Supporting Information

Molecular Amino-Phosphonate Cobalt-Lanthanide Clusters

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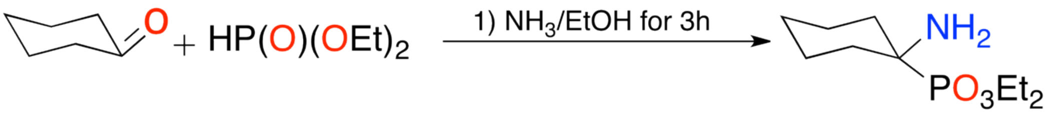
Experimental Details

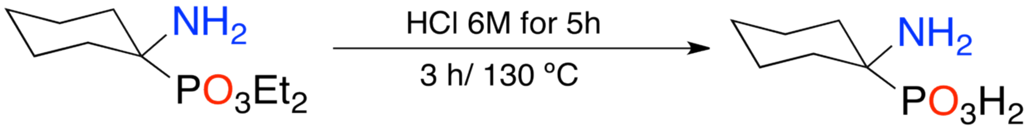
Synthesis of starting materials

Unless stated otherwise, all reagents and solvents were purchased from Aldrich Chemicals and used without further purification. $[Co_2(\mu\text{-}OH_2)(O_2C^tBu)_4(HO_2C^tBu)_4]$[6] **6** was prepared according to established methods. $[Ln_2(O_2C^tBu)_6(HO_2C^tBu)_6]$[7] (Ln = Gd, **7**; Tb, **8**, Dy, **9**) were synthesized by refluxing Ln_2O_3 (3.62 g, 10 mmol) and excess pivalic acid (30 g, 300 mmol) at 160 ºC for 5 hrs to form a clear solution. Followed by cooling the solution to room temperature and white precipitate came out. 50 ml toluene was added to dissolve the access pivalic acid and filtered in vacuum and 50 ml *n*-hexane were used to wash the product (yield ca. 13 g, 87 %).

Synthesis of (1-amino-1-cyclohexyl)phosphonic acid[5]



Diethyl 1-aminocyclohexylphosphonate: a solution of cyclohexanone (9.1 mL, 0.088 mol), diethyl phosphite (11.2 mL, 0.087 mol) and 52 mL of NH_3/EtOH (2M, 0.1 mol) was heated in an ampule to 100 ºC for 7 hours. Excess NH_3 and EtOH were removed under reduced pressure. The resultant oil was a mixture of diethyl 1-aminocyclohexylphosphonate and diethyl phosphite. The oily product (22 g) was dissolved in acetone (38 mL) and a solution of oxalic acid (5.4 g, 60 mmol) in acetone (13.7 mL) was added. The mixture was refrigerated overnight and the precipitated product was separated by filtration and washed with cold acetone (3 x 25 mL). The dry product was treated with a saturated solution of $NaHCO_3$ and extracted with DCM until the extracted DCM became colourless. The solution was concentrated under reduced pressure to afford pure diethyl 1-aminocyclohexylphosphonate (13.13 g, 84 %).



1-aminocyclohexylphosphonate acid: diethyl 1-aminocyclohexylphosphonate (3 g, 13 mmol) and HCl 6M (45 mL) were heated in an ampule for 3 hours at 120 ºC. then the solution was evaporated until the odour of HCl disappeared. The product was then dissolved in H_2O and precipitated with MeCN to give 1-aminocyclohexylphosphonic acid (2.0 g, 88 %). The product contains one molecule of water of crystallization. Elemental analysis, calcd (%) for $C_6H_{14}NPO_3 \bullet H_2O$: C36.55, H 8.18, N 7.10, P 15.71; Found: C 36.53, H 7.92, N 7.05, P 15.57.

Synthesis of compound 1 to 2

1 was obtained by mixing **6** (0.036 g, 0.04 mmol), **7** (0.165 g, 0.1 mmol), Et_3N (0.1 ml, 1 mmol) and $H_2O_3PC_6H_{10}NH_2$ (0.036 g, 0.2 mmol) in MeCN (8 ml) were stirred at room temperature for a few minutes. The resulting slurry was transferred into a 10 mL Teflon-lined autoclave, which was heated at 150 ^{o}C for 12 hrs. and then cooled to room temperature at a rate of 0.05 ^{o}C min^{-1}. Pink block-shape crystals were collected (yield 10 mg, 10 %, based on **7**). EA for $Co_4Gd_{10}P_{12}N_{10}O_{66}C_{124}H_{236}$, found (calc); C 28.96 (29.18), H 4.67 (4.66), Co 4.34 (4.62), Gd 29.65 (30.81), N 2.65 (2.74) and P 7.21 (7.28). **2** was obtained by mixing **6** (0.036 g, 0.04 mmol), **9** (0.165 g, 0.1 mmol), Et_3N (0.1 ml, 1 mmol) and $H_2O_3PC_6H_{10}NH_2$ (0.036 g, 0.2 mmol) in MeCN (8 ml) were stirred at room temperature for a few minutes. The resulting slurry was transferred into a 10 mL Teflon-lined autoclave, which was heated at 150 ^{o}C for 12 hrs. and then cooled to room temperature at a rate of 0.05 ^{o}C min^{-1}. Pink block-shape crystals were collected (yield 10 mg, 10 %, based on **9**). EA for $Co_4Dy_{10}P_{12}N_{10}O_{66}C_{124}H_{236}$, found (calc); C 28.47 (28.89), H 4.53 (H 4.61), Co 4.48 (4.57), Dy 31.23 (31.52), N 2.65 (2.72) and P 7.18 (7.21).

Synthesis of compound 3 to 5

3 to **5** were synthesized from similar reaction, replacing the lanthanide source. **6** (0.095 g, 0.1 mmol), **7**, **8** or **9** (0.075 mmol), Et_3N (0.1 ml, 0.7 mmol), Na_3PO_3 (0.05g, 0.3 mmol) and $H_2O_3PC_6H_{10}NH_2$ (0.018 g, 0.1 mmol) in MeCN (8 ml) were stirred at room temperature for a few minutes. The resulting slurry was transferred into a 10 mL Teflon-lined autoclave, which was heated at 150 ^{o}C for 12 hrs. and then cooled to room temperature at a rate of 0.05 ^{o}C min^{-1}. Block-shape purple crystals were collected. EA for **3** (yield 20 mg, 18.50 % based on **7**) $Co_6Gd_4Na_2O_{46}N_6P_6C_{96}H_{186}$, found (calc for **3** with loss of 2 MeCN and gain of 2 H_2O); C 32.52 (34.16), H 5.12 (5.55), Co 10.44 (10.48), Gd 17.90 (18.64), P 5.63 (5.51), N 3.12 (2.49) and Na 1.37 (1.36). EA for **4** (yield 18 mg, 16.6 % based on **8**) $Co_6Tb_4Na_2O_{46}N_6P_6C_{96}H_{186}$, found (calc for **4** with loss of 2 MeCN and gain of 2 H_2O); C 32.72 (34.09), H 5.35 (5.54), Co 10.85 (10.46), Tb 18.31 (18.79), P 5.21 (5.49), N 3.20 (2.5) and Na 1.23 (1.35). EA for **5** (yield 16 mg, 14.6% based on **9**) $Co_6Dy_4Na_2O_{44}N_8P_6C_{100}H_{188}$, found (calc); C 35.23 (34.89), H 5.28 (5.50), Co 10.98 (10.27), Dy 18.46 (18.88), P 5.71 (5.39), N 2.98 (3.25) and Na 1.41 (1.33).

Crystallography

The data of **1** to **5** were collected on a Bruker SMART CCD diffractometer with MoKα radiation (λ = 0.71073 Å). The data of 5 were collected on a oxford SMART CCD diffractometer with MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined on *F2* using SHELXTL. CCDC 922115-922117 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Crystal data for **1** [$C_{124}H_{214}Co_4Gd_{10}N_{10}O_{66}P_{12}\cdot 3(C_2H_3N)$]: M_r = 5226.25, triclinic, space group *P-1, T* = 100.15 K, *a* = 18.2190 (2), *b* = 22.4563 (3), *c* = 27.5752 (4) Å, α = 70.1022 (12), β = 84.55267 (11), γ = 79.3776 (12)º, *V* = 10420.1 (2) Å^3, *Z* = 2, ρ = 1.666 g cm^{-3}, total data 84001, independent reflections 42000 (R_{int} = 0.083), μ = 3.61 mm^{-1}, 1975 parameters, R_1 = 0.095 for $I \geq 2\sigma(I)$ and wR_2 = 0.218. CCDC 922116

Crystal data for **2** [$C_{124}H_{228}Co_4Dy_{10}N_{10}O_{66}P_{12}\cdot C_4N_2H_6$]: M_r = 5229.68, triclinic, space group *P-1, T* = 100.15 K, *a* = 17.0917 (3), *b* = 20.9589 (3), *c* = 30.4298 (4) Å, α = 108.0775 (13), β = 101.8103 (13), γ = 92.1947 (12)º, *V* = 10082.3 (3) Å^3, *Z* = 2, ρ = 1.725 g cm^{-3}, total data 79235, independent reflections 40171 (R_{int} = 0.062), μ = 4.14 mm^{-1}, 1877 parameters, R_1 = 0.087 for $I \geq 2\sigma(I)$ and wR_2 = 0.194. CCDC 922115

Crystal data for **3** [$C_{100}H_{186}Co_6Gd_4N_8Na_2O_{44}P_6\cdot 2(C_2H_3N)$]: M_r = 3501.06, triclinic, space group *P2₁/n, T* = 100.15 K, *a* = 15.8683 (5), *b* = 27.0973 (8), *c* = 19.4683 (6) Å, β = 112.274 (13)º, *V* = 7746.5 (4) Å^3, *Z* = 2, ρ = 1.501 g cm^{-3}, total data 42633, independent reflections 15760 (R_{int} = 0.060), μ = 2.45 mm^{-1}, 771 parameters, R_1 = 0.055 for $I \geq 2\sigma(I)$ and wR_2 = 0.139. CCDC 922117

Crystal data for **4** (unite cell) [$Co_6Tb_4P_6N_9O_{43}C_{100}H_{188}$]: monoclinic, space group *P2₁/n, T* = 100.15 K, *a* = 15.8615(4), *b* = 27.2388(6), *c* = 19.440(5) Å, γ = 111.837(3)º, *V* = 7797.9(3) Å^3.

Crystal data for **5** (unite cell) [$Co_6Dy_4P_6N_{10}O_{44}C_{104}H_{192}$]: monoclinic, space group *P2₁/n, T* = 100.15 K, *a* = 15.810(3), *b* = 27.065(6), *c* = 19.386(4) Å, β = 111.888(5), *V* = 7697.12 Å^3.

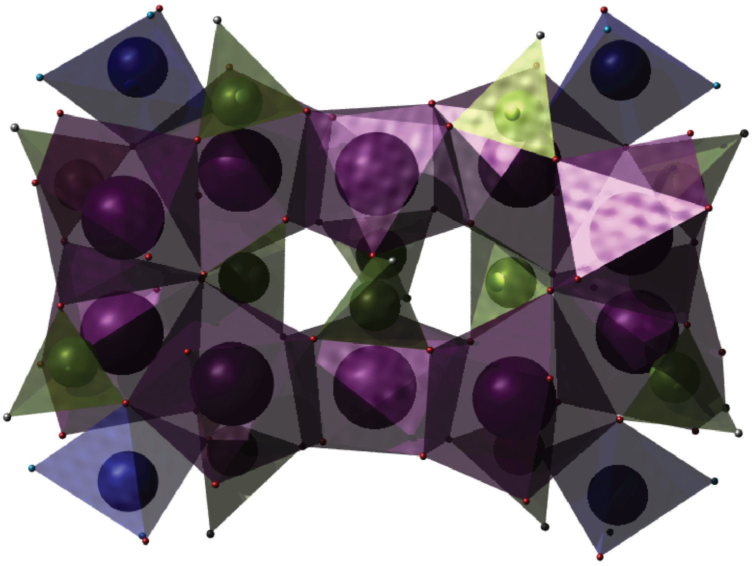


Figure S1. Polyhedral representation of $Co_4Dy_{10}P_{12}$. Scheme: Dy, purple; Co, blue; P, green; O, orange; C, grey; N, cyan.

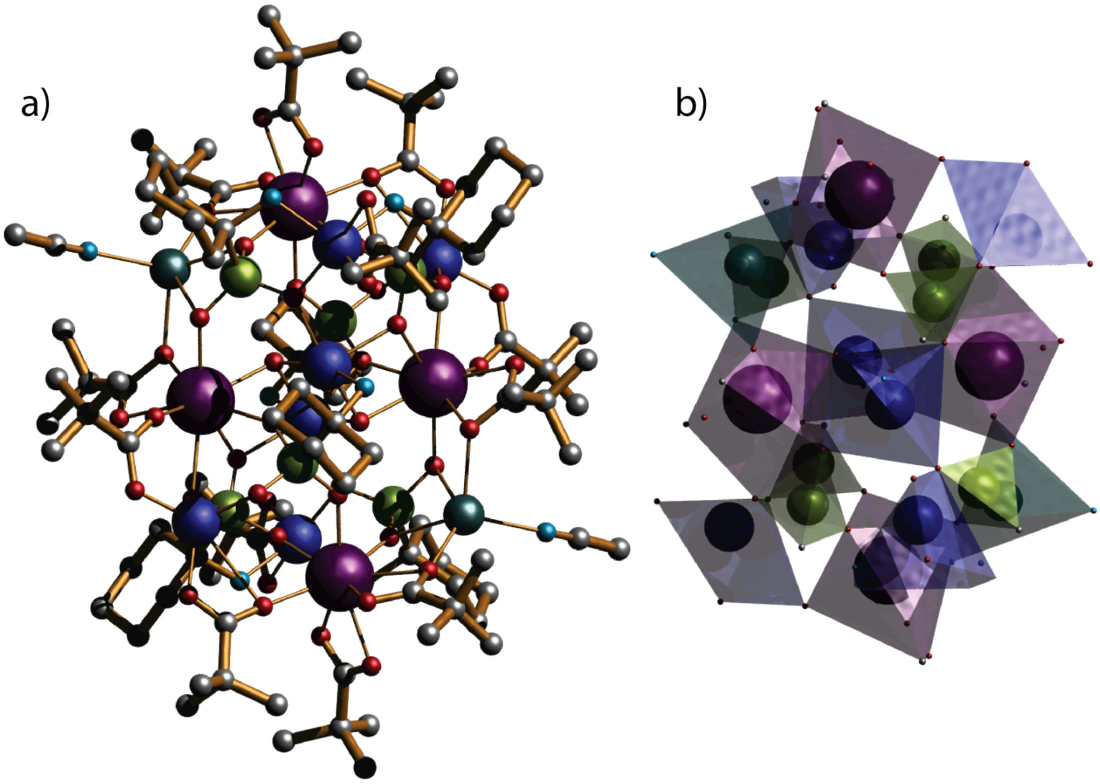


Figure S2. a) Full structure and polyhedral representation of $Co_6Gd_4P_6$ cluster; b) Polyhedral representation of $Co_6Gd_4P_6$. Scheme: Gd, purple; Co, blue; P, green; O, orange; C, grey; N, cyan; (H omitted for clarity).

Magnetic measurements

The magnetic properties of polycrystalline samples of **1-5** were performed with a Quantum Design MPMS-XL7 SQUID. The samples were ground, placed in a gel capsule and fixed with a small amount of eicosanoid acid to avoid movement during the measurement. The data were corrected for diamagnetism from the gel capsule, diamagnetic contribution from the eicosanoid acid and diamagnetic contribution calculated from Pascal constants.

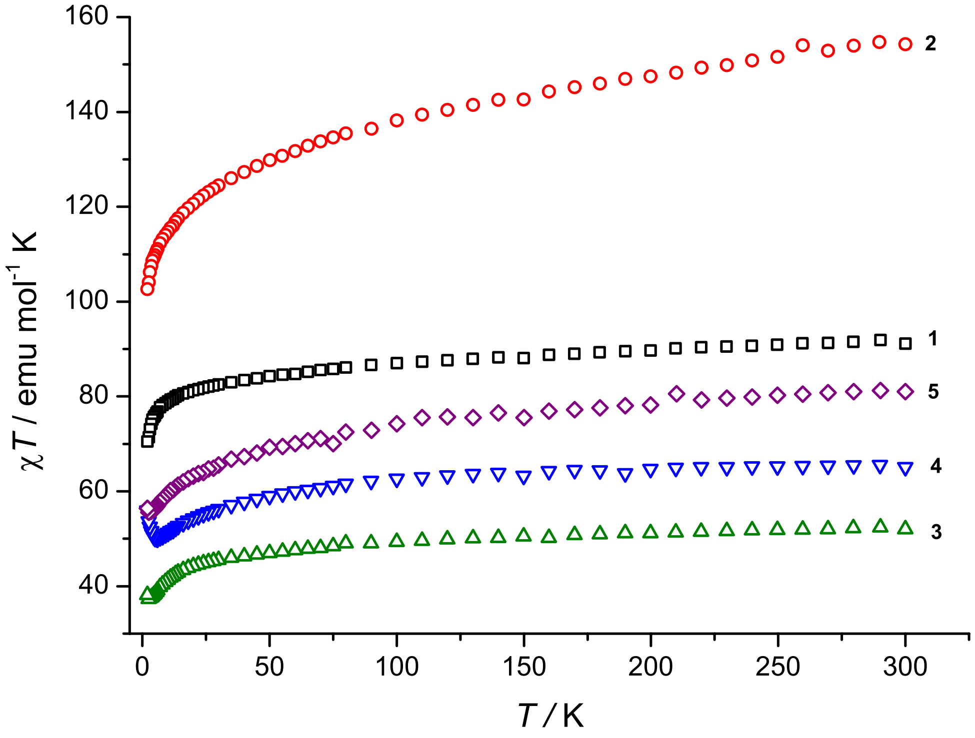


Figure S3. a) Molar magnetic susceptibility (χT) vs. *T* plot for **1-5** under 1 kG DC field.

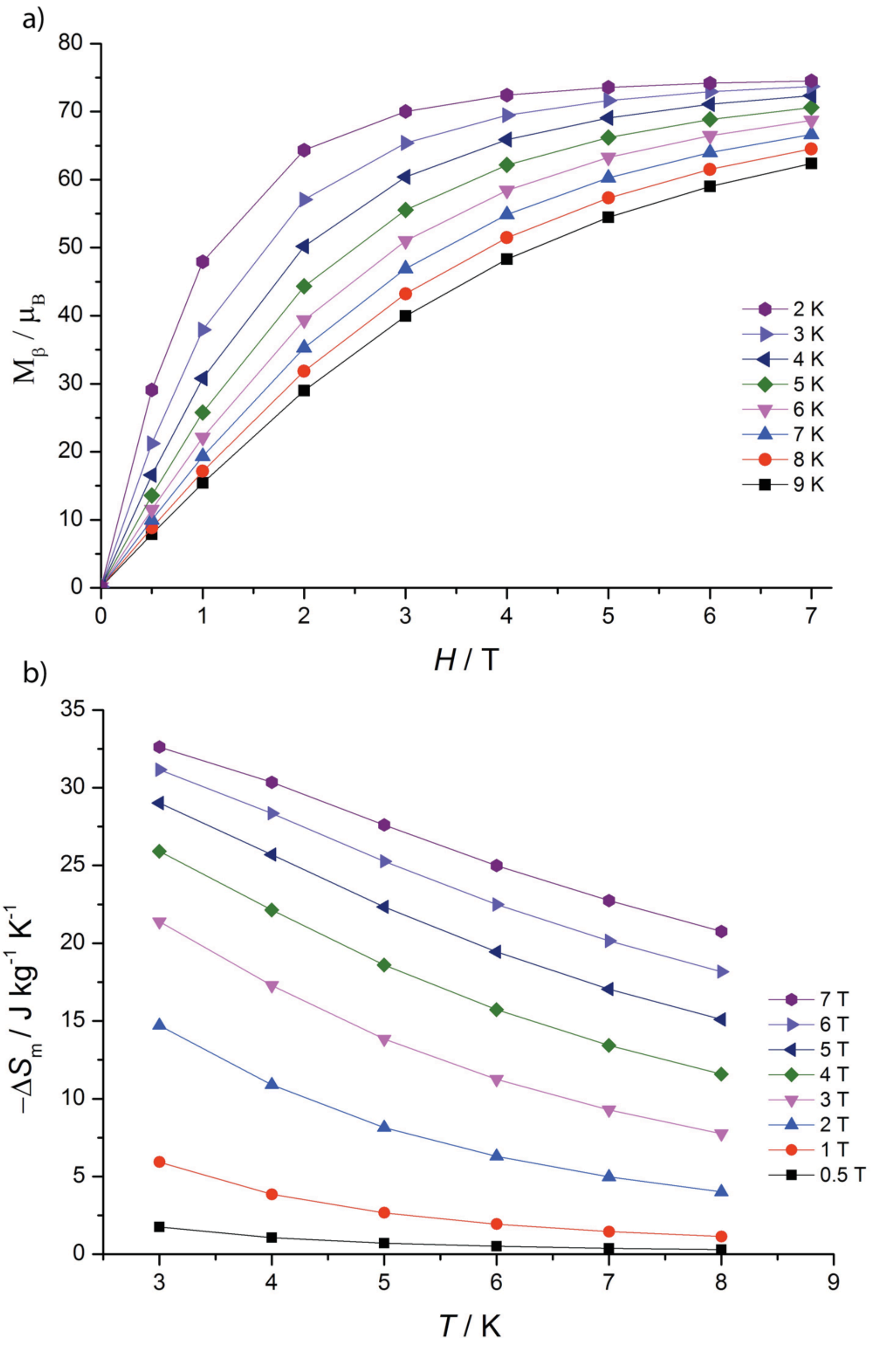


Figure S4. a) M/N$_{\mu\beta}$ magnetization of **1** at different temperatures; b) Magnetic Entropy change of **1**.

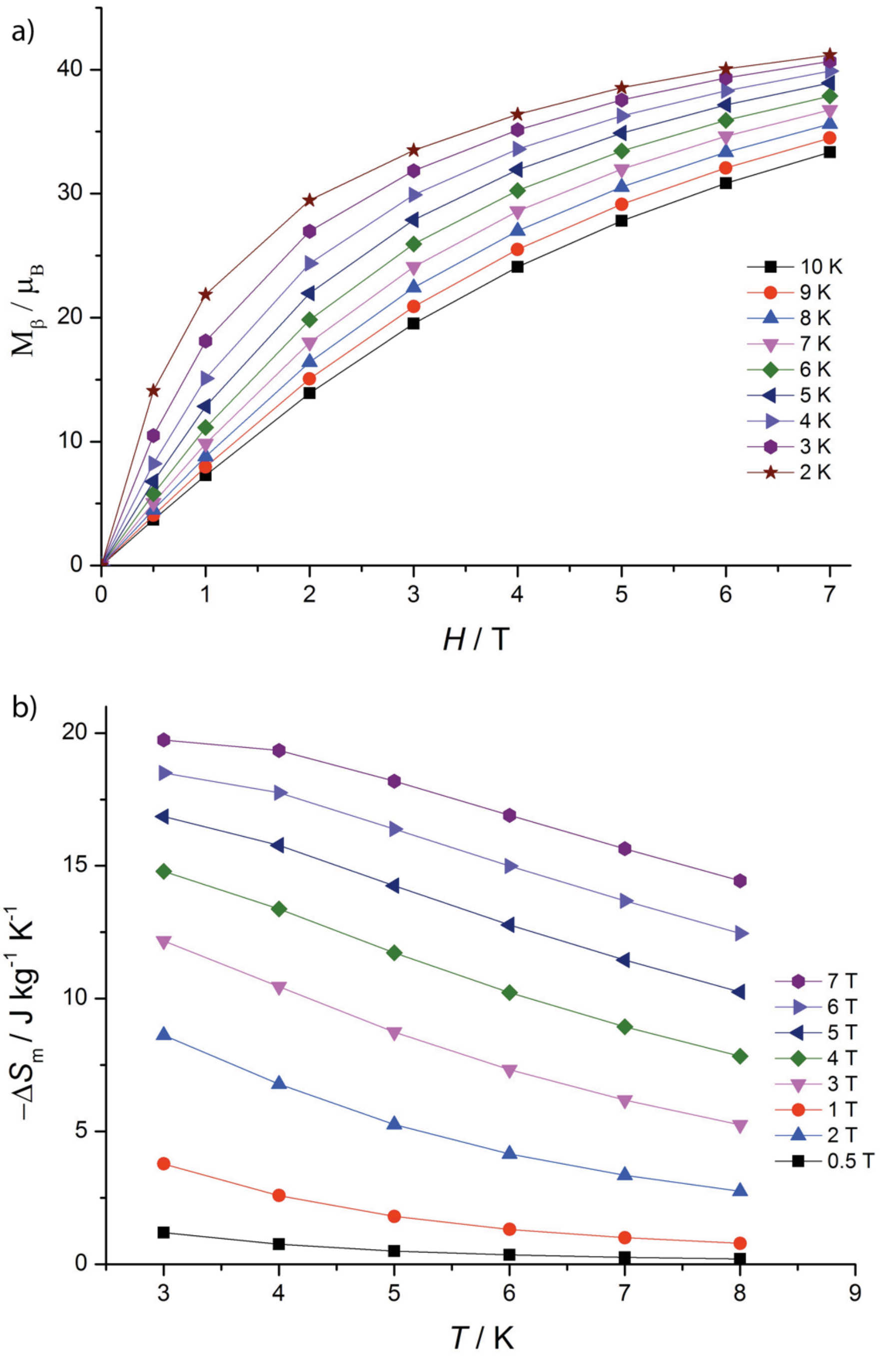


Figure S5. a) M/N$_{\mu\beta}$ magnetization of **3** at different temperatures; b) Magnetic Entropy change of **3**.