

Supplementary information

Syntheses, crystal structures, magnetism, thermal stabilities and luminescence of four new metal phosphonates

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Table S1. Selected bond lengths (Å) and angles (°) for **2**.

Mn(1)-N(1)	2.336(5)	Mn(2)-O(1)	2.233(4)
Mn(1)-N(2) ^c	2.366(5)	Mn(2)-O(1) ^a	2.233(4)
Mn(1)-O(1)	2.281(4)	Mn(2)-O(1) ^b	2.233(4)
Mn(1)-O(2) ^a	2.042(4)	Mn(2)-O(1) ^d	2.237(4)
Mn(1)-O(3) ^b	2.070(5)	Mn(2)-O(1) ^e	2.233(4)
Mn(1)-O(4)	2.299(6)	Mn(2)-O(1) ^f	2.233(4)
N(1)-Mn(1)-N(2) ^c	98.49(17)	O(1)-Mn(2)-O(1) ^a	91.88(14)
N(1)-Mn(1)-O(1)	82.75(14)	O(1)-Mn(2)-O(1) ^b	88.12(14)
N(1)-Mn(1)-O(2) ^a	152.4(2)	O(1)-Mn(2)-O(1) ^d	88.12(14)
N(1)-Mn(1)-O(3) ^b	102.07(18)	O(1)-Mn(2)-O(1) ^e	180.0
N(1)-Mn(1)-O(4)	70.86(17)	O(1)-Mn(2)-O(1) ^f	91.88(14)
N(2) ^c -Mn(1)-O(1)	177.14(18)	O(1) ^a -Mn(2)-O(1) ^b	88.12(14)
N(2) ^c -Mn(1)-O(2) ^a	88.29(19)	O(1) ^a -Mn(2)-O(1) ^d	179.997(1)
N(2) ^c -Mn(1)-O(3) ^b	91.28(19)	O(1) ^a -Mn(2)-O(1) ^e	88.12(14)
N(2) ^c -Mn(1)-O(4)	84.3(2)	O(1) ^a -Mn(2)-O(1) ^f	91.88(14)
O(1)-Mn(1)-O(2) ^a	91.77(16)	O(1) ^b -Mn(2)-O(1) ^d	91.88(14)
O(1)-Mn(1)-O(3) ^b	85.94(16)	O(1) ^b -Mn(2)-O(1) ^e	91.88(14)
O(1)-Mn(1)-O(4)	98.54(18)	O(1) ^b -Mn(2)-O(1) ^f	180.0
O(2) ^a -Mn(1)-O(3) ^b	104.5(2)	O(1) ^d -Mn(2)-O(1) ^e	91.88(14)
O(2) ^a -Mn(1)-O(4)	83.4(2)	O(1) ^d -Mn(2)-O(1) ^f	88.12(14)
O(3) ^b -Mn(1)-O(4)	170.91(18)	O(1) ^e -Mn(2)-O(1) ^f	88.12(14)
Symmetry codes: a - y + 1, x - y + 1, z; b x - y + 2/3, x + 1/3, - z + 1/3; c y - 1, - x + y, - z; d y - 1/3, - x + y + 1/3, - z + 1/3; e - x + 2/3, - y + 4/3, - z + 1/3; f - x + y, - x + 1, z.			

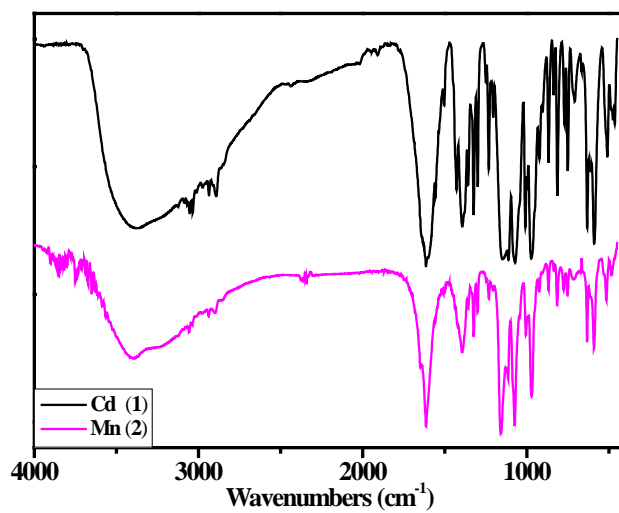


Fig. S1 IR curves of **1** and **2**.

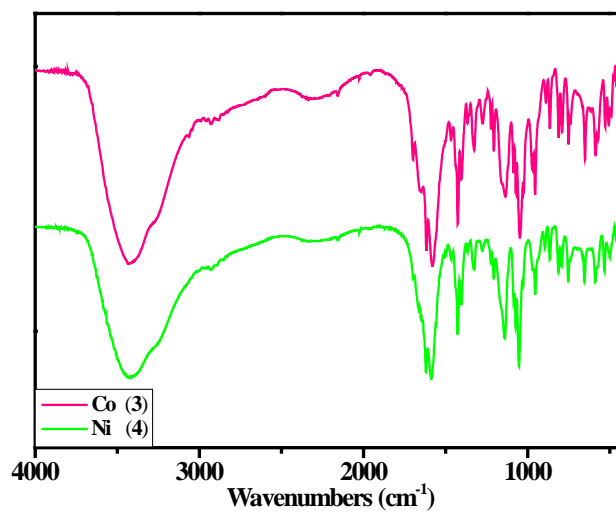


Fig. S2 IR curves of **3** and **4**.

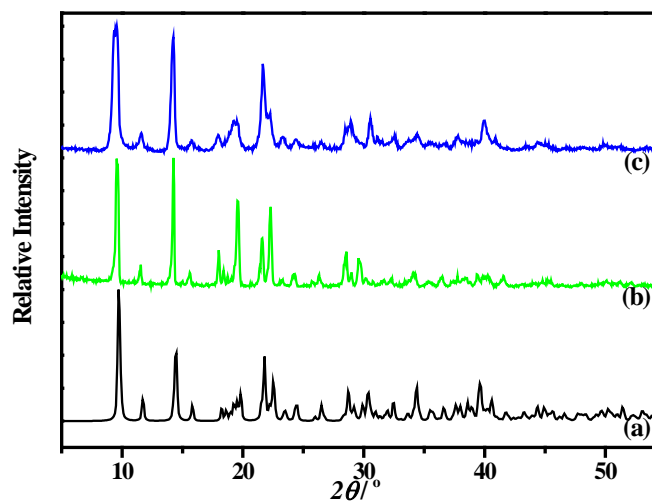


Fig. S3 XRD patterns of **3** (a) simulated from single-crystal X-ray data, and experimental data for solids **3** (b) and **4** (c).

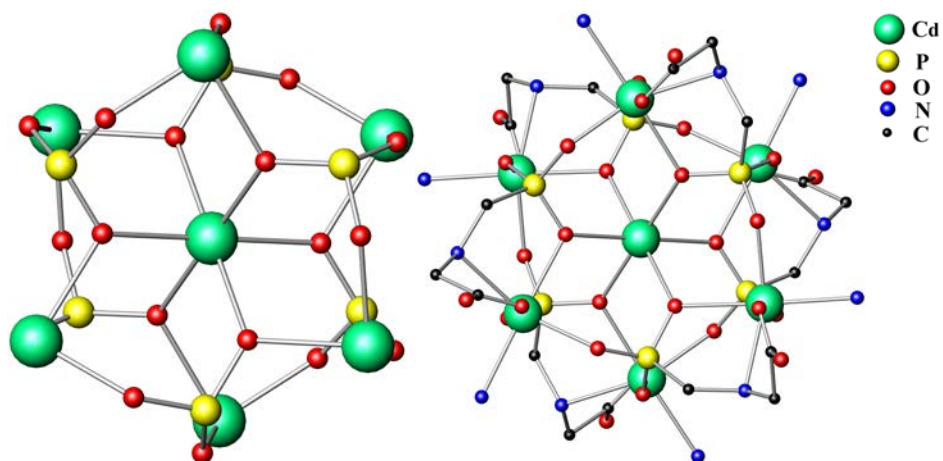


Fig. S4 Ball-stick view of the Cd₇ hepta-nuclear unit in **1**.

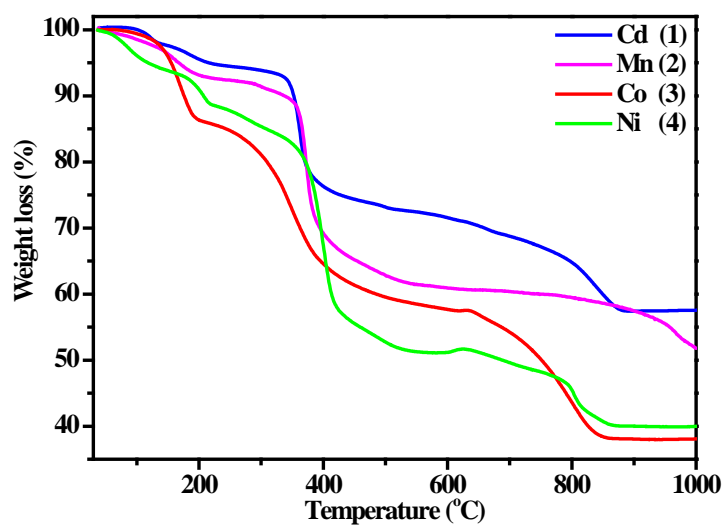


Fig. S5 TGA curves of 1-4.

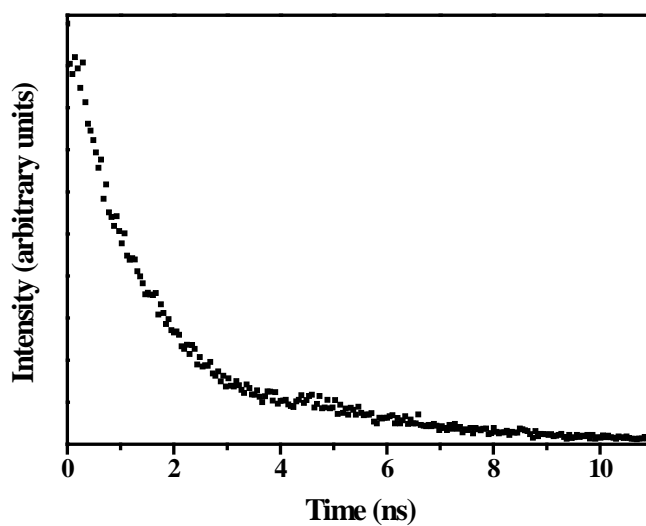


Fig. S6 Room-temperature solid-state fluorescent intensity as a function of time for **1** with $\lambda_{em} = 430$ nm.

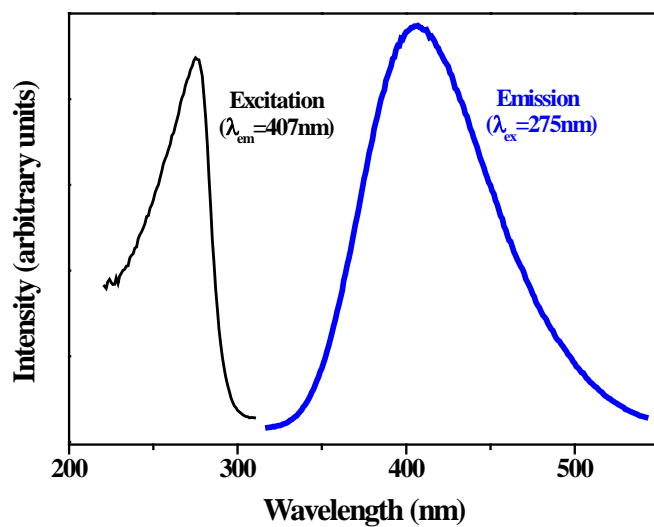


Fig. S7 Emission and excitation spectra for **1** at room temperature.

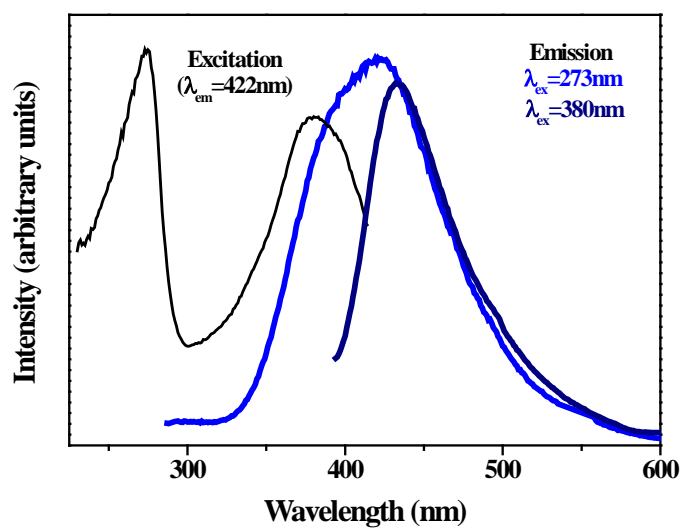


Fig. S8 Emission and excitation spectra for solid **1-200** at room temperature.

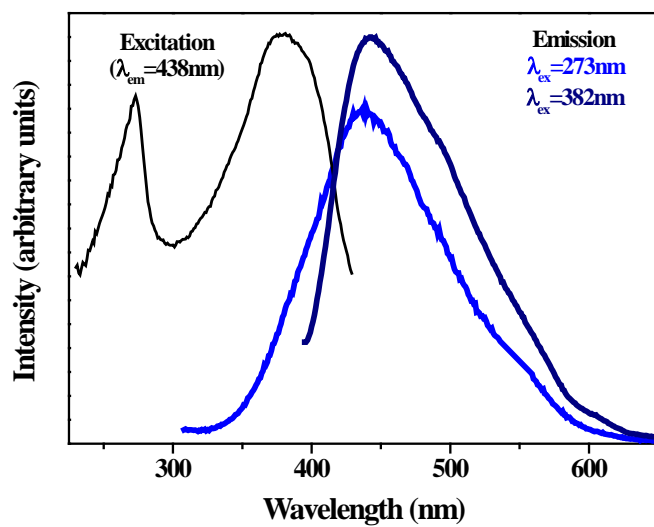


Fig. S9 Emission and excitation spectra for solid 1-250 at room temperature.

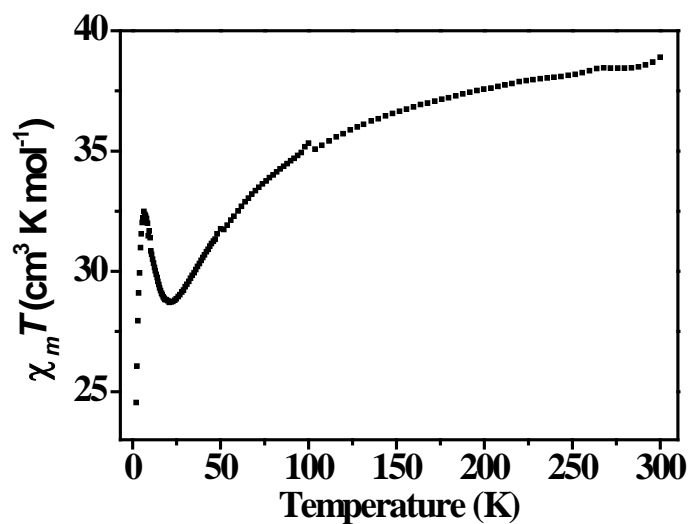


Fig. S10 The $\chi_m T$ versus T curve per Mn_7 unit in 2.

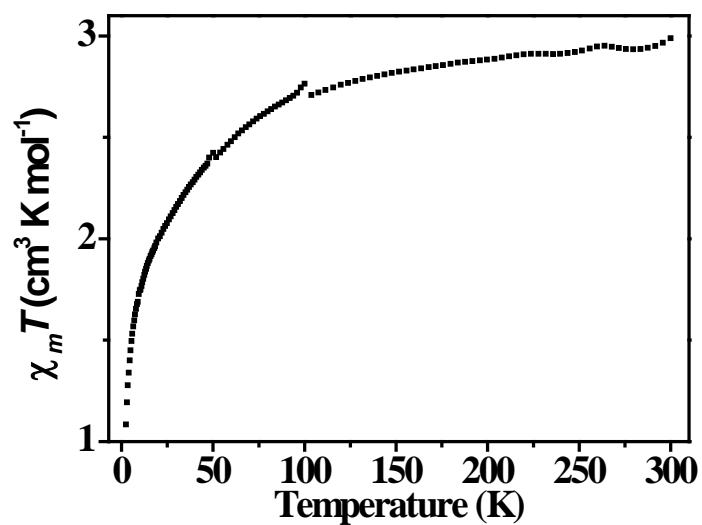


Fig. S11 The $\chi_m T$ versus T curve per Co unit in **3**.

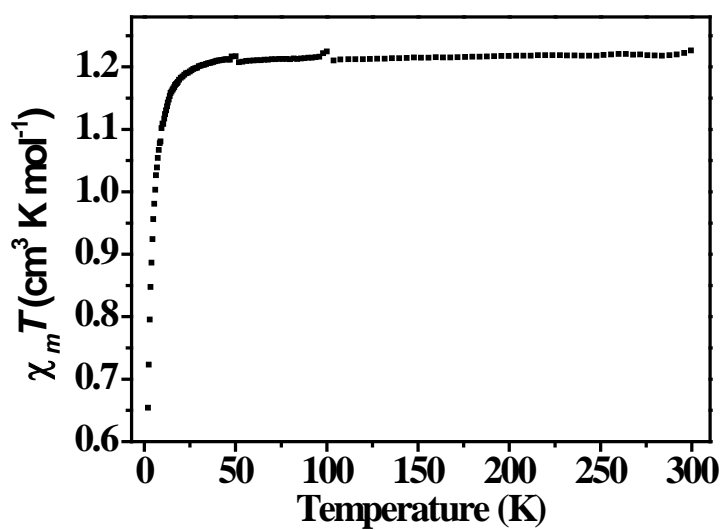


Fig. S12 The $\chi_m T$ versus T curve per Ni unit in **4**.