## **Supporting Information**

Linking heterometallic Ln-Cu chain unit with 2-methylenesuccinate bridge to form 2D network exhibiting large magnetocaloric effect

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Gd(1)-O(10)	2.372(3)	Gd(1)-O(6)#2	2.543(3)
Gd(1)-O(1)	2.387(3)	Gd(1)-O(5)#2	2.566(3)
Gd(1)-O(11)	2.390(3)	Gd(1)-C(9)#1	2.871(4)
Gd(1)-O(9)	2.423(3)	Gd(1)-C(6)#2	2.933(4)
Gd(1)-O(5)	2.431(3)	Cu(1)-O(2)	1.929(3)
Gd(1)-O(8)#1	2.479(3)	Cu(1)-O(4)#3	1.978(3)
Gd(1)-O(7)#1	2.508(3)		
$O(9)_Gd(1)_O(8)\#1$	71 54(11)	$O(11)_{Gd}(1)_{O}(8)\#1$	138 32(11)
O(9) C d(1) O(7) # 1	71.34(11) 74.20(12)	O(11) - O(1) - O(3) + 1	136.32(11) 145.17(11)
O(9) - O(1) - O(7) # 1	74.39(12)	O(11) - Ga(1) - O(7) # 1	(143.1/(11))
O(9)-Gd(1)- $O(6)$ #2	127.61(11)	O(11)-Gd(1)-O(6)#2	69.41(11)
O(9)-Gd(1)-O(5)#2	150.90(11)	O(11)-Gd(1)-O(5)#2	/1./6(10)
O(9)-Gd(1)-O(5)	114.56(11)	O(11)-Gd(1)-O(5)	78.99(11)
O(9)-Gd(1)-C(9)#1	71.74(12)	O(10)-Gd(1)-O(9)	72.46(13)
O(8)#1-Gd(1)-O(7)#1	51.99(10)	O(10)-Gd(1)-O(8)#1	86.01(13)
O(8)#1-Gd(1)-O(6)#2	68.96(10)	O(10)-Gd(1)-O(7)#1	132.95(13)
O(8)#1-Gd(1)-O(5)#2	83.44(10)	O(10)-Gd(1)-O(6)#2	71.80(11)
O(7)#1-Gd(1)-O(6)#2	105.05(11)	O(10)-Gd(1)-O(5)#2	121.38(11)
O(7)#1-Gd(1)-O(5)#2	78.59(10)	O(10)-Gd(1)-O(5)	153.08(13)
O(6)#2-Gd(1)-O(5)#2	50.62(9)	O(10)-Gd(1)-O(11)	79.50(13)
O(5)-Gd(1)-O(8)#1	120.90(10)	O(10)-Gd(1)-O(1)	80.18(13)
O(5)-Gd(1)-O(7)#1	72.41(10)	O(1)-Gd(1)-O(9)	69.13(11)
O(5)-Gd(1)-O(6)#2	114.77(10)	O(1)-Gd(1)-O(8)#1	140.60(11)
O(5)-Gd(1)-O(5)#2	65.94(11)	O(1)-Gd(1)-O(7)#1	117.22(11)
O(2)-Cu(1)-O(4)#3	89.59(14)	O(1)-Gd(1)-O(6)#2	137.70(11)
O(2)#3-Cu(1)-O(4)#3	90.41(14)	O(1)-Gd(1)-O(5)#2	134.93(10)
O(2)#3-Cu(1)-O(2)	180.000(1)	O(1)-Gd(1)-O(5)	78.72(11)
O(11)-Gd(1)-O(9)	137.27(11)	O(1)-Gd(1)-O(11)	74.89(11)

 Table S1. Selected bond lengths (Å) and angles (°) for 2.

Symmetry codes: #1 -x+2, -y+1, -z; #2 -x+1, -y+1, -z; #3 x+1, y, z.



Fig. S1 The 2D layer structure of 1.



**Fig. S2** Packing View of the 2D layer structure of **2** viewed along [011] axis. The free water molecules are shown in space-filling mode, and the hydrogen atoms have been omitted for clarity.



Fig. S3 The IR spectra of 1-4.



Fig. S4 TG curves for 1–4 in a nitrogen atmosphere (10 °C/min).



Fig. S5 The simulated and experimental powder X-ray diffraction patterns of 1-4.



Fig. S6 Temperature dependence of the  $\chi_M$  values for 1 at 1000 Oe dc magnetic field. The red solid line represents the best fit to the data of 1 with the parameters in the text.



Fig. S7 Field dependence of the magnetization of 1 at 2.0 K.



Fig. S8 Field dependence of the magnetization of 3 and 4 at 2.0 K.