Supporting Information

M_8L_{12} cubic cages with all facial Δ or facial Λ configuration: Effects of surface anions on occupancy of the cage and anion exchange

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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 and Measurements and Instrumentation

^{1}H, ^{13}C, ^{19}F and COSY NMR spectra were recorded on Bruker 300, 400 and 600 MHz instruments for protons. Chemical shifts (δ) for ^{1}H NMR spectra are reported in parts per million (ppm) and are reported relative to the TMS as reference. Hexafluorobenzene (C_6F_6) was used as the internal standard (–164.9 ppm) for ^{19}F NMR spectra. Electrospray ionization (ESI) mass spectra were measured by a PE SCIEX API 150EX system. HRMS was recorded on Waters Q-TOF premier mass spectrometer. Elemental analyses were performed on an Elementar Analysensysteme GmbH Vario EL elemental analyzer.

Synthesis of ligand

To a solution of 1-methyl-2-imidazolecarboxaldehyde (220 mg, 2 mmol) in ethanol (15 mL), *m*-xylenediamine (136 mg, 1mmol) was added dropwise with constant stirring. After stirring for 24 h at room temperature, the solution was concentrated by rotary evaporation to obtain a yellow hygroscopic liquid (yield: 97%). The ligand was then used for metalation without further purification. ^{1}H NMR (400 MHz, d_6-DMSO): δ 8.40 (s, 2H), 7.37–7.26 (m, 4H), 7.26–7.18 (m, 2H), 7.04 (d, J = 1.0 Hz, 2H), 4.77 (s, 4H), 3.89 (s, 6H). ^{13}C NMR (150 MHz, d_6-DMSO): δ 154.1, 142.4, 139.6, 128.8, 128.5, 127.1, 126.3, 125.7, 64.1, 34.8. ESI-MS: m/z 321.2 $[M + H]^+$, 343.2 $[M + Na]^+$. HRMS (ESI-MS): m/z $[M + H]^+$ (calc. 321.1828): found 321.1843.

Procedure for the self-assembly synthesis of the complexes

A solution of ligand (0.3 mmol) and metal salt (manganese hexafluorophosphate, zinc hexafluoroantimonate, or cadmium trifluoromethanesulfonate; 0.2 mmol) in acetonitrile/methanol (15 mL/3 mL) were stirred at room temperature for 4 h. The crude compound was isolated by filtration after precipitation by diethyl ether. Slow diffusion of isopropyl ether into acetonitrile and methanol solution of redissolved crude compound gave crystalline product.

$[Mn_8\mathbf{L}_{12}](PF_6)_{16}$: yield: 71%. ESI-MS: 1505.9 $[Mn_8\mathbf{L}_{12}](PF_6)_{12}^{4+}$, 1175.4 $[Mn_8\mathbf{L}_{12}](PF_6)_{11}^{5+}$, 955.4 $[Mn_8\mathbf{L}_{12}](PF_6)_{10}^{6+}$ and 798.5 $[Mn_8\mathbf{L}_{12}](PF_6)_9^{7+}$. CHN elemental analysis: calc. for $Mn_8(C_{18}H_{20}N_6)_{12}(PF_6)_{16}\cdot 7H_2O\cdot 5CH_3OH\cdot 5CH_3CN$: C, 38.76; H, 4.05; N, 14.87; Found: C, 38.76; H, 4.03; N, 14.94%. $[Zn_8\mathbf{L}_{12}](SbF_6)_{16}$: yield: 68%. ESI-MS: 1798.1 $[Zn_8\mathbf{L}_{12}](SbF_6)_{12}^{4+}$, 1390.6 $[Zn_8\mathbf{L}_{12}](SbF_6)_{12}^{5+}$, 1120.4 $[Zn_8\mathbf{L}_{12}](SbF_6)_{12}^{6+}$ and 927.1 $[Zn_8\mathbf{L}_{12}](SbF_6)_{12}^{7+}$. CHN elemental analysis: calc. for $Zn_8(C_{18}H_{20}N_6)_{12}(SbF_6)_{16}\cdot 27H_2O\cdot CH_3CH_2OH$: C, 30.19; H, 3.49; N, 11.63; Found: C, 30.23; H, 3.56; N, 11.61%. ^{1}H NMR (400 MHz, CD_3CN): δ 7.65 (s, 1H), 7.47 (s, 1H), 7.30 (d, *J* = 0.9 Hz, 1H), 6.50 (s, 1H), 6.02 (s, 2H), 4.86 (d, *J* = 14.4 Hz, 1H), 4.79 (d, *J* = 14.4 Hz, 1H), 3.55 (s, 3H). ^{13}C NMR (150 MHz, CD_3CN): δ 152.5, 142.1, 138.0, 128.1, 128.0, 127.7, 126.5, 126.4, 63.3, 33.4. $[Cd_8\mathbf{L}_{12}](OTf)_{16}$: yield: 82%. ESI-MS: 1632.8 $[Cd_8\mathbf{L}_{12}](OTf)_{12}^{4+}$, 1276.5 $[Cd_8\mathbf{L}_{12}](OTf)_{11}^{5+}$, 1038.7 $[Cd_8\mathbf{L}_{12}](OTf)_{10}^{6+}$, and 869.6 $[Cd_8\mathbf{L}_{12}](OTf)_9^{7+}$. CHN elemental analysis: calc. for $Cd_8(C_{18}H_{20}N_6)_{12}(OTf)_{16}\cdot 4H_2O$: C, 38.69; H, 3.47; N, 14.00; Found: C, 38.60; H, 3.48; N, 14.09 %. ^{1}H NMR (400 MHz, CD_3CN): δ 7.90–7.63 (m, 2H), 7.31 (d, *J* = 0.9 Hz, 1H), 6.74 (s, 1H), 6.17 (d, *J* = 7.7 Hz, 1H), 5.78 (t, *J* = 7.7 Hz, 1H), 5.08 (d, *J* = 13.9 Hz, 1H), 4.77 (d, *J* = 13.9 Hz, 1H). 3.58 (s, 3H). ^{13}C NMR (150 MHz, CD_3CN): δ 151.8, 142.0, 138.3, 129.1, 128.9, 127.8, 126.8, 126.8, 123.2, 121.0, 63.0, 33.2. Protons of $[Zn_8\mathbf{L}_{12}](SbF_6)_{16}$ and $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ are assigned with the help of ^{1}H–^{1}H COSY spectra (Figures S3 and S4).

Procedure of titrations between $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ and different anions

To study the anion exchange, the changes of NMR spectra were monitored during titrations of $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ which were dissolved in CD_3CN (0.5 mL; 1mM) with different anions (Bu_4NSbF_6, Bu_4NNTf_2, Bu_4NNO_3 and Bu_4NOTs; 0.25 M) at 300 K. In case

of titration between $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ (1 mM) and Bu_4NSbF_6 (from 0 to 35 equiv.; 0.25 M), Bu_4NSbF_6 was added to the solution of $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ in an NMR tube in small portions (1–10 μL). After every addition, the solution was thoroughly mixed by gentle shaking. After recording every ^{1}H NMR spectrum, ^{19}F NMR spectrum was measured. ^{19}F NMR spectra of titration between $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ and Bu_4NSbF_6 are shown in Figure S5. ^{1}H NMR spectra of titration between $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ and Bu_4NNTf_2 are shown in Figure S6. ^{1}H NMR spectra of titrations between $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ and Bu_4NNO_3 and $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ and Bu_4NOTs are shown in Figures S7 and S8, respectively. Binding constants were estimated using the equation $K_{TfO\text{-}/anion}$ = [(anion)⊂Cage]/[(TfO^-)⊂Cage](anion).

X-ray crystallographic analysis

Single crystal diffraction data of $[Mn_8\mathbf{L}_{12}](PF_6)_{16}$ was collected at 173(2) K on an Oxford Diffraction Gemini S Ultra X-ray single crystal diffractometer using monochromatized Cu-Kα radiation (λ = 1.54178 Å). Single crystal diffraction data of $[Zn_8\mathbf{L}_{12}](SbF_6)_{16}$ was collected at 100(2) K on an Bruker Proteum X8 X-ray single crystal diffractometer using multilayer mirror monochromatized Cu-Kα radiation (λ = 1.54178 Å). Single crystal diffraction data of $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ was collected at 100(2) K using synchrotron radiation (λ = 0.78 Å) on beamline 3W1A of the Beijing Synchrotron Radiation Facility at the Institute of High Energy Physics, Chinese Academy of Sciences. All structures were solved by direct methods using SHELXS and refined by full-matrix least-squares on $|F^2|$ algorithm (SHELXL) using Olex2 program. Some solvent molecules and anions in the structures were omitted using SQUEEZE routing of PLATON program as they were highly disordered and could not been resolved unambiguously. Due to the weak diffraction feature of $[Zn_8\mathbf{L}_{12}](SbF_6)_{16}$, the reflection data were cut off at 1.0 Å. Crystallographic data of all the complexes are given in Table S1.

Table S1. Crystallographic data for $[Mn_8\mathbf{L}_{12}](PF_6)_{16}$, $[Zn_8\mathbf{L}_{12}](SbF_6)_{16}$ and $[Cd_8\mathbf{L}_{12}](OTf)_{16}$.

Complex	$[Mn_8\mathbf{L}_{12}](PF_6)_{16}$	$[Zn_8\mathbf{L}_{12}](SbF_6)_{16}$	$[Cd_8\mathbf{L}_{12}](OTf)_{16}$
Empirical formula	$C_{240}H_{240}F_{39}Mn_8N_{84}P_{6.5}$	$C_{216}H_{228}F_{96}N_{72}Sb_{16}Zn_8$	$C_{232}H_{240}Cd_8F_{48}N_{72}O_{48}S_{16}$
Formula weight	5682.99	8127.65	7129.11
Temperature/K	173	100	100
Crystal system	cubic	cubic	cubic
Space group	Pn $\bar{3}$n	Pa $\bar{3}$	Pa $\bar{3}$
a=b=c/Å	26.6801(3)	40.8424(9)	41.313(5)
α=β=γ/°	90.00	90	90
Volume/Å^3	18991.6(6)	68129(5)	70510(30)
Z	2	8	8
ρ_{calc}g/cm^3	0.994	1.585	1.343
μ/mm^{-1}	2.925	11.392	0.660
F(000)	5833.0	31584.0	28736.0
Crystal size/mm^3	0.35 × 0.33 × 0.28	0.3 × 0.3 × 0.3	0.5 × 0.5 × 0.5
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	Synchrotron Radiation (λ = 0.78)
2θ range for data collection/°	6.62 to 143.44	3.746 to 98.256	1.708 to 53.784
Independent reflections	3103	11183	24838
Data/restraints/ parameters	3103/7/173	11183/59/1203	24838/654/1380
Goodness-of-fit on F^2	1.325	1.086	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.1287, wR_2 = 0.3681	R_1 = 0.0977, wR_2 = 0.2862	R_1 = 0.1225, wR_2 = 0.3472

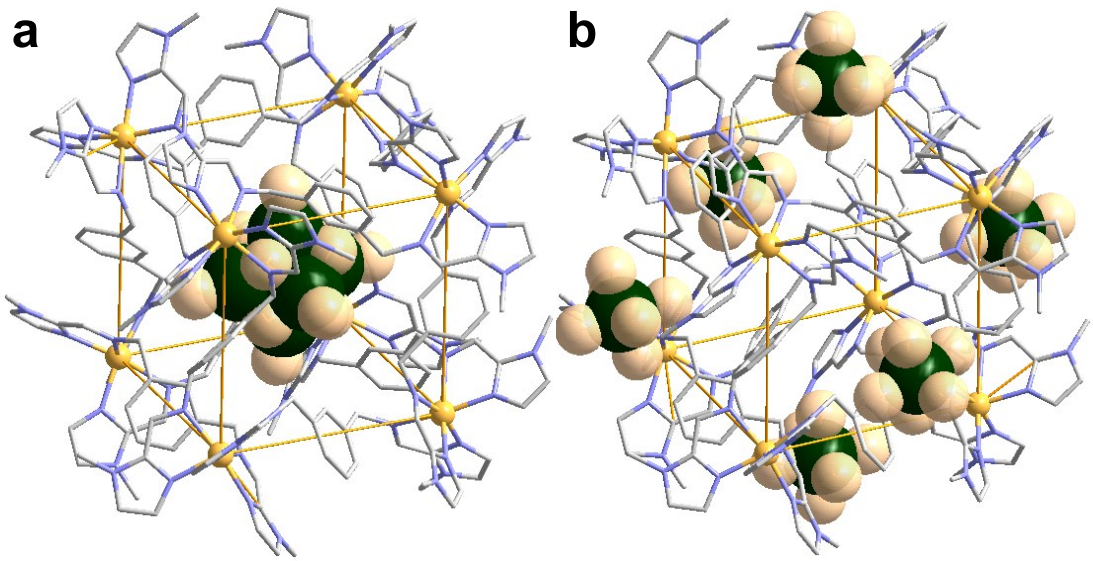

Figure S1. X-ray crystal structure of $[Zn_8\mathbf{L}_{12}](SbF_6)_{16}$ with (a) the encapsulated anion (disorder heavily) and (b) the exterior anions shown in space filling model.

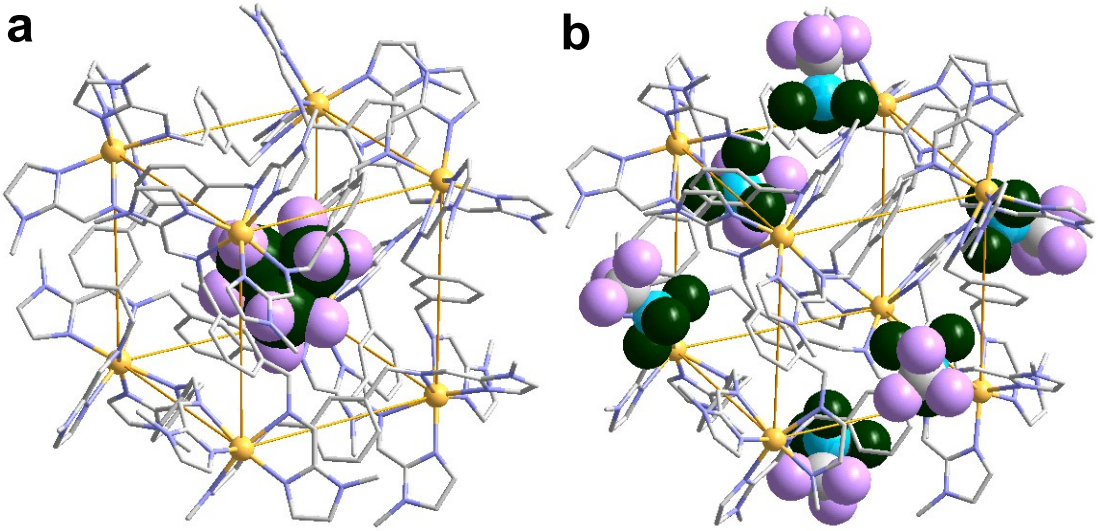

Figure S2. X-ray crystal structure of $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ with (a) the encapsulated anion (disorder heavily) and (b) the exterior anions shown in space filling model.

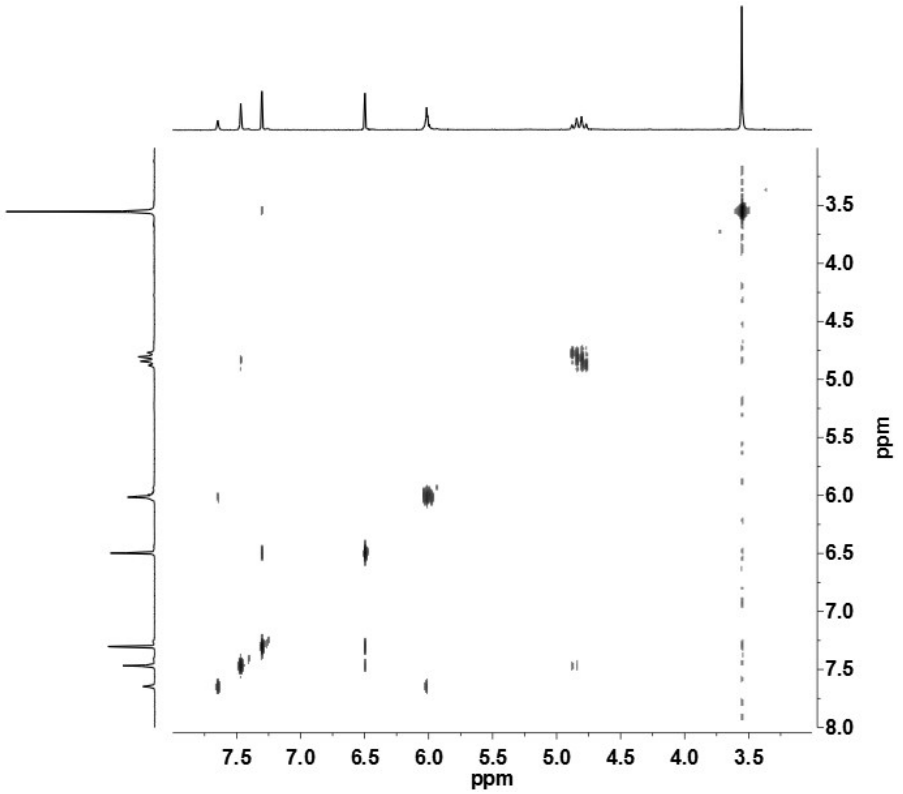

Figure S3. ^{1}H–^{1}H COSY spectrum of $[Zn_8\mathbf{L}_{12}](SbF_6)_{16}$ in CD_3CN.

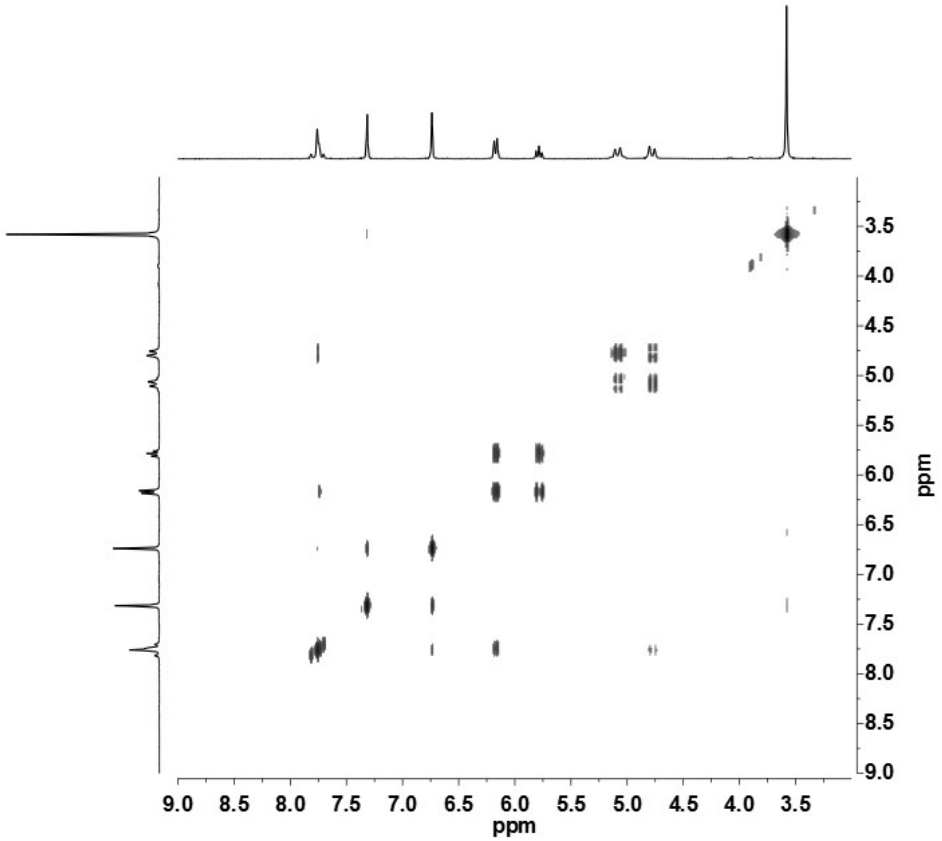

Figure S4. ^{1}H–^{1}H COSY spectrum of $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ in CD_3CN.

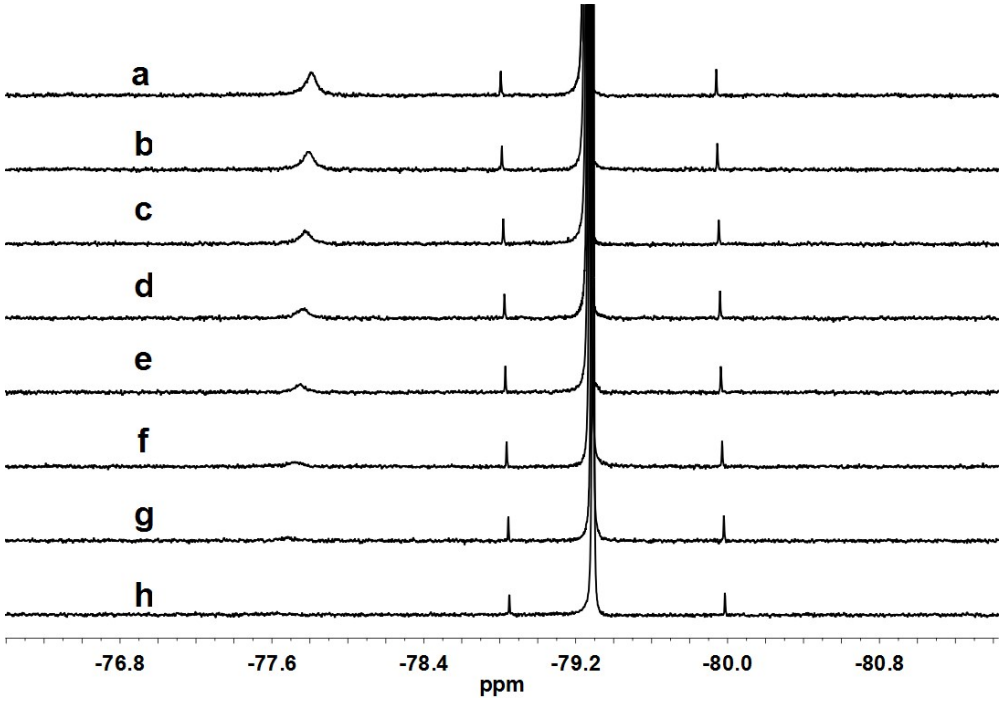

Figure S5. ^{19}F NMR spectra of titration between $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ and Bu_4NSbF_6 in CD_3CN (from a to h: 0, 1, 3, 5, 7, 11, 20 and 35 equiv.).

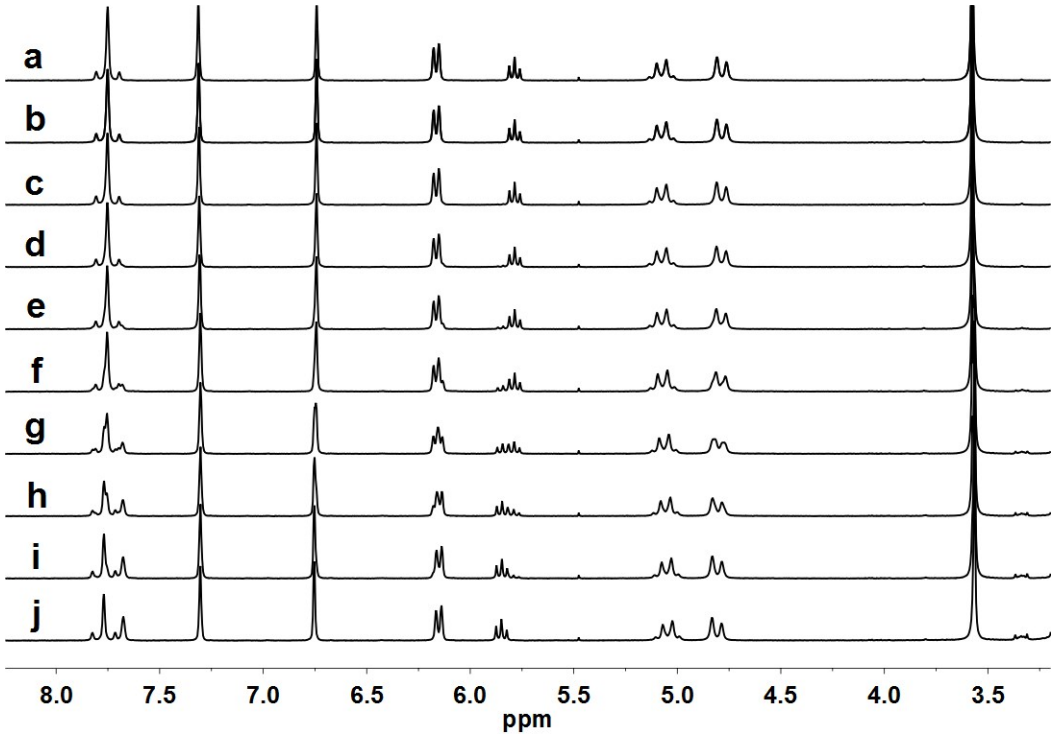

Figure S6. ^{1}H NMR spectra of titration between $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ and Bu_4NNTf_2 in CD_3CN (from a to j: 0, 1, 3, 5, 10, 20, 40, 60, 75 and 100 equiv.).

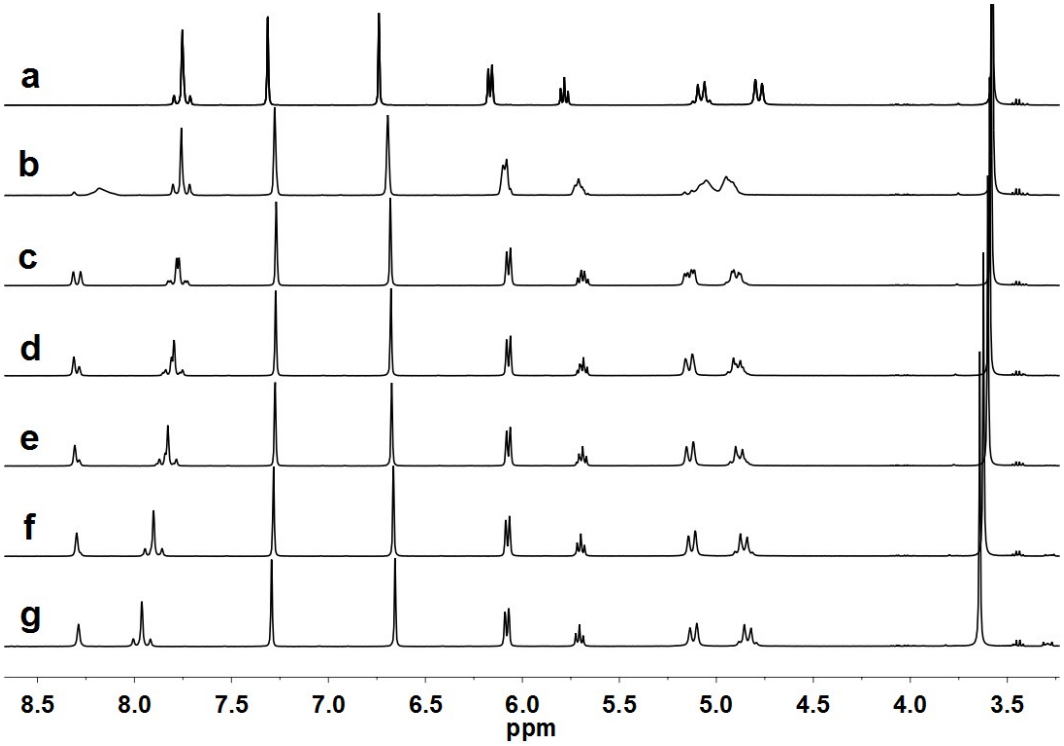

Figure S7. ^{1}H NMR spectra of titration between $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ and Bu_4NNO_3 in CD_3CN (from a to g: 0, 1, 3, 5, 8, 20 and 50 equiv.).

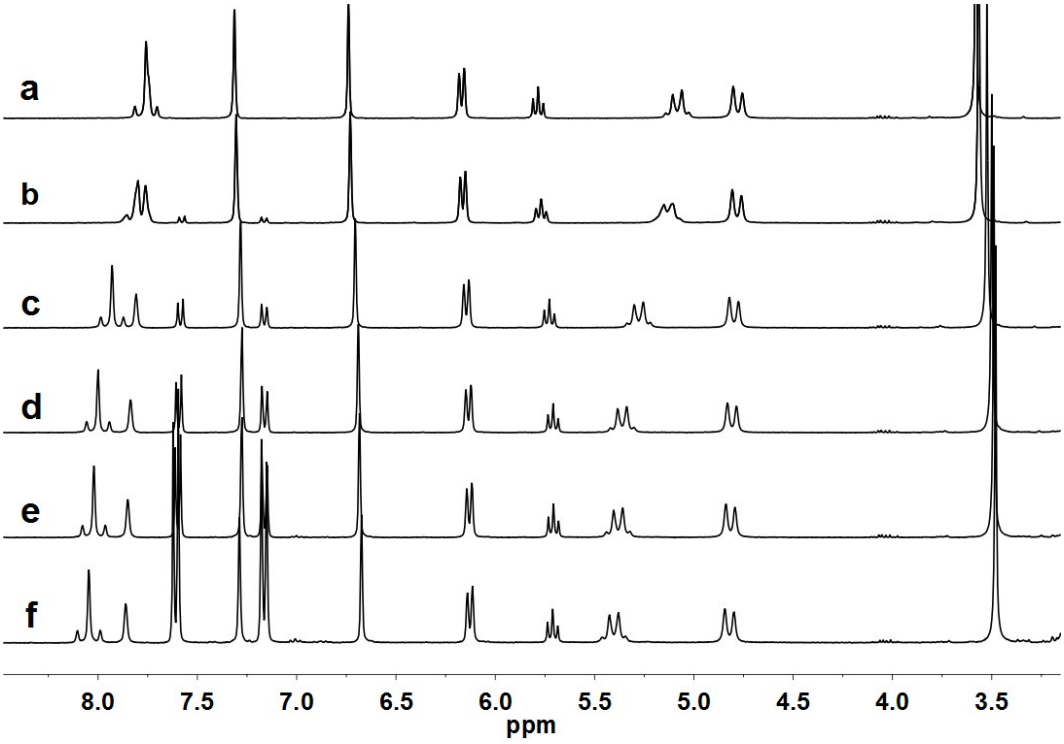

Figure S8. ^{1}H NMR spectra of titration between $[Cd_8\mathbf{L}_{12}](OTf)_{16}$ and Bu_4NOTs in CD_3CN (from a to f: 0, 1, 5, 10, 15 and 35 equiv.).