Electronic Supplementary Material (ESI) for Dalton Transactions.

Zn_2Ln_2 complexes with carbonate bridges formed by fixation of carbon dioxide in the atmosphere: single-molecule magnet behaviour and magnetocaloric effect

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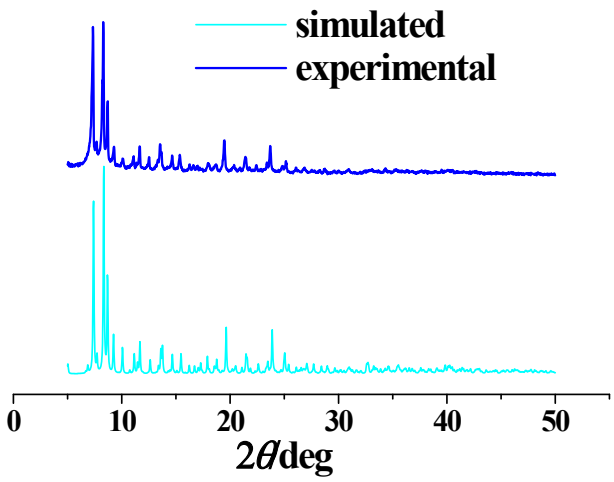

Fig. S1. The simulative and experimental powder X-ray diffraction patterns for **1**.

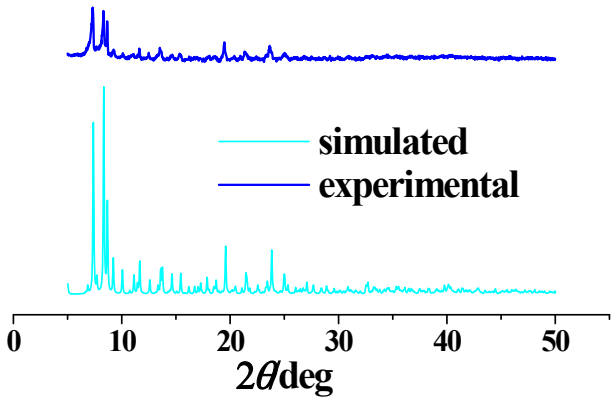

Fig. S2. The simulative and experimental powder X-ray diffraction patterns for **2**.

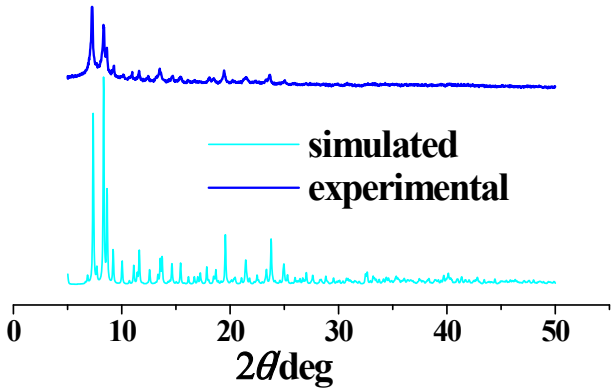

Fig. S3. The simulative and experimental powder X-ray diffraction patterns for **3**.

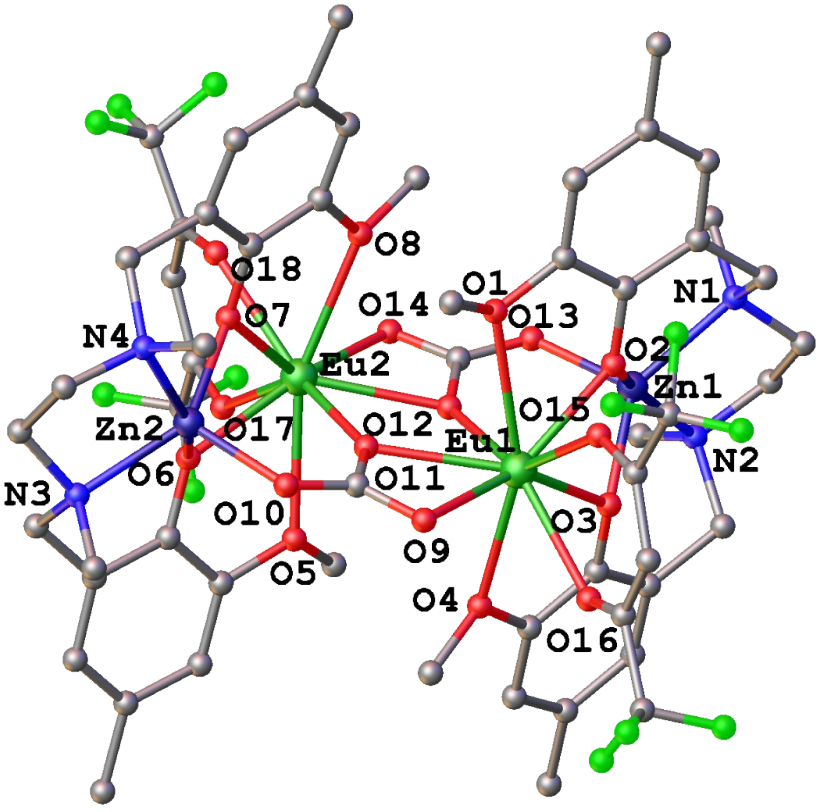

Fig. S4. Crystal structure of **2**, all hydrogen atoms, one solvent methanol molecule and some disordered F atoms are omitted for clarity.

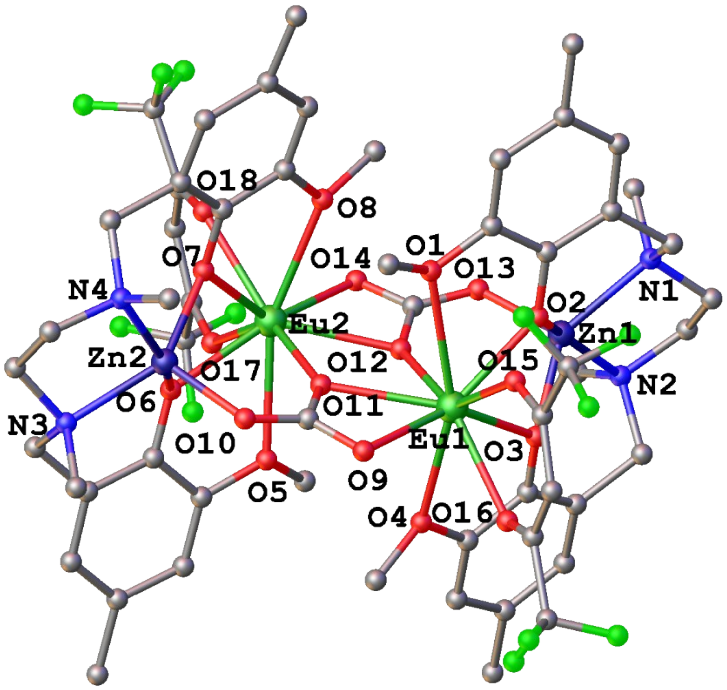

Fig. S5. Crystal structure of **3**, all hydrogen atoms, one solvent methanol molecule and some disordered F atoms are omitted for clarity.

Table S1 Selected Bond Lengths (Å) and Angles (°) of **1-3**.

	Complex **1** (Ln = Dy)	Complex **2** (Ln = Gd)	Complex **3** (Ln = Eu)
Ln(1)-O(1)	2.7368(18)	2.7333(17)	2.742(3)
Ln(1)-O(2)	2.2635(18)	2.2898(16)	2.304(2)
Ln(1)-O(3)	2.3265(16)	2.3534(15)	2.368(2)
Ln(1)-O(4)	2.5443(17)	2.5561(16)	2.577(3)
Ln(1)-O(9)	2.3875(17)	2.4252(16)	2.433(2)
Ln(1)-O(11)	2.3787(17)	2.4061(16)	2.419(2)
Ln(1)-O(12)	2.4228(16)	2.4355(15)	2.449(2)
Ln(1)-O(15)	2.3844(18)	2.4046(17)	2.419(3)
Ln(1)-O(16)	2.4672(18)	2.4863(17)	2.502(3)
Ln(2)-O(5)	2.6159(17)	2.6265(17)	2.640(3)
Ln(2)-O(6)	2.2798(17)	2.3124(15)	2.317(2)
Ln(2)-O(7)	2.3219(17)	2.3454(15)	2.363(2)
Ln(2)-O(8)	2.5756(18)	2.5824(16)	2.598(3)
Ln(2)-O(11)	2.3773(16)	2.3932(15)	2.403(2)
Ln(2)-O(12)	2.3791(17)	2.4073(16)	2.418(2)
Ln(2)-O(14)	2.3847(16)	2.4210(15)	2.427(2)
Ln(2)-O(17)	2.4255(17)	2.4419(16)	2.453(3)
Ln(2)-O(18)	2.4198(19)	2.4446(17)	2.457(3)
Zn(1)-N(1)	2.119(2)	2.124(2)	2.130(3)
Zn(1)-N(2)	2.151(2)	2.151(2)	2.151(3)
Zn(1)-O(2)	2.0365(17)	2.0338(16)	2.040(3)
Zn(1)-O(3)	2.0351(17)	2.0362(16)	2.039(2)
Zn(1)-O(13)	1.9654(18)	1.9648(17)	1.966(3)
Zn(2)-N(3)	2.111(2)	2.114(2)	2.115(3)
Zn(2)-N(4)	2.157(2)	2.157(2)	2.161(3)
Zn(2)-O(6)	2.0731(17)	2.0678(16)	2.074(2)
Zn(2)-O(7)	2.0188(17)	2.0241(16)	2.024(2)
Zn(2)-O(10)	1.9674(18)	1.9671(17)	1.968(3)
Ln(2)-O(11)-Ln(1)	117.73(7)	117.56(6)	117.35(10)
Ln(2)-O(12)-Ln(1)	115.94(7)	115.88(6)	115.64(9)
N(1)-Zn(1)-N(2)	84.70(8)	84.65(8)	84.53(12)
N(3)-Zn(2)-N(4)	85.05(9)	85.08(8)	84.94(13)
O(3)-Zn(1)-O(2)	75.66(7)	76.38(6)	76.44(10)
O(7)-Zn(2)-O(6)	74.16(7)	74.93(6)	74.93(10)

Table S2. Continuous Shape Measures calculation for Dy1 atom in **1**.

Dy1 structure

EP-9	1 D9h	Enneagon
OPY-9	2 C8v	Octagonal pyramid
HBPY-9	3 D7h	Heptagonal bipyramid
JTC-9	4 C3v	Johnson triangular cupola J3
JCCU-9	5 C4v	Capped cube J8
CCU-9	6 C4v	Spherical-relaxed capped cube
JCSAPR-9	7 C4v	Capped square antiprism J10
CSAPR-9	8 C4v	Spherical capped square antiprism
JTCTPR-9	9 D3h	Tricapped trigonal prism J51
TCTPR-9	10 D3h	Spherical tricapped trigonal prism
JTDIC-9	11 C3v	Tridiminished icosahedron J63
HH-9	12 C2v	Hula-hoop
MFF-9	13 Cs	Muffin

Structure	EP-9	OPY-9	HBPY-9	JTC-9	JCCU-9	CCU-9	JCSAPR-9	**CSAPR-9**	JTCTPR-9	TCTPR-9	JTDIC-9	HH-9	**MFF-9**
ABOXIY	33.182	23.113	18.465	14.778	10.773	9.217	3.196	**2.115**	4.341	2.965	10.889	9.392	**2.119**

Table S3. Continuous Shape Measures calculation for Dy2 atom in **1**.

Dy2 structure

EP-9	1 D9h	Enneagon
OPY-9	2 C8v	Octagonal pyramid
HBPY-9	3 D7h	Heptagonal bipyramid
JTC-9	4 C3v	Johnson triangular cupola J3
JCCU-9	5 C4v	Capped cube J8
CCU-9	6 C4v	Spherical-relaxed capped cube
JCSAPR-9	7 C4v	Capped square antiprism J10
CSAPR-9	8 C4v	Spherical capped square antiprism
JTCTPR-9	9 D3h	Tricapped trigonal prism J51
TCTPR-9	10 D3h	Spherical tricapped trigonal prism
JTDIC-9	11 C3v	Tridiminished icosahedron J63
HH-9	12 C2v	Hula-hoop
MFF-9	13 Cs	Muffin

Structure	EP-9	OPY-9	HBPY-9	JTC-9	JCCU-9	CCU-9	JCSAPR-9	CSAPR-9	JTCTPR-9	**TCTPR-9**	JTDIC-9	HH-9	MFF-9
ABOXIY	36.122	21.994	17.738	15.457	8.672	7.125	3.623	2.442	4.371	**2.005**	8.931	9.787	2.848

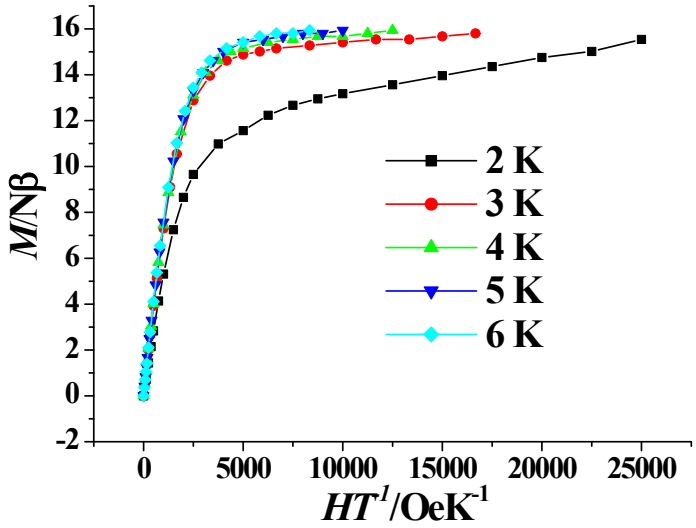

Fig. S6. *M* versus *H*/*T* plots at 2-6 K of **1**.

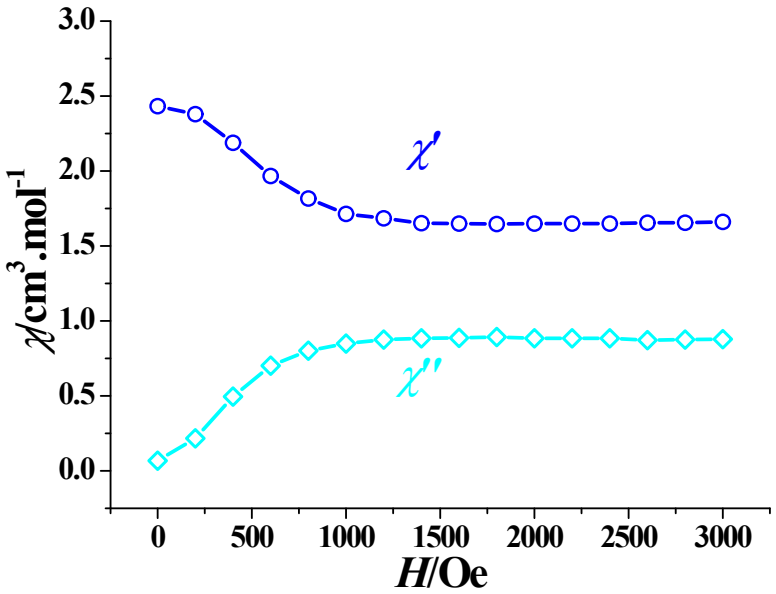

Fig. S7. AC susceptibilities measured at 2.5 Oe ac magnetic field with variable dc fields at 997 Hz and 12 K for **1**.

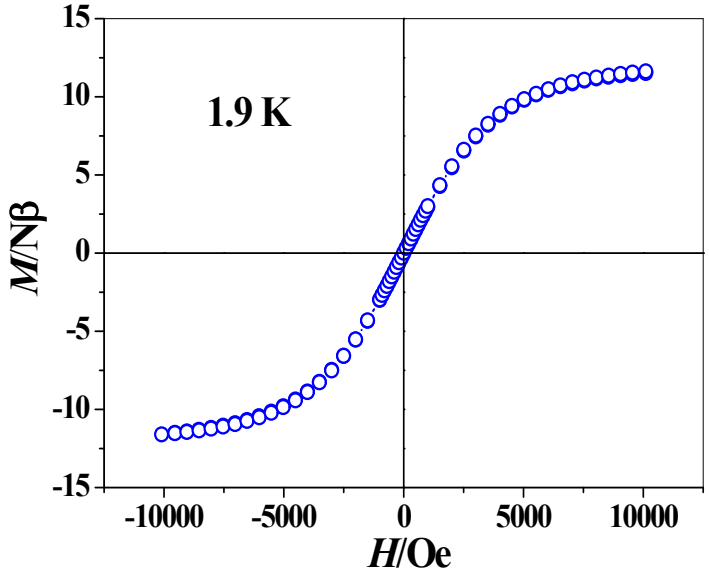

Fig. S8. Hysteresis loop for **1** at 1.9 K.

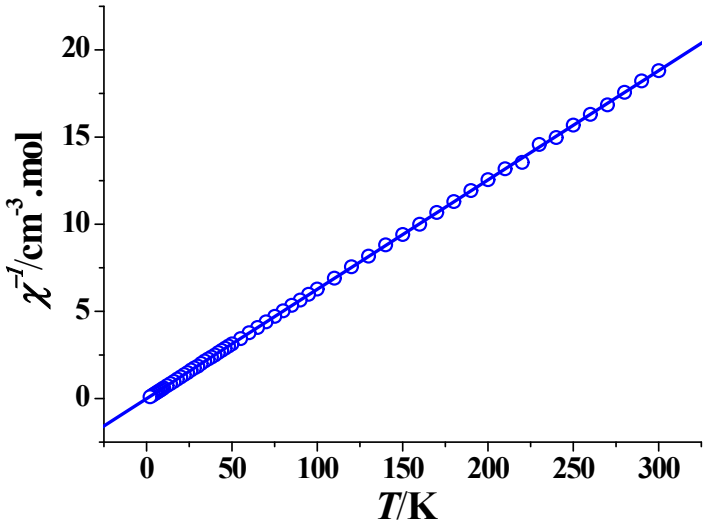

Fig. S9. Plots of χ^{-1} versus T of **2**.