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An exceptionally stable 3D Gd^{III}-organic framework for use as a magnetocaloric refrigerant

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Supporting Information:

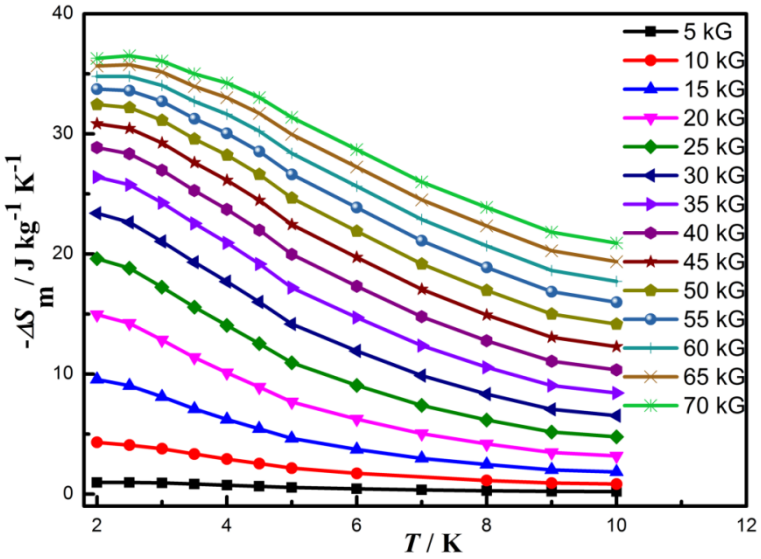

Fig. S1 The entropy change ($-\Delta S_m$) calculated from the magnetization data at T = 2 – 10 K and 5 – 70 kOe.

Table 1 Summary of $-\Delta S_m^{max}$ for 3D Gd^{III}-containing selected molecule-based materials.

Compounds	$-\Delta S_m^{max}$ ($J \cdot kg^{-1} \cdot K^{-1}$) ($\Delta H$)	$-\Delta S_m^{max}$ ($mJ \cdot cm^{-3} \cdot K^{-1}$)	Ligands' formula (M_r $g \cdot mol^{-1}$)
$\{Gd(OH)CO_3\}_n$ [S1]	66.4 (7 T)	355	CO_3^{2-} (60.0)
$\{Gd(HCOO)_3\}_n$ [S2]	55.9 (7 T)	215.7	$HCOO^-$ (45.0)
$[Gd_4(\mu_4\text{-}SO_4)_3(\mu_3\text{-}OH)_4(\mu_2\text{-}C_2O_4)(\mu_2\text{-}H_2O)(H_2O)_4]_n \cdot nH_2O$ [S3]	51.5 (7 T)	190.5	$C_2O_4^{2-}$ (88.0)
$[Gd_4(SO_4)_4(\mu_3\text{-}OH)_4(H_2O)_4]_n$ [S4]	51.3 (7 T)	198.9	–
$[Gd_6(OH)_8(suc)_5(H_2O)_2]_n \cdot 4nH_2O$ [S5]	48.0 (7 T)	144	$C_4H_4O_4^{2-}$ (116.1)
$[Gd(HCOO)(C_8H_4O_4)]_n$ [S6]	47.0 (9 T)	125.11	$C_8H_4O_4^{2-}$ (164.1)
$\{[Gd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu_4\text{-}ClO_4)_4(H_2O)_6](OH)_4\}_n$ [S7]	46.6 (7 T)	206.8	–
$[Ln(C_4O_4)(C_2O_4)_{0.5}(H_2O)_2]_n$ [S8]	44 (7 T)	127.6	$C_4O_4^{2-}$ (112.0)
$[Gd_2(OH)_2(suc)_2(H_2O)]_n \cdot 2nH_2O$ [S5]	42.8 (7 T)	120	$C_4H_4O_4^{2-}$ (116.1)
$\{[Gd_2(IDA)_3] \cdot 2H_2O\}_n$ [S9]	40.6 (7 T)	100.7	$C_4H_4NO_4^{2-}$ (130.1)
$[Gd(OH)(H_2O)(abtc)_{0.5}]_n \cdot nH_2O$ (This work)	36.6 (7 T)	97.5	$C_{16}H_6N_2O_8^{4-}$ (354.2)
$[Gd_2(N\text{-}BDC)_3(dmf)_4]_n$ [S10]	29.0 (7 T)	41.2	$C_8H_5NO_4^{2-}$ (179.1)
$[Gd_2(azdc)_3(DMA)_2]_n \cdot 2n(DMA)$ [S11]	22.3 (7 T)	34.9	$C_{14}H_8N_2O_4^{2-}$ (268.2)
$[Gd_2(fum)_3(H_2O)_4]_n \cdot 3nH_2O$ [S12]	20.7 (5 T)	52.1	$C_4H_2O_4^{2-}$ (114.1)

(S1) Y. C. Chen, L. Qin, Z. S. Meng, D. F. Yang, C. Wu, Z. D. Fu, Y. Z. Zheng, J. L. Liu, R. Tarasenko, M. Orendáč, J. Prokleška, V. Sechovský and M. L. Tong, *J. Mater. Chem. A.,* 2014, **2**, 9851.
(S2) G. Lorusso, J. W. Sharples, E. Palacios, O. Roubeau, E. K. Brechin, R. Sessoli, A. Rossin, F. Tuna, E. J. L. Mclnnes, D. Collison and M. Evangelisti, *Adv. Mater.,* 2013, **25**, 4653.

(S3) S. D. Han, X. H. Miao, S. J. Liu and X. H. Bu, *Chem. Asian. J.,* 2014, **9**, 3116.
(S4) S. D. Han, X. H. Miao, S. J. Liu and X. H. Bu, *Inorg. Chem. Front.,* 2014, **1**, 549.
(S5) Y. C. Chen, F. S. Guo, Y. Z. Zheng, J. L. Liu, J. D. Leng, R. Tarasenko, M. Orendáč, J. Prokleška, V. Sechovský and M. L. Tong, *Chem. Eur. J.,* 2013, **19**, 13504.
(S6) R. Sibille, T. Mazet, B. Malaman, and M. François, *Chem. Eur. J.,* 2012, **18**, 12970.
(S7) Y. L. Hou, G. Xiong, P. F. Shi, R. R. Cheng, J. Z. Cui and B. Zhao, *Chem. Commun.,* 2013, **49**, 6066.
(S8) S. Biswas, H. S. Jena, A. Adhikary, and S. Konar, *Inorg. Chem.,* 2014, **53**, 3926.
(S9) J. M. Jia, S. J. Liu, Y. Cui, S. D. Han, T. L. Hu, and X. H. Bu, *Cryst. Growth Des.,* 2013, **13**, 4631.
(S10) G. Lorusso, M. A. Palacios, G. S. Nichol, E. K. Brechin, O. Roubeau, and M. Evangelisti, *Chem. Commun.,* 2012, **48**, 7592.
(S11) S. W. Zhang, W. Shi, L. L. Li, E. Y. Duan, and P. Cheng, *Inorg. Chem.,* 2014, **53**, 10340.
(S12) L. Sedláková, J. Hanko, A. Orendáčová, M. Orendáč, C. L. Zhou, W. H. Zhu, B. W. Wang, Z. M. Wang, and S. Gao, *J. Alloys Compd.,* 2009, **487**, 425.

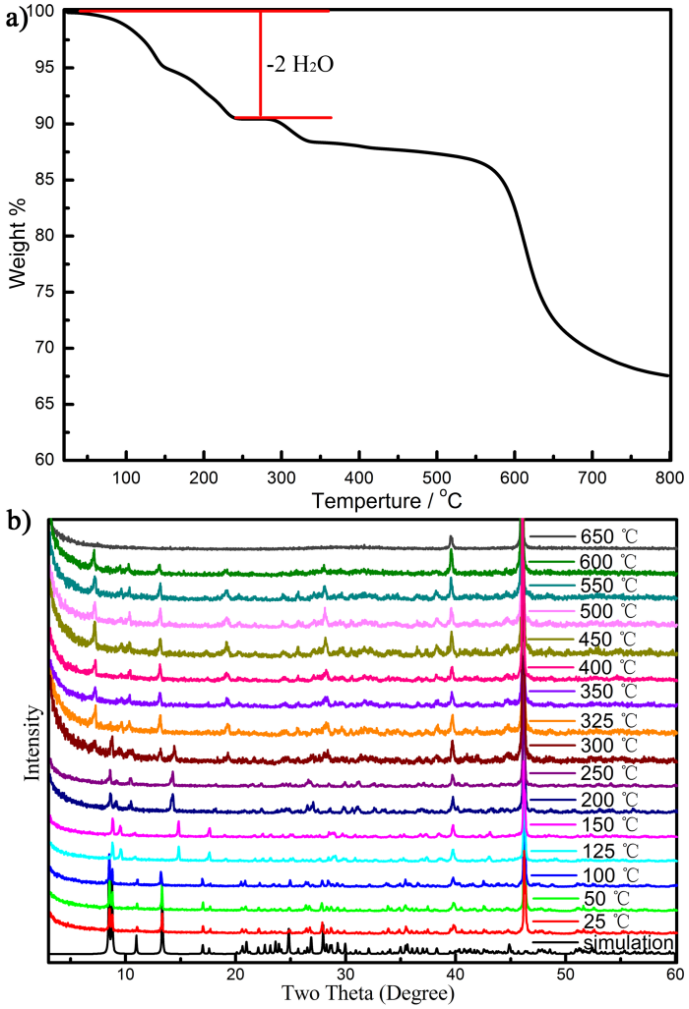

Fig. S2 (a) The TG curve of **1** on crystalline sample in a N_2 atmosphere in the range of 25 – 800 ºC; (b) The in-situ temperature-variable PXRD pattern for **1**, measured on a Pt sample platform under N_2 atmosphere in the range of 25 – 650 °C. The peaks observed at *ca.* 40° and 46.3° are derived from the Pt sample platform.

TG Analysis and Temperature–variable in-situ PXRD

The thermal stability of **1** was investigated on the crystalline sample under the N_2 atmosphere from 25 to 800 ˚C, and the thermogravimetric (TG) curve of **1** exhibits slow weight loss in the tested range (Fig. S2a). The weight loss of 9.41% between 25 and 250 ˚C corresponds to the remove of one lattice water molecule and one coordinated water molecule (calcd. 9.30%). Meanwhile, the temperature-variable *in-situ* PXRD pattern of **1** was also examined on a Pt sample platform from 25 to 650 ˚C (Fig. S2b). The corresponding PXRD patterns indicate that the structure of **1** remains unchanged after heated to 100 ˚C. As the temperature increases from 125 ˚C, the peaks start to shift, which is assumed as the remove of one coordinated water molecule. Above 250 ˚C, the peaks observed at *ca.* 8 – 10° begin to decrease gradually and disappear finally, and a new peak at *ca.* 7.3° appears, which may indicate that the framework rearranges to produce a new structure or phase, however, we were unfortunately unable to identify or solve the structure of the high-temperature phase. Upon further heating, the diffraction peaks are barely noticeable, implying that the framework of **1** begins to collapse and becomes amorphous. Moreover, the results are consistent with the TG analysis.