# *Electronic Supplementary Information (ESI)*

## Three-dimensional two-fold interpenetrated $Cr^{III}$-$Gd^{III}$ heterometallic framework as an attractive cryogenic magnetorefrigerant

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**Table S1** Comparison of $-\Delta S_m^{max}$ (larger than 30.0 J kg$^{-1}$ K$^{-1}$ with $\Delta H$ = 7/9 T) among **1** and 3*d*-Gd$^{III}$ complexes associated with potential molecule-based magnetic coolers.

| Complex | Dimensionality | $-\Delta S_m^{max}$ [J kg$^{-1}$ K$^{-1}$] ($\Delta H$) | $-\Delta S_m^{max}$ [mJ cm$^{-3}$ K$^{-1}$] |
|---|---|---|---|
| $\{[Mn(H_2O)_6][MnGd(oda)_3]_2 \cdot 6H_2O\}_n$[S2] | 3D | 50.1 (7 T) | 114.28 |
| $[Co_{10}Gd_{42}]$[S3] | 0D | 41.26 (7 T) | 112.64 |
| $\{[CrGd(IDA)_2(C_2O_4)]\}_\infty$ (**1**) | 3D | 39.86 (7 T) | 93.69 |
| $[Cr_2Gd_3]$[S4] | 0D | 38.3 (7 T) | 57.79 |
| $[Ni_{10}Gd_{42}]$[S3] | 0D | 38.2 (7 T) | 105.47 |
| $[Gd_3Mn_2]_\infty$[S5] | 3D | 40.3 (7 T) | 92.32 |
| $[Ni_{12}Gd_{36}]$[S6] | 0D | 36.3 (7 T) | 83.49 |
| $[Cu_3Gd_6]_\infty$[S7] | 3D | 35.76 (7 T) | -- |
| $[Cu_2Gd_7]$[S8] | 0D | 34.6 (9 T) | 63.70 |
| $[Ni_2Gd_2(hmp)_4(OAc)_6]$[S9] | 0D | 34.4 (7 T) | 65.57 |
| $[Mn_4Gd_6P_6]$[S10] | 0D | 33.7 (7 T) | 54.12 |
| $[Fe_2Gd_3]$[S4] | 0D | 33.1 (7 T) | 50.71 |
| $[Cu_4Gd_{12}]$[S8] | 0D | 33.0 (9 T) | 62.90 |
| $[Co_4Gd_{10}]$[S9] | 0D | 32.6 (7 T) | 54.31 |
| $[Cu_5Gd_4]$[S12] | 0D | 31 (9 T) | 61.66 |
| $[ZnGd_5]_\infty$[S13] | 3D | 30.7 (7 T) | 57.96 |

$-\Delta S_m^{max}$ [mJ cm$^{-3}$ K$^{-1}$] = $-\Delta S_m^{max}$ [J kg$^{-1}$ K$^{-1}$]*$\rho_{cald}$ [g cm$^{-3}$]. odaH = oxydiacetate acid, $H_2$IDA = iminodiacetate acid, hmpH = 2-(hydroxymethyl)pyridine

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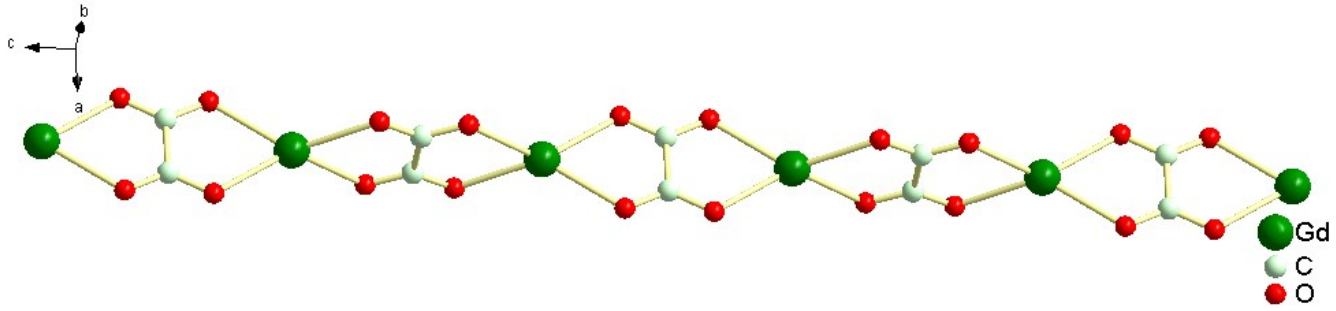
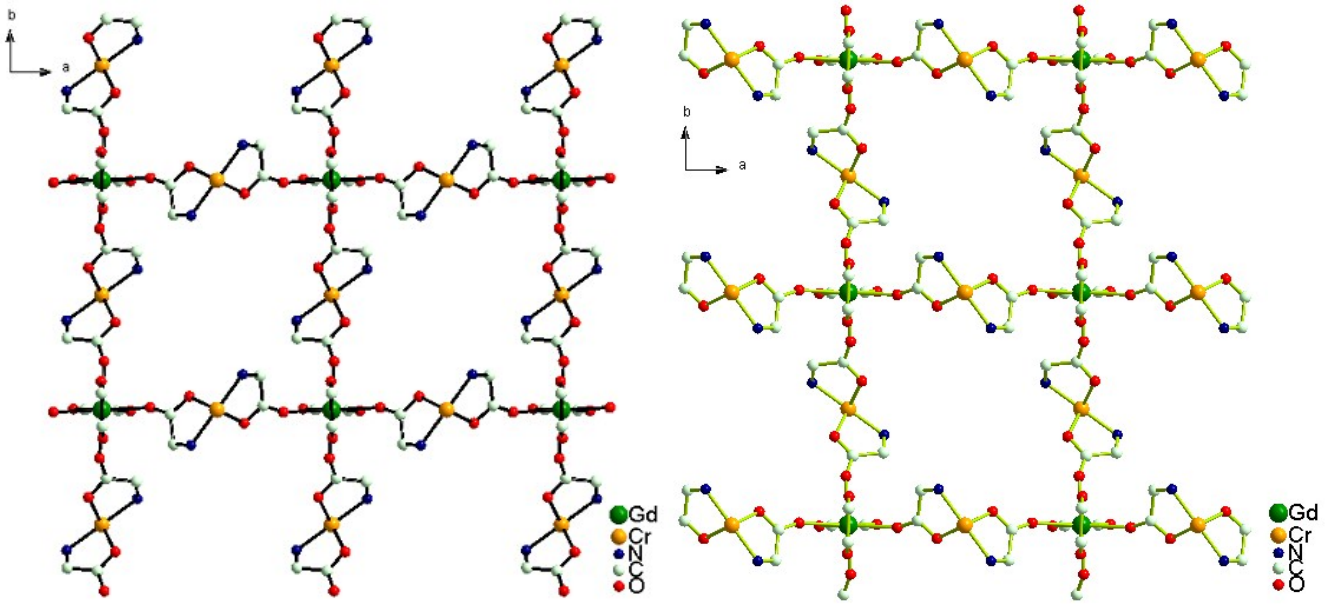
**Table S2.** Selected bond lengths (Å) and angles (°) for **1**[a]

| | | | |
|---|---|---|---|
| N1—Cr1 | 2.054 (8) | O2—Gd1 | 2.364 (4) |
| O1—Cr1 | 1.985 (4) | O4—Gd1 | 2.415 (4) |
| | | | |
| O1$^{\#3}$—Cr1—O1 | 88.0(3) | O1—Cr1—N1 | 82.7(2) |
| O1$^{\#4}$—Cr1—O1 | 92.0(3) | O1$^{\#5}$—Cr1—N1 | 97.3(2) |
| O1—Cr1—N1$^{\#5}$ | 97.3(2) | O2$^{\#6}$—Gd1—O2$^{\#7}$ | 99.0(3) |
| O4$^{\#7}$—Gd1—O4$^{\#6}$ | 132.4(2) | O2$^{\#6}$—Gd1—O2 | 149.6(2) |
| O4—Gd1—O4$^{\#6}$ | 67.31(19) | O2$^{\#7}$—Gd1—O2 | 88.9(3) |
| O2—Gd1—O4$^{\#6}$ | 138.73(14) | O2—Gd1—O4$^{\#7}$ | 76.86(17) |
| O2$^{\#7}$—Gd1—O4$^{\#6}$ | 77.90(16) | O2—Gd1—O4 | 71.66(14) |
| O4$^{\#7}$—Gd1—O4 | 135.4(2) | | |

[a]Symmetry codes: #3: $-x+2, -y+1, z$; #4: $-y+3/2, -x+3/2, -z+1/2$; #5: $-x+2, -y, z$; #6: $-x+2, -y, -z+1$; #7: $-y+3/2, -x+3/2, -z+1/2$.




(a)




(b)

**Fig. S1.** Views of (a) the $\{Gd(ox)\}_{\infty}$ chain in **1**; (b) the two interpenetrating 3D networks along *c* direction.

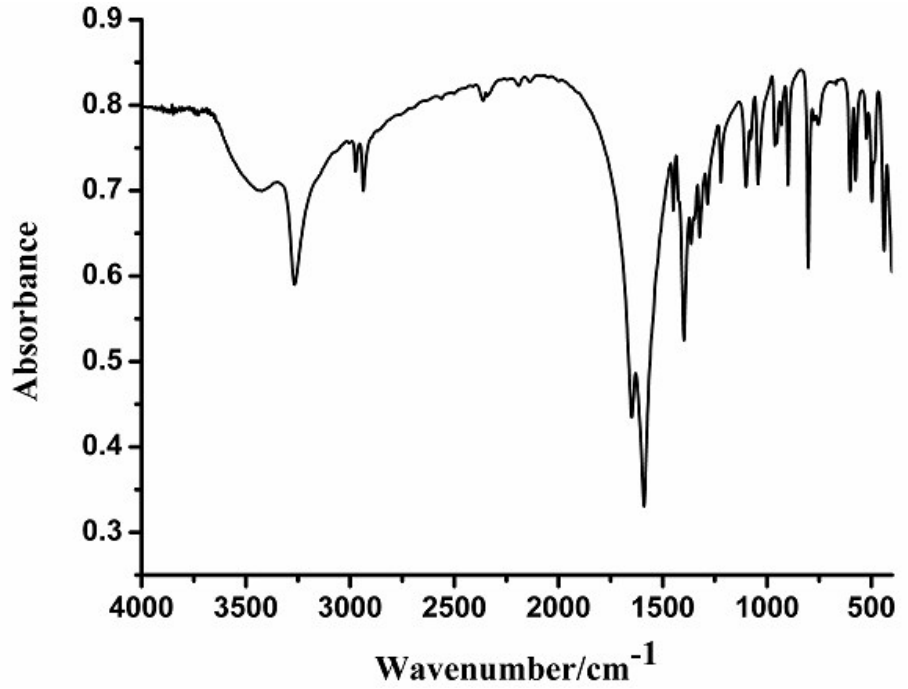



**Fig. S2.** The IR spectrum of **1**.

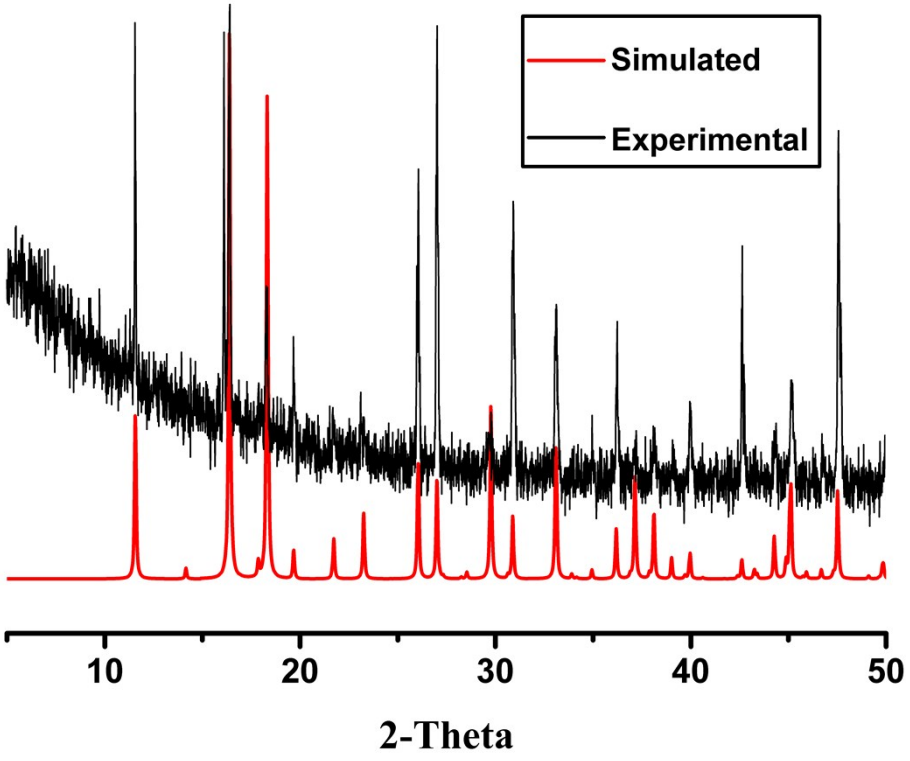



**Fig. S3**. The XRPD patterns of **1**.

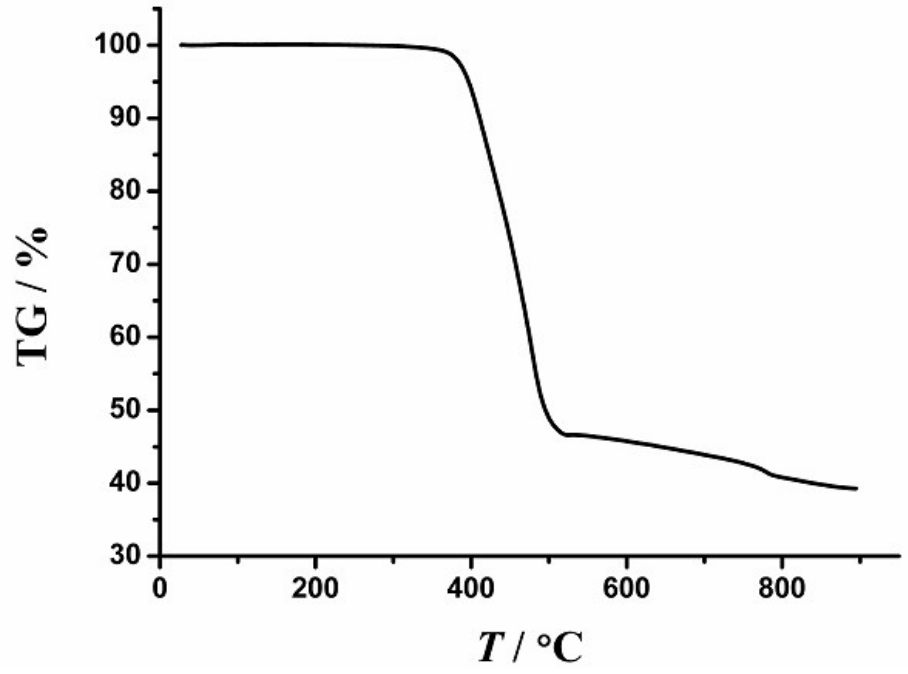



**Fig. S4**. The TGA curve for **1**.

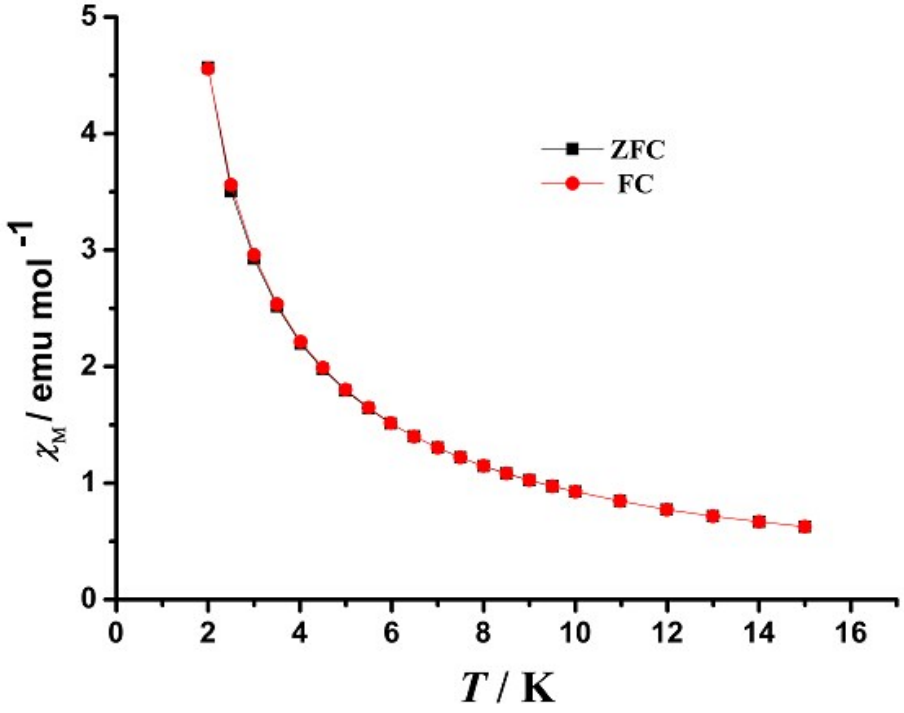



**Fig. S5.** The ZFC/FC curves under 50 Oe field of **1**.