Supporting Information

# Octametallic 4f-phosphonate horseshoes

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## Experimental Details

All reagents, metal salts and ligands were used as obtained from Aldrich. Analytical data were obtained by the microanalytical service of the University of Manchester.

### Preparation of compounds 1 to 3

Compound **1** was synthesised by refluxing a mixture of pivalic acid ($HO_2C^tBu$) (0.8 g, 7.83 mmol), $Gd(NO_3)_3•6H_2O$ (0.25 g, 0.55 mmol), *tert*-butyl phosphonic acid ($H_2O_3P^tBu$) (0.07 g, 0.51 mmol) and isopropylamine ($^iPrNH_2$) (0.1 mL, 1.16 mmol) in *iso*-butyl alcohol ($^iBuOH$) (15 ml) for 3 hrs to form a clear solution. The solution was filtered and then allowed to stand undisturbed at room temperature for four days. Colourless crystals of **1** suitable for X-ray were collected. Yield 150 mg (50 %), based on $Gd(NO_3)_3•6H_2O$. Elemental analysis for $C_{94}H_{197}Gd_8N_2O_{47}P_6$, found (calc); C 31.68 (31.79); H 5.41 (5.59); N 0.81 (0.79); Gd 35.38 (35.42); P 5.21 (5.23).

A similar procedure was used to synthesise **2** except that $Tb(NO_3)_3•6H_2O$ was used in place of $Gd(NO_3)_3•6H_2O$. Yield 165 mg (55%), based on $H_2O_3P^tBu$. Elemental analysis for $C_{94}H_{197}Tb_8N_2O_{47}P_6$, found (calc); C 31.77 (31.67); H 5.48 (5.57); N 0.83 (0.79); Gd 35.59 (35.67); P 4.16 (5.21).

A similar procedure was used to synthesise **3** except that $Dy(NO_3)_3•5H_2O$ was used instead of $Gd(NO_3)_3•6H_2O$. Yield 180 mg (59 %), based on $H_2O_3P^tBu$. Elemental analysis for, $C_{94}H_{197}Dy_8N_2O_{47}P_6$, found (calc); C 31.47 (31.41); H 5.49 (5.52); N 0.80 (0.78); Dy 36.25 (36.17); P 5.21 (5.17).

**Crystallography**

The data of **1** to **3** were collected on Agilent SuperNova CCD diffractometer with MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined on *F2* using SHELXTL. CCDC 953479-953481 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 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** [$C_{94}H_{195}Gd_8N_2O_{47}P_6$]: *M*r = 3549.33, triclinic, space group *P-1*, *T* = 150.01 K, *a* = 14.0956(4), *b* = 24.0968(7), *c* = 26.5567(8) Å, *α* = 76.758(2), *β* = 74.883(2), *γ* = 82.741(2) °, *V* = 8455.2(4) Å$^3$, *Z* = 2, ρ = 1.393 g cm$^{-3}$, total data = 47337, independent reflections 34034[$R_{(int)}$ = 0.0380], μ = 3.208 mm$^{-1}$, 1284 parameters, $R_1$ = 0.0640 for $I \geq 2\sigma$ (I) and w$R_2$ = 0.1717.

Crystal data for **2** [$C_{94}H_{195}Tb_8N_2O_{47}P_6$]: *M*r = 3562.79, triclinic, space group *P-1*, *T* = 150.05 K, *a* = 14.0342(7), *b* = 24.0928(11), *c* = 26.4594(12) Å, *α* = 76.727(4), *β* = 75.084(4), *γ* = 82.955(4) °, *V* = 8394.9(7) Å$^3$, *Z* = 2, ρ = 1.409 g cm$^{-3}$, total data = 46176, independent reflections 33802 [$R_{(int)}$ = 0.0899), μ = 3.441 mm$^{-1}$, 1206 parameters, $R_1$ = 0.0782 for $I \geq 2\sigma$ (I) and w$R_2$ = 0.2034.

Crystal data for **3** [$C_{94}H_{196}Dy_8N_2O_{47}P_6$]: *M*r = 3592.34, triclinic, space group *P-1*, *T* = 128.35 K, *a* = 14.0658(3), *b* = 24.0994(6), *c* = 26.4957(6) Å, *α* = 76.637(2), *β* = 75.300(2), *γ* = 83.1827(19) °, *V* = 8435.1(4) Å$^3$, *Z* = 2, ρ = 1.414 g cm$^{-3}$, total data = 67875, independent reflections 34418 [$R_{(int)}$ = 0.0407), μ = 3.614 mm$^{-1}$, 1253 parameters, $R_1$ = 0.0499 for $I \geq 2\sigma$ (I) and w$R_2$ = 0.1293. All three compounds crystallise with large solvent voids and the electron density in these voids has been handled using SQUEEZE.

**Magnetic measurements**

The magnetic properties in the temperature range 1.8K-300K were performed on polycrystalline samples either constrained in eicosane or lastly powdered, using a Quantum Design MPMS-XL7 SQUID magnetometer armed with a 7 T magnet. Data were corrected for the diamagnetism of the compounds (Pascal constants) and for diamagnetic contribution of eicosane and the sample holder by measurement.

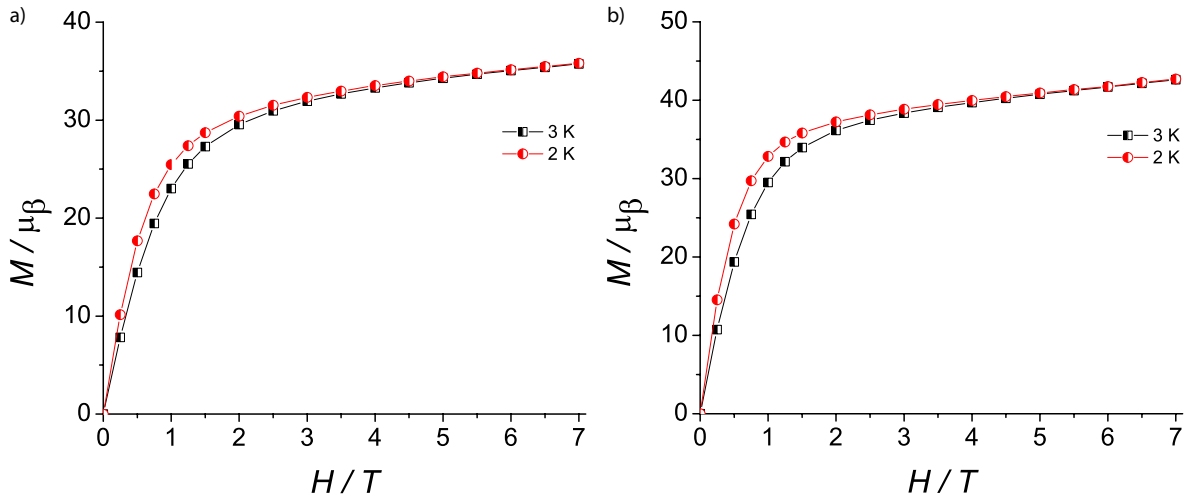


**Figure S1**. a) $M/N_{\mu\beta}$ magnetization of **2** at different temperatures; b) $M/N_{\mu\beta}$ magnetization of **3** at different temperatures.

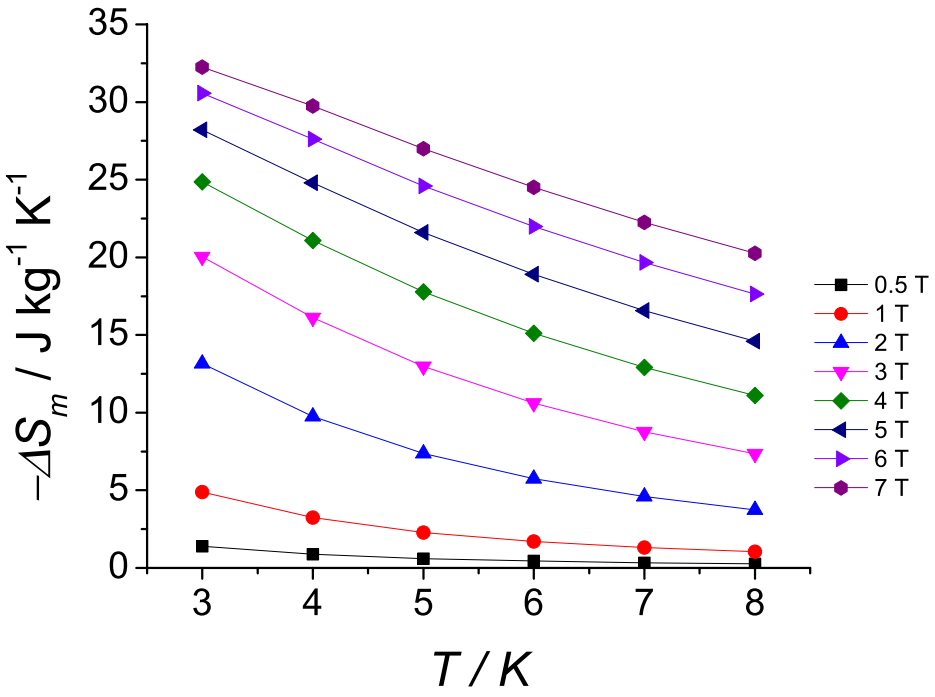


**Figure S2**. Magnetic entropy change of **1.**