Supporting Information:

A new approach to fabricate the Mn(II)-based magnetic refrigerant through incorporation of diamagnetic {LiO_4} spacer

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Contents

1. Experiment Section

1.1 Materials and Physical Measurements

All the materials were purchased from the commercial sources and used without any further purification. Thermogravimetric (TG) analysis was performed using a GA/ NETZSCH STA449C instrument heated from room temperature to 800ºC. Elemental analyses (C, H and N) were carried out with a Vario EL III analyzer. The IR spectrum of **1** was measured on Perkin-Elmer FT-IR spectrometer with KBr pellets in the range 4000−500 cm^{-1}. The X-ray powder diffraction (XPRD) spectrum was collected using Miniflex II (Cu-Kα radiation: λ = 1.54056 Å) in the range of 5° < 2θ < 60°. The magnetic susceptibility was measured with a Quantum Design PPMS−9T system. Diamagnetic corrections were estimated by using Pascal's constants and background corrections by experimental measurement on sample holders.

1.2 Synthesis of the Compound

A mixture of $Mn(CH_3COO)_2{\cdot}4H_2O$ (0.25 mmol, 61 mg), isophthalic acid (H_2ip, 0.50 mmol, 84 mg) and LiOH (0.5 mmol, 12 mg) was kept in a 20 mL of Teflon-lined stainless steel vessel with 6 mL isopropanol and 8 drops of glacial acetic acid were added. After stirred for about 10 minutes, the mixture was heated to 120°C. After being maintained for 72 h, the reaction vessel was cooled to room temperature in another 72 h. Colorless rod-like crystal of **1** were obtained. Yield: 92.0 mg (85% based on Mn). Anal. Calcd for $C_{16}H_{12}Li_2MnO_{10}$: C 44.33, H 2.77; found: C 44.18, H 2.86. IR (KBr, cm^{-1}): 3465 m, 1618 vs, 1553 vs, 1445 m, 1400 vs, 1268 vs, 1170 vs, 1075 s, 1020 vs, 925 vs, 838 s, 733 vs, 565 s, 519 vs.

1.3 Crystal Structure Analysis

X-ray single-crystal diffraction data were collected on Rigaku 724 CCD area-detector Diffractometer with a graphite monochromator utilizing Mo Kα radiation (λ = 0.71073 Å). CrystalClear software was used for data reduction and empirical absorption correction. The structure was solved by direct methods using SHELXS-97[1] and refined by full-matrix least-squares on F^2 using *SHELX-2016* program[2]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to carbon were generated geometrically (C−H 0.97 or 0.93 Å) and U(H) values set as 1.2

times Ueq(C). A summary of crystal data and structure refinements of **1** is provided in Table S1. Selected bond lengths and angles are given in Table S2.

2. Results and Discussion.

2.1 IR Spectroscopic Analysis

In the IR spectrum of **1** (Fig. S5, ESI†), the peak observed at 3467 cm^{-1} suggests the presence of water molecules. On the other hand, the presence of carboxylate is proved by three obvious signals at about 1622, 1558, and 1398 cm^{-1}. The strong bands at 750 cm^{-1} indicate the meta-substitution of carboxyl groups in the benzene ring of the H_2ip ligand.

2.2 Magnetic Susceptibility Analysis:

The analysis of the magnetic data for 1D regular Mn(II) chain was performed based on the Hamiltonian $H = -J\Sigma S_i S_{i+1}$ (J stands for the exchange constant between the adjacent Mn(II) ions and S_i are the classical spin vectors), and the magnetic susceptibility can be written as $\chi_m = [Ng^2\beta^2 S(S + 1)/3KT][(1 + (coth(JS(S + 1)/KT) - KT/JS(S + 1)))/(1 - (coth(JS(S + 1)/KT) - KT/JS(S + 1)))]$.

3. Tables and Figures.

Table S1. Crystallographic data for **1**.

	1
formula	$C_{16}H_{12}MnLi_2O10$
formula mass	433.08
crystal system	Monoclinic
space group	*C2/c*
a/Å	16.390(6)
b/Å	10.753(4)
c/Å	10.349(4)
α/°	90.00
β/°	111.528(5)
γ/°	90.00
V/Å^3	1696.8(11)
Z	4
D_{calc}/g cm^{-3}	1.695
μ/mm^{-1}	4.943
F(000)	876.0
Parameters	126
R_1[a],wR_2[b] [I>2σ(I)]	0.0348/0.0840
R_1[a],wR_2[b] [all data]	0.0392/0.0866
GOF on F^2	1.039

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.

Table S2. Selected bond lengths (Å) and angles (º) for **1**.

Mn1−O3B	2.2167(17)	Mn1−O3C	2.2167
Mn1O1	2.2361(14)	Mn1−O1A	2.2361(14)
Mn1−O2	2.4064(15)	Mn1−O2A	2.4064(15)
Li1−O2	1.923(4)	Li1−O3E	1.957(4)
Li1−O1F	1.959(4)	Li1−O5	1.977(4)
Mn1−O1	2.2361(14)	Mn1−O1A	2.2361(14)
Mn1−O2	2.4064(15)	Mn1−O2A	2.4064(15)
Li1D−O1−Mn1	95.77(12)	Li1−O2−Mn1	118.46(13)
Li1H−O3−Mn1G	96.45(13)		

Symmetry codes: (A) 1 − x, + y, − 1/2− z; (B) 1/2 − x, − 1/2 + y, − 1/2− z; (C) 1/2 + x,− 1/2 + y, + z; (D) + x,− y, − 1/2 + z; (E) 1/2 + x, 1/2 − y , 1/2 + z; (F) + x, − y, 1/2 + z; (G) − 1/2 + x, 1/2 − y, − 1/2 + z; (H) − 1/2 + x,1/2 − y, − 1/2 + z;

Table S3. The $-\Delta S_m$ of **1** and 3d−based compounds.

complexes	$-\Delta S_m$(J kg^{-1} K^{-1})	T(K)	ΔH(T)	Ref
$[Mn^{II}(glc)_2(H_2O)_2]$	60.3	1.8	7	3
$[NH_3CH_3][CrMn(HCOO)_6]$	48.2	2	7	4
$[CH_3NH_2CH_3][CrMn(HCOO)_6]$	43.93	2	7	5
$[Mn(Me\text{-}ip)(DMF)]_n$	42.4	2	8	6
1	30.4	2	8	This work
$[Fe_2(L)_2](BF_4)_2\cdot 2(H_2O)$	27.7	3	7	6
$[Fe_2(L)_2](Cl)_2\cdot 2(CH_3OH)\cdot 4(H_2O)$	26.5	3	7	6
$[Mn^{III}_6Mn^{II}_8(OH)_2(Hpeol)_4(H_2peol)_6I_4(EtOH)_6]I_4$	25	3.8	7	7
$[Fe_2(L)_2](NO_3)_2\cdot 3(CH_3OH)\cdot 2(H_2O)$	24.1	3	7	6
$[Fe_2(L)_2](ClO_4)(Cl)\cdot 4(CH_3OH)\cdot 2(H_2O)$	22.9	3	7	6
$Fe^{II}_{14}O_6(ta)_6(OMe)_{18}Cl_6$	20.3	6	7	8
$[Mn^{II}_4(N_3)_{7.3}Cl_{0.7}(dafo)_4]$	19.3	4	5	9
$[Mn^{II}(bipy)_3]_{1.5}[Mn^{II}_{24}Mn^{IV}_8(thme)_{16}(bipy)_{24}(N_3)_{12}(OAc)_{12}](ClO_4)_{11}$	18.2	1.6	7	10
$Fe^{III}_{14}O_6(bta)_6(OMe)_{18}Cl_6$	17.6	6	7	11, 12
$[Mn^{III}_6Mn^{II}_8(OH)_2(Hpeol)_4(H_2peol)_6I_4(EtOH)_6]I_4\cdot 12EtOH$	17.0	3.8	7	7
$Fe^{III}(acetate)_3[9\text{-}MC_{FeN(shi)}\text{-}3](MeOH)_3\cdot MeOH\cdot 7H_2O$	15.4	3	7	13
$\{Na_2Mn^{II}(SO_4)_3(OH)_3\}_n$	14.4	13.5	7	14
$[Mn^{II}_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH.4H_2O$	13.8	13.8	5	15
$[Mn^{III}_{11}Mn^{II}_6O_8Cl_4(dmp)_{10}(OAc)_{2.66}Cl_{2.34}(py)_3(MeCN)_2]\cdot 7MeCN$	13.3	5.2	9	16
$\{[Co^{II}_5(Me{-}ip)_4(Me{-}Hip)_2(H_2O)_4].6H_2O\}n$	13.2	4.0	8	17
$[Mn^{III}_6Mn^{II}_4(OH)_6(amp)_4(ampH)_4I_4(EtOH)_4]\ I_4\cdot 12EtOH$	13.0	2.2	7	9, 18
$[Mn^{III}_6Mn^{II}_4O_4(mptH)_6(N_3)_3Br_2](N_3)_{0.7}Br_{0.3}\cdot 3MeCN\cdot 2MeOH$	10.3	2.6	9	16
$[Na_2Mn^{III}_{11}Mn^{II}_4O_8(hmpH)_{10}(OAc)_2(H_2O)_2(MeO)_{1.5}(N_3)_{2.5}](OAc)_{10}H_2O\cdot 2MeOH$	9.5	6	7	18
$[Mn^{III}_{12}Mn^{II}_7O_8(hmpH)_{12}(N_3)_3(MeO)_{5.5}(MeOH)_{3.5}(H_2O)_{1.5}$	9.0	9	7	18

$(OH)_{0.5}](OAc)\cdot 10H_2O$				
$[Mn^{III}_{12}Mn^{II}_7O_8(bhmmp)_{12}$	8.9	4.2	7	18
$(MeCN)_6]Cl_2\cdot 10MeOH.MeCN$				
$[Fe^{III}_{17}O_{16}(OH)_{12}(py)_{12}Br_4]Br_3$	8.9	2.7	7	19
$Fe^{III}(benzoate)_3$[9-$MC_{FeN(shi)}$-3]	7.4	7	7	13
$(MeOH)_3\cdot MeOH\cdot 4H_2O$				
$[Mn^{II}(glc)_2]_n$	6.9	7.0	7	3
$NiCl_2(bipy)$	6	7	7	20
$[Mn^{III}_8Mn^{IV}_4O_{12}(2-ClPhCO_2)_{16}$	4.3	~2.5	3	21
$(H_2O)_4]CH_2Cl_2\cdot 5H_2O$				
$\{Co^{II}_4(OH)_2(SBA)_3\}_n$	2.4	10	5	22
$[Mn^{II}_3(OH)_2(tdc)_2]_n$	<1.7	25	5	23

Abbrevation: glc = glycolates; H_2Me-ip = 5-methylisophthalic acid; H_2L = N′1,N′4-bis(2-hydroxybenzylidene)succinohydrazide; H_2peol = pentaerythritol; taH = 1,2,3-triazole; dafo = 4,5-diazafluoren-9-one; bipy = bipyridyl; thme = methyl-hexane; bta = benzotriazole; H_2dmp = 2,2-dimethyl-1,3-propanediol; py = pyridine; H_2amp = 1,3-propanediol; H_3mpt = 3-methylpentan-1,3,5-triol; H_3hmp = 2,6-bis(hydroxymethyl)-4-methylpheno; bhmmp = 2,6-bis(hydroxymethyl)-4-methylphenol; SBA = sebacic acid; tdc = thiophene-2,5-dicarboxylic acid.

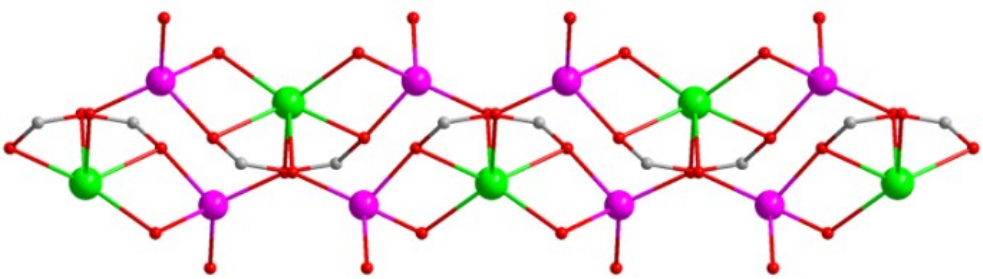

Figure S1. View of the −Mn−Li_2−Mn−Li_2− chain in **1**.

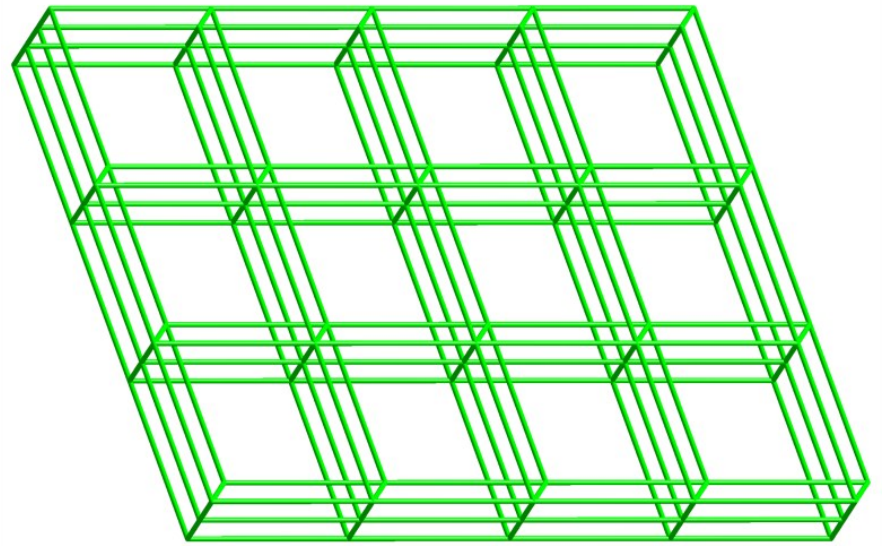

Figure S2. View of the 6-connected topological network of **1**.

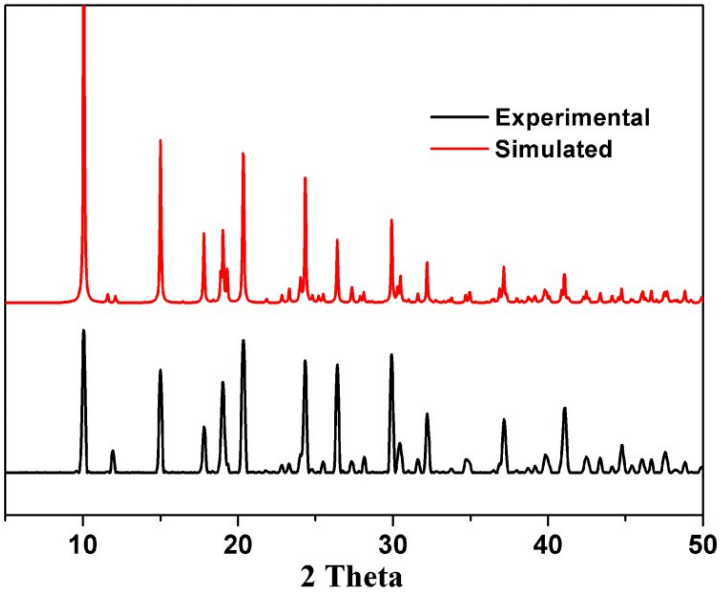

Figure S3. The PXRD of **1**.

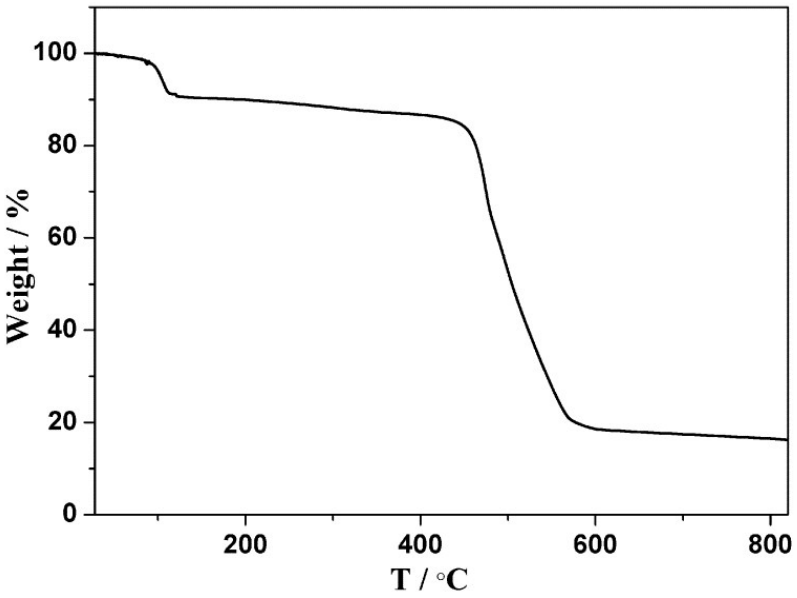

Figure S4. The TG curve of compound **1**.

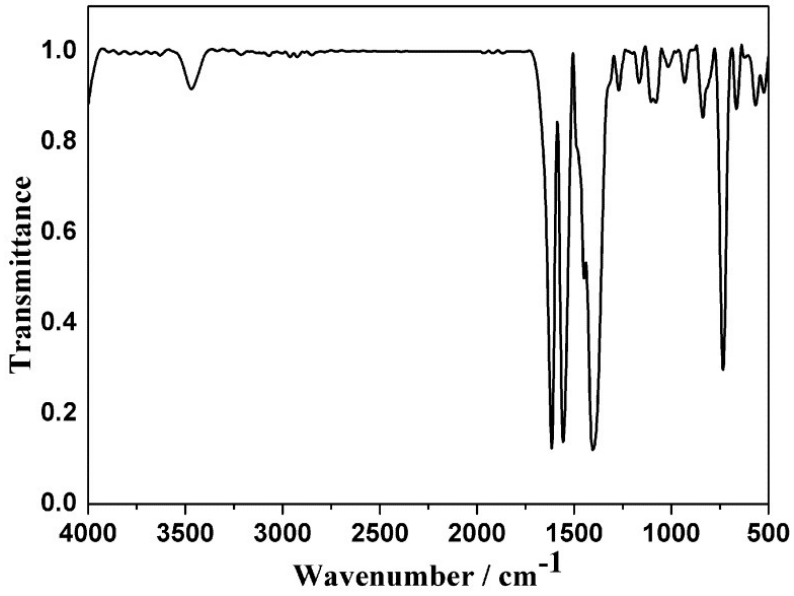

Figure S5. The IR spectrum of compound **1**.

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