Electronic Supplementary Information (ESI)

Coordination-driven self-Assembly of $M_{10}L_8$ metal-organic bi-capped square antiprisms with adaptable cavity

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General Procedure

Starting materials, reagents, and solvents were purchased from commercial sources (Alfa Aesar, J&K, TCI and Aldrich) and used without further purification. FT-IR spectra were measured using a Nicolet Avatar 360 FT-IR spectrophotometer (vs = very strong, s = strong, m = middle, w = weak). Elemental analyses were carried out with an Elementar vario EL Cube equipment. Mass spectra were recorded on an LTQ Orbitrap XL™ Hybrid Ion Trap-Orbitrap Mass Spectrometer from Thermo Scientific. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Biospin Avance (400 MHz) equipment.

Syntheses of the ligand and complexes

Ligand synthesis. A methanol solution (10.0 mL) of 1,3-diaminopropane (0.741 g, 10 mmol) was added to a methanol solution (25.0 mL) of imidazole-4-carbaldehyde (1.922 g, 20 mmol). The mixture was stirred overnight at 50 °C. A product of light-yellow powder (H_2L) was obtained by evaporation under reduced pressure (1.564 g, yield 68.0 %). ^{1}H NMR (400 MHz, MeOD): 8.17 (s, 2H), 7.67 (s, 2H), 7.43 (s, 2H), 3.56-3.53 (t, 3H), 1.98-1.91 (m, 4H). ^{13}C NMR (100 MHz, MeOD): 31.6, 58.1, 122.9, 134.9, 137.0, 154.5. MS: m/z for $C_{11}H_{15}N_6$ ($[M+H]^+$), calculated: 231.1; found: 231.1. IR spectrum (KBr, pellets, cm^{-1}): 3118(w), 2939(w), 2837(w), 2776(m), 2667(w), 2599(w), 1650(s), 1460(m), 1112(m), 998(m), 946(m), 859(m), 629(m). Elemental analysis (CHN): $C_{11}H_{16}N_6$, calculated (%): C 57.38, H 6.13, N 36.50; found (%): C 57.17, H 6.09, N 36.83.

Synthesis of cage 1: A mixture of $Cu(ClO_4)_2 \cdot 6H_2O$ (18.5 mg, 0.05 mmol), H_2L (9.2 mg, 0.04 mmol), and DMF/ methanol mixed solvent (2.5 mL, 1:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 100 °C for 72 hours and cooled to room temperature at a rate of 5 °C/h. The green rhombohedron-like crystals were obtained (10.0 mg, yield 60.6 %, based on $Cu(ClO_4)_2 \cdot 6H_2O$). IR spectrum (KBr, pellets, cm^{-1}): 3459(w), 2934(w), 1617(vs), 1465(m), 1266(m), 1114(s), 1031(m), 960(m), 873(m),655(m), 624(v). Elemental analysis (CHN): $C_{100}H_{148}N_{52}O_{32}Cl_4Cu_{10}$

(corresponding to $[Cu_{10}L_8]\cdot 4ClO_4\cdot 6DMF\cdot 24H_2O$), calculated (%): C 38.21, H 5.63, N 22.70; found (%): C 38.14, H 5.64, N 22.66.

Synthesis of cage 2: A mixture of $CuSiF_6$ (10.3 mg, 0.05 mmol), H_2L (9.2 mg, 0.04 mmol), and DMF/ ethanol mixed solvent (2.5 mL, 4:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 100 °C for 72 hours and cooled to room temperature at a rate of 5 °C/h. The green rhombohedron-like crystals were obtained with low yield (2.0 mg). IR spectrum (KBr, pellets, cm^{-1}): 3443(w), 3127(w), 1631(m), 1611(vs), 1456(m), 1465(m), 1112(s), 1079(m), 727(s), 671(m), 654.1(m). Elemental analysis (CHN): $C_{100}H_{152}N_{53}O_{22}F_{12}Si_2Cu_{10}$ (corresponding to $[Cu_{10}L_8]\cdot 2SiF_6\cdot 6DMF\cdot 14H_2O$), calculated (%): C 35.66, H 4.55, N 22.04; found (%): C 35.68, H 4.44, N 21.82.

Synthesis of cage 3: A mixture of $CuBr_2$ (11.2 mg, 0.05 mmol), H_2L (9.2 mg, 0.04 mmol), and DMF/ methanol mixed solvent (2.5 mL, 4:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 110 °C for 72 hours and cooled to room temperature at a rate of 5 °C/h. The dark cyan square-like crystals were obtained (7.5 mg, yield 62.5 %, based on $CuBr_2$). IR spectrum (KBr, pellets, cm^{-1}): 3426(w), 2925(w), 1654(m), 1617(vs), 1468(m), 1343(s), 1263(m), 1114(s), 1081(m), 1034(m),

655(m). Elemental analysis (CHN): $C_{88}H_{150}N_{48}O_{27}Cu_{10}Br_4$ (corresponding to $[Cu_{10}L_8]\cdot 4Br\cdot 27H_2O$), calculated (%): C 32.35, H 4.63, N 20.58; found (%): C 32.32, H 4.07, N 20.05.

Synthesis of cage 4: A mixture of $CuCl_2\cdot 2H_2O$ (8.5 mg, 0.05 mmol), H_2L (9.2 mg, 0.04 mmol), and DMF/ methanol mixed solvent (2.5 mL, 4:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 100 °C for 72 hours and cooled to room temperature at a rate of 5 °C/h. The green powders were obtained (5.1 mg, yield 40.8%, based on $CuCl_2\cdot 2H_2O$) IR spectrum (KBr, pellets, cm^{-1}): 3421(w), 2917(w), 1647(m), 1616(vs), 1540(m), 1458(m), 1263(m), 1115(s), 1080(m),1031(m), 653(m).Elemental analysis (CHN): $C_{91}H_{148}N_{48}O_{23}Cl_4Cu_{10}$ (corresponding to $[Cu_{10}L_8]\cdot 4Cl\cdot 3CH_4O\cdot 20H_2O$), calculated (%): C 35.72, H 4.88, N 21.97; found (%): C 35.63, H 4.37, N 21.76.

Synthesis of single crystals of cage 4 transformed: A mixture of **1** (10 mg, 0.004 mmol), KCl (7.4 mg, 0.1 mmol), and DMF/ methanol mixed solvent (2.5 mL, 4:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 100 °C for 72 hours and cooled to room temperature at a rate of 5 °C/h. The dark-green block crystals belong to cage **1** were obtained.

Synthesis of coordination polymer 5： A mixture of $Cu(ClO_4)_2\cdot 6H_2O$ (14.8 mg, 0.04 mmol), H_2L (9.2 mg, 0.04 mmol), and DEF/ methanol mixed solvent (2.5 mL, 1:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 100 °C for 72 hours and cooled to room temperature at a rate of 5 °C/h. The light green needle-like crystals were collected were obtained (8.0 mg, yield 43.6 %, based on $Cu(ClO4)_2\cdot 6H_2O$). IR spectrum (KBr, pellets, cm^{-1}): 3435(w), 2930(w), 2859(w), 1621(vs), 1464(m), 1260(m), 1121(s), 1036(m), 654(m), 625(m).

Synthesis of coordination polymer 6： A mixture of $CuSiF_6$ (8.2 mg, 0.04 mmol), H_2L (9.2 mg,0.04 mmol), and DMF/ methanol mixed solvent (2.5 mL, 4:1, v/v) was sealed

in a Pyrex glass tube and heated in an oven at 100 °C for 72 hours and cooled to room temperature at a rate of 5 °C/h. The light green polyhedron-like crystals were collected were obtained (6.8 mg, yield 46.7 %, based on $Cu(SiF_6)_2$). IR spectrum (KBr, pellets, cm^{-1}): 3127(w), 1631(m), 1611(vs), 1465(m), 1113(s), 1079(m), 890(m), 727(vs), 671(m), 654(m), 474(m).

Synthesis of coordination polymer 7： A mixture of $CuBr_2$ (9.0 mg, 0.04 mmol), H_2L (9.2 mg, 0.04 mmol), and DMF/ methanol mixed solvent (2.5 mL, 4:1, v/v) was sealed in a Pyrexglass tube and heated in an oven at 100 °C for 72 hours and cooled to room temperature at a rate of 5 °C/h. The blue square-like crystals were collected were obtained (4.6 mg, yield 30.9 %, based on $CuBr_2$). IR spectrum (KBr, pellets, cm^{-1}): 3427(w), 2925(w), 1655(m), 1618(vs), 1468(m), 1343(s), 1264(m), 1114(s), 1081(m), 1034(m), 655(m).

Synthesis of coordination polymer 8： A mixture of $CuCl_2{\cdot}2H_2O$ (6.8 mg, 0.04 mmol), H_2L (9.2 mg, 0.04 mmol), and DMF/ ethanol mixed solvent (2.5 mL, 4:1, v/v) was sealed in a Pyrex glass tube and heated in an oven at 100 °C for 72 hours and cooled to room temperature at a rate of 5 °C/h. The green cubic crystals were collected were obtained (5.2 mg, yield 39.6 %, based on $CuCl_2{\cdot}2H_2O$). IR spectrum (KBr, pellets, cm^{-1}): 3421(w), 2917(m), 2849(m), 1616(vs), 1458(m), 1263(m), 1115(vs), 1032(m), 654(s), 442(m).

Crystal Structure Analysis and Additional Characterization

Crystallographic Studies

Single crystal structures of compounds **1-8** were measured by X-ray diffraction. Data collection was performed on a XtaLab PRO MM007HF DW Diffractometer System equipped with a MicroMax-007DW MicroFocus X-ray generator and Pilatus 200 K silicon diarray detector (Rigaku, Japan, Cu Kα, λ = 1.54178 Å). All crystals were measured at 100 K. The structures were solved by direct methods and refined by full-matrix least-squares refinements based on *F*2. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. The crystallographic calculations were performed using the SHELXL-2018/3 programs. The treatment for the disordered guest molecules in the cavities of all complexes involved the use of the SQUEEZE program of PLATON. Crystal data and structure refinement were summarized in Table S1-S4. CCDC nos. 1866613-1866620.

Table S1 Crystal data of cages **1** and **2**.

Parameter	**1**	**2**
Chemical formula	$C_{106}H_{140}Cl_4Cu_{10}N_{54}O_{23}$	$C_{88}H_{98}Cu_{10}F_6N_{48}OSi$
Formula weight	3315.91	2621.63
Temperature (K)	100	100
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	22.28850(10)	22.2435(2)
b (Å)	25.78600(10)	26.0724(2)
c (Å)	26.57420(10)	26.5968(2)
α (deg)	90.00	90.00
β (deg)	110.7950(10)	111.0710(10)
γ (deg)	90.00	90.00
Volume (Å^3)	14278.08(13)	14393.2(2)
Z	4	4
D_{calcd} (g cm^{-3})	1.543	1.202
μ (mm^{-1})	2.959	2.138
Reflections collected	83018	39436
Unique reflections	29158	13495
R_{int}	0.0187	0.0237
Goodness-of-fit on F^2	1.072	1.053
R_1[a] [I > 2σ(I)]	0.0656	0.0348
wR_2[b] [I > 2σ(I)]	0.1877	0.0964
R_1[a] [all refl.]	0.0699	0.0387
wR_2[b] [all refl.]	0.1910	0.0986
CCDC number	1866613	1866614

[a] $R_1=\sum(||F_0|- |F_c||)/\sum|F_0|$; [b] $wR_2=[\sum w(F_0^2- F_c^2)^2/\sum w(F_0^2)^2]^1$

Table S2 Crystal data of cages **3** and **4**.

Parameter	**3**	**4**
Chemical formula	$C_{88}H_{96}BrCu_{10}N_{48}$	$C_{88}H_{96}ClCu_{10}N_{48}$
Formula weight	2541.43	2496.97
Temperature (K)	100	100
Crystal system	tetragonal	tetragonal
Space group	*P4/n*	*P4/n*
a (Å)	19.2461(2)	19.3296(3)
b (Å)	19.2461(2)	19.3296(3)
c (Å)	14.4823(3)	14.3057(4)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
Volume (Å^3)	5364.42(16)	5345.1(2)
Z	2	2
D_{calcd} (g cm^{-3})	1.573	1.551
μ (mm^{-1})	3.086	2.889
Reflections collected	15561	16694
Unique reflections	5222	5431
R_{int}	0.0446	0.0773
Goodness-of-fit on F^2	1.044	1.026
R_1[a] [I > 2σ(I)]	0.0491	0.0658
wR_2[b] [I > 2σ(I)]	0.1195	0.1606
R_1[a] [all refl.]	0.0761	0.1277
wR_2[b] [all refl.]	0.1310	0.1922
CCDC number	1866615	1866616

[a] $R_1=\sum(||F_0|- |F_c||)/\sum|F_0|$; [b] $wR_2=[\sum w(F_0^2- F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

Table S3 Crystal data of one-dimensional coordination polymers **5** and **6**.

Parameter	**5**	**6**
Chemical formula	$C_{22}H_{25}ClCu_2N_{12}O_4$	$C_{22}H_{26}Cu_2F_6N_{12}Si$
Formula weight	684.07	727.72
Temperature (K)	100	100
Crystal system	orthorhombic	monoclinic
Space group	*Pbcn*	$P2_1/c$
a (Å)	9.4211(5)	8.61500(10)
b (Å)	14.8334(5)	14.2500(2)
c (Å)	21.6671(10)	10.57550(10)
α (deg)	90	90
β (deg)	90	93.0570(10)
γ (deg)	90	90
Volume (Å^3)	3027.9(2)	1296.44(3)
Z	2	2
D_{calcd} (g cm^{-3})	1.501	1.864
μ (mm^{-1})	2.968	3.235
Reflections collected	14261	6081
Unique reflections	2886	2563
R_{int}	0.0772	0.0124
Goodness-of-fit on F^2	1.138	1.060
R_1[a] [I > 2σ(I)]	0.0660	0.0280
wR_2[b] [I > 2σ(I)]	0.1807	0.0745
R_1[a] [all refl.]	0.0787	0.0283
wR_2[b] [all refl.]	0.1918	0.0748
CCDC number	1866617	1866618

[a] $R_1=\sum(||F_0|- |F_c||)/\sum|F_0|$; [b] $wR_2=[\sum w(F_0^2- F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

Table S4 Crystal data of one-dimensional coordination polymers **7** and **8**.

Parameter	**7**	**8**
Chemical formula	$C_{11}H_{13}BrCuN_6$	$C_{11}H_{13}ClCuN_6$
Formula weight	372.72	328.26
Temperature (K)	100	100
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	9.1003(2)	9.16170(10)
b (Å)	9.0877(2)	9.33540(10)
c (Å)	15.9711(3)	15.0311(2)
α (deg)	90	90
β (deg)	90.770(2)	91.9370(10)
γ (deg)	90	90
Volume (Å^3)	1320.70(5)	1284.85(3)
Z	4	4
D_{calcd} (g cm^{-3})	1.875	1.697
μ (mm^{-1})	5.847	4.279
Reflections collected	5685	5921
Unique reflections	2446	2618
R_{int}	0.0782	0.0243
Goodness-of-fit on F^2	1.044	1.105
R_1[a] [I > 2σ(I)]	0.0455	0.0378
wR_2[b] [I > 2σ(I)]	0.1181	0.1066
R_1[a] [all refl.]	0.0568	0.0396
wR_2[b] [all refl.]	0.1332	0.1077
CCDC number	1866619	1866620

[a] $R_1=\sum(||F_0|- |F_c||)/\sum|F_0|$; [b] $wR_2=[\sum w(F_0^2- F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

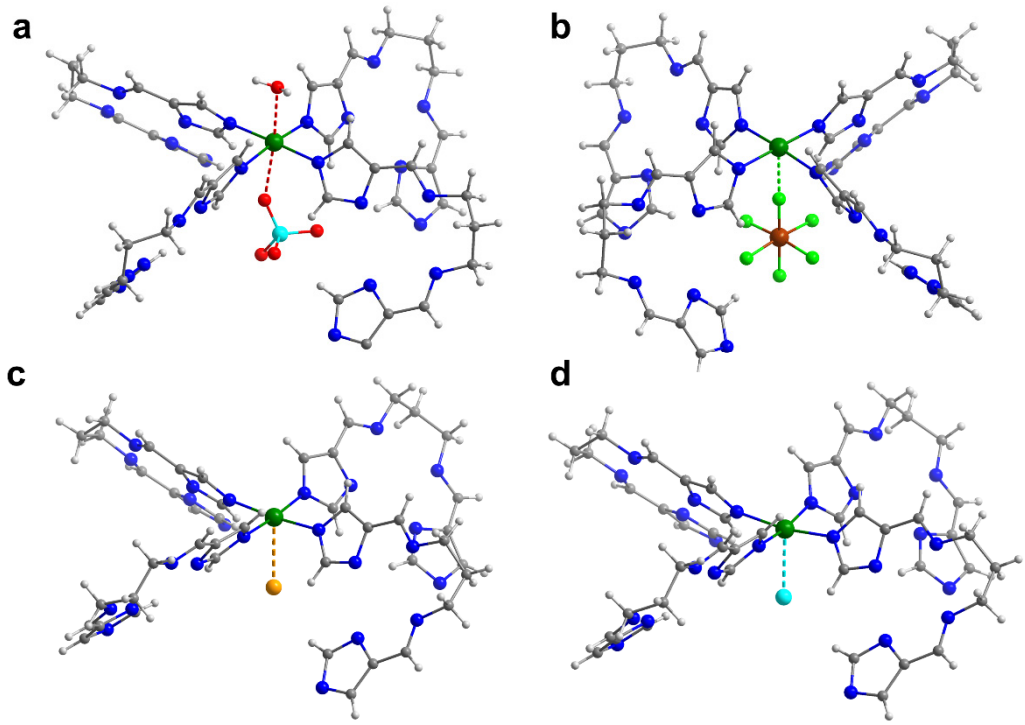

Fig. S1. Surrounding environment of the axial Cu(II) in (a) cage **1** (binding with a ClO_4^- and a water molecule), (b) cage **2** (binding with a SiF_6^{2-} and a water molecule), (c) cage **3** (binding with a Br^-), (d) cage **4** (binding with a Cl^-). Color codes: C grey, O red, N blue, H bright grey, F bright green, Cl cyan, Br light orange, Si brown and Cu green.

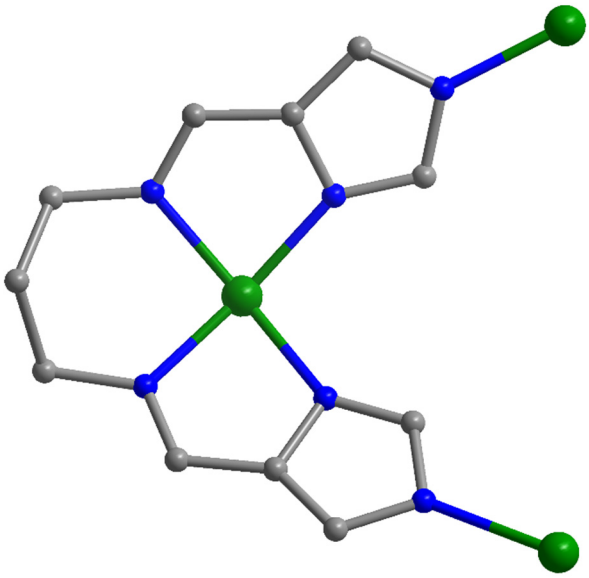

Fig. S2. The coordination geometry of ligand. Color codes: C grey, N blue, Cu green.

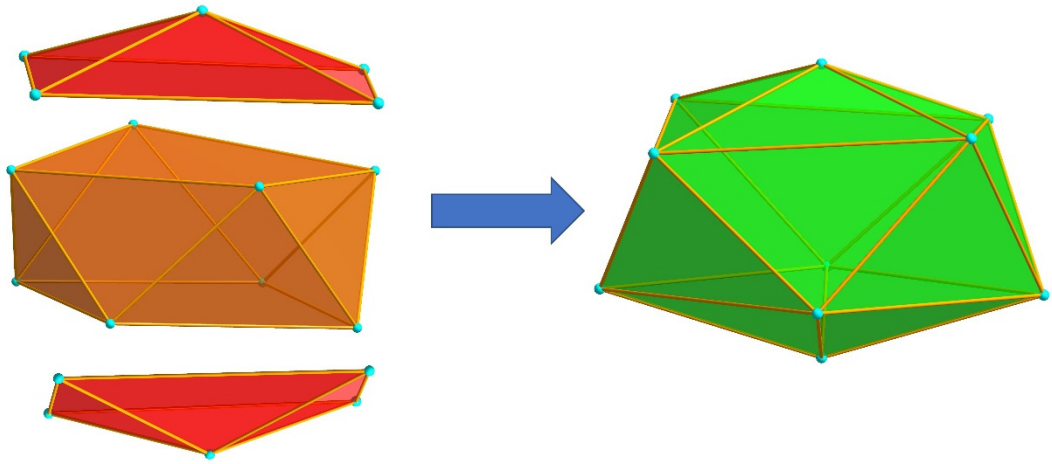

Fig. S3. Schematic diagram of formation a *closo* bicapped square antiprism.

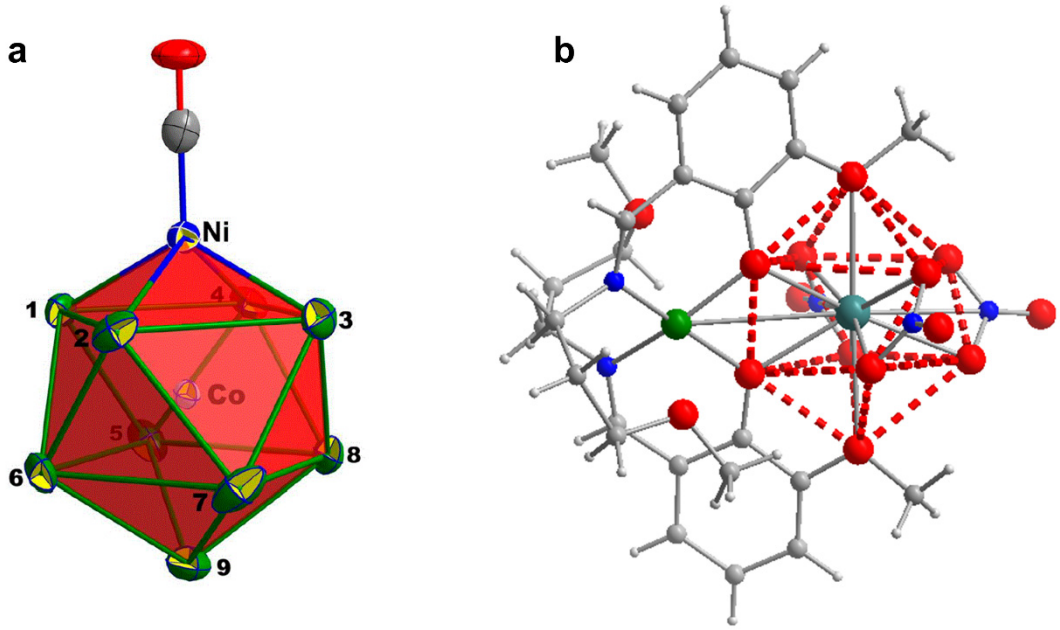

Fig. S4. Bicapped square antiprism geometry of (a) the $[Co@Sn9Ni(CO)]^{3-}$ cluster[1] (copyright 2018 American Chemical Society) and (b) coordination geometry of Tb^{III} ion. [2] Color codes: C grey, O red, N blue, H bright grey, Tb teal, and Cu green.

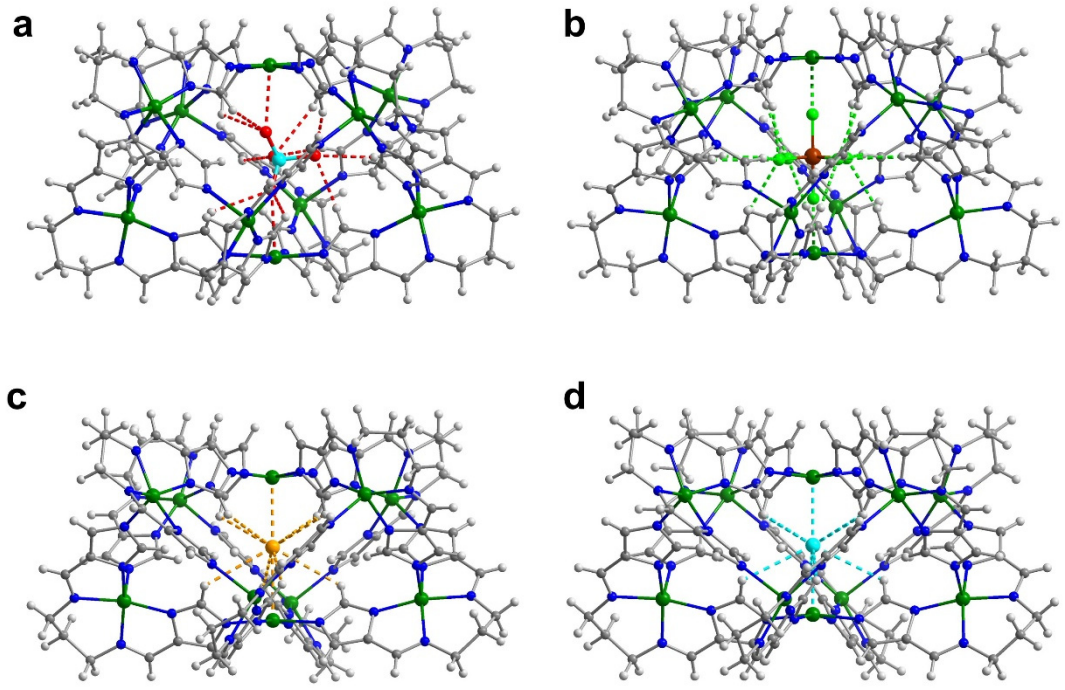

Fig. S5. X-ray crystal structure of cages **1** (a), **2** (b), **3** (c), and **4** (d) encapsulating ClO_4^-, SiF_6^{2-}, Br^-, and Cl^-, respectively. Multiple interactions exist between cages and anions, which are highlighted with dashed lines. In cages **1-4,** the coordination interactions of Cu_a and O (**1** Cu-O: 2.721 ~ 2.744 Å), Cu_a and F (**2** Cu- F: 2.172 ~ 2.278 Å), Cu_a and Br^- (**3** Cu-Br:2.892 ~ 2.960 Å), and Cu_a and Cl^- (**4** Cu-Cl：2.714 ~ 2.752 Å) exist between axial copper ions and anions, respectively. On the other hand, the multiple weak hydrogen bonds: C-H···O (H···O: 2.324 ~ 2.836 Å) for **1**, C-H···F (H···F: 2.619(3) ~ 2.787(7) Å) for **2**, C-H···Br (H···Br: 3.074~3.192 Å) for **3**, and C-H···Cl (H···Cl: 3.043~3.142 Å) for **4** exist between correspond anions and imidazolate groups, respectively. Color codes: C grey, O red, N blue, H bright grey, F bright green, Cl cyan, Br light orange, Si brown and Cu green.

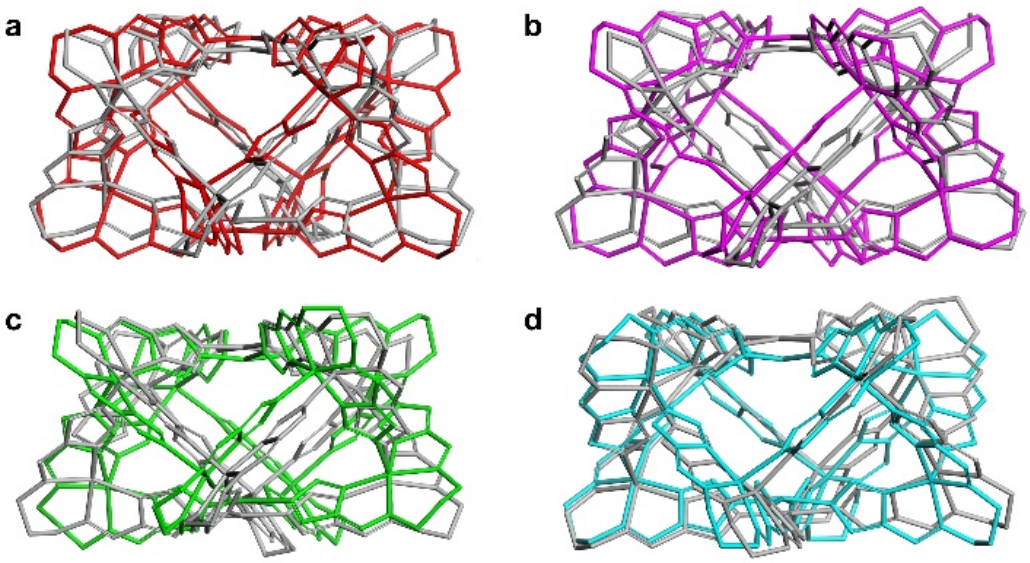

Fig. S6. View of two superimposed cage crystal structures: cage **1** (red, a), **2** (purple, b), **3** (green, c), **4** (cyan, d) and calculated cages (grey, a-d), respectively. Anions and hydrogen atoms were removed for clarity.

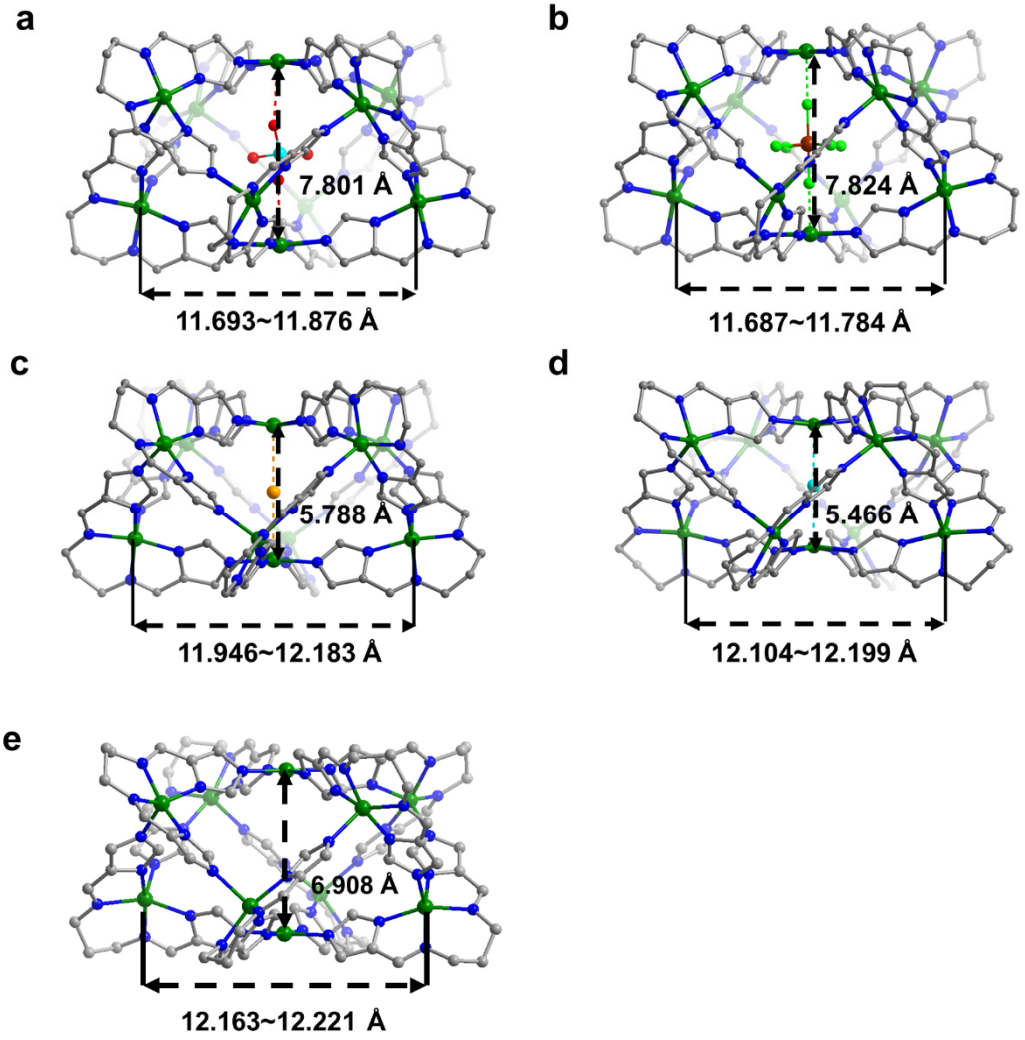

Fig. S7. The distances of $Cu_a \cdots Cu_a$ between two axial Cu(II) and diagonal distances of $Cu_e \cdots Cu_e$ on equatorial plane of the cage (a) **1**, (b) **2**, (c) **3**, (d) **4** and (e) DFT calculated cage **5** without encapsulated anions. Color codes: C grey, O red, N blue, F bright green, Cl cyan, Br light orange, Si brown and Cu green.

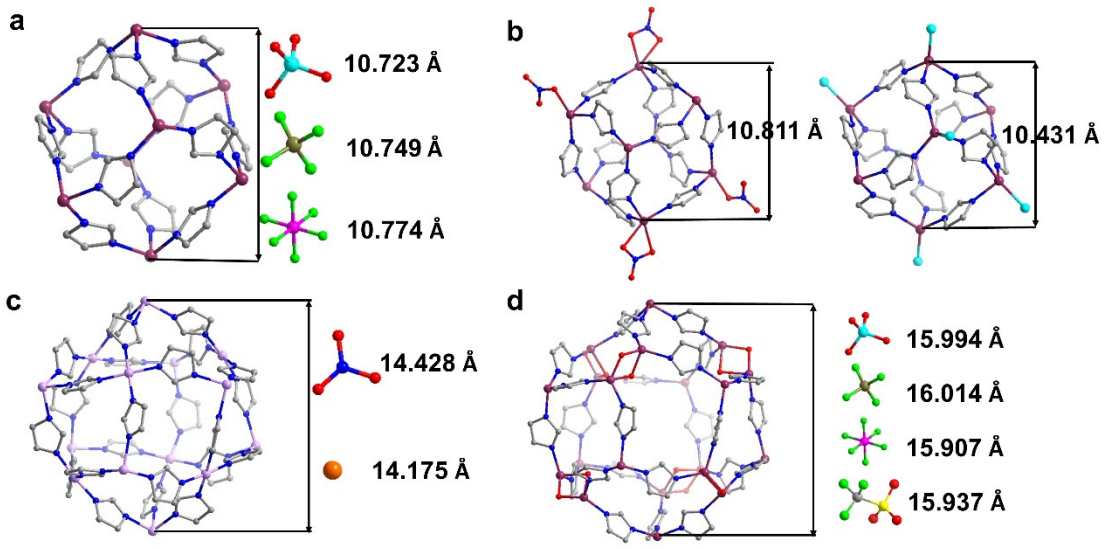

Fig. S8. X-ray crystal structure of cages M_8L_6 (a,b), $M_{14}L_{24}$ (c), and $M_{20}L_{12}(OH)_{12}$ (d) and their varied anions (ClO_4^-, BF_4^-, PF_6^{2-}, NO_3^-, Cl^-, Br^- and $CF_3SO_3^-$). Their sizes for each type of cage are very close, although the anions are changed. The substitution groups and hydrogen atoms on imidazolate are omitted for clarity. Color codes: C grey, O red, N blue, H bright grey, F bright green, Cl cyan, Br light orange, P pink, S yellow, Co plum, and Ni lavender.

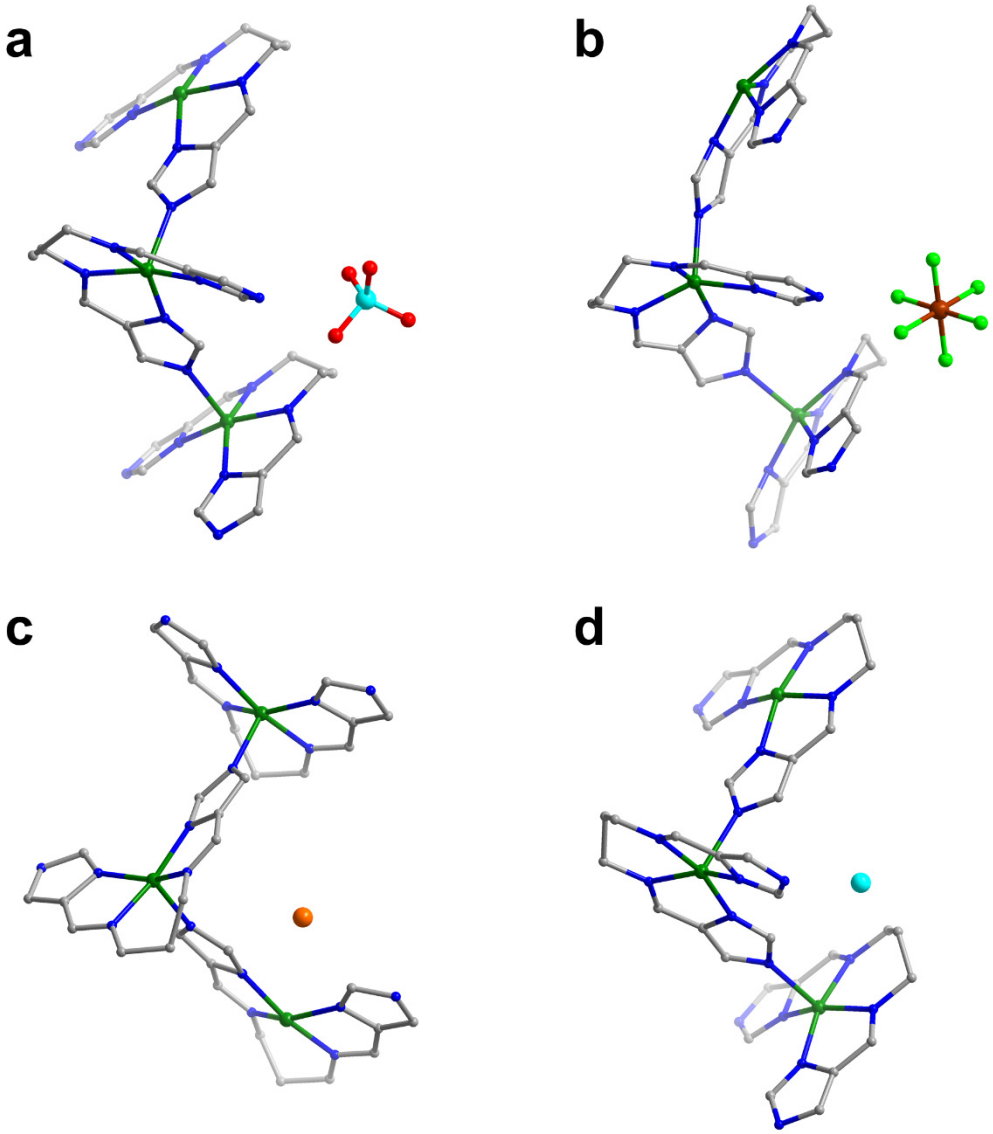

Fig. S9. X-ray crystal structure of one-dimensional coordination polymers **5** (a), **6** (b), **7** (c), and **8** (d) and their balancing anions ClO_4^-, SiF_6^{2-} , Br^-, and Cl^-, respectively. Color codes: C grey, O red, N blue, H bright grey, F bright green, Br light orange, Si brown and Cu green.

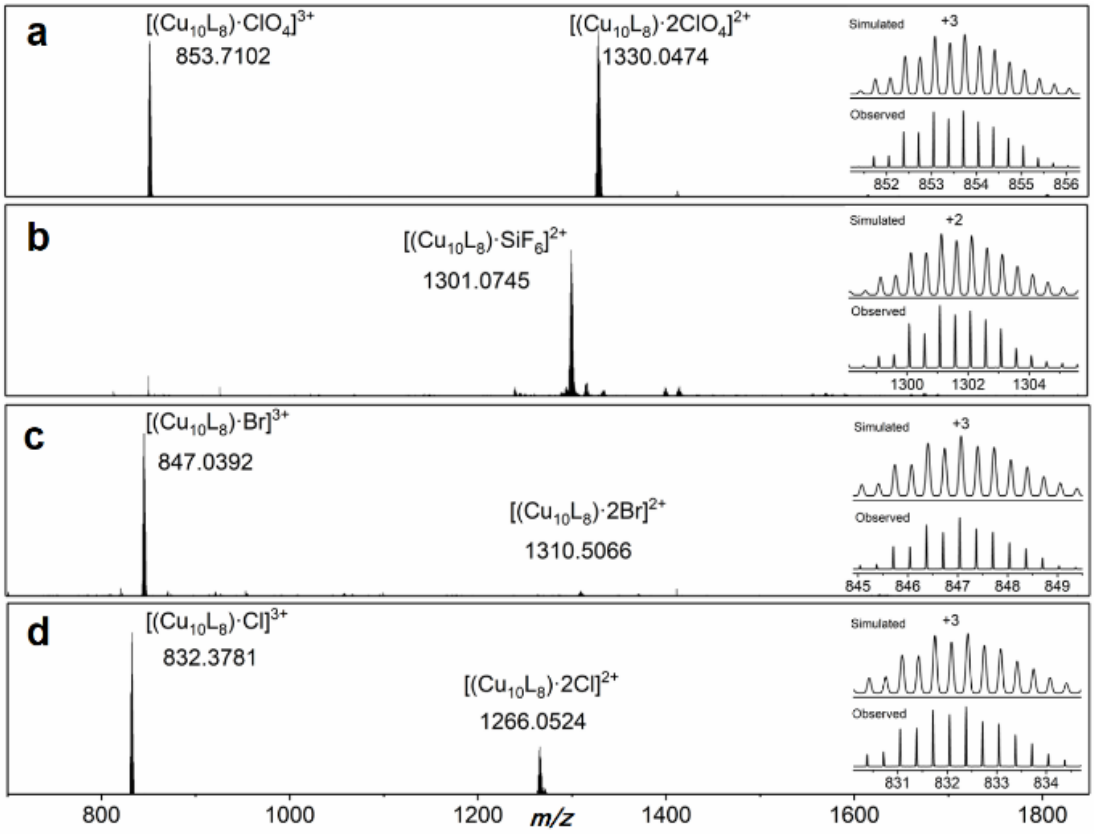

Fig. S10. Mass spectra of cages **1** (a), **2** (b), **3** (c), and **4** (d), respectively. Insets show the observed patterns of $[(Cu_{10}L_8)\cdot ClO_4]^{3+}$, $[(Cu_{10}L_8)\cdot SiF_6]^{2+}$, $[(Cu_{10}L_8)\cdot Br]^{3+}$, and $[(Cu_{10}L_8)\cdot Cl]^{3+}$ and their corresponding simulated isotope patterns, respectively.

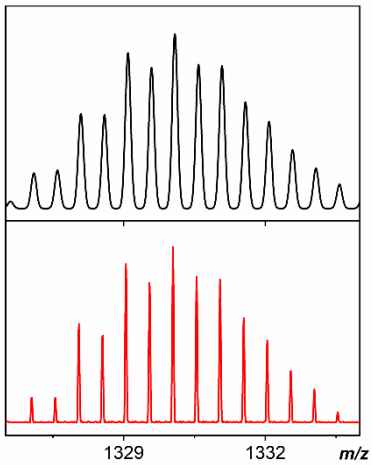

Fig. S11. Observed and simulated isotope patterns for the $[(Cu_{10}L_8)\cdot 2ClO_4]^{2+}$ of cage **1**. Black: simulated; red: observed.

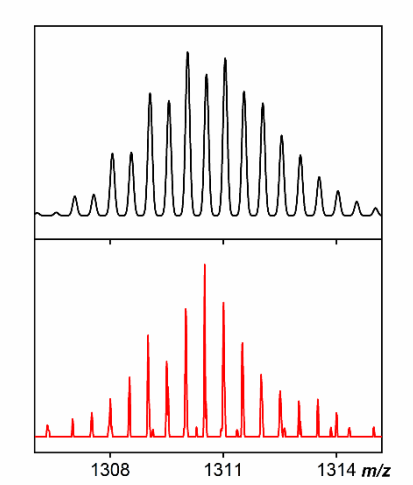

Fig. S12. Observed and simulated isotope patterns for the $[(Cu_{10}L_8)\cdot 2Br]^{2+}$ of cage **3**. Black: simulated isotope patterns; red: observed isotope patterns.

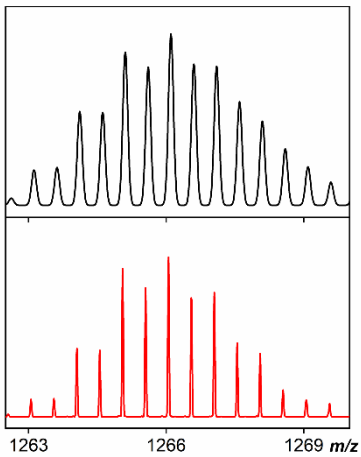

Fig. S13. Observed and simulated isotope patterns for the $[(Cu_{10}L_8)\cdot 2Cl]^{2+}$ of cage **4**. Black: simulated isotope patterns; red: observed isotope patterns.

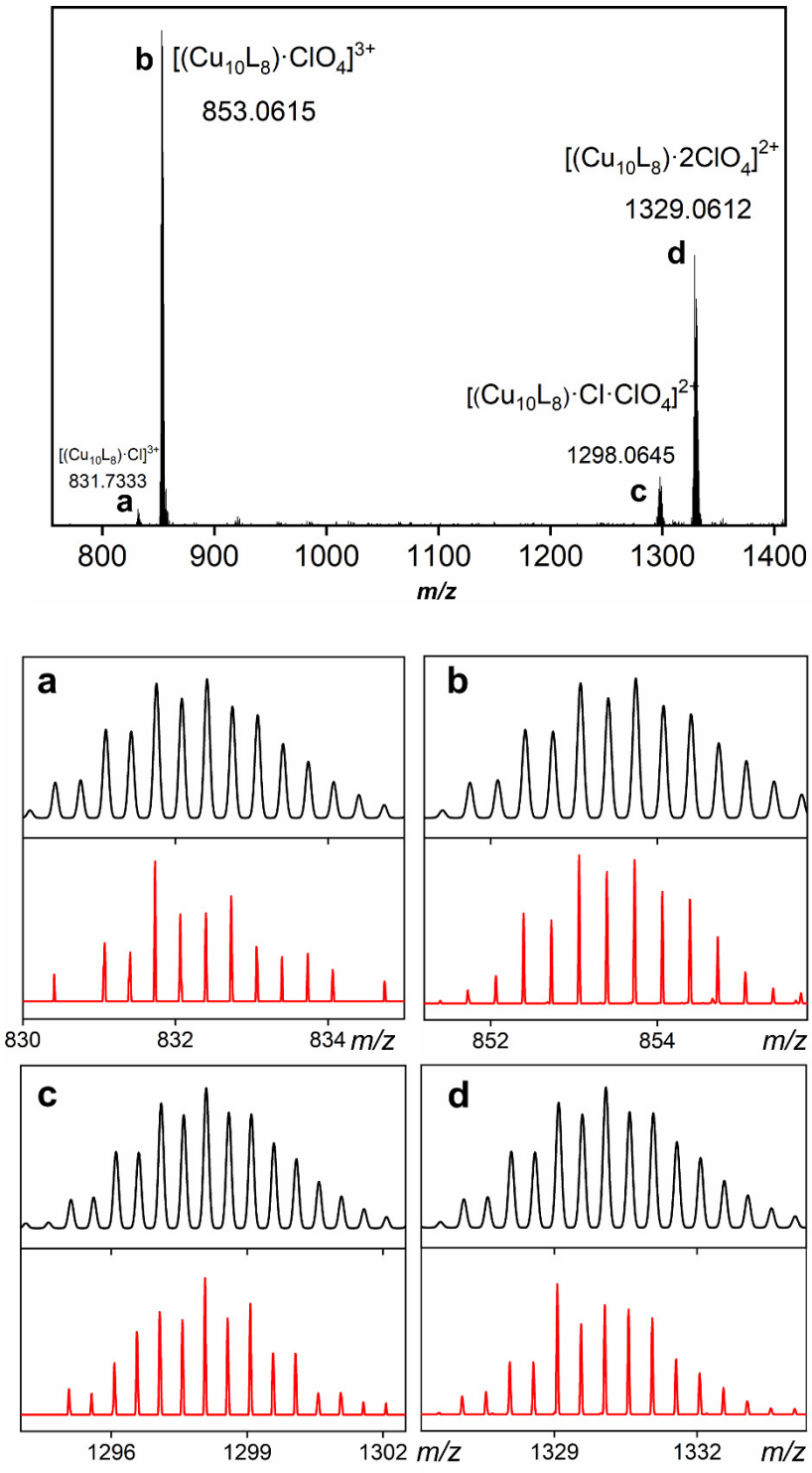

Fig. S14. Mass spectrum of the transformed product obtained under room temperature (top), and the observed and simulated isotopic patterns (bottom) of $[(Cu_{10}L_8)\cdot Cl]^{3+}$ (a), $[(Cu_{10}L_8)\cdot ClO_4]^{3+}$ (b), the $[(Cu_{10}L_8)\cdot Cl\cdot ClO_4]^{2+}$ (c), and $[(Cu_{10}L_8)\cdot 2ClO_4]^{2+}$ (d), respectively. Black: simulated isotope patterns; red: observed isotope patterns.

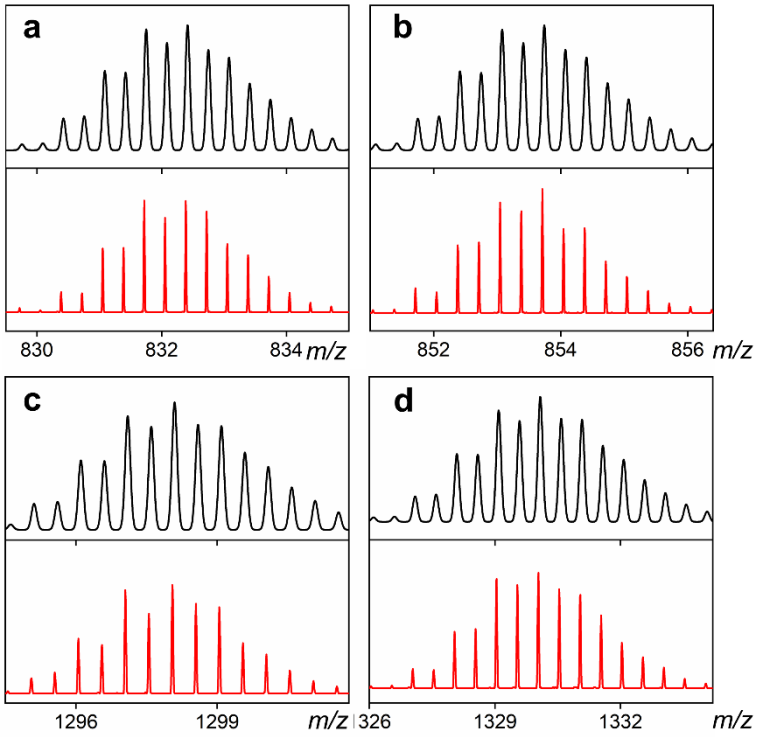

Fig. S15. Observed and simulated isotopic patterns of $[(Cu_{10}L_8)\cdot Cl]^{3+}$ (a), $[(Cu_{10}L_8)\cdot ClO_4]^{3+}$ (b), $[(Cu_{10}L_8)\cdot Cl\cdot ClO_4]^{2+}$ (c), and $[(Cu_{10}L_8)\cdot 2ClO_4]^{2+}$ (d), respectively. Black: simulated isotope patterns; red: observed isotope patterns.

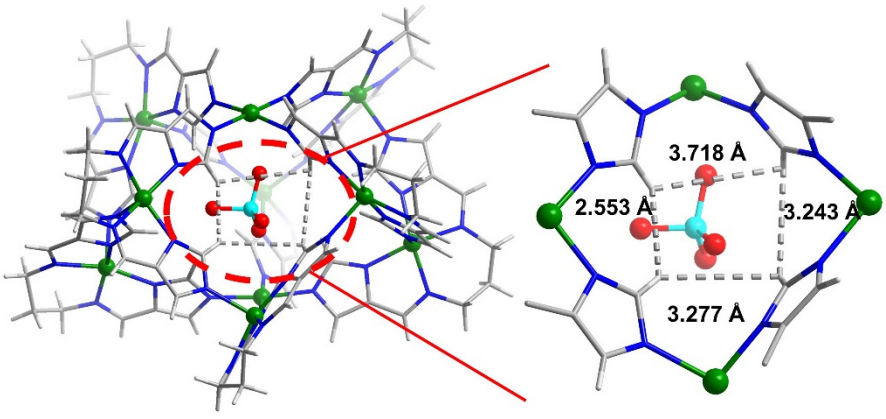

Fig. S16. Crystal structure shows the small windows in cage **1**, which is smaller than the diameter of ClO_4^- (5.0 Å).

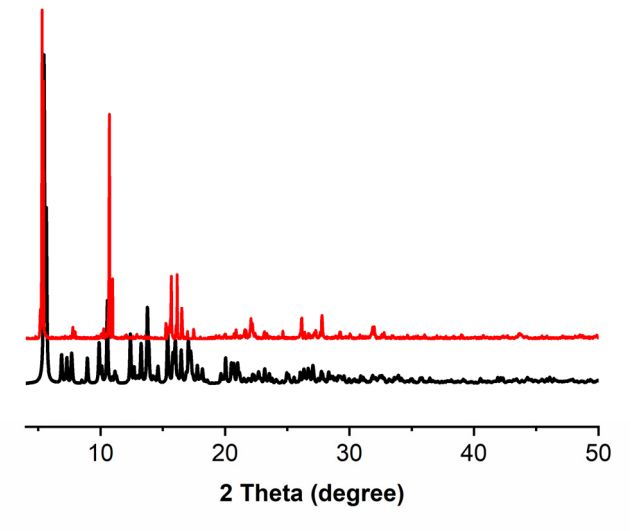

Fig. S17. PXRD patterns for simulated (black line) and as-synthesized (red line) samples of cage **1**.

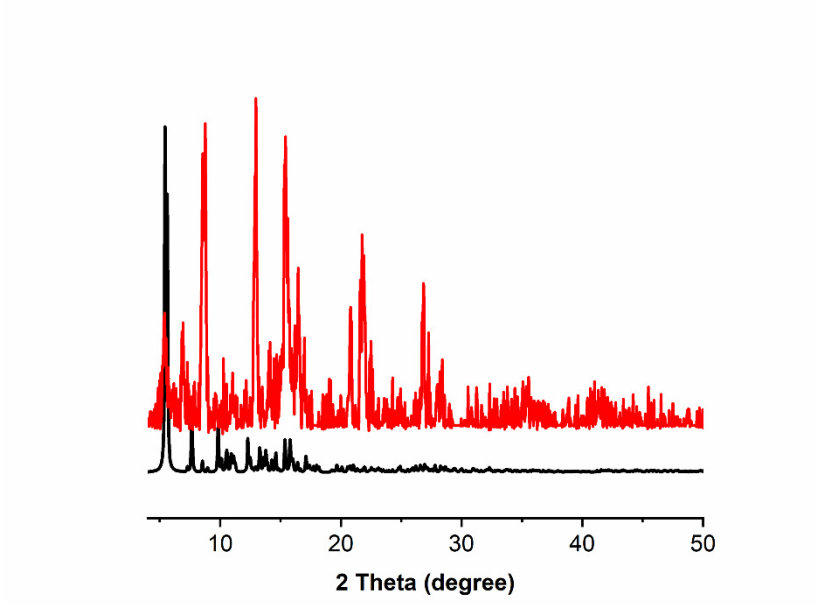

Fig. S18. PXRD patterns for simulated (black line) and as-synthesized (red line) samples of cage **2**.

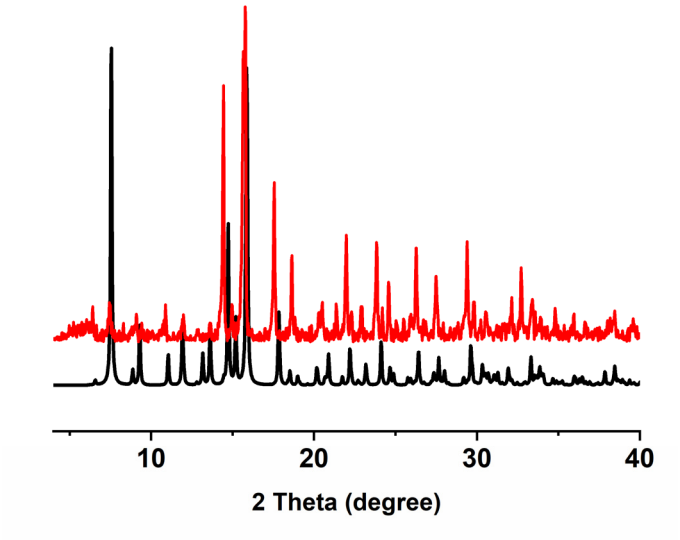

Fig. S19. PXRD patterns for simulated (black line) and as-synthesized (red line) samples of cage **3**.

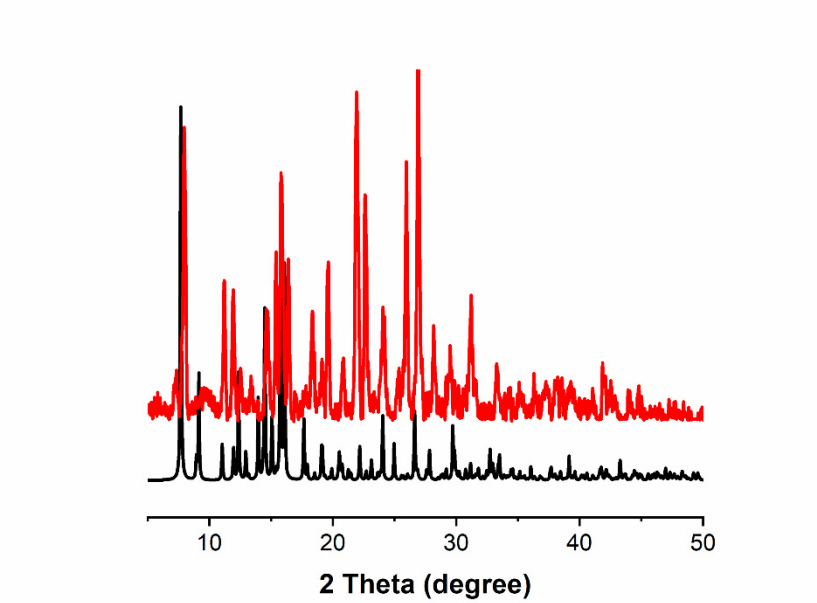

Fig. S20. PXRD patterns for simulated (black line) and as-synthesized (red line) samples of cage **4**.

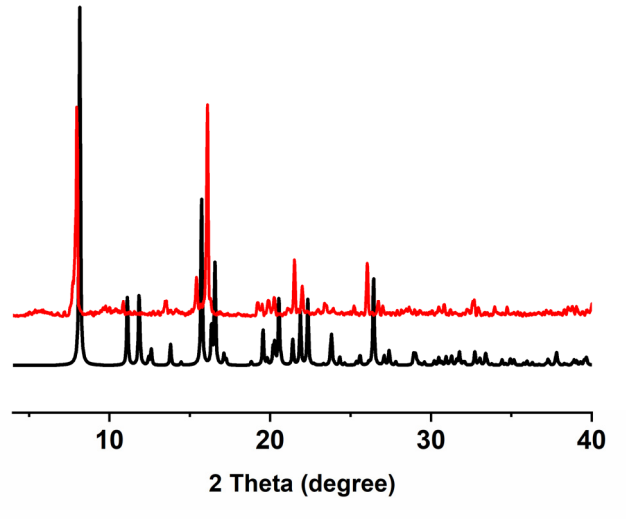

Fig. S21. PXRD patterns for simulated (black line) and as-synthesized (red line) samples of coordination polymer **5**.

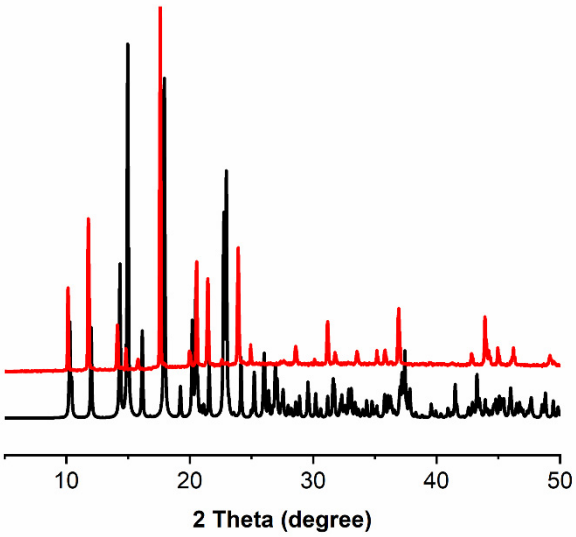

Fig. S22. PXRD patterns for simulated (black line) and as-synthesized (red line) samples of coordination polymer **6**.

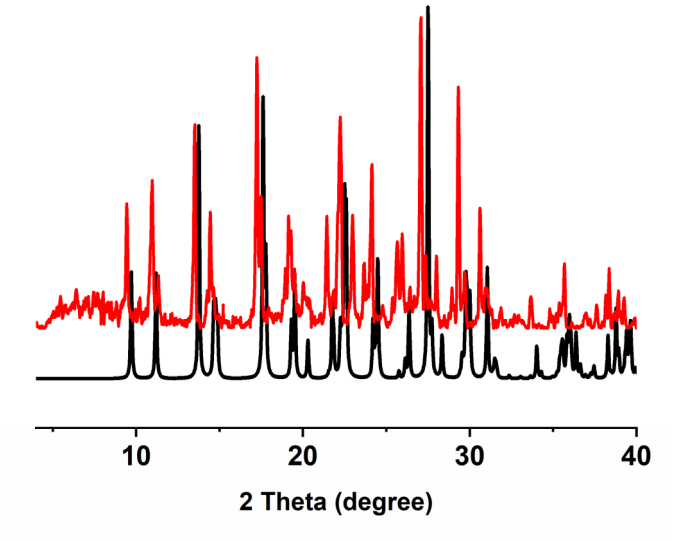

Fig. S23. PXRD patterns for simulated (black line) and as-synthesized (red line) samples of coordination polymer **7**.

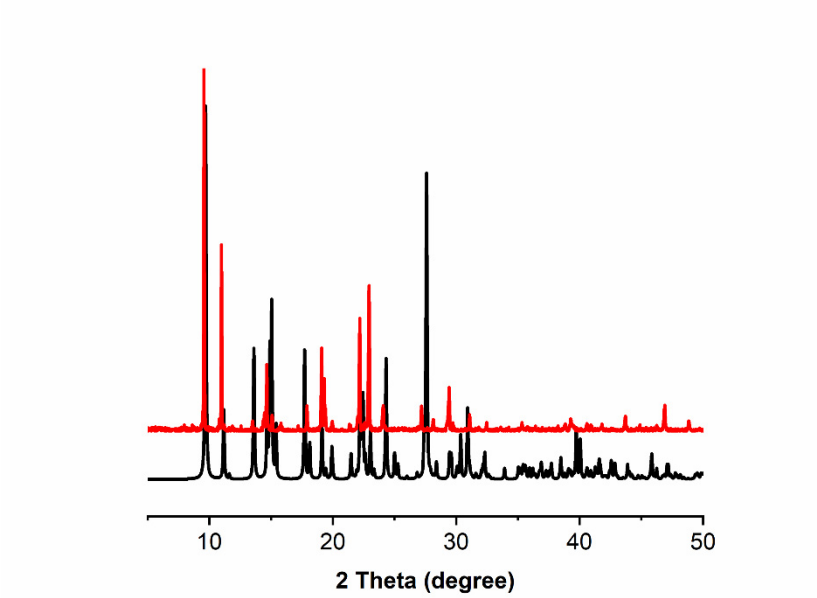

Fig. S24. PXRD patterns for simulated (black line) and as-synthesized (red line) samples of coordination polymer **8**.

Computational Detail

The geometry of $Cu_{10}L_8$ cage without encapsulated anion was optimized by density functional theory (DFT) calculations using PBE functional[3] in Amsterdam Density Function 2016 (ADF 2016)[4] program package (table S3). Slater type TZP basic sets with a small frozen core approximation were used for all atoms.[5] Scalar relativistic effects were considered by using the zeroth-order regular approximation (ZORA).[6] The optimized geometry was confirmed as minimum on the potential energy surfaces by the absence of imaginary eigenvalues in the Hessian matrix. [7]

Table S3 Atomic coordinates of optimized $Cu_{10}L_8$ cage without encapsulated anion calculated from ADF 2016 program.

atoms	x	y	z
Cu	-1.68562	6.335701	18.94539
H	5.240615	14.40336	13.90812
N	-1.48711	6.181361	16.94125
N	-1.87717	6.594053	20.93837
N	0.307588	6.278812	19.1457
N	-3.67572	6.396051	18.74362
Cu	-1.90049	7.166558	12.72639
N	-0.83147	5.451708	12.55293
N	-3.37537	8.502717	12.89164
N	-2.80893	6.845837	10.9109
N	-1.73191	6.649298	14.75613
N	-0.2169	8.525741	12.53046
Cu	-1.33132	8.35317	24.86586
N	-2.50229	6.785548	25.38523
N	0.212812	9.543257	24.43089
N	-0.41264	8.3508	26.70498
N	-1.57013	7.46467	22.98682
N	-2.91924	9.84043	24.7987

Cu	-6.07796	11.55597	14.30375
N	-6.94258	10.41431	15.69977
N	-5.51047	13.10552	13.1202
N	-5.00383	10.01854	13.21805
N	-8.02942	11.7324	13.68107
N	-4.51211	12.32199	15.45829
Cu	3.040381	12.11846	22.42116
N	3.8285	10.6544	21.31437
N	1.90068	10.8934	23.8099
N	2.569646	13.90942	23.25185
N	4.998826	12.2949	23.02866
N	1.504807	12.71057	21.12733
Cu	-7.73214	7.869895	19.0996
N	-5.79005	7.120327	18.95281
N	-8.11894	6.116504	18.15665
N	-7.79286	9.121521	17.33157
N	-7.39514	9.29758	20.45541
N	-9.54101	7.80202	20.07509
Cu	-5.62907	12.44959	22.82518
N	-4.38108	12.92288	21.22642
N	-4.3786	11.23916	23.81187
N	-6.62107	14.05827	22.092
N	-6.22689	12.88489	24.74161
N	-6.88999	10.92918	21.91835
Cu	4.427496	7.379782	18.52639
N	2.465269	6.796693	18.81002
N	4.585441	8.96792	20.03185
N	4.724936	5.817765	19.79382

N	4.181531	8.558774	16.92649
N	6.27842	7.131932	17.68109
Cu	-1.48293	13.20243	18.2212
N	-0.2057	13.25887	19.77782
N	0.070447	13.06665	16.9633
N	-3.03493	13.35585	19.48255
N	-2.76461	13.03468	16.67688
Cu	2.639482	11.3278	13.9763
N	1.319526	10.00787	13.24072
N	3.808554	9.955669	15.2022
N	3.325376	11.25313	12.04514
N	1.417708	12.20235	15.39122
N	3.716537	13.01559	14.34627
H	5.565402	13.7915	11.60508
H	3.82002	13.97118	11.82627
C	-2.91227	6.056555	24.39792
C	-2.84922	6.468034	26.76533
C	-0.47791	4.90819	13.6729
C	-0.49769	4.839404	11.27252
C	-8.3231	10.40594	15.57667
C	-6.67865	9.634369	16.75114
C	-3.87359	9.442625	13.69844
C	-4.23232	8.464086	11.80329
C	-0.75932	5.257128	16.23964
C	-2.05817	6.990492	16.00221
C	5.202064	10.5638	21.47794
C	3.513111	9.684686	20.45176
C	0.739879	10.28698	23.45545

C	1.082003	9.676972	25.5021
C	-2.64956	5.873277	21.81056
C	-1.24288	7.533888	21.6973
C	2.125487	10.51126	25.10054
C	1.204208	7.047461	18.46439
C	2.392536	5.789838	19.75942
C	-3.88346	7.558241	10.75396
C	-2.33126	5.956527	9.855586
C	-4.46313	13.74808	13.52553
C	-6.2287	13.50344	11.91579
C	0.701713	9.017581	26.71163
C	-0.91852	7.716278	27.91943
C	1.053737	5.479448	19.97176
C	-5.23873	9.405288	12.02159
C	-4.51328	7.342411	19.25741
C	-5.79162	5.94928	18.2119
C	-4.4792	5.510013	18.07582
C	-2.45578	6.40315	23.08187
C	1.556	14.51111	22.71806
C	3.315855	14.5094	24.3519
C	-7.07299	5.429751	17.82759
C	-9.46623	5.626033	17.89652
C	-0.91482	5.537667	14.88601
C	-8.83607	9.605416	16.59678
C	5.65672	9.518842	20.67327
C	-8.86582	11.12928	14.4701
C	-8.49257	12.42223	12.47994
C	0.804727	12.38099	20.04276

C	-0.13148	14.21601	20.75479
C	-6.49572	10.20627	20.83981
C	-8.45541	9.436808	21.33698
C	5.790523	11.46872	22.41433
C	5.507013	13.19825	24.05883
C	0.266155	12.07601	16.04757
C	1.168507	13.88045	16.8735
C	-3.87131	13.33796	14.7669
C	-3.82804	12.18411	16.59256
C	-3.24999	12.60344	20.59985
C	-4.93045	13.95747	20.48606
C	3.641154	5.272728	20.24393
C	6.043235	5.325697	20.17624
C	3.328655	9.407043	16.34637
C	5.301865	8.555168	16.11082
C	-4.09873	14.21546	19.40214
C	0.293373	9.222475	13.57721
C	1.5013	9.807072	11.88144
C	-3.43366	10.31257	23.6352
C	-4.4996	11.37984	25.1855
C	0.931949	13.88534	21.58779
C	-3.58548	10.51158	25.78313
C	-2.78513	13.76952	15.52112
C	0.53899	8.891902	11.45475
C	5.053593	9.419859	15.04429
C	-6.12722	14.55701	21.00505
C	-7.77823	14.65266	22.74935
C	-5.51386	12.27805	25.64209

C	-7.34221	13.74928	25.1196
C	-9.59471	8.608264	21.09236
C	-10.6947	6.987231	19.70024
C	-8.12598	10.44757	22.24037
C	2.598314	10.49745	11.27859
C	4.510313	11.93327	11.52928
C	2.001578	13.35466	15.89186
C	6.408261	7.767541	16.5557
C	7.387701	6.37022	18.24963
H	-3.42037	9.737296	14.6415
H	0.287076	10.41479	22.47542
H	0.11671	3.985143	13.69947
H	1.321489	9.089337	27.61562
H	-4.16611	8.16665	19.87433
H	-3.5672	5.189314	24.55798
H	1.198055	15.47834	23.09659
H	-4.49328	7.483199	9.843568
H	-0.18506	4.476598	16.73016
H	-7.15826	4.470397	17.29932
H	-2.54915	11.85026	20.9493
H	-4.05332	14.59361	12.95652
H	0.91027	7.760864	17.69962
H	-9.94843	11.15483	14.28562
H	6.870165	11.45207	22.61679
H	-2.73153	7.804547	16.25638
H	-5.67598	9.413348	17.10856
H	-3.10995	9.951611	22.6619
H	-3.27556	5.047371	21.48558

H	-0.52451	8.237477	21.28555
H	0.60135	4.75708	20.64471
H	-4.08239	4.642614	17.55657
H	-0.46299	11.29309	15.8602
C	3.230852	13.77026	15.27856
C	4.915326	13.39299	13.60805
H	2.996034	10.83944	25.66226
H	2.499229	9.472904	20.12109
H	-9.87125	9.367344	16.82718
H	2.348647	9.652095	16.74811
H	3.669883	4.432911	20.95141
H	-1.64996	8.402733	28.38295
H	-0.09811	7.581707	28.64424
C	-1.60246	6.37375	27.65469
H	6.670937	9.154973	20.53154
H	-5.54497	10.37221	20.33893
H	-0.09509	9.126893	14.5881
H	1.025554	11.52586	19.40962
H	-1.55121	6.493425	9.285805
H	-3.14997	5.734005	9.150574
C	-1.73997	4.652047	10.39239
H	-6.0913	9.65642	11.39603
H	-4.20008	14.94148	18.60088
H	-9.57055	12.64083	12.56276
H	-8.36684	11.73475	11.62388
C	-7.72279	13.71226	12.19245
H	-3.41284	5.521134	26.80339
H	-3.51232	7.265199	27.14362

H	-4.09627	11.49454	17.38829
H	3.142574	13.90102	25.2566
H	2.933846	15.52346	24.55567
C	4.81891	14.56416	24.05147
H	6.596282	13.32773	23.9428
H	5.340586	12.72208	25.0421
H	-1.91254	5.960027	28.6259
H	-0.88704	5.66103	27.21658
H	-6.5858	15.42423	20.51062
H	4.987617	15.07203	23.08946
H	5.295171	15.18203	24.8273
H	-0.00403	3.86726	11.43826
H	0.225065	5.495221	10.75715
H	-5.69495	12.43099	26.71463
H	-0.8216	15.05343	20.80137
H	-1.44893	4.037316	9.527496
H	-2.5046	4.085381	10.94546
H	1.290593	14.76223	17.49589
H	-8.70164	10.83283	23.07791
H	-6.10071	12.7081	11.16132
H	-5.78894	14.42693	11.50317
H	-7.85104	14.42596	13.02068
H	-8.16903	14.17456	11.29901
H	-2.04525	14.53537	15.30786
H	5.69322	9.670283	14.20202
H	-9.42071	4.616771	17.45413
H	-9.93835	6.293251	17.15514
C	-10.3113	5.601617	19.1773

H	-10.4877	8.669005	21.72895
H	3.722891	14.70646	15.5751
H	-9.78616	5.029497	19.95742
H	-11.2433	5.060121	18.95575
H	2.826263	10.37671	10.21093
H	-11.2466	7.525084	18.90813
H	-11.3798	6.886275	20.55887
H	-8.61373	13.93393	22.69043
H	-8.08692	15.56652	22.21506
C	-7.48425	14.97846	24.21977
H	7.339271	7.720003	15.97509
H	-3.38431	10.34762	26.83856
H	-7.23402	14.06618	26.17049
H	-8.26987	13.15254	25.05576
H	5.943843	4.394495	20.7585
H	6.511333	6.079015	20.83358
C	6.93752	5.088712	18.95308
H	7.840678	4.560879	19.29406
H	6.427102	4.422209	18.24128
H	7.904014	7.015706	18.98311
H	8.120385	6.127702	17.46165
H	0.362629	8.497864	10.45745
H	4.47269	11.97237	10.4275
H	5.394721	11.3293	11.80131
C	4.685373	13.34501	12.09212
H	-6.58372	15.60769	24.2874
H	-8.32276	15.57773	24.605
H	5.721845	12.69002	13.88011

Calculation of the volume of cages:

The size of the inner cavity volumes of **1-5** were determined using VOIDOO calculations.[8] The calculations were based on the crystal structure of **1-4** and on the optimized structure of **5**. A virtual probe with a radius of 1.4 Å (set by default, water-sized) was employed, and the following parameters were changed from their default settings:

Maximum number of volume-refinement cycles:	30
Minimum size of secondary grid:	3
Grid for plot files:	0.1
Primary grid spacing:	0.1
Plot grid spacing:	0.1

All anions were full optimized at B3LYP[9]/cc-pVDZ[10] theoretical level with Gaussian09 suit of program[11] to obtain the stable geometry and electronic structure. Based on the stable structure, the Connolly surface of each anion was generated by Material Studio 2018. The values of Connolly surface occupied volume utilized here as anion volumes. In the isosurfaces generation, the grid resolution of ultra-fine and vdW scale factor of 1.1000 was employed.

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