Supporting Information for

Large cryogenic magnetocaloric effect exhibited at low field by a 3D ferromagnetically coupled Mn(II)-Gd(III) framework material

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Experimental Section

$[Mn(H_2O)_6][MnGd(oda)_3]_2 \cdot 6H_2O$ (**1**) was prepared following a modified procedure.[11] A mixture of $odaH_2$ (161 mg, 1.2 mmol) and NaOH (64 mg, 1.6 mmol) were dissolved in 10 mL of deionized water. Then, an aqueous solution (10 mL) containing $Gd(NO_3)_3 \cdot 5H_2O$ (173 mg. 0.4 mmol) and $Mn(NO_3)_2 \cdot 4H_2O$ (251 mg, 0.6 mmol) was subsequently added under vigorous stirring. After rapid filtration, the solution was mixed with 10 mL of anhydrous ethanol and left to stand at room temperature. Colorless cubic crystals suitable for X-ray crystallography formed in ~20% yield (based on Gd^{3+}) after two days. Phase purity was confirmed by Powder X-ray diffraction study (Figure S1). Elemental analysis (%) calcd for $C_{24}H_{48}Gd_2Mn_3O_{42}$: C 19.37, H 3.25; found: C 19.75, H 3.10. Infra-red (KBr disc, cm^{-1}): 3395 (m), 1596 (m), 1463(w), 1441(s), 1359(m), 1309(m), 1241(w), 1053(w), 738(w).

Physical Characterization: The magnetic measurements were carried out with the use of a Quantum Design MPMS XL-7 SQUID magnetometer MPMS. Measurements were performed on the polycrystalline samples. Diamagnetism was estimated from Pascal constants. Specific heat was studied in Quantum Design PPMS system in the temperature range 0.3 – 30.2 K in magnetic fields up to 30 kG using relaxation technique.

CCDC 900845 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

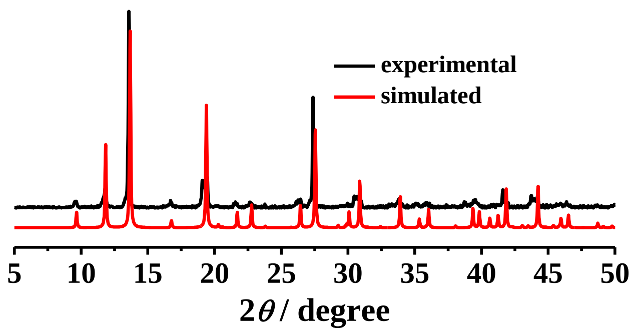

Figure S1. PXRD patterns of complex **1**.

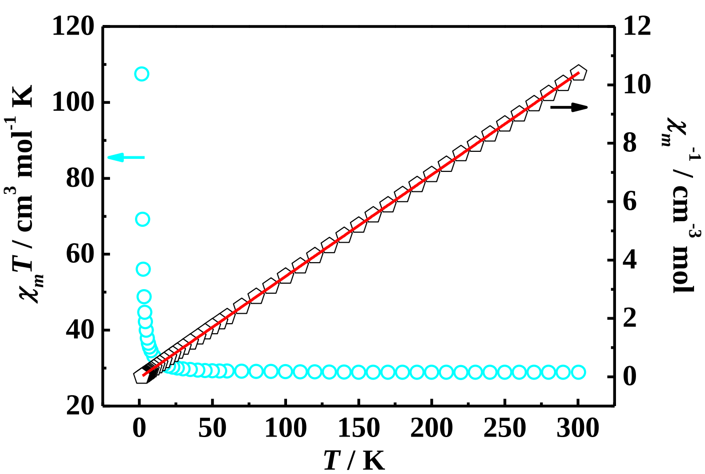

Figure S2 Plots of the χT and the inverse molecular susceptibility versus temperature for complex **1** in the 300-1.8 K temperature range in an applied magnetic field of 0.5 kG. The red solid line represents least-square fit using a Curie-Weiss law.

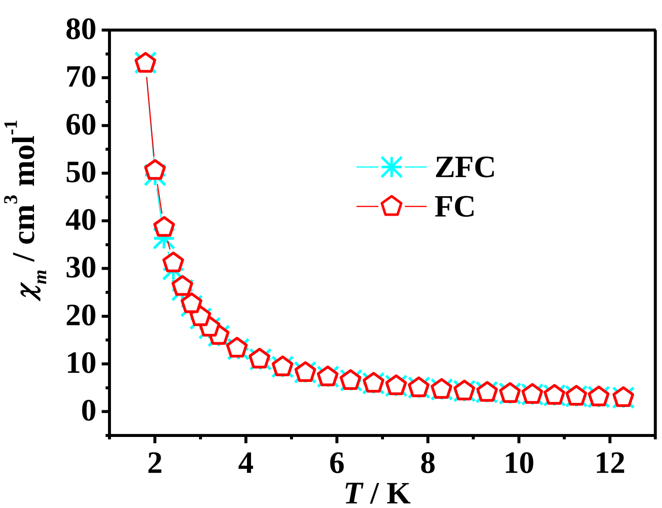

Figure S3. The zero-field-cooled (ZFC) and field-cooled (FC) molar magnetic susceptibility of **1** obtained in a dc applied field of 10Gs.

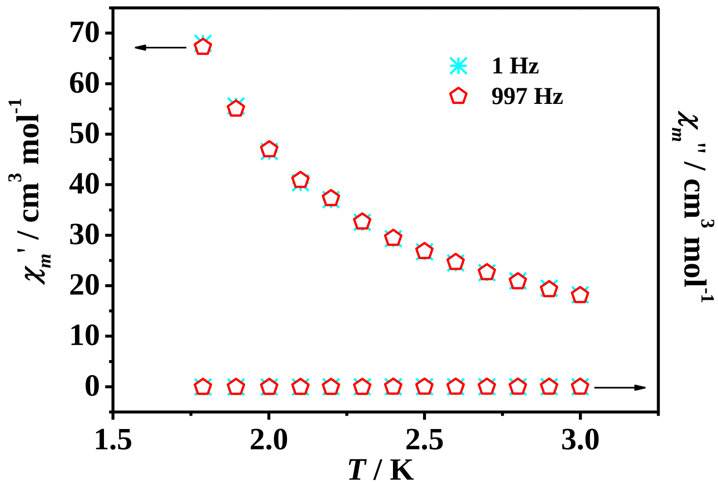

Figure S4. Temperature dependence of the in-phase (χ') and the out-of-phase (χ'') ac susceptibility component at indicated frequencies for **1** (H_{ac}=5 Gs and H_{dc}=0 Gs).

Table S1. -ΔS_m data upon ΔH at a given temperature for selected 3*d*/3*d*-4*f*/4*f* complexes.

Category	Complex	-ΔS_m / $Jkg^{-1}K^{-1}$	*H*/kG	*T*/K	Ref
3*d*	$\{Mn^{III}_6Mn^{II}_8\}$	25.0	70	3.8	A
	$\{Fe_{14}\}$	20.3	70	6	B
3*d*-4*f*	$\{Mn^{III}_4Gd^{III}_4\}$	19.0	70	3	C
	$\{Mn^{II}_4Gd^{III}_6\}$	33.7	70	3	D
	$\{Mn^{II}_3Gd^{III}_2\}_n$	50.1	70	1.8	This work
	$\{Co^{II}_6Gd^{III}_8\}$	28.6	70	3	E
	$\{Ni^{II}_{12}Gd^{III}_{36}\}$	36.6	70	3	F
	$\{Cu^{II}_5Gd^{III}_4\}$	31	90	3	G
4*f*	$[Gd_2(OAc)_6(H_2O)_4]\cdot 4H_2O$	41.6	70	1.8	H
	$[Gd(OAc)_3(H_2O)_{0.5}]_n$	47.7	70	1.8	I
	$[Gd(HCO_2)(OAc)_2(H_2O)_2]_n$	45.9	70	1.8	J
	$[Gd(HCO_2)(C_8H_4O_4)]_n$	47.0	90	2.3	K
Reference	$Gd_3Ga_5O_{12}$	27	50	5	L

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