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ARTICLE

Two Gd^{III} complexes derived from dicarboxylate ligands as cryogenic magnetorefrigerants

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Two Gd^{III} complexes, namely $[Gd_2(OH)_2(oda)_2(H_2O)_4]_\infty$ (**1**) and $\{[Gd(fum)(ox)_{0.5}(H_2O)_2]\cdot 2H_2O\}_\infty$ (**2**) (H_2oda = oxydiacetic acid, H_2fum = fumaric acid and H_2ox = oxalic acid), have been constructed *via* hydrothermal reactions. Complex **1** is a one-dimensional chain structure based on hydroxyl-bridged Gd_2O_2 cores, while complex **2** exhibits a three-dimensional framework consisting of Gd_6 macrocycles, and also can be seen as a 3D layer-pillar structure with intersected channels occupied by guest water. Magnetic studies indicate weak antiferromagnetic and ferromagnetic interactions between adjacent Gd^{III} ions exist in **1** and **2**, which display large magnetocaloric effects with $-\Delta S_m^{max} = 43.3$ and 37.1 J kg^{-1} K^{-1} for $\Delta H = 7$ T, respectively. Notably, the maximum entropy changes ($-\Delta S_m^{max}$) of **1** and **2** reach 29.9 and 28.5 J kg^{-1} K^{-1} at 2 K for a moderate field change ($\Delta H = 3$ T). Therefore, **1** and **2** could be regarded as potential magnetorefrigerants for low-temperature applications.

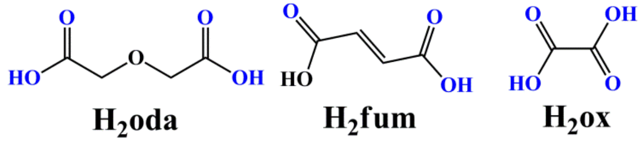
Introduction

Recently, considerable interest has been focused on the investigation of molecular cryogenic magnetorefrigerants because they have been proposed as environmentally friendly and energy-efficient cooling materials.[1] The refrigeration process is based on the magnetocaloric effect (MCE), which describes the adiabatic temperature change (ΔT_{ad}) or the isothermal magnetic entropy change (ΔS_m) of a solid in a varying magnetic field.[2] With the key applications in single-chain magnets, single-ion magnets, spin qubits and high-performance and easy-accessible molecule-based magnetorefrigerants, Gd^{III} complexes [including Gd^{III} clusters and Gd^{III} coordination polymers (CPs)] have attracted much more attention considering the inherent properties of Gd^{III} ion, such as negligible magnetic anisotropy (D), large spin ground state (S) and low-lying excited spin states.[3] Additionally, weak interactions usually occur in the Gd^{III} complexes because of the shielding of the f orbitals and the consequent poor overlap with bridging ligand orbitals, which is profitable to enhance the MCE.[4] Thus, this work aims to produce new Gd-based molecular magnetic materials with larger MCEs in fields of less than 20 kOe, which can be generated by commercial Nd-Fe-B permanent magnets.

Because of the synthetic challenge of high-nuclearity Gd^{III} clusters, the MCE exploration of Gd^{III} CPs has become more active in recent years.[5] In this context, the control of magnetic density (M_W/N_{Gd} ratio) and magnetic interaction (θ) between Gd^{III} ions is pivotal,[6] suggesting that the use of light organic molecules and suitable magnetic exchange channels should be necessary. Among kinds of light organic ligands, carboxylate ligands displaying various coordination modes could take part in coordination of the complicated and fantastic frameworks with interesting properties.[7] According to literatures,[8] monocarboxylate ligands have been extensively employed to construct the Gd^{III}-based magnetorefrigerants, however, the Gd^{III} CPs based on dicarboxylate ligands have become more preferred for preparing the high-performance cryogenic magnetorefrigerants. It is because that dicarboxylates could bear much more coordination modes compared with monocarboxylate ligands and transmit weak magnetic interactions.[9]

Previous literatures indicate hydrothermal reaction is an efficient method toward the construction of rare earth magnetic coolers,[10] during which *in situ* synthesis frequently occurs. In other words, some new ligands could be generated *in situ* and further coordinate to Gd^{III} ions to form the Gd^{III} complexes, giving rise to a variety of functional Gd^{III} complexes. Based on above consideration, Gd_2O_3 and $Gd(NO_3)_3$ were selected as metal ion sources, while oxydiacetic acid (H_2oda) and fumaric acid (H_2fum) were employed as primary ligands. We believe that the use of these two dicarboxylate ligands will be helpful for the synthesis of Gd^{III} CPs.

As an extension of our previous studies on molecule-based magnetic coolers,[2a,6b,11] we report herein two Gd^{III} CPs derived from dicarboxylate ligands, namely $[Gd_2(OH)_2(oda)_2(H_2O)_4]_\infty$ (**1**) and $\{[Gd(fum)(ox)_{0.5}(H_2O)_2]\cdot 2H_2O\}_\infty$ (**2**) (H_2oda = oxydiacetic acid, H_2fum = fumaric acid and H_2ox = oxalic acid). Magnetic investigations indicate weak antiferromagnetic (AF) and ferromagnetic (F) interactions between adjacent Gd^{III} ions in **1** and **2**, which display large magnetocaloric effects with $-\Delta S_m^{max}$ = 43.3 and 37.1 J kg^{-1} K^{-1} for ΔH = 7 T, respectively.



Scheme 1. The ligands used and formed *in situ* for the synthesis of **1** and **2**.

Experimental

Materials and instrumentation

All chemicals were of reagent grade and used as purchased without further purification. Elemental analysis (C, H and N) was performed on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). The X-ray powder diffraction (PXRD) spectra were recorded on a Rigaku D/Max-2500 diffractometer at 60 kV, 300 mA for a Cu-target tube and a graphite monochromator. Simulation of the PXRD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the Internet at http://www.iucr.org. IR spectra were measured in the range of 400–4000 cm^{-1} on a Bruker ALPHA FT-IR spectrometer using KBr pellets (Bruker, German). Magnetic data were measured by a Quantum Design MPMS-XL-7 SQUID magnetometer. Diamagnetic corrections were estimated by using Pascal constants and background corrections by experimental measurement on sample holders.

Preparation of 1 and 2. $[Gd_2(OH)_2(oda)_2(H_2O)_4]_\infty$ (1): A mixture of Gd_2O_3 (181 mg, 0.5 mmol) and H_2oda (134 mg, 1 mmol) in 10 mL H_2O was stirred for about 15 min, sealed in a 25 mL Teflon-lined autoclave, and heated to 160 ℃ for 3 days. After the autoclave was cooled to room temperature in 12 h, block colorless crystals were collected with ~30% yield based on Gd^{III}. Anal. Calcd for $C_4H_9GdO_8$: C, 14.03; H, 2.65%. Found: C, 14.25; H, 2.34%. IR spectrum is shown in Fig. S5a (ESI).

$\{[Gd(fum)(ox)_{0.5}(H_2O)_2]\cdot 2H_2O\}_\infty$ (2): A mixture of $Gd(NO_3)_3\cdot 6H_2O$ (270 mg, 0.6 mmol) and H_2fum (522 mg, 4.5 mmol) in 9 mL H_2O was sealed in a 25 mL Teflon-lined autoclave, and heated to 140 ℃ for 2 days. After the autoclave was cooled to room temperature in 48 h, block colorless crystals were collected with ~35% yield based on Gd^{III}. Anal. Calcd for $C_5H_{10}GdO_{10}$: C, 15.50; H, 2.60%. Found: C, 15.96; H, 2.80%. IR spectrum is shown in Fig. S5b (ESI).

Crystallographic data and structure refinements. The single-crystal X-ray diffraction data of **1** and **2** were collected on a Rigaku SCX-mini diffractometer at 293(2) K with Mo-Kα radiation (λ = 0.71073 Å) by ω scan mode. The program *CrystalClear*[12] was used for the integration of the diffraction profiles. The structures were solved by direct method using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied by using the SADABS program).[13] The non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. All hydrogen atoms of ligands were generated theoretically at the specific atoms and refined isotropically with fixed thermal factors. The hydrogen atoms of water molecules and hydroxyl groups in **1** and **2** were added by the difference Fourier maps and refined with suitable constrains. A summary of the crystallographic data, data collection and refinement parameters for **1** and **2** is provided in Table 1.

Table 1. Crystallographic data, data collection and refinement parameters for **1** and **2**

	1	**2**
formula	$C_4H_9GdO_8$	$C_5H_{10}GdO_{10}$
M_r	342.36	387.38
crystal system	monclinic	orthrhombic
space group	$P2_1/c$	$Fddd$
a[Å]	10.950(2)	9.6867(19)
b[Å]	6.8081(14)	15.449(3)
c[Å]	11.381(2)	27.303(6)
β[°]	95.76(3)	90
V[Å^3]	844.2(3)	4085.9(14)
ρ[g cm^{-3}]	2.694	2.519
Z	4	16
F(000)	644	2944
μ[mm^{-1}]	7.871	6.535
collected reflections	6792	10269
unique reflections	1462	1176
R_{int}	0.0975	0.0375
R_1^a/wR_2^b [I>2σ(I)]	0.0551/0.1296	0.0244/0.0432
GOF on F^2	1.180	1.167

$^aR = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$. $^bRw = [\Sigma w(|F_0|^2 - |F_C|^2)^2/(\Sigma w|F_0|^2)^2]^{1/2}$.

Results and discussion

Syntheses

Compared with lanthanide salts, the use of Gd_2O_3 provides not only a slow-release Ln^{III} ion source and a pH regulator of the reactions, but also the possibility of the introduction of hydroxyl.[6b,11] Additionally, oxalate anion could be formed *in situ* when using dicarboxylates as organic ligands under hydrothermal conditions.[14]

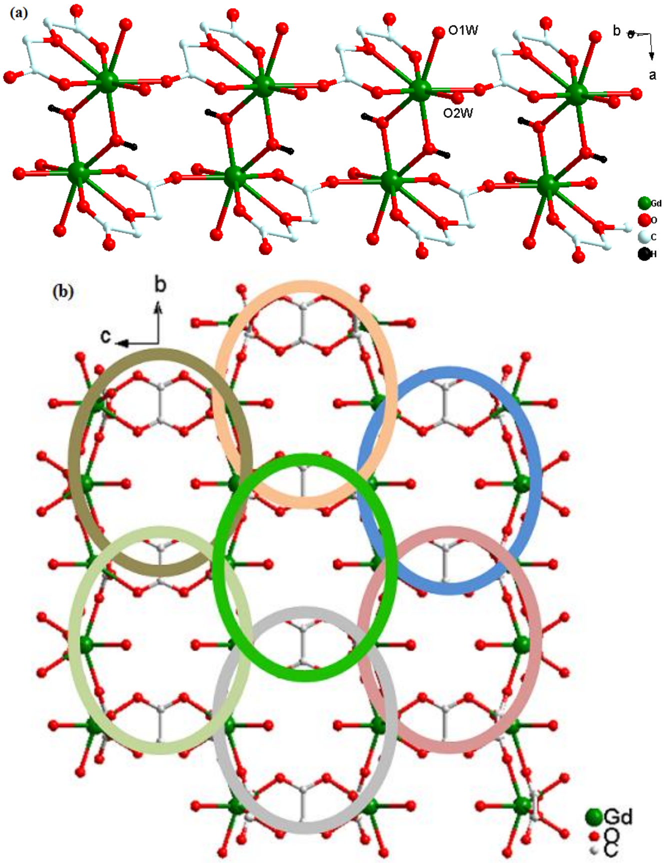


Fig. 1. Views of (a) the 1D chain structure of **1** and (b) the 3D structure of **2** composed of Gd_6 macrocycles along *a* direction.

Description of crystal structures

Isostructural structures of **1** and **2** have been reported previously,[15] therefore we herein present only a relatively brief description of their structures. Complex **1** crystallizes in the monoclinic space group $P2_1/c$, and the structure is shown in Fig. 1a. Each Gd^{III} ion shows an eight-coordinated environment and is surrounded by two oda^{2-} ligands, two hydroxyls and two water molecules (O1W and O2W). A pair of adjacent Gd^{III} ions is connected by hydroxyl O atoms to form a dinuclear unit (Gd_2). Each two neighboring Gd_2 units are further bridged through *syn*,*anti* carboxylate groups to form 1D ladder Gd^{III} chains. The $Gd_2(OH)_2$ unit is centrosymmetric with a Gd−Gd distance of 3.8049(16) Å and a Gd−O−Gd angle of 113.9(4)°. The 3D packing structure (Fig. S1, ESI) indicates the existence of the weak intermolecular C−H⋯O hydrogen bonds because of the short distances (Table S4, ESI).

Complex **2** possesses a 3D porous framework consisting of ox-pillared Gd-fum layers (Fig. S2b, ESI). The unique Gd^{III} ion is eight-coordinated by four fum^{2-} ligands, two water molecules and one bis-chelating ox^{2-}, in a bi-capped trigonal prism (Fig. S2a, ESI). The Gd-fum layer extends in the *ab* plane. In this layer, the Gd^{III} ions are linked by two *syn*,*anti* carboxylate bridges into a chain along one diagonal direction (*a*+*b*), while the neighboring parallel chains are connected along the other diagonal direction (*a*-*b*). The two coordinated waters and the ox of each Gd^{III} ion stretch out of the Gd-fum layer, residing on the two sides of the layer and associated with opposite orientations for the neighboring Gd^{III} ion. Along the *c* direction, the Gd-fum layers are pillared by the ox^{2-}, thus resulting in a 3D framework (Fig. S2b, ESI). Interestingly, the 3D structure could be composed of Gd_6 macrocycles, all of which arrange neatly along the *a* axis with adjacent Gd_6 macrocycles sharing two or three Gd^{III} ions (Fig. 1b), exhibiting an aesthetic appeal. The intersected channels are occupied by lattice water molecules, that is, two per formula. The framework possesses a solvent accessible per unit cell volume of 4085.9 Å^3, 22.1% of the unit cell without consideration of water molecules calculated by PLATON.[16] In addition, the topological analysis of **2** has not been provided for the typical 3D layer-pillar structure (or chain-based structure).

Magnetic Studies

Before the magnetic measurements, the PXRD measurements of the crushed crystalline samples of **1** and **2** were carried out to confirm their phase purities (Fig. S2 in the ESI).

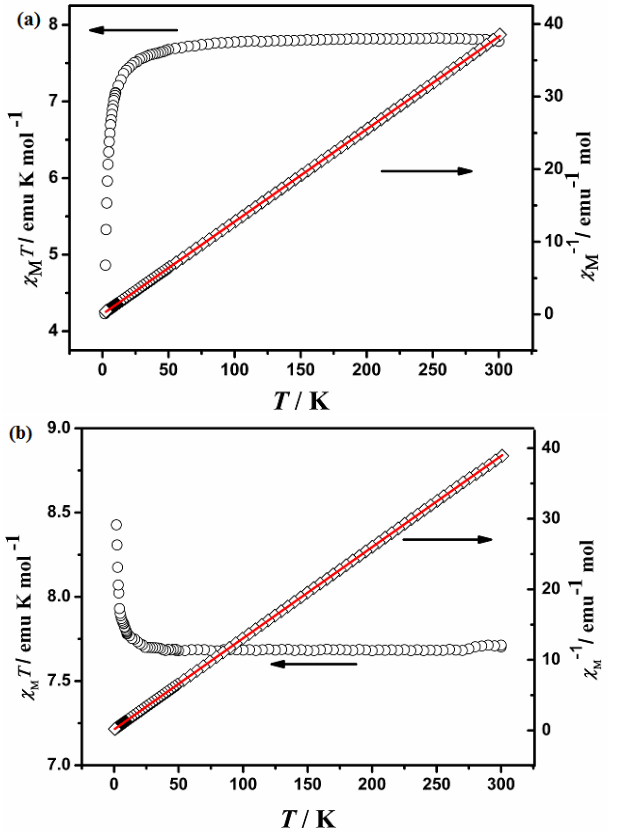


Fig. 2. Plots of $\chi_M T$ *vs.* T and χ_M^{-1} *vs.* T (red part for the Curie-Weiss fitting) for **1** (a) and **2** (b) (red lines represent the best fitting).

The magnetic properties of **1** and **2** were studied by solid state magnetic susceptibility measurements in 2.0−300 K range at 1 kOe dc field and the isothermal field-dependent magnetizations *M*(*H*) at fields up to 70 kOe at 2.0 K. The magnetic properties of **1** and **2** in the form of $\chi_M T$ *vs.* T plots are shown in Fig. 2. The room-temperature $\chi_M T$ products estimated as 7.78 emu K mol^{-1} (**1**) and 7.70 (**2**) emu K mol^{-1} are in relatively good agreement with the presence of per Gd^{III} ion ($S = 7/2$, $g = 2$, $C = 7.88$ emu K mol^{-1}). For **1**, as the temperature decreases, the $\chi_M T$ value stays nearly constant in the high temperature range with a value of 7.77 emu K mol^{-1} at 100 K. Upon further cooling the temperature to 1.8 K, $\chi_M T$ rapidly decreases to a minimum value (4.23 emu K mol^{-1}), indicating the AF interaction between Gd^{III} ions. For **2**, upon lowering of the temperature to 1.8 K, $\chi_M T$ value stays nearly constant at high temperatures, and then increases sharply to a maximum value (8.43 emu K mol^{-1}), which indicates F interaction between Gd^{III} ions.

The χ_M^{-1} vs. T plots of **1** and **2** are shown in Fig. 2. Curie-Weiss fitting [$\chi_M = C/(T\text{-}\theta)$] of the magnetic data in the range of 1.8–300 K gives C = 7.85 emu K mol^{-1}, θ = -1.06 K for **1**, and C = 7.69 emu K mol^{-1}, θ = 0.03 K for **2**. The very small θ values for **1** and **2** also indicate weak magnetic couplings between the Gd^{III} ions. The *M vs. H* curves are shown in Fig. 3. For **1**, the magnetization slowly increases and approaches to 7.35 Nβ at 70 kOe. The experimental magnetization curve is below the red line that presents the Brillouin function for one magnetically uncoupled Gd^{III} ion with S = 7/2 and g = 2.1, which also supports the weak antiferromagnetism. For **2**, the magnetization increases fast and tends to 6.98 Nβ at 70 kOe. The change of M could be well described by the Brillouin function with the parameters derived from the static susceptibility data, which confirms the weak F interaction between Gd^{III} ions. All mentioned above is in good agreement with the prediction of the weak Gd$^{III}\cdot\cdot$Gd^{III} coupling.

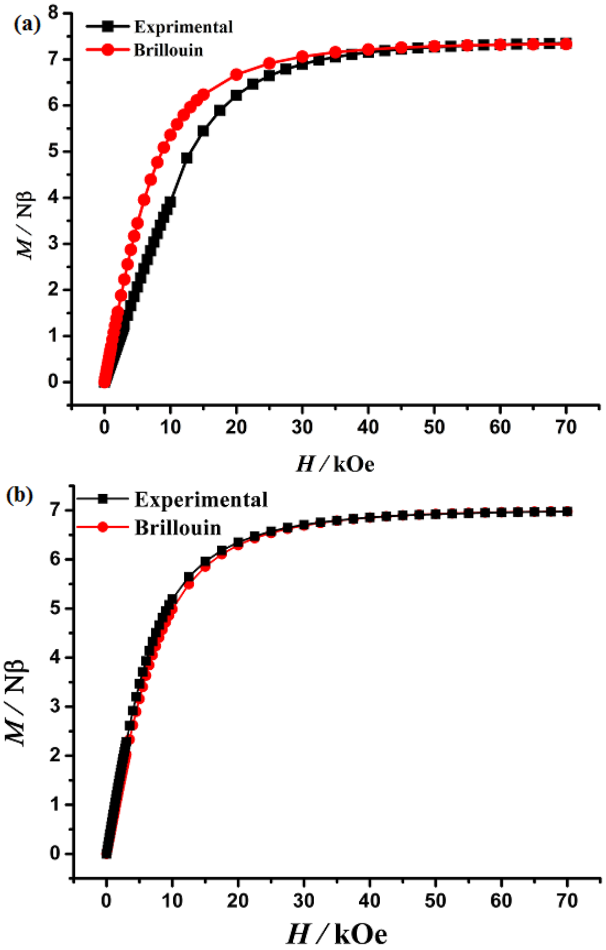


Fig. 3. The curves of M *vs.* H for **1** (a) and **2** (b) in the field range 0-70 kOe.

Considering the weak magnetic couplings between the Gd^{III} ions and potential application of Gd^{III} complexes for magnetic refrigeration, we herein also investigated the magnetocaloric properties of **1** and **2**. As a vital parameter in evaluating the MCE, the magnetic entropy change (ΔS_m) can be derived by applying the Maxwell equation ($\Delta S_m(T)_{\Delta H} = \int[\partial M(T,H)/\partial T]_H dH$)[17] to the experimentally obtained magnetization data (Fig. S4, ESI). The entropy changes at various magnetic fields and temperatures are summarized in Fig. 4, with an impressive $-\Delta S_m$ = 43.3 J kg^{-1} K^{-1} for **1** and 37.1 J kg^{-1} K^{-1} for **2** at 2 K when ΔH = 7 T. The values of $-\Delta S_m$ is smaller than the theoretical values of 50.5 J kg^{-1} K^{-1} and 44.6 J kg^{-1} K^{-1} calculated by $-\Delta S_m^{max} = R\ln(2S+1)$, respectively,

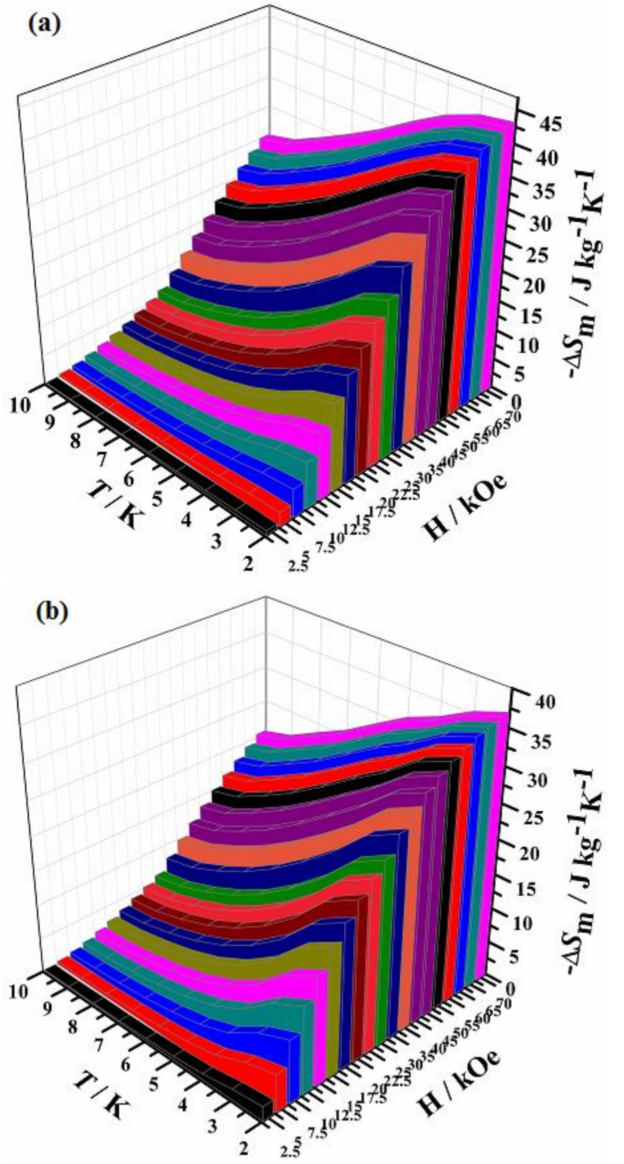


Fig. 4. Experimental $-\Delta S_m$ calculated by using the magnetization data of **1** (a) and **2** (b) at different fields and temperatures.

which is attributed to the weak couplings between the Gd^{III} ions. Among the reported magnetic coolers based on Gd^{III} CPs, the ΔS_m is limited up to $-\Delta S_m^{max}$ =37.0 J kg^{-1} K^{-1}, as listed in Table S1 (ESI). Notably, the maximum entropy changes ($-\Delta S_m^{max}$) of complexes **1** and **2** reach 29.9 and 28.5 J kg^{-1} K^{-1} at 2 K for a moderate field change (ΔH = 3 T). Indeed, evaluating the MCE of molecular materials from the volumetric aspect is more meaningful for practical application in cryogenic magnetic refrigeration. Therefore, considering from the volumetric aspect, the values of $-\Delta S_{\rm m}^{\rm max}$ are 116.6 and 93.4 mJ cm^{-3} K^{-1}, respectively, which are relatively large values among reported $\mathrm{Gd^{III}}$ CPs (Table S1, ESI).

In order to study the main factors toward the MCE of $\mathrm{Gd^{III}}$ CPs, the magnetic density ($M_{\rm W}/N_{\rm Gd}$) and magnetic interaction (θ) were used to contrast. As shown in Table S1 (ESI), when the $M_{\rm W}/N_{\rm Gd}$ ratios are close, the smaller the value of $|\theta|$, the larger the MCE ($-\Delta S_{\rm m}$). On the other hand, when the θ values are almost the same, the smaller the $M_{\rm W}/N_{\rm Gd}$ ratios, the larger the value of $-\Delta S_{\rm m}$. In addition, weak F coupling is also favor for the large MCE of $\mathrm{Gd^{III}}$ complexes. The reason can be described as following. The total $-\Delta S_{\rm m}$ is the linear addition of each individual ion when the magnetic coupling is weak, indicated by the formulae $-nR\ln(2S + 1)$ (n = the number of uncoupled $\mathrm{Gd^{III}}$). Strong AF interactions that lead to the cancellation of the adjacent magnetic moments will inevitably reduce the $-\Delta S_{\rm m}$s. The $-\Delta S_{\rm m}^{\rm max}$ will be given by $-R\ln(2nS + 1)$ when the magnetic coupling is strong F, which is smaller, but it is very likely that $-\Delta S_{\rm m}$ at low fields will be much greater (i.e. a higher magnetic susceptibility at low fields).[1b] Therefore, both the large magnetic density and weak magnetic coupling (especially for weak F coupling) could lead to the large MCE of $\mathrm{Gd^{III}}$ complexes.

Conclusions

Two $\mathrm{Gd^{III}}$ coordination polymers take 1D chain and 3D layer-pillar structures, and exhibit large magnetocaloric effects with $-\Delta S_{\rm m}^{\rm max}$ = 43.3 J kg^{-1} K^{-1} (116.6 mJ cm^{-3} K^{-1}) for **1** and 37.1 J kg^{-1} K^{-1} (93.4 mJ cm^{-3} K^{-1}) for **2**, respectively. By comparison, the large magnetic density (high $M_{\rm w}/N_{\rm Gd}$) and weak magnetic coupling (low $|\theta|$ value) could lead to the large magnetocaloric effect of $\mathrm{Gd^{III}}$ complexes. This study not only enriches the existing field of $\mathrm{Gd^{III}}$ coordination polymers with excellent refrigeration performance but also corroborates that light dicarboxylate ligands are good candidates for the construction of $\mathrm{Gd^{III}}$ coordination polymers with a large magnetocaloric effect.

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Notes and references

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†Electronic supplementary information (ESI) available: X-ray crystallographic data file in CIF format for CCDC 1042007 (**1**) and 1042008 (**2**), supplementary Tables, and additional characterizations. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00000.

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