**Supporting information**

# Dodecanuclear hexagonal prismatic $M_{12}L_{18}$ coordination cages by subcomponent self-assembly

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Contents

## Experimental

### Chemicals and Starting Materials

The solvents used for synthesis were of analytical grade. All starting chemicals were of reagent-grade quality and were obtained commercially and used as received without further purification.

### Physical Measurements and Instrumentation

$^1$H, COSY and NOESY NMR spectra were recorded on Bruker 400 MHz instruments. The $^1$H and chemical shift was referred to TMS as reference. Electrospray (ESI) mass spectra were measured by a PE SCIEX API 150EX system. Elemental analyses were performed on a Vario EL elemental analyzer. CD spectra were recorded on a Biokin MOS-450 instrument with a 3 mm cell at 25 °C.

**General procedure for the subcomponent self-assembly synthesis of the complexes.** 2-pyridinecarboxaldehyde (210 mg, 2 mmol), *m*-xylenediamine (140 mg, 1 mmol) and manganese(II) or cadmium perchlorate (0.67 mmol) in mixture of acetonitrile (20 ml) and methanol (4 ml) were stirred at room temperature for 24 h. Crude compounds were isolated by filtration after precipitation by diethyl ether. Slow diffusion of diethyl ether into acetonitrile solution of redissolved crude compounds gave crystalline products. Products were isolated by filtration. $[Mn_{12}\mathbf{L}_{18}](ClO_4)_{24}$: Yield: 380 mg (79%). ESI-MS: 1641.0 $[Mn_{12}\mathbf{L}_{18}](ClO_4)_{19}^{5+}$, 1350.9 $[Mn_{12}\mathbf{L}_{18}](ClO_4)_{18}^{6+}$, and 1143.5 $[Mn_{12}\mathbf{L}_{18}](ClO_4)_{17}^{7+}$; CHN elemental analysis: calc. for $C_{360}H_{324}N_{72}Mn_{12}Cl_{24}O_{96}\cdot 40H_2O$: C, 45.87; H, 4.32; N, 10.70; Found: C, 45.79; H, 4.41; N, 10.70%. $[Cd_{12}\mathbf{L}_{18}](ClO_4)_{24}$: Yield: 370 mg (71%). ESI-MS: 1778.6 $[Cd_{12}\mathbf{L}_{18}](ClO_4)_{19}^{5+}$, 1466.1 $[Cd_{12}\mathbf{L}_{18}](ClO_4)_{18}^{6+}$,and 1424.2 $[Cd_{12}\mathbf{L}_{18}](ClO_4)_{17}^{7+}$; CHN elemental analysis: calc. for $C_{360}H_{324}N_{72}Cd_{12}Cl_{24}O_{96}\cdot 50H_2O$: C, 42.00; H, 4.15; N, 9.80; Found: C, 42.05; H, 4.25; N, 9.75%. Both $[Mn_{12}\mathbf{L}_{18}](ClO_4)_{24}$ and $[Cd_{12}\mathbf{L}_{18}](ClO_4)_{24}$ give similar UV-Vis spectrum (Figure S7) and the pale yellow solid $[Cd_{12}\mathbf{L}_{18}](ClO_4)_{24}$ gives an emission at 380 nm in MeCN.

**X-ray crystallographic analysis**.

$[Mn_{12}\mathbf{L}_{18}](ClO_4)_{24}$: Single crystal diffraction data was collected at 173(2) K on an Oxford Diffraction Gemini S Ultra X-ray single crystal diffractometer using graphite monochromatized Cu-Kα radiation (λ = 1.54178 Å). The crystal was extremely easy to lost solvent. It cracked and lost the shiny appearance almost immediately after leaving solvent. However, with the help of dry ice, it was successfully mounted and satisfactory intensity data were obtained. Space group *R*3, a = 25.886(1), b = 25.886(1), c = 59.139(3) Å, $V$ = 34318(2) Å$^3$, $Z$ = 3 $D_c$ = 1.276 Mg m$^{-3}$, $F_{000}$ = 13524,

27590 reflections measured, 17237 unique, $R_{int}$ = 0.0388, R = 0.1059 (I > 2σ(I)) and 0.1253 (for all data), $wR_2$ = 0.2702 (I > 2σ(I)) and 0.2930 (for all data), Flack parameter: 0.073(8).

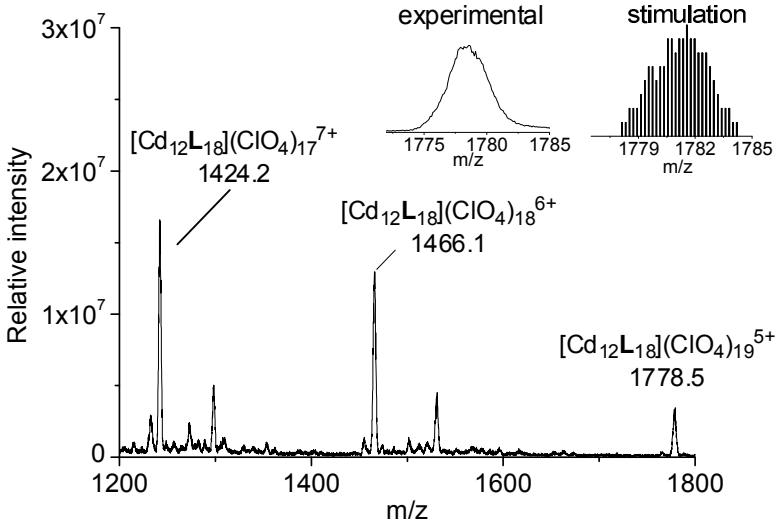



Figure S1. ESI-MS spectrum of the $[Cd_{12}\mathbf{L}_{18}](ClO_4)_{24}$, the inset showing the isotopic distribution of $[Cd_{12}\mathbf{L}_{18}](ClO_4)_{19}^{5+}$

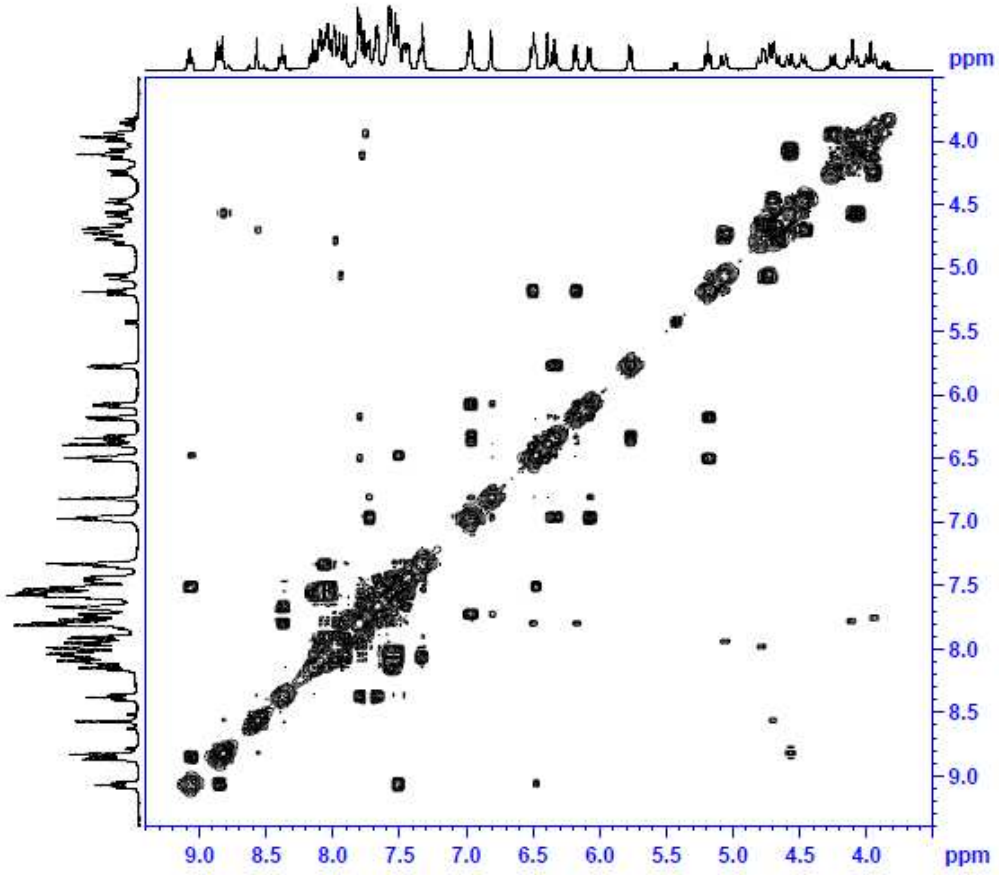



Figure S2 COSY spectrum of $[Cd_{12}\mathbf{L}_{18}](ClO_4)_{24}$ in $CD_3CN$

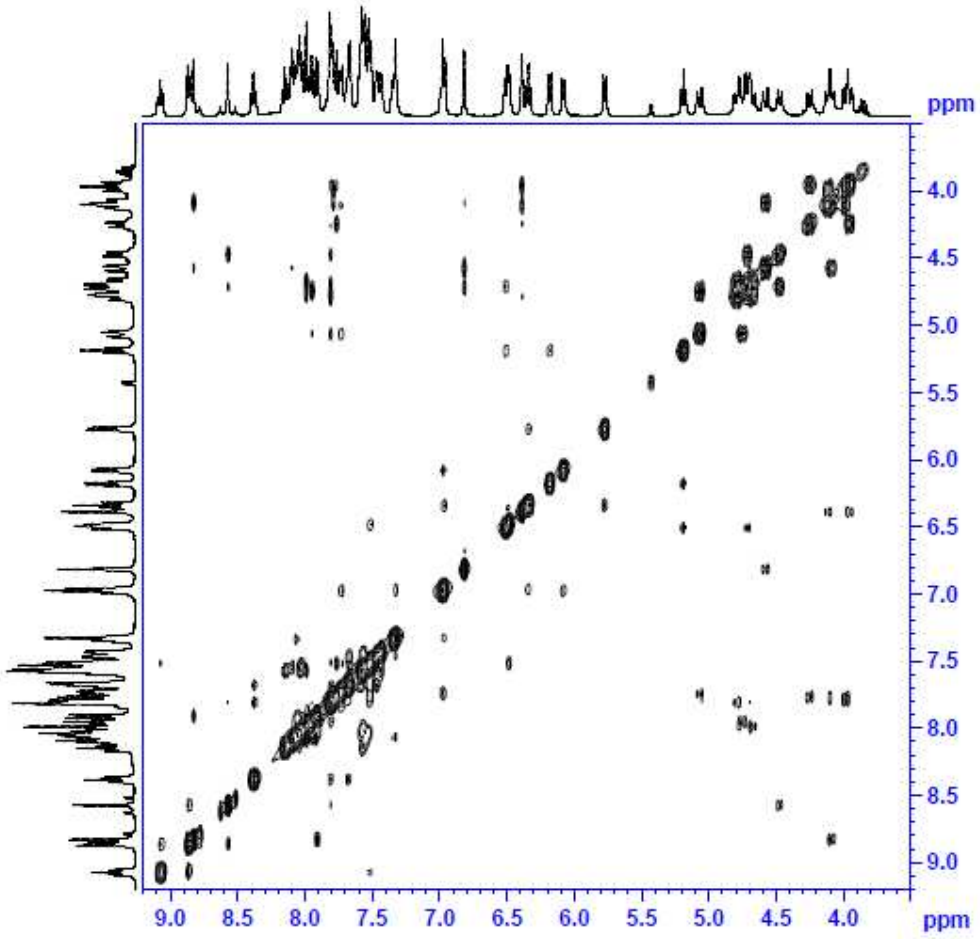
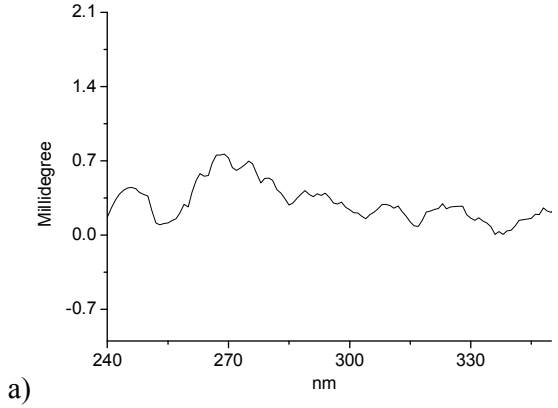
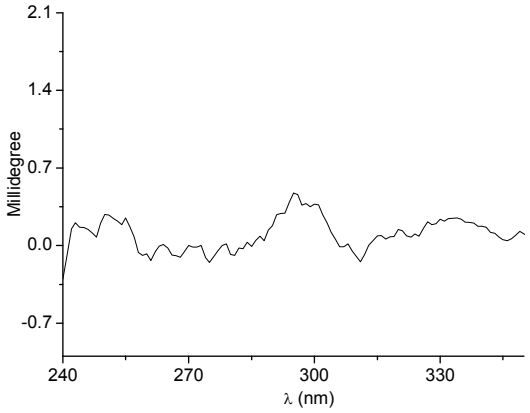



Figure S3 NOESY spectrum of $[Cd_{12}\mathbf{L}_{18}](ClO_4)_{24}$ in $CD_3CN$




a)




b)

Figure S4 a) CD of a solution of a piece of single crystal of $[Mn_{12}\mathbf{L}_{18}](ClO_4)_{24}$ in MeCN, and b) CD spectrum of a solution of precipitate of $[Cd_{12}\mathbf{L}_{18}](ClO_4)_{24}$ for comparsion.

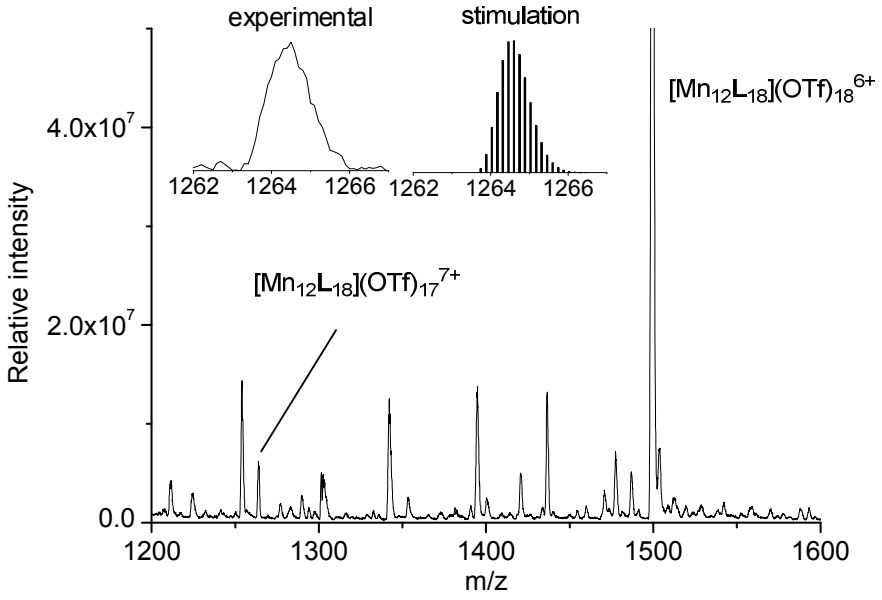



Figure S5 ESI-MS spectrum of $[Mn_{12}\mathbf{L}_{18}](OTf)_{24}$, the inset showing the isotopic distribution of $[Mn_{12}\mathbf{L}_{18}](OTf)_{17}^{7+}$

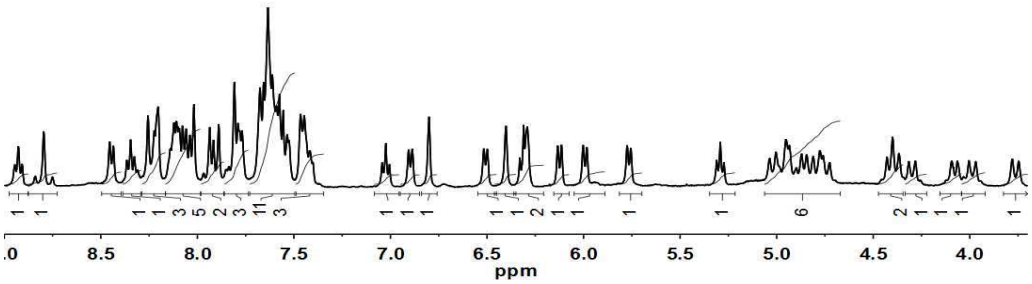



Figure S6 $^{1}$H NMR spectrum of $[Cd_{12}\mathbf{L}_{18}](OTf)_{24}$ in $CD_3CN$

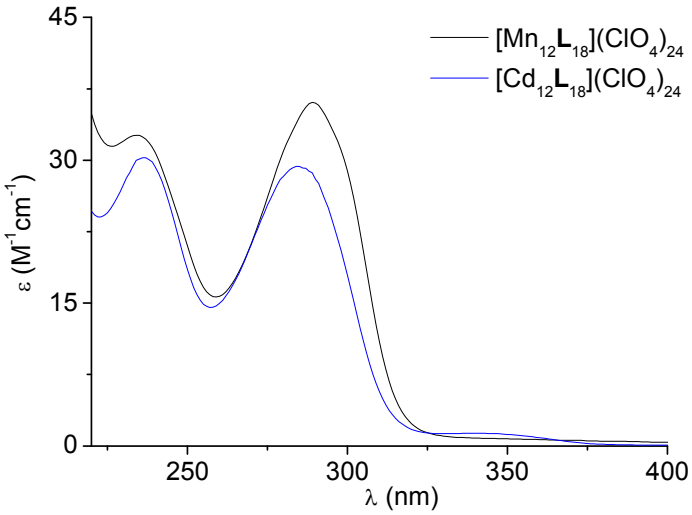



Figure S7 UV–Vis spectrum of $[Mn_{12}\mathbf{L}_{18}](ClO_4)_{24}$ and $[Cd_{12}\mathbf{L}_{18}](ClO_4)_{24}$ in MeCN.