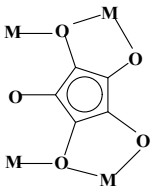

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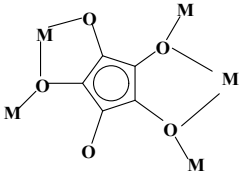
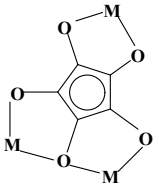


XVI

Pentadentate ligand



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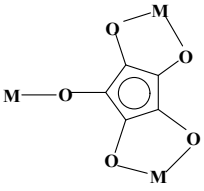

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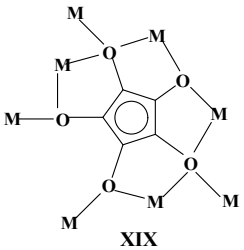

XIX

Scheme S1 The coordination modes of croconate dianions with metal cations.

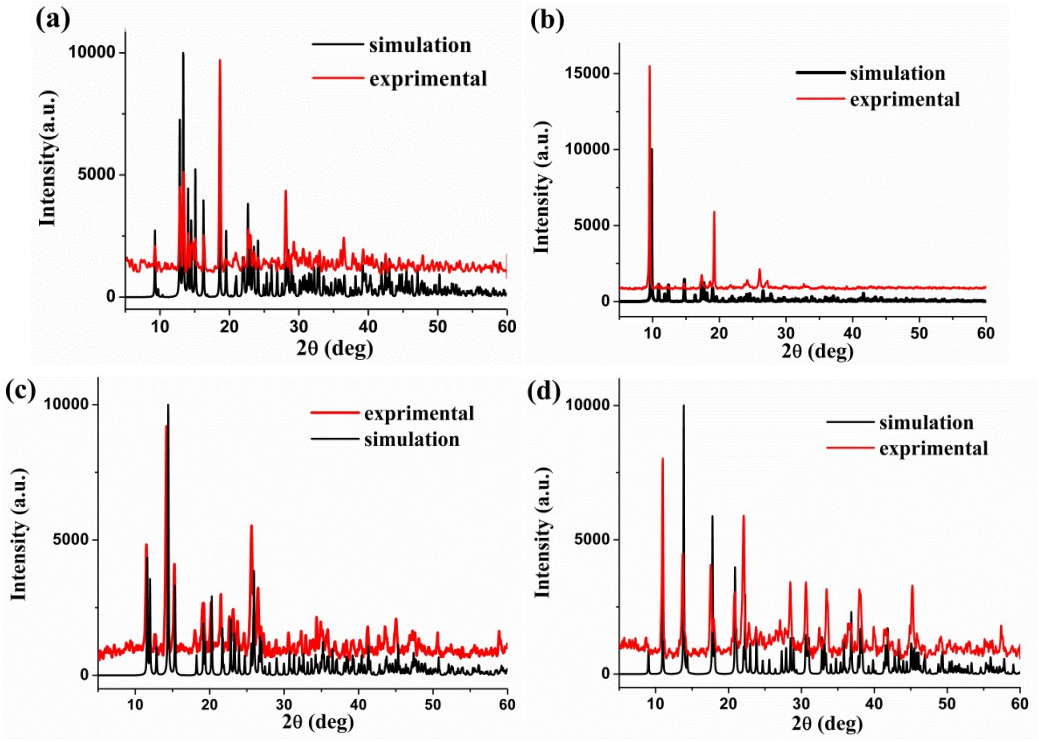

Fig. S2 Comparison of the simulated and experimental XRPD patterns of **1** (a), **2** (b), **3** (c) and **4** (d).

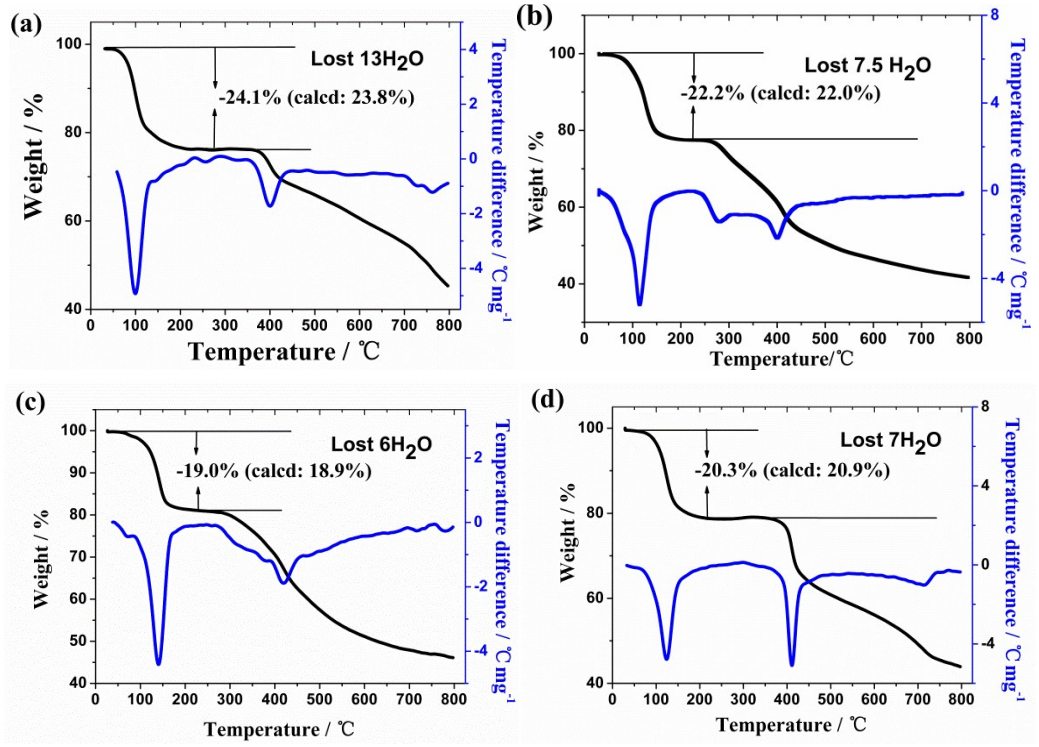

Fig. S3 TGA and DSC curves of **1** (a), **2** (b), **3** (c) and **4** (d).

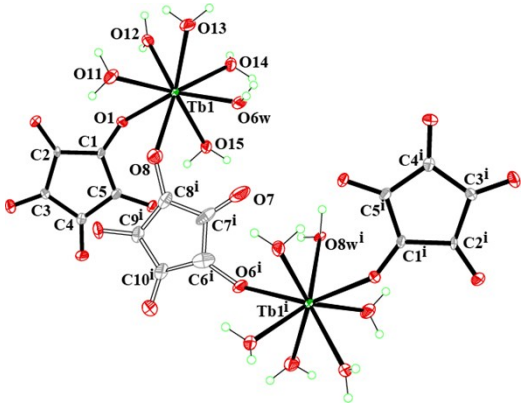

Fig. S4 The coordination of compound **1** and displacement ellipsoids are drawn at the 30% probability (Symmetry codes: i -x+2, -y+2, -z+2). O6 and O6w share one site, while O8 and O8w choose the same mode. The bridged croconate $C_5O_5^{2-}$ marked by open line shows the other part of the croconate with the occupancy of 50%.

Table S2 Selected bond lengths(Å) and bond angles (°)of compound **1**.

Tb(1)—O(15)	2.340(5)	Tb(1)—O(1)	2.359(4)
Tb(1)—O(8W)	2.366(13)	Tb(1)—O(11)	2.373(5)
Tb(1)—O(13)	2.381(5)	Tb(1)—O(8)^{i}	2.386(17)
Tb(1)—O(6)	2.389(5)	Tb(1)—O(14)	2.399(6)
Tb(1)—O(12)	2.401(5)		
O(15)—Tb(1)—O(1)	74.84(16)	O(15)—Tb(1)—O(8W)	80.8(4)
O(1)—Tb(1)—O(8W)	84.4(4)	O(15)—Tb(1)—O(11)	140.24(17)
O(1)—Tb(1)—O(11)	77.06(17)	O(8W)—Tb(1)—O(11)	69.0(4)
O(15)—Tb(1)—O(13)	144.93(18)	O(1)—Tb(1)—O(13)	137.24(16)
O(8W)—Tb(1)—O(13)	111.0(4)	O(11)—Tb(1)—O(13)	72.6(2)
O(15)—Tb(1)—O(8)^{i}	74.3(4)	O(1)—Tb(1)—O(8)^{i}	75.6(4)
O(8W)—Tb(1)—O(8)^{i}	9.9(5)	O(11)—Tb(1)—O(8)^{i}	71.9(4)
O(13)—Tb(1)—O(8)^{i}	120.6(4)	O(15)—Tb(1)—O(6)	79.69(19)
O(1)—Tb(1)—O(6)	148.25(16)	O(8W)—Tb(1)—O(6)	72.9(4)
O(11)—Tb(1)—O(6)	113.4(2)	O(13)—Tb(1)—O(6)	73.13(18)
O(8)^{i}—Tb(1)—O(6)	79.5(4)	O(15)—Tb(1)—O(14)	72.2(2)
O(1)—Tb(1)—O(14)	114.4(2)	O(8W)—Tb(1)—O(14)	140.5(4)
O(11)—Tb(1)—O(14)	146.38(19)	O(13)—Tb(1)—O(14)	79.3(2)
O(8)^{i}—Tb(1)—O(14)	140.4(4)	O(6)—Tb(1)—O(14)	74.3(2)
O(15)—Tb(1)—O(12)	112.53(19)	O(1)—Tb(1)—O(12)	71.31(16)
O(8W)—Tb(1)—O(12)	147.0(4)	O(11)—Tb(1)—O(12)	83.76(18)
O(13)—Tb(1)—O(12)	76.06(18)	O(8)^{i}—Tb(1)—O(12)	142.4(4)
O(6)—Tb(1)—O(12)	137.42(17)	O(14)—Tb(1)—O(12)	71.69(18)

Symmetry codes: (i) $-x$, $-y$, $-z$.

Table S3 Hydrogen–bond geometry (Å) and bond angles (°) of compound **1**.

D—H···A	D—H	H···A	D···A	D—H···A
O(11)—H(11A) ···O(4)^{i}	0.82	1.87	2.667(8)	161.9
O(11)—H(11B) ···O(10)^{ii}	0.82	1.99	2.765(13)	155.8
O(12)—H(12A) ···O(2)^{iii}	0.83	2.01	2.711(7)	141.7
O(12)—H(12A) ···O(1)^{iii}	0.83	2.60	3.260(6)	137.3
O(12)—H(12B) ···O(4)^{iv}	0.82	2.27	3.073(10)	165.1
O(13)—H(13A) ···O(5)^{i}	0.83	2.04	2.763(6)	145.4
O(15)—H(15A) ···O(5)	0.84	1.86	2.685(6)	168.8
O(15)—H(15B) ···O(3)^{v}	0.82	2.00	2.679(8)	139.5

Symmetry codes: (i) $x+1, y, z$; (ii) $x, y+1, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x, -y+1, -z+1$; (v) $x, y-1, z$.

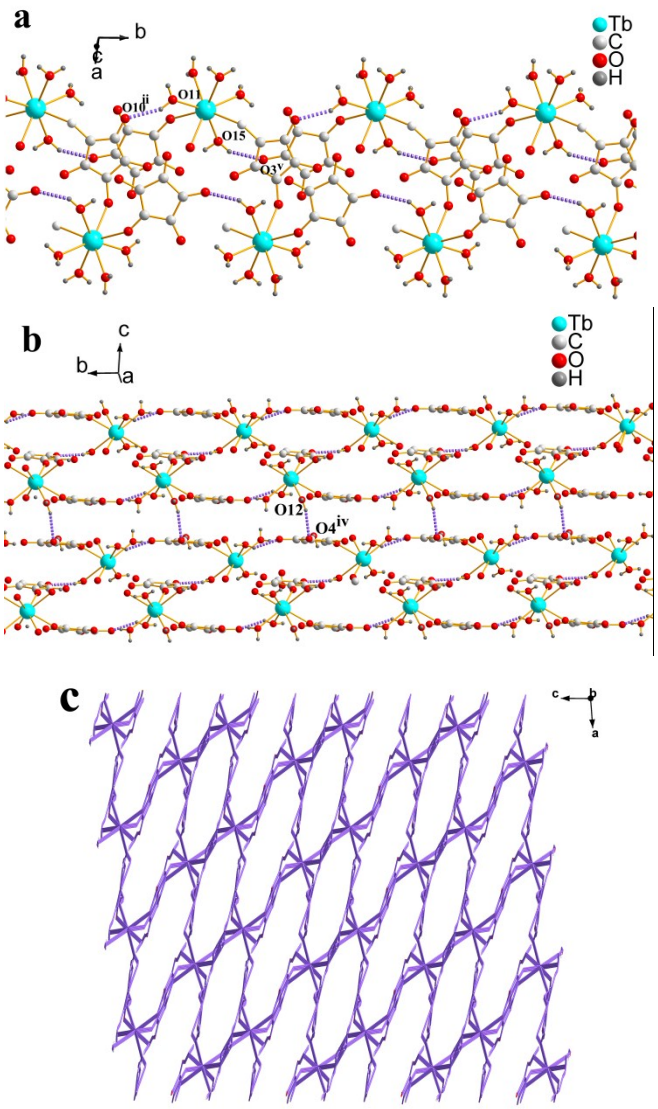

Fig. S5 Molecule packing diagram for the complex **1** connecting by O-H···O hydrogen bonds, a) along *b* axis, forming 1D chains. b) in *bc* plane, forming 2D sheet. c) 3D net structure with large rectangular channels along *b* direction. (Symmetry codes: i $x + 1, y, z$; ii $x, y + 1, z$; iii $–x + 1, –y + 1, –z + 1$; iv $–x, –y + 1, –z +1$; v $x, y–1, z$) .

Table S4 Selected bond lengths(Å) and bond angles (°)of compound **2**.

Tb(1)—O(7)	2.368 (5)	Tb(1)—O(7)^{i}	2.368 (5)
Tb(1)—O(1)	2.369(5)	Tb(1)—O(1)^{i}	2.369(5)
Tb(1)—O(8)	2.370 (5)	Tb(1)—O(8)^{i}	2.370 (5)
Tb(1)—O(6)	2.391(6)	Tb(1)—O(6)^{i}	2.391(6)
Tb(1)—K(1)^{i}	4.357(5)	Tb(1)—H(6B)	2.4650
K(1)—O(1)	3.178(7)	K(1)—O(6)	2.693(7)
K(1)—O(5)	2.783(9)	K(1)—O(3)^{ii}	2.940(8)
K(1)—O(4)^{ii}	3.057(8)	K(1)—C(1)^{i}	3.463(9)
K(1)—H(6A)	3.0050	K(1)—H(6B)	3.0065
O(7)—Tb(1)—O(7)^{i}	143.3(3)	O(7)—Tb(1)—O(1)^{i}	73.93(18)
O(7)^{i}—Tb(1)—O(1)^{i}	140.59(18)	O(7)—Tb(1)—O(1)	140.59(18)
O(7)^{i}—Tb(1)—O(1)	73.92(18)	O(1)—Tb(1)—O(1)^{i}	76.2(3)
O(7)—Tb(1)—O(8)^{i}	71.54(19)	O(7)^{i}—Tb(1)—O(8)^{i}	80.0(2)
O(1)^{i}—Tb(1)—O(8)^{i}	113.56 (19)	O(1)—Tb(1)—O(8)^{i}	145.57 (18)
O(7)—Tb(1)—O(8)	80.0 (2)	O(7)^{i}—Tb(1)—O(8)	71.54 (19)
O(1)^{i}—Tb(1)—O(8)	145.57 (18)	O(1)—Tb(1)—O(8)	113.56 (19)
O(8)^{i}—Tb(1)—O(8)	77.8 (3)	O(7)—Tb(1)—O(6)	76.9 (2)
O(7)^{i}—Tb(1)—O(6)	114.3 (2)	O(1)^{i}—Tb(1)—O(6)	80.03 (19)

O(1)—Tb(1)—O(6)	73.07 (19)	O(8)^{i}—Tb(1)—O(6)	139.64 (18)
O(8)—Tb(1)—O(6)	72.38 (18)	O(7)—Tb(1)—O(6)^{i}	114.3 (2)
O(7)^{i}—Tb(1)—O(6)^{i}	76.9 (2)	O(1)^{i}—Tb(1)—O(6)^{i}	73.07 (19)
O(1)—Tb(1)—O(6)^{i}	80.02 (19)	O(8)^{i}—Tb(1)—O(6)^{i}	72.38 (18)
O(8)—Tb(1)—O(6)^{i}	139.64 (18)	O(6)—Tb(1)—O(6)^{i}	145.7 (2)
O(7)—Tb(1)—K(1)^{i}	111.04 (17)	O(7)^{i}—Tb(1)—K(1)^{i}	96.85 (16)
O(1)^{i}—Tb(1)—K(1)^{i}	45.37 (14)	O(8)^{i}—Tb(1)—K(1)^{i}	60.51 (15)
O(8)^{i}—Tb(1)—K(1)^{i}	101.64 (15)	O(8)—Tb(1)—K(1)^{i}	168.34 (15)
O(6)—Tb(1)—K(1)^{i}	112.93 (15)	O(6)^{i}—Tb(1)—K(1)^{i}	33.11 (14)
O(7)—Tb(1)—H(6B)	58.9	O(7)^{i}—Tb(1)—H(6B)	133.2
O(1)^{i}—Tb(1)—H(6B)	68.9	O(1)—Tb(1)—H(6B)	86.7
O(8)^{i}—Tb(1)—H(6B)	127.8	O(8)—Tb(1)—H(6B)	78.5
O(6)—Tb(1)—H(6B)	19.7	O(6)^{i}—Tb(1)—H(6B)	141.7
K(1)^{i}—Tb(1)—H(6B)	110.1	O(6)—K(1)—O(5)	113.8 (3)
O(6)—K(1)—O(3)^{ii}	150.9 (3)	O(5)—K(1)—O(3)^{ii}	78.0 (2)
O(6)—K(1)—O(4)^{ii}	102.2 (2)	O(5)—K(1)—O(4)^{ii}	133.1 (3)
O(3)^{ii}—K(1)—O(4)^{ii}	56.74 (19)	O(6)—K(1)—O(1)	57.00 (19)
O(5)—K(1)—O(1)	57.70 (18)	O(3)^{ii}—K(1)—O(1)	132.6 (2)
O(4)^{ii}—K(1)—O(1)	152.2 (2)	O(6)—K(1)—C(1)^{i}	65.1 (2)
O(5)—K(1)—C(1)^{i}	81.3 (2)	O(3)^{ii}—K(1)—C(1)^{i}	92.3 (2)
O(4)^{ii}—K(1)—C(1)^{i}	88.1 (2)	O(1)—K(1)—C(1)^{i}	66.91 (19)
O(6)—K(1)—H(6A)	15.4	O(5)—K(1)—H(6A)	125.7
O(3)^{ii}—K(1)—H(6A)	151.9	O(4)^{ii}—K(1)—H(6A)	96.1
O(1)—K(1)—H(6A)	68.0	C(1)^{i}—K(1)—H(6A)	78.7
O(6)—K(1)—H(6B)	15.6	O(5)—K(1)—H(6B)	117.1
O(3)^{ii}—K(1)—H(6B)	135.4	O(4)^{ii}—K(1)—H(6B)	90.8
O(1)—K(1)—H(6B)	64.8	C(1)^{i}—K(1)—H(6B)	53.4
H(6A)—K(1)—H(6B)	25.5		

Symmetry codes: (i) $-x$, y, $-z + 1/2$; (ii) x, $-y + 1$, $z + 1/2$.

Table S5 Hydrogen–bond geometry (Å) and bond angles (°) of compound **2**.

D—H···A	D—H	H···A	D···A	D—H···A
O(6) —H(6A) ···O(2)^{iii}	0.82	2.31	2.774(8)	115.9
O(8) —H(8B) ···O(5)^{iv}	0.83	1.97	2.718(7)	148.4
O(8) —H(8A) ···O(3)^{iii}	0.85	1.78	2.631(8)	179.8
O(7) —H(7B) ···O(4)^{ii}	0.83	1.88	2.676(8)	162.5
O(7) —H(7A) ···O(2)^{i}	0.83	2.04	2.695(8)	135.4

Symmetry codes: (i) $-x$, y, $-z + 1/2$; (ii) $-x$, $y + 1$, $-z + 1/2$. (iii) x, $-y + 2$, $z + 1/2$; (iv) x, $y + 1$, z;

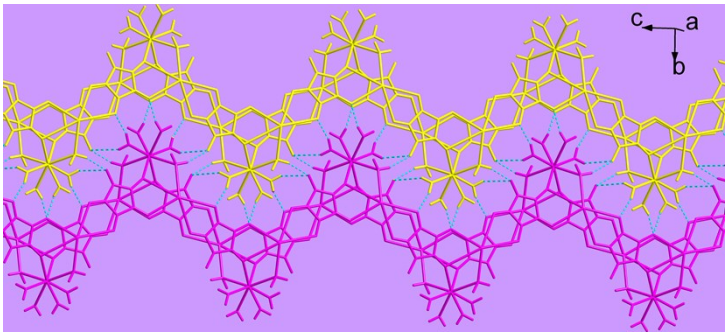

Fig. S6 Molecule packing diagram for the complex **2**, forming 2D layer in the *bc* plane.

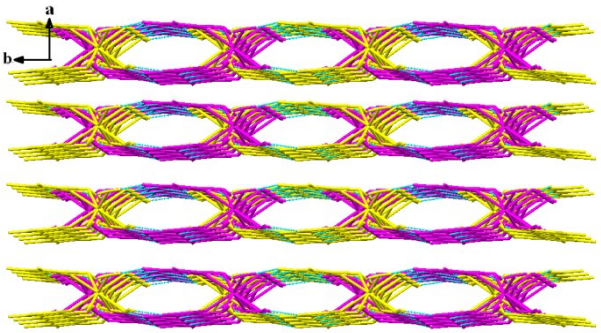

Fig. S7 Molecule packing diagram for the complex **2** along *c* axis.

Table S6 Selected bond lengths(Å) and bond angles (°)of compound **3**.

Tb(1)—O(6)	2.318(6)	Tb(1)—O(11)	2.350(6)
Tb(1)—O(1)	2.365(5)	Tb(1)—O(12)	2.368(4)
Tb(1)—O(14)	2.377(5)	Tb(1)—O(13)	2.403(4)
Tb(1)—O(10)	2.404(5)	Tb(1)—N(1)	2.602(5)
O(6)—Tb(1)—O(11)	140.8(2)	O(6)—Tb(1)—O(1)	141.09(18)
O(11)—Tb(1)—O(1)	77.47(19)	O(6)—Tb(1)—O(12)	107.00(14)
O(11)—Tb(1)—O(12)	85.26(15)	O(1)—Tb(1)—O(12)	76.98(15)
O(6)—Tb(1)—O(14)	75.56(17)	O(11)—Tb(1)—O(14)	74.55(18)
O(1)—Tb(1)—O(14)	122.67(16)	O(12)—Tb(1)—O(14)	146.40(16)
O(6)—Tb(1)—O(13)	78.98(14)	O(11)—Tb(1)—O(13)	115.34(15)
O(1)—Tb(1)—O(13)	75.31(14)	O(12)—Tb(1)—O(13)	140.29(16)
O(14)—Tb(1)—O(13)	73.29(15)	O(6)—Tb(1)—O(10)	72.28(17)
O(11)—Tb(1)—O(10)	75.41(18)	O(1)—Tb(1)—O(10)	142.32(15)
O(12)—Tb(1)—O(10)	75.18(16)	O(14)—Tb(1)—O(10)	73.91(18)
O(13)—Tb(1)—O(10)	140.64(16)	O(6)—Tb(1)—N(1)	64.82(18)
O(11)—Tb(1)—N(1)	151.44(19)	O(1)—Tb(1)—N(1)	80.86(15)
O(12)—Tb(1)—N(1)	71.82(14)	O(14)—Tb(1)—N(1)	133.55(15)
O(13)—Tb(1)—N(1)	76.15(15)	O(10)—Tb(1)—N(1)	113.26(16)

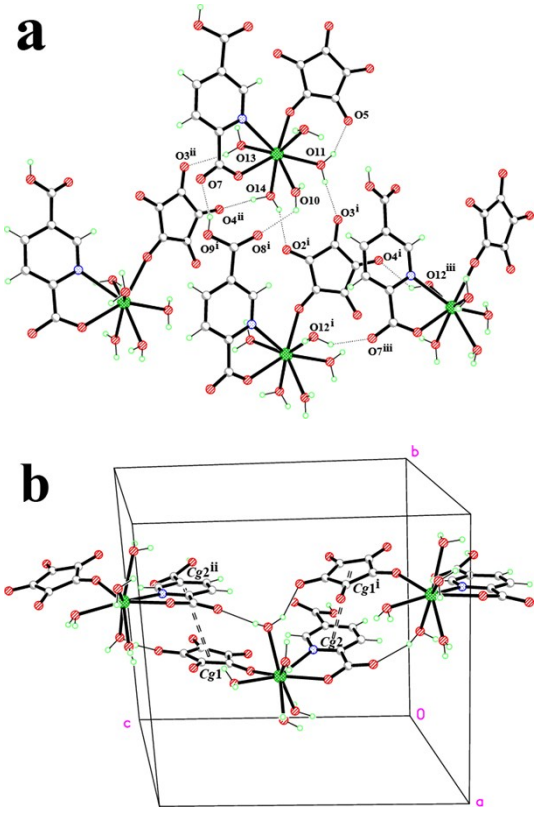

Fig. S8 (a) Molecule packing diagram for the complex **3** connecting by O-H···O intermolecular hydrogen bonds (Symmetry codes: i -*x*, *y*, -*z*+1/2; ii *x*, -*y*+1, *z*+1/2; iii *x*, -*y*+1, *z*-1/2) and (b) π···π interactions between the centroids of $C_5O_5^{2-}$ and pyridine.

Table S7 Hydrogen–bond geometry (Å) and bond angles (°) of compound **3**.

D—H···A	D—H	H···A	D···A	D—H···A
O(15)—H(15B) ···O(1)^{i}	0.85	2.57	3.048(6)	116.4
O(15)—H(15B) ···O(2)^{i}	0.85	2.04	2.870(7)	166.8
O(15)—H(15A) ···O(5)^{ii}	0.85	1.86	2.698(7)	169.7
O(14)—H(14B) ···O(2)^{iii}	0.86	1.99	2.742(7)	146.2
O(14)—H(14A) ···O(4)^{iv}	0.86	1.89	2.716(6)	161.7
O(13)—H(13B) ···O(3)^{iv}	0.89	2.17	3.039(7)	165.9
O(13)—H(13A) ···O(15)^{v}	0.89	1.85	2.700(7)	160.2
O(12)—H(12B) ···O(4)^{vi}	0.86	2.10	2.738(6)	130.7
O(12)—H(12A) ···O(7)^{vii}	0.86	1.93	2.688(6)	147.4
O(11)—H(11B) ···O(5)	0.85	2.13	2.671(9)	120.7
O(11)—H(11A) ···O(3)^{iii}	0.85	2.15	2.886(8)	144.5
O(10)—H(10B) ···O(8)^{iii}	0.83	2.28	2.765(7)	117.4
O(10)—H(10A) ···O(15)^{viii}	0.92	1.85	2.760(6)	167.4
O(9)—H(9) ···O(7)^{ix}	0.82	1.77	2.549(7)	158.7

Symmetry codes: (i) *x*, *y*, *z* + 1; (ii) *x* – 1/2, –*y* + 1/2, *z* + 1/2; (iii) *x* + 1, *y*, *z*; (iv) *x* + 1/2, –*y* + 1/2, *z* – 1/2; (v) *x*, *y*, *z*–1; (vi) *x*, –*y*, *z* – 1/2; (vii) *x*, –*y*, *z* + 1/2; (viii) *x* + 1/2, *y* – 1/2, *z* – 1; (ix) *x* – 1, *y*, *z*.

Table S8 Selected bond lengths(Å) and bond angles (°)of compound **4**.

Tb(1)—O(9)	2.309(4)	Tb(1) —O(6)	2.360(6)
Tb(1) —O(2)^{i}	2.373(4)	Tb(1) —O(2)	2.373(4)
Tb(1) —O(8)^{i}	2.444(2)	Tb(1) —O(8)	2.444(2)
Tb(1) —O(7)	2.620(6)	Tb(1) —O(1)	2.623(4)
Tb(1) —O(1)^{i}	2.623(4)	Tb(1) —K(1)^{ii}	4.3164(18)
K(1) —O(7)^{iii}	2.844(6)	K(1) —O(4)^{iv}	2.854(3)
K(1) —O(4)	2.855(3)	K(1) —O(4)^{v}	2.900(4)
K(1) —O(4)^{vi}	2.900(4)	K(1) —O(8)^{vii}	2.967(4)
K(1) —O(8)^{viii}	2.967(4)	K(1) —O(5)^{iv}	3.180(4)
K(1) —O(5)	3.180(4)	K(1) —O(6)^{vii}	3.359(7)
K(1) —K(1)^{vi}	4.2339(9)	K(1) —K(1)^{ix}	4.2338(9)
O(9) —Tb(1) —O(6)	100.2(2)	O(9) —Tb(1) —O(2)	79.49(13)
O(6) —Tb(1) —O(2)	131.69(9)	O(6) —Tb(1) —O(2)^{i}	131.68(9)
O(9) —Tb(1) —O(2)^{i}	79.48(13)	O(2)^{i}—Tb(1) —O(2)	96.14(17)
O(9) —Tb(1) —O(8)^{i}	142.09(7)	O(6) —Tb(1) —O(8)^{i}	74.9(2)
O(2) —Tb(1) —O(8)^{i}	132.11(17)	O(2)^{i} —Tb(1) —O(8)^{i}	76.98(15)
O(6) —Tb(1) —O(8)	74.9(2)	O(9) —Tb(1) —O(8)	142.09(7)
O(2) —Tb(1) —O(8)	76.97(15)	O(2)^{i} —Tb(1) —O(8)	132.11(17)
O(9) —Tb(1) —O(7)	123.65(18)	O(8)^{i} —Tb(1) —O(8)	74.04(11)
O(2)—Tb(1) —O(7)	64.28(12)	O(6) —Tb(1) —O(7)	136.10(14)
O(8)^{i}—Tb(1) —O(7)	70.40(19)	O(2)^{i}—Tb(1) —O(7)	64.28(12)
O(9) —Tb(1) —O(1)	72.14(11)	O(8) —Tb(1) —O(7)	70.40(19)
O(2)^{i}—Tb(1) —O(1)	149.06(11)	O(6) —Tb(1) —O(1)	67.05(11)
O(8)^{i}—Tb(1) —O(1)	133.73(16)	O(2) —Tb(1) —O(1)	67.12(11)
O(7) —Tb(1) —O(1)	123.09(8)	O(8) —Tb(1) —O(1)	71.48(14)
O(6) —Tb(1) —O(1)^{i}	67.05(11)	O(9) —Tb(1) —O(1)^{i}	72.14(11)
O(2) —Tb(1) —O(1)^{i}	149.06(10)	O(2)^{i} —Tb(1) —O(1)^{i}	67.12(11)
O(8) —Tb(1) —O(1)^{i}	133.73(16)	O(8)^{i} —Tb(1) —O(1)^{i}	71.48(14)
O(1) —Tb(1) —O(1)^{i}	113.81(16)	O(7) —Tb(1) —O(1)^{i}	123.09(8)
O(6) —Tb(1) —K(1)^{ii}	50.64(18)	O(9) —Tb(1) —K(1)^{ii}	150.89(12)
O(2) —Tb(1) —K(1)^{ii}	118.17(10)	O(2)^{i} —Tb(1) —K(1)^{ii}	118.17(10)
O(8) —Tb(1) —K(1)^{ii}	41.51(10)	O(8)^{i} —Tb(1) —K(1)^{ii}	41.51(10)
O(1) —Tb(1) —K(1)^{ii}	92.77(10)	O(7) —Tb(1) —K(1)^{ii}	85.46(14)
O(7)^{iii} —K(1) —O(4)^{iv}	76.50(13)	O(1)^{i} —Tb(1) —K(1)^{ii}	92.76(10)
O(4)^{iv} —K(1) —O(4)	67.12(13)	O(7)^{iii} —K(1) —O(4)	76.50(13)
O(4)^{iv} —K(1) —O(4)^{v}	174.75(8)	O(7)^{iii} —K(1) —O(4)^{v}	108.74(13)
O(7)^{iii} —K(1) —O(4)^{vi}	108.74(13)	O(4) —K(1) —O(4)^{v}	113.21(10)
O(4) —K(1) —O(4)^{vi}	174.75(8)	O(4)^{iv} —K(1) —O(4)^{vi}	113.22(10)
O(7)^{iii} —K(1) —O(8)^{vii}	142.03(10)	O(4)^{v} —K(1) —O(4)^{vi}	65.93(12)

O(4) —K(1) —O(8)^{vii}	99.61(14)	O(4)^{iv} —K(1) —O(8)^{vii}	67.58(12)
O(4)^{vi} —K(1) —O(8)^{vii}	76.06(14)	O(4)^{v} —K(1) —O(8)^{vii}	107.39(13)
O(4)^{iv} —K(1) —O(8)^{viii}	99.61(14)	O(7)^{iii} —K(1) —O(8)^{viii}	142.03(10)
O(4)^{v} —K(1) —O(8)^{viii}	76.06(14)	O(4) —K(1) —O(8)^{viii}	67.58(12)
O(8)^{vii} —K(1) —O(8)^{viii}	59.46(11)	O(4)^{vi} —K(1) —O(8)^{viii}	107.39(12)
O(4)^{iv} —K(1) —O(5)^{iv}	57.70(9)	O(7)^{iii} —K(1) —O(5)^{iv}	63.95(7)
O(4)^{v} —K(1) —O(5)^{iv}	124.55(10)	O(4) —K(1) —O(5)^{iv}	117.07(10)
O(8)^{vii} —K(1) —O(5)^{iv}	86.04(8)	O(4)^{vi} —K(1) —O(5)^{iv}	65.99(9)
O(7)^{iii} —K(1) —O(5)	63.95(7)	O(8)^{viii} —K(1) —O(5)^{iv}	144.95(10)
O(4) —K(1) —O(5)	57.70(9)	O(4)^{iv} —K(1) —O(5)	117.07(10)
O(4)^{vi} —K(1) —O(5)	124.55(10)	O(4)^{v} —K(1) —O(5)	65.99(9)
O(8)^{viii} —K(1) —O(5)	86.04(8)	O(8)^{vii} —K(1) —O(5)	144.95(10)
O(7)^{iii} —K(1) —O(6)^{vii}	156.7(2)	O(5)^{iv} —K(1) —O(5)	127.00(13)
O(4) —K(1) —O(6)^{vii}	122.09(11)	O(4)^{iv} —K(1) —O(6)^{vii}	122.09(11)
O(4)^{vi} —K(1) —O(6)^{vii}	52.99(10)	O(4)^{v} —K(1) —O(6)^{vii}	52.99(10)
O(8)^{viii} —K(1) —O(6)^{vii}	54.58(13)	O(8)^{vii} —K(1) —O(6)^{vii}	54.58(13)
O(5) —K(1) —O(6)^{vii}	111.84(7)	O(5)^{iv} —K(1) —O(6)^{vii}	111.84(7)
O(4)^{iv} —K(1) —K(1)^{ix}	43.04(7)	O(7)^{iii} —K(1) —K(1)^{ix}	102.44(13)
O(4)^{v} —K(1) —K(1)^{ix}	133.44(8)	O(4) —K(1) —K(1)^{ix}	43.04(7)
O(8)^{vii} —K(1) —K(1)^{ix}	58.30(12)	O(4)^{vi} —K(1) —K(1)^{ix}	133.44(8)
O(5)^{iv} —K(1) —K(1)^{ix}	99.87(7)	O(8)^{viii} —K(1) —K(1)^{ix}	58.30(12)
O(6)^{vii} —K(1) —K(1)^{ix}	100.89(11)	O(5) —K(1) —K(1)^{ix}	99.87(7)
O(4)^{iv} —K(1) —K(1)^{vi}	140.70(7)	O(7)^{iii} —K(1) —K(1)^{vi}	84.50(13)
O(4)^{v} —K(1) —K(1)^{vi}	42.21(7)	O(4) —K(1) —K(1)^{vi}	140.70(7)
O(8)^{vii} —K(1) —K(1)^{vi}	115.98(13)	O(4)^{vi} —K(1) —K(1)^{vi}	42.21(7)
O(5)^{iv} —K(1) —K(1)^{vi}	83.08(7)	O(8)^{viii} —K(1) —K(1)^{vi}	115.98(13)
O(6)^{vii} —K(1) —K(1)^{vi}	72.17(11)	O(5) —K(1) —K(1)^{vi}	83.08(7)
K(1)^{vi} —K(1) —K(1)^{ix}	173.06(8)		

Symmetry code: (i) $-x + 1, y, z$; (ii) $x - 1/2, y - 1/2, z$; (iii) $-x + 3/2, -y + 3/2, z - 1/2$; (iv) $-x + 2, y, z$; (v) $x, -y + 2, z - 1/2$; (vi) $-x + 2, -y + 2, z - 1/2$; (vii) $x + 1/2, y + 1/2, z$; (viii) $-x + 3/2, y + 1/2, z$; (ix) $-x + 2, -y + 2, z + 1/2$;

Table S9 Hydrogen–bond geometry (Å) and bond angles (°) of compound **4**.

D–H···A	D–H	H···A	D···A	D—H···A
O(6)—H(6A) ···O(10)^{i}	0.82	2.37	3.041(7)	139.9
O(6)—H(6A) ···O(4)^{i}	0.82	2.29	2.822(6)	123.7
O(7)—H(7A) ···O(10)^{v}	0.82	2.40	3.183(6)	158.8
O(7)—H(7A) ···O(5)^{v}	0.82	2.81	3.203(5)	111.5
O(8)—H(8A) ···O(3)^{i}	0.87	1.79	2.653(5)	171.4
O(8)—H(8B) ···O(5)^{ii}	0.91	1.95	2.759(7)	146.7
O(8)—H(8B) ···O(7)	0.91	2.43	2.923(8)	113.7
O(9)—H(9A) ···O(10)^{iv}	0.82	1.95	2.759(4)	168.8
O(9)—H(9A) ···O(2)^{iii}	0.82	2.92	3.370(5)	117.1
O(10)—H(10A) ···O(1)^{ii}	0.85	1.94	2.774(6)	167.7
O(10)—H(10B) ···O(3)^{i}	0.86	1.98	2.838(5)	177.1

Symmetry codes: (i) $-x + 3/2, -y + 3/2, z - 1/2$; (ii) $-x + 3/2, -y + 3/2, z + 1/2$; (iii) $-x + 1, -y + 2, z - 1/2$; (iv) $x - 1/2, y + 1/2, z$; (v) $x - 1/2, -y + 3/2, z + 1/2$.

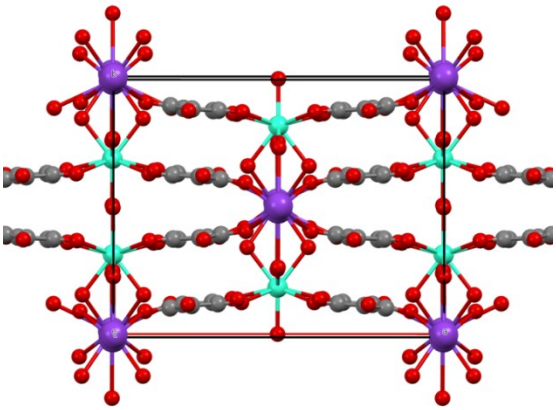

Fig. S9 Molecule packing diagram for the complex **4** linked by coordinated water molecules along crystallographic *b* resulting in the formation of the 2D square grids. K atoms are shown in purple, Tb atoms in blue,

carbon atoms in gray, oxygen atoms in red and hydrogen atoms were omitted for clarity.

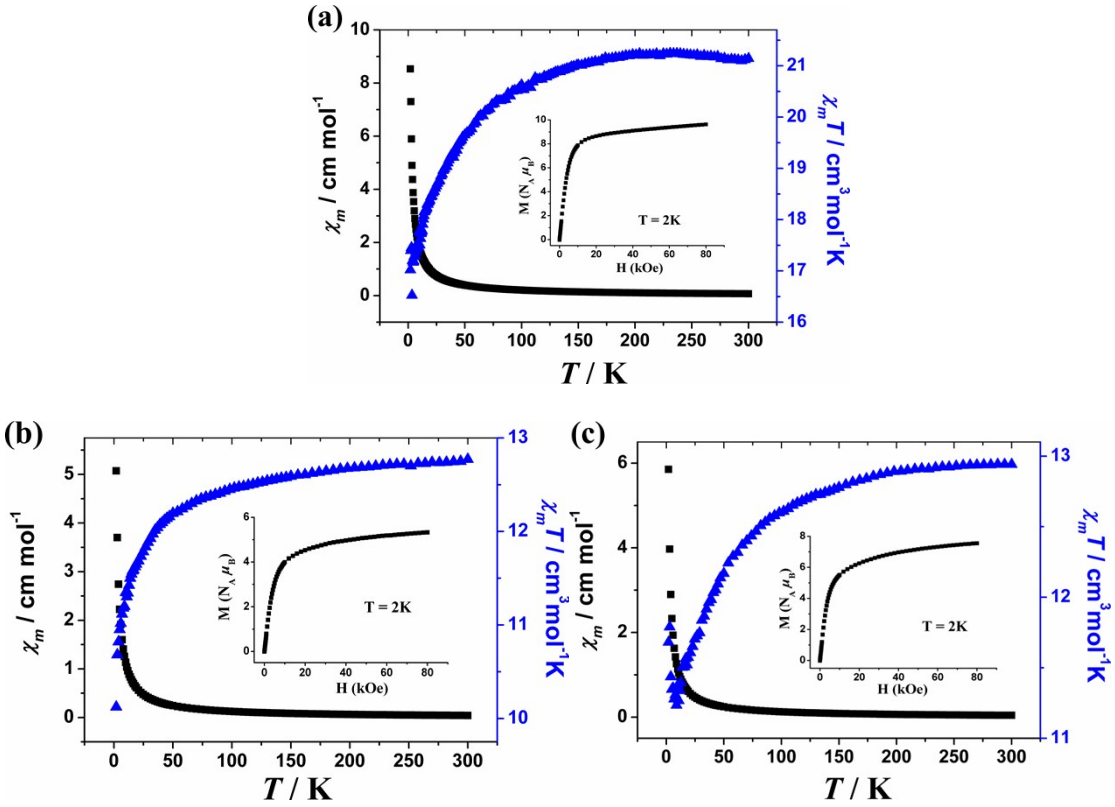

Fig. S10 Temperature dependence of $\chi_m T$ and χ_m collected in an applied field of 1000 Oe for complexes **1** (a), **2** (b) and **3** (c), where χ_m is the molar susceptibility. Magnetic moment data as a function of field are shown in the inset.

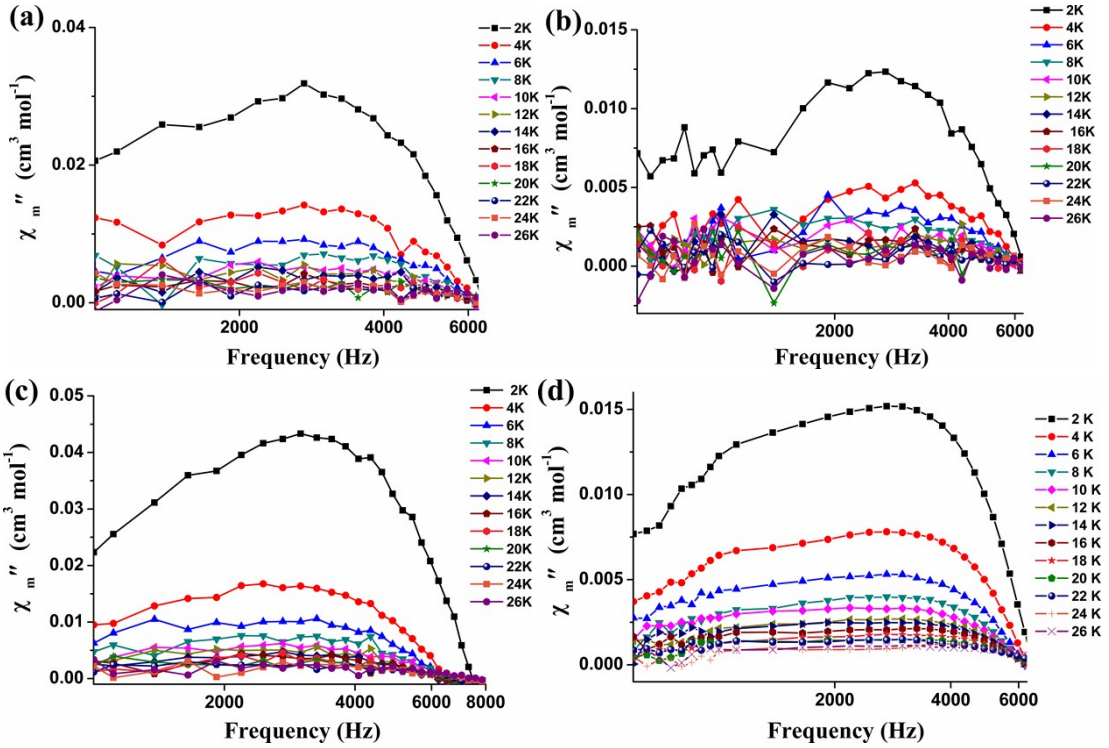

Fig. S11 Out-of-phase *ac* magnetic susceptibility (χ_m'') for **1**-**4** from 2 to 26 K with 2 K intervals.

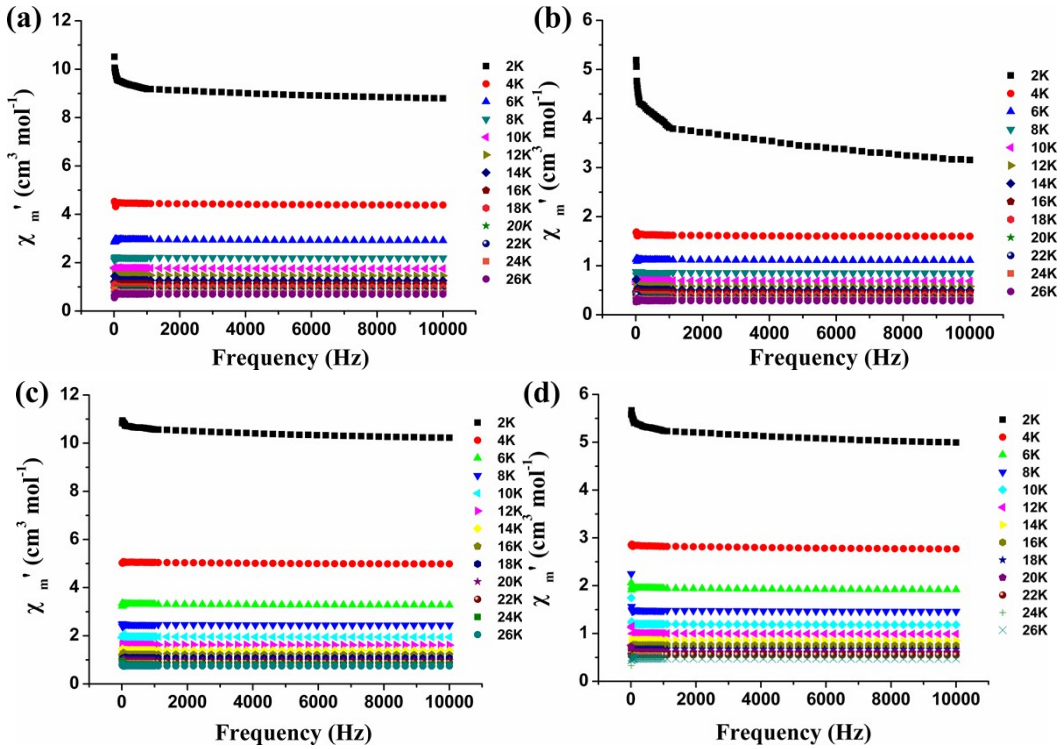

Fig. S12 In-phase *ac* magnetic susceptibility (χ_m') for **1**-**4** from 11 to 10000 Hz at temperatures from 2 to 26 K with 2 K intervals.