Electronic Supplementary Information (ESI) for

One-dimensional Gd^{III}-M^{II} (M = Mn, Co) acetate chains exhibiting large cryogenic magnetocaloric effect at ΔH = 3T

Yin-Yin Pan, Yan Yang, La-Sheng Long*, Rong-Bin Huang and Lan-Sun Zheng

State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. E-mail: lslong@xmu.edu.cn

Experimental section:

Single-Crystal Structure Determination. Suitable single crystals of **1-2** were carefully selected under an optical microscope and glued to thin glass fibers. Diffraction data were collected on Rigaku Image Plate and Oxford Gemini S Ultra diffractometers equipped with Mo $K\alpha$ (λ = 0.71073 Å). The crystal structures were solved and refined using the SHELXTL program suite.[1] Direct methods yielded all nonhydrogen atoms, which were refined anisotropically, while all hydrogen atoms were calculated geometrically and were riding on their respective atoms. In all compounds, disordered lattice water molecules were removed during structural refinement via application of the Squeeze function in PLATON.[2]

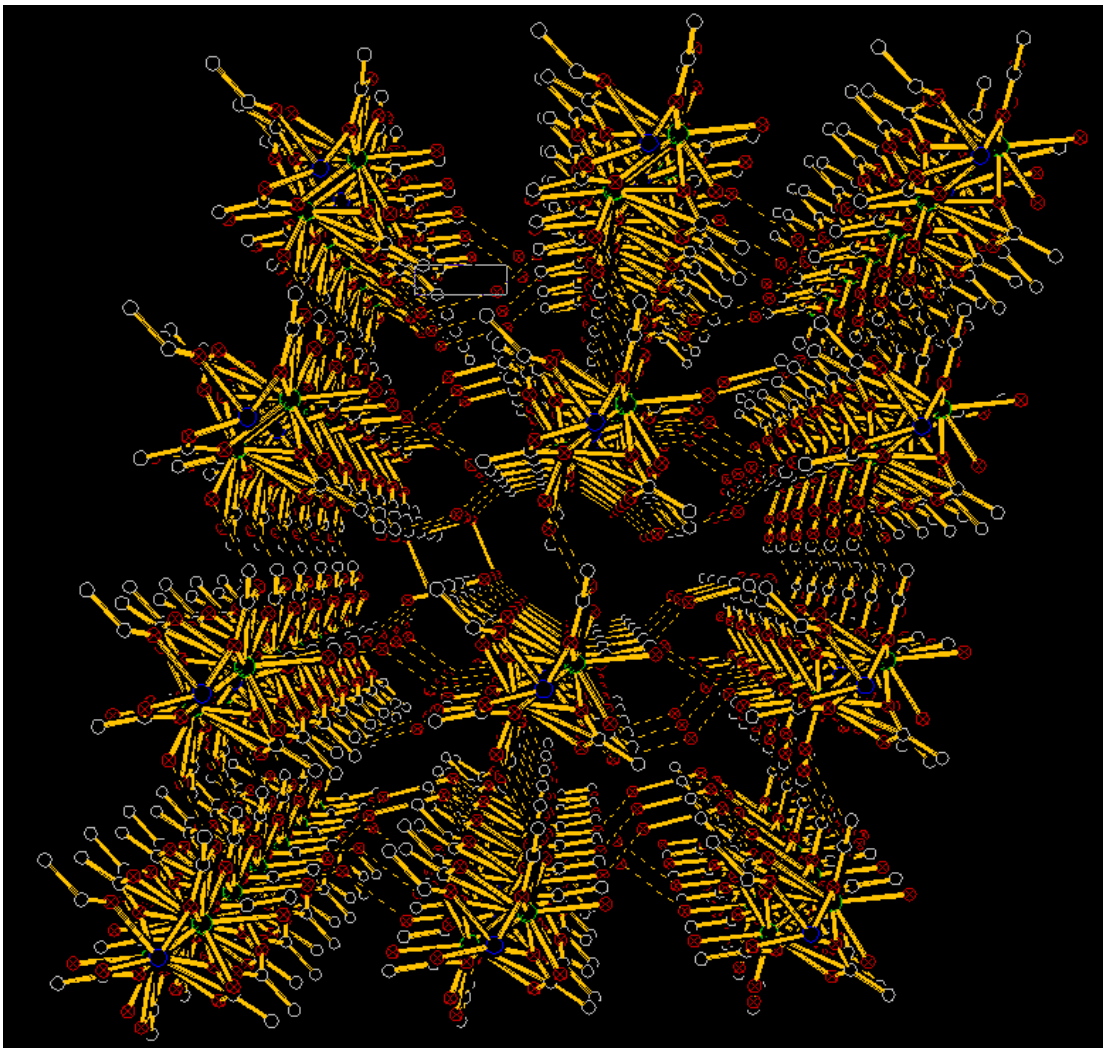

Fig. S1 3D structure of **1** viewed along *c* axis

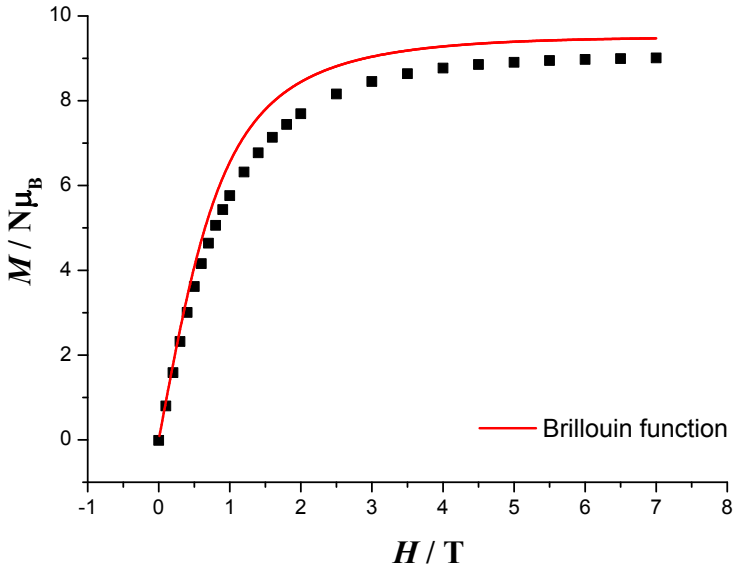

Figure S2. The red line is calculated through Brillouin function for one Gd^{3+} ion and a half Mn^{2+} ion (magnetically isolated) with $s_{Gd} = 7/2$, $g_{Gd} = 2.0$, $s_{Mn} = 5/2$, $g_{Mn} = 2.0$ at $T = 2$ K.

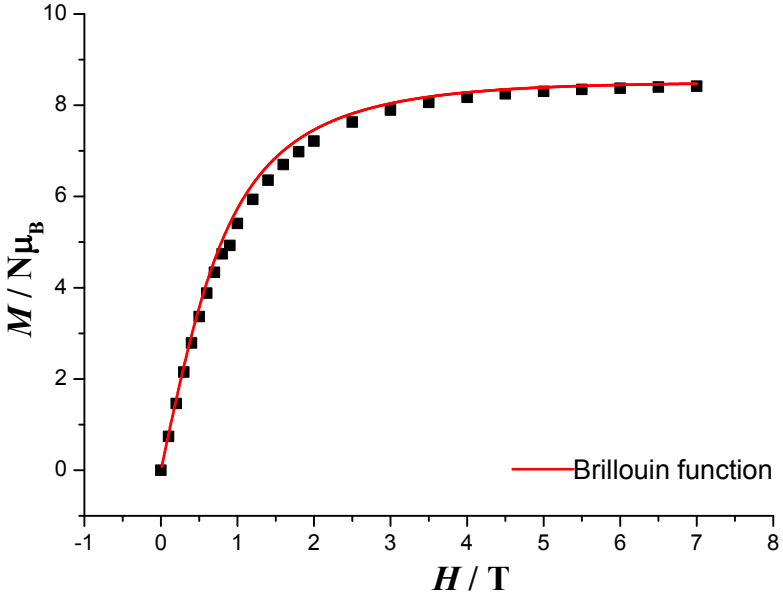

Figure S3. The red line is calculated through Brillouin function for one Gd^{3+} ion and a half Co^{2+} ion (magnetically isolated) with $s_{Gd} = 7/2$, $g_{Gd} = 2.0$, $s_{Co} = 3/2$, $g_{Co} = 2.0$ at $T = 2$ K.

Other Experimental details

All reagents were of commercial origin and were used as received. The C, H, and N microanalyses were carried out with a CE instruments EA 1110 elemental analyzer. The IR spectra (KBr pellets) were recorded in the range of 400-4000 cm^{-1} on a Nicolet 5DX spectrometer. Powder X-ray diffraction (PXRD) studies were performed on Panalytical X-Pert PRO diffractometer with Cu $K\alpha$ radiation (λ = 0.15418 nm, 40.0 kV, 30.0 mA) (Figures S2-3). TGA curve was prepared on a SDT Q600 thermal analyzer. Samples were placed in open alumina pans in the temperature range 25-1000 °C and were purged with a stream of dry N_2 flowing at 100 mL min^{-1} with heating rate 10 °C (Figure S3). Magnetic susceptibility was measured by a Quantum Design MPMS superconducting quantum interference device (SQUID).

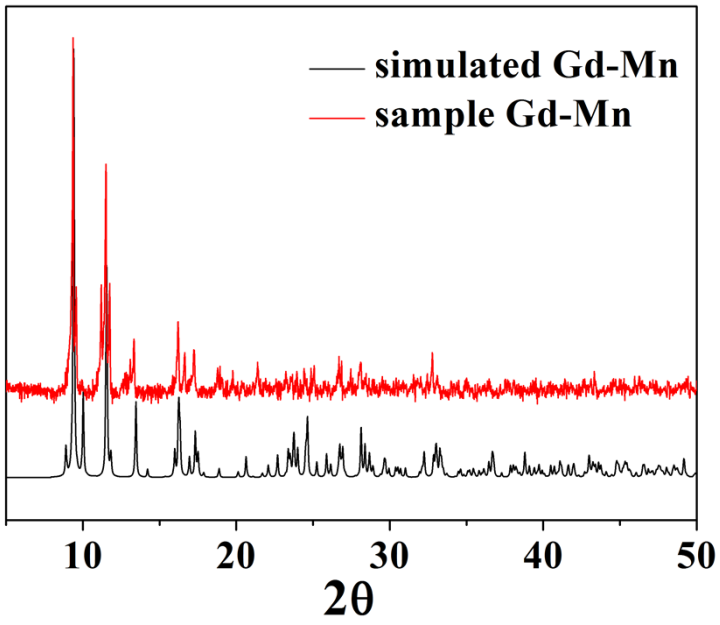

Figure S4. The PXRD pattern of **1** and simulated one.

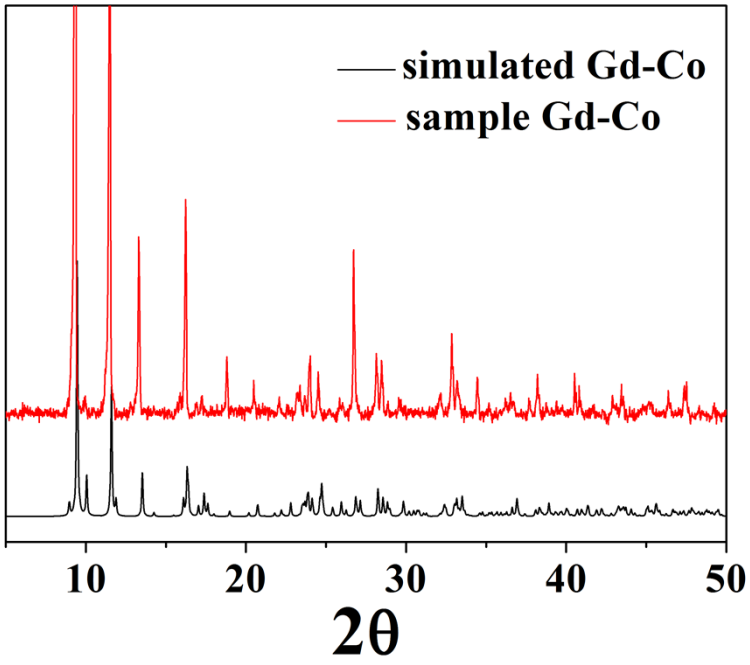

Figure S5. The PXRD pattern of **2** and simulated one.

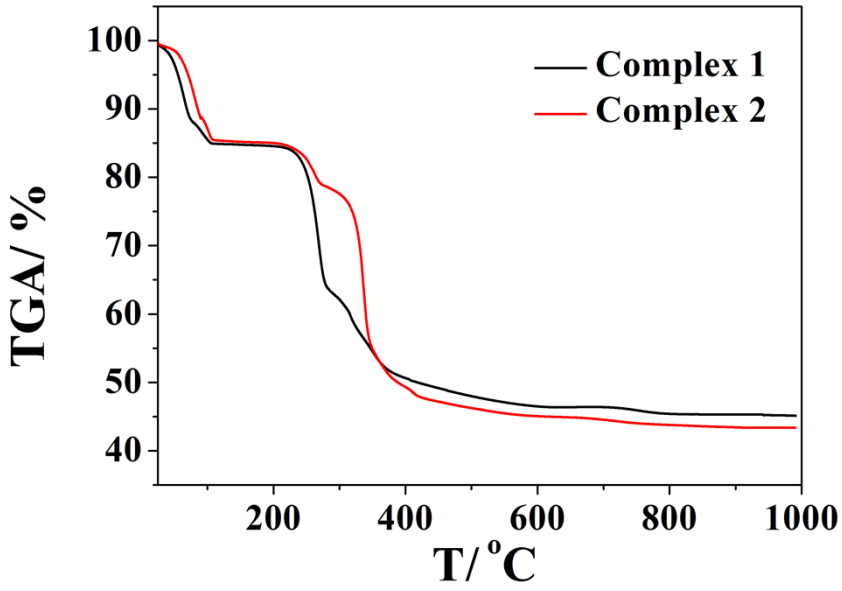

Figure S6. Thermogravimetric analyses of **1** and **2**.

The thermogravimetric analysis for **1** exhibits the first weight loss of 10.72% in the temperature range from 25 to 75°C, corresponding to the weight loss of three lattice water molecules(calc. 10.57%), and the second weight loss of 3.68% in the temperature range from 75 to 110°C, corresponding to the loss of one coordination

water molecule in **1** (calc. 3.52%), and then the metal-organic complex starts to decompose with the loss of acetate ligands and the other one coordination water molecule which has intramolecular hydrogen bonds with acetate ligand**s** (O10—H10A…O1 and O10—H10A…O6). The TGA curve of **2** is similar to that of **1**, the first and second weight loss of complex **2** are 10.65% (calc.10.53%) and 3.72% (calc.3.51%), corresponding to the weight loss of three lattice water molecules and one coordination water molecule respectively. Then the metal-organic complex starts to decompose**.**

Reference:

(1) G. M. Sheldrick, *SHELXTL 6.12*; Bruker AXS, Inc.: Madison, WI, 2003.

(2) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool;* Utrecht University: Utrecht, The Netherlands, 2001.