Electronic Supplementary Information for:

**Waterproof Architectures through Subcomponent Self-Assembly**

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1. General Experimental Procedures

Reagents were purchased from commercial suppliers and used without further purification. All manipulations were carried out in dry glassware under an inert atmosphere using standard Schlenk techniques. All solvents were distilled prior to use. Flash column chromatography was performed using Silica Gel high purity grade (pore size 60 Å, 230-400 mesh particle size, Sigma-Aldrich). TLC analyses were performed on Merck TLC Silica Gel 60 F254 Glass plates. Product spots were visualized under UV light (λmax = 254 nm). Centrifugation of samples was carried out using a Grant-Bio LMC-3000 low speed benchtop centrifuge.

NMR spectra were recorded on a Bruker Advance DPX 400 MHz Avance III HD Smart Probe (routine $^1$H, $^1$H wide-sweep, $^{13}$C, and $^{19}$F NMR) or Bruker Advance Cryo 500 spectrometer unless otherwise specified. Chemical shifts for $^1$H, $^{13}$C, and $^{19}$F are reported in ppm on the δ scale; all coupling constants are reported in Hz. Signals on $^1$H and $^{13}$C spectra recorded in D$_2$O were referenced to an internal standard of tert-Butanol (δ = 1.24 ppm for $^1$H and 30.29 ppm for $^{13}$C{$^1$H}) dissolved in D$_2$O at a concentration of 1.0 mM. Signals on $^1$H spectra recorded in CD$_3$CN were referenced to the residual solvent peak (δ = 1.94 ppm). Chemical shifts (δ) for $^{19}$F NMR spectra are reported relative to C$_6$F$_6$ (as an external standard in a capillary tube) at −164.9 ppm. DOSY experiments were performed using a maximum gradient strength of 6.57 G/cmÅ. The standard Bruker pulse program, ledbpgp2s, employing a stimulated echo and longitudinal eddy-current delay (LED) using bipolar gradient pulses for diffusion using 2 spoil gradients was utilized. Rectangular gradients were used with a total duration of 1.5 ms. Gradient recovery delays were 950–1400 μs. Diffusion times were 100 ms. Individual rows of the S4 quasi-2D diffusion databases were phased and baseline corrected. Hydrodynamic radii were calculated through the Stokes-Einstein equation by using the viscosity value of ηH$_2$O = 0.890 × 10$^{-3}$ kg/m·s, 298 K.

The $^1$H wide-sweep paramagnetic NMR spectra were recorded in the analogue digitization mode with a spectral width (SW) of 372.98 ppm, a transmitter frequency offset (O1P) of 100.00 ppm and the line width set to 10.0 Hz. Due to the experimental difficulties associated with collecting NMR data for $^1$H nuclei with vastly different relaxation times,
differences between measured and theoretical integration values were in some cases observed. While the paramagnetic nature of the complex precluded complete assignment of the proton environments, we suggest that the extent of downfield shifting of each resonance can be associated to the bond proximity of the proton environment to the Co\textsuperscript{II} centres; this has been proposed and observed in previous reports.\textsuperscript{1,2}

Electrospray ionization (ESI-MS) mass spectra were obtained on a Micromass Quattro LC mass spectrometer infused from a Harvard syringe pump at a rate of 10 μL min\textsuperscript{-1}. The diverse sulfate derivatives of metal-organic capsules were dissolved in distilled H\textsubscript{2}O (unless otherwise specified) and filtered prior to acquisition using different experimental conditions according to each metal ion: Co\textsuperscript{II}: cone voltage 22 eV; desolvation temp. 313 K; ionization temp. 313 K. Ni\textsuperscript{II}: cone voltage 33 eV; desolvation temp. 353 K; ionization temp. 353 K. Zn\textsuperscript{II}: cone voltage 22 eV; desolvation temp. 353 K; ionization temp. 353 K. Cd\textsuperscript{II}: cone voltage 22 eV; desolvation temp. 353 K; ionization temp. 353 K. The diverse acetonitrile-soluble metal-organic capsules (obtained as triflate, triflimide or tetrafluoroborate salts) were dissolved in acetonitrile and filtered prior to acquisition using different experimental conditions according to each metal ion: Co\textsuperscript{II}: cone voltage 22 eV; desolvation temp. 313 K; ionization temp. 313 K. Ni\textsuperscript{II}: cone voltage 33 eV; desolvation temp. 313 K; ionization temp. 313 K. Zn\textsuperscript{II}: cone voltage 18 eV; desolvation temp. 313 K; ionization temp. 313 K. Cd\textsuperscript{II}: cone voltage 18 eV; desolvation temp. 313 K; ionization temp. 313 K.

The construction of the diverse metal-organic capsules reported in this study entailed the in situ formation of dynamic imine bonds resulting from condensation of 2-formylpyridine with aniline-based subcomponents A–C. Likewise, reaction of formylpyridine-based subcomponents D–H with p-methoxy-aniline (anisidine), tris(2-aminoethyl)amine (TREN), or tris(3-aminopropyl)amine (TRPN) afforded the target ligand fragments (L). The different subcomponents A–H (Charts S1 and S2) employed in this study were prepared following previously reported methods:

(A) zinc(II) 5,10,15,20-tetrakis(4-aminophenyl)-21H, 23H-porphine\textsuperscript{3}

(B) 1,3,5-tris(4’-aminophenyl)benzene\textsuperscript{4}

(C) 4,4’-diaminobiphenyl\textsuperscript{5}

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(D) 1,3,5-tris(4′,4''',4'''-formylpyridine)benzene

(E) 6,6′-diformyl-3,3′-bipyridine

(F) 5,5′-(1,4-Phenylene)bis-2-pyridinecarboxaldehyde

(G) 2,2′-(2,5-dimethyl-1,4-phenylene)bis-2-pyridinecarboxaldehyde

(H) 5,5′-(Perfluoro-1,4-phenylene)bis-2-pyridinecarboxaldehyde.

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Chart S1. Aniline-based subcomponents A–C used to make metal-organic cages.
Chart S2. Formyl-pyridine subcomponents D–H used to make metal-organic cages.
2. Synthesis of acetonitrile-soluble cobalt(II)–based capsules and their anion-exchange sequences

The direct self-assembly of the cobalt(II)-based sulfate cages was attempted with porphyrin A and CoSO₄ in DMF or DMF/H₂O without success. Similarly, CoSO₄ was treated with subcomponents B–E in 1:1 CH₃CN/H₂O, 1:1 CH₃OH/H₂O, or 1:1:1 CH₃CN/CH₃OH/H₂O solvent systems in order to prepare the corresponding water-soluble capsules; it was not possible to obtain the target sulfate salts of the cages. Hence, the preparation of the sulfate salts of Co²⁺-based cages was only accessible via anion exchange with sulfate from preformed acetonitrile-soluble subcomponent self-assembled cages.

The outcome of the diverse self-assembly reactions with Co²⁺ ions to form the acetonitrile-soluble cages was sensitive to the identity of the counter anions involved. The reaction of aniline B with Co(OTf)₂ resulted in a mixture containing insoluble materials that could not be characterized as well as a products in solution, a Co₂L₃ helicate and the Co₄L₄ tetrahedral structure. Although the reaction of B and CoSO₄ afforded the target water-soluble capsule Co–2•SO₄ as the major product, some amount of a Co₂L₃ water-soluble helicate was also formed and it could not be separated. Conversely, reaction of subcomponent B and Co(NTf₂)₂ gave tetrahedron Co–2•NTf₂ as a clean product.

Aniline C reacted with diverse CoX₂ (X = OTf⁻, NTf₂⁻, BF₄⁻) salts to give a mixture of diastereomers of Co₄L₆ cages (Co–3•X). We previously observed C to self-assemble with Fe²⁺ salts to produce mixtures of T, C₃, and S₄ diastereomers in different ratios depending on the anion.⁵,¹¹ The use of Co(BF₄)₂ provided the simplest NMR spectrum where seven intense signals could be distinguished that are consistent with the presence of the T-symmetric diastereomer as the major product, as when BF₄⁻ was used in the construction of the analogous Fe²⁺-based cage to yield the T-symmetric diastereomer.

Likewise, cage Co–5 was obtained through the reported method¹ that uses Co(OTf)₂ as the metal salt, whereas other salts produced different structures to the tetrahedral capsule.¹²
2.1 Synthesis of the water-soluble Co–I$$\text{SO}_4$$ cube and its reversible conversion into acetonitrile-soluble Co–I$$\text{OTf}$$

Subcomponent A (10.0 mg, 0.014 mmol, 6 equiv), 2-formylpyridine (5.2 μL, 0.054 mmol, 24 equiv), cobalt(II) triflate dihydrate (7.1 mg, 0.019 mmol, 8 equiv), and 2.0 mL of DMF were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles and heated to 100°C overnight. After this time, the mixture was cooled to room temperature and diethyl ether (5 mL) was added leading to precipitation of a dark purple solid that was inferred to contain cube Co–I$$\text{OTf}$$, the mixture was centrifuged and the supernatant DMF/Et₂O was decanted. The product was then twice dissolved in MeCN (2 mL) and precipitated with Et₂O (5 mL). Co–I$$\text{OTf}$$ was recovered as a purple solid (19.6 mg, yield 92%). Then, Co–I$$\text{OTf}$$ was dissolved in CH₃CN and tetrabutylammonium sulfate (TBA₂SO₄) solution 50wt % in H₂O (24 equivalents per cage) was added leading to precipitation of a purple solid, which was washed with CH₃CN:H₂O (9:1) and then with CH₃CN. Cube Co–I$$\text{SO}_4$$ was recovered as a dark purple solid (14.6 mg, yield 90%). $^1$H NMR (400 MHz, D₂O, 298 K): δ = 245.2, 91.2, 75.5, 53.5, 17.8, 14.0, 8.7, 0.3, –3.4, –4.8, –63.9. ESI-MS (5:1 H₂O/CH₃CN): m/z = 635.6 [Co–I(O Tf)₄]$$^{+12}$$, 707.5 [Co–I(O Tf)₃]$$^{+11}$$, 793.0 [Co–I(O Tf)₆]$$^{+10}$$, 897.8 [Co–I(O Tf)₇]$$^{+9}$$, 1028.4 [Co–I(O Tf)₈]$$^{+8}$$, 1196.7 [Co–I(O Tf)₉]$$^{+7}$$, 1421.3 [Co–I(O Tf)₁₀]$$^{+6}$$. Elemental analysis (%) calcd for C₄₀₈H₂₆₄Co₈N₇₀O₅₂S₈Zn₆•8H₂O•CH₃CN: C 61.61, H 3.57, N 12.79; found: C 61.82, H 3.54, N 12.70.
Figure S1. Wide sweep $^1$H NMR spectrum (400 MHz, D$_2$O, 298 K) of cube Co-1•SO$_4$.

Figure S2. ESI-MS spectrum of cube Co-1•SO$_4$ (5:1 H$_2$O/CH$_3$CN).

Addition of 24 equivalents of LiOTf (3 equiv per sulfate) to a D$_2$O solution of Co-1•SO$_4$ (3.2 mg in 500 μL) induced precipitation of a purple solid in quantitative yield (3.5 mg, yield 92%), the mixture was centrifuged and the supernatant H$_2$O:D$_2$O was decanted; this
process was repeated two times with H$_2$O. NMR and ESI-MS analyses in CH$_3$CN confirmed that this solid corresponded to the former Co-1•OTf complex (Figures S3 and S4); spectroscopic details as follows: $^1$H NMR (400 MHz, CD$_3$CN, 298 K): δ = 246.3, 90.0, 75.3, 53.1, 17.8, 14.0, 7.9, 0.2, –3.3, –5.1, –64.5. ESI-MS (CH$_3$CN): m/z = 524.0 [Co-1(OTf)$_2$]$^{+14}$, 575.7 [Co-1(OTf)$_3$]$^{+13}$, 636.0 [Co-1(OTf)$_4$]$^{+12}$, 707.4 [Co-1(OTf)$_5$]$^{+11}$, 793.0 [Co-1(OTf)$_6$]$^{+10}$, 897.7 [Co-1(OTf)$_7$]$^{+9}$, 1028.9 [Co-1(OTf)$_8$]$^{+8}$, 1197.0 [Co-1(OTf)$_9$]$^{+7}$, 1421.4 [Co-1(OTf)$_{10}$]$^{+6}$. Elemental analysis (%) calcd for C$_{424}$H$_{264}$Co$_8$F$_{48}$N$_{72}$O$_{48}$S$_{16}$Zn$_6$•3H$_2$O: C 53.03, H 2.98, N 10.50; found: C 53.17, H 2.84, N 10.48. Notably, X-ray quality crystals were obtained from this solution corroborating the molecular structure of the Co-1 framework and further confirming the reversibility of the anion exchange process to regenerate the original Co-1•OTf complex (see X-ray crystallography section, vide infra).

Further addition of TBA$_2$SO$_4$ to an acetonitrile solution of this freshly regenerated Co-1•OTf induced precipitation of the water-soluble Co-1•SO$_4$. The complete Co-1•OTf→Co-1•SO$_4$→Co-1•OTf anion exchange cycle was carried twice out multiple times, with 90-94% recovery by weight per cycle.
Figure S3. Wide sweep $^1$H NMR spectrum (400 MHz, CD$_2$CN, 298 K) of cube Co–1•OTf obtained upon reversible anion exchange from Co–1•SO$_4$.

Figure S4. ESI-MS spectrum of cube Co–1•OTf (CH$_3$CN) obtained upon reversible anion exchange from Co–1•SO$_4$. 

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2.2 Synthesis of the water-soluble Co–2•SO₄ cage and its reversible conversion into the acetonitrile-soluble Co–2•NTf₂

Subcomponent B (8.7 mg, 0.025 mmol, 4 equiv), 2-formylpyridine (6.9 μL, 0.075 mmol, 12 equiv), cobalt(II) triflimide (15.3 mg, 0.025 mmol, 4 equiv), and 2.0 mL of CH₃CN were placed in a thick-walled 25 mL sealed Schlenk tube. The mixture was degassed by three evacuation/nitrogen fill cycles and heated to reflux overnight. Cage Co-2•NTf₂ was precipitated from the crude solution by addition of diethyl ether (5 mL), this suspension was centrifuged and the supernatant CH₃CN/Et₂O was decanted; the product was again dissolved in MeCN (2 mL) and precipitated with Et₂O (5 mL). Clean Co-2•NTf₂ tetrahedron was recovered as an orange solid (27.9 mg, yield 91%). Then, Co-2•NTf₂ cage was dissolved in CH₃CN and tetrabutylammonium sulfate (TBA₂SO₄) 50wt % solution in H₂O (12 equiv per cage) was added, inducing precipitation of a red solid, the mixture was centrifuged and the supernatant was decanted; this process was repeated with CH₃CN:H₂O (9:1), then with CH₃CN, and the excess solvent was removed with N₂. Cage Co-2•SO₄ was obtained as a dark orange solid (16.00 mg, yield 92%). ¹H NMR (400 MHz, D₂O, 298 K): δ = 241.2, 87.3, 72.7, 51.3, 15.2, 1.5, –13.4, –19.6. ESI-MS (5:1 H₂O/CH₃CN): m/z = 426.9 [Co-2(NTf₂)]⁺⁷, 545.1 [Co-2(NTf₂)$_2$]⁺⁶, 710.3 [Co-2(NTf₂)$_3$]⁺⁵, 957.9 [Co-2(NTf₂)$_4$]⁺⁴, 1370.4 [Co-2(NTf₂)$_5$]⁺⁶. Elemental analysis (%) calcd for C$_{168}$H$_{120}$Co$_4$N$_{24}$O$_{16}$S$_4$•2.5H₂O: C 64.26, H 4.01, N 10.71; found: C 64.46, H 3.98, N 10.76.
Figure S5. Wide sweep $^1$H NMR spectrum (400 MHz, D$_2$O, 298 K) of Co–2•SO$_4$.

Figure S6. ESI-MS spectrum of cube Co–2•SO$_4$ (5:1 H$_2$O/CH$_3$CN).
Addition of 12 equivalents of LiNTf₂ (1.5 equiv per sulfate) to a D₂O solution of Co-2•SO₄ (4.2 mg in 500 μL) induced precipitation of a bright orange solid; the mixture was centrifuged and the solvent decanted (6.4 mg, yield 95%). NMR and ESI-MS analyses in CH₃CN confirmed that this solid corresponded to the former Co-2•NTf₂ complex (Figures S7–S8); spectroscopic details as follows: ¹H NMR (400 MHz, CD₃CN, 298 K): δ = 240.2, 86.3, 72.3, 50.8, 15.0, 1.44, –13.3, –20.2. ESI-MS (CH₃CN): m/z = 338.1 [Co-2]⁺⁸, 426.9 [Co-2(N Tf₂)]⁺⁷, 545.1 [Co-2(N Tf₂)₂]⁺⁶, 710.2 [Co-2(N Tf₂)₃]⁺⁵, 957.9 [Co-2(N Tf₂)₄]⁺⁴, 1370.5 [Co-2(N Tf₂)₅]⁺³. Elemental analysis (%) calcd for C₁₈₄H₁₂₀Co₄F₄₈N₃₂O₃₂S₁₆•H₂O: C 44.47, H 2.47, N 9.02; found: C 44.96, H 2.61, N 9.11.

Further addition of TBA₂SO₄ to an acetonitrile solution of this Co-2•NTf₂ induced a second precipitation of the water-soluble Co-2•SO₄. The complete Co-2•NTf₂→Co-2•SO₄→Co-2•NTf₂ anion exchange cycle was carried out multiple times, with 90-95% recovery by weight per cycle.

Figure S7. Wide sweep ¹H NMR spectrum (400 MHz, CD₃CN, 298 K) of Co–2•NTf₂ obtained upon reversible anion exchange from Co–2•SO₄.
Figure S8. ESI-MS spectrum of Co–2•NTf₂ (CH₃CN) obtained upon reversible anion exchange from Co–2•SO₄.

2.3 Synthesis of acetonitrile-soluble Co–3•BF₄ and its disassembly as Co–3•SO₄ in water

Subcomponent C (3.6 mg, 0.019 mmol, 6 equiv), 2-formylpyridine (3.6 μL, 0.039 mmol, 12 equiv), cobalt(II) tetrafluoroborate hexahydrate (4.4 mg, 0.013 mmol, 4 equiv), and 1.0 mL of CH₃CN were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles and heated at 80°C overnight. Tetrahedron Co-3•BF₄ was precipitated from the crude solution by addition of diethyl ether, this suspension was
centrifuged and the supernatant CH$_3$CN/Et$_2$O was decanted; this process was repeated with Et$_2$O and the excess solvent was removed by a gentle N$_2$ flow. Clean Co-3•BF$_4$ cage was recovered as a dark orange solid (7.2 mg, yield 92%). $^1$H NMR [Peaks corresponding to the main species, the T–symmetric isomer] (400 MHz, CD$_3$CN, 298 K): $\delta = 240.5$, 85.9, 73.6, 51.3, 16.4, −2.1, −27.7. ESI-MS (CH$_3$CN): $m/z = 356.7$ [Co-3(BF$_4$)$_4$]$^{+7}$, 430.6 [Co-3(BF$_4$)$_2$]$^{+6}$, 534.1 [Co-3(BF$_4$)$_3$]$^{+5}$, 689.3 [Co-3(BF$_4$)$_4$]$^{+4}$, 948.3 [Co-3(BF$_4$)$_5$]$^{+3}$, 1465.5 [Co-3(BF$_4$)$_6$]$^{+2}$. Elemental analysis (%) calcd for C$_{144}$H$_{108}$B$_8$Co$_4$F$_{32}$N$_{24}$•2CH$_3$CN: C 55.78, H 3.61, N 11.43; found: C 56.12, H 3.72, N 11.38.

Figure S9. Wide sweep $^1$H NMR spectrum (400 MHz, CD$_3$CN, 298 K) of Co–3•BF$_4$. Deconvolution of the imine region can be observed as indication of the presence of different diasteromers (T, C$_3$, S$_4$); major peaks in the spectrum correspond to the T isomer that is estimated to account for ca. 72% of the total distribution.
Then, Co-3•BF$_4$ cage was dissolved in CH$_3$CN and tetrabutylammonium sulfate (TBA$_2$SO$_4$) solution 50wt % in H$_2$O (12 equivalents per cage) was added leading to precipitation of a dark orange solid that was inferred to contain cage Co-3•SO$_4$; the mixture was centrifuged and the supernatant was decanted; this process was repeated with CH$_3$CN and the excess solvent was removed with N$_2$. Although this dark orange solid could be dissolved in pure water, it rapidly decomposed as evidenced by cloudiness of the red solution and precipitation of dianiline C within the first 10 minutes after dissolution.
2.4 Synthesis of acetonitrile-soluble \textit{Co}–4\textit{OTf} and its disassembly as \textit{Co}–4\textit{SO}_4 in water

Subcomponent D (4.0 mg, 0.010 mmol, 4 equiv), 4-methoxyaniline (3.7 mg, 0.031 mmol, 12 equiv), cobalt(II) triflate dihydrate (4.0 mg, 0.010 mmol, 4 equiv), and 1.0 mL of CH$_3$CN were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles and heated at 80°C overnight. Tetrahedron \textit{Co}–4\textit{OTf} was precipitated from the crude solution by addition of diethyl ether, this suspension was centrifuged and the supernatant CH$_3$CN/Et$_2$O was decanted; this process was repeated with Et$_2$O. Clean \textit{Co}–4\textit{OTf} cage was recovered as a dark orange solid (6.88 mg, yield 87%). $^1$H NMR (400 MHz, CD$_3$CN, 298 K): δ = 246.4, 75.8, 71.1, 10.6, 8.0, 0.9, –12.1, –21.6. ESI-MS (CH$_3$CN): $m/z$ = 460.4 [Co-4(OTf)]$^+$, 561.8 [Co-4(OTf)$_2$]$^+$, 703.7 [Co-4(OTf)$_3$]$^+$, 917.6 [Co-4(OTf)$_4$]$^+$, 1273.3 [Co-4(OTf)$_5$]$^+$. Elemental analysis (%) calcd for C$_{188}$H$_{144}$Co$_4$F$_{24}$N$_{24}$O$_{36}$S$_8$·H$_2$O: C 52.52, H 3.47, N 7.82; found: C 52.62, H 3.55, N 7.88.
**Figure S11.** Wide sweep $^1$H NMR spectrum (400 MHz, CD$_3$CN, 298 K) of Co–4•OTf.

**Figure S12.** ESI-MS spectrum of Co–4•OTf (CH$_3$CN).
Then, Co-4•OTf capsule was dissolved in CH$_3$CN and tetrabutylammonium sulfate (TBA$_2$SO$_4$) solution 50wt % in H$_2$O (12 equivalents per cage) was added leading to precipitation of a dark orange solid that was inferred to contain cage Co-4•SO$_4$; the mixture was centrifuged and the supernatant was decanted; this process was repeated with CH$_3$CN and the excess solvent was removed with N$_2$. Although the dark orange solid could be dissolved after immediate addition of pure water, it rapidly decomposed as evidenced by cloudiness of the orange solution and precipitation of aldehyde D within the first 10 minutes after dissolution.

2.5 Synthesis of acetonitrile-soluble Co–5•OTf and its disassembly as Co–5•SO$_4$ in water

Capsule Co-5•OTf was prepared following our previously reported method.1 Subcomponent E (4.0 mg, 0.019 mmol, 6 equiv), 2-formylpyridine (3.6 μL, 0.039 mmol, 12 equiv), cobalt(II) triflate dihydrate (4.6 mg, 0.013 mmol, 4 equiv), and 1.0 mL of CH$_3$CN were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles and heated at 80°C overnight. Clean Co-5•OTf cage was recovered as a dark orange solid by addition of diethyl ether (9.9 mg, yield 86%). The NMR and ESI-MS data fully correspond to those previously obtained. ESI-MS (CH$_3$CN): $m/z = 512.8$ [Co-5(OTf)$_2$]$^{+6}$, 643.7 [Co-5(OTf)$_3$]$^{+5}$, 842.0 [Co-5(OTf)$_4$]$^{+4}$, 1172.3 [Co-5(OTf)$_5$]$^{+3}$. 

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Next, Co-5•OTf capsule was dissolved in CH₃CN and tetrabutylammonium sulfate (TBA₂SO₄) solution 50wt % in H₂O (12 equivalents per cage) was added leading to precipitation of a dark orange solid that was inferred to contain cage Co-5•SO₄; the mixture was centrifuged and the supernatant was decanted; this process was repeated with CH₃CN and the excess solvent was removed with N₂. Although the dark orange solid could be dissolved after immediate addition of pure water, it rapidly decomposed as evidenced by cloudiness of the red solution and precipitation of aldehyde E within the first 10 minutes after dissolution.
3. Synthesis of water-soluble nickel(II)–based capsules and their anion-exchange sequences

The direct self-assembly of the nickel(II)-based sulfate tetrahedral Ni-2 to Ni-4 cages was possible through combination of subcomponents B–D with NiSO₄. Conversely, all attempts to generate the corresponding water-soluble cube from direct assembly of porphyrin A with NiSO₄ were unsuccessful in the following mixtures of solvents: 1:1 CH₃CN/H₂O, 1:1 DMF/H₂O, or in pure DMF; however, the water-soluble target capsule was obtained via anion exchange with sulfate salts.

3.1 Synthesis of the water-soluble Ni–I•SO₄ cube and its reversible conversion into the acetonitrile-soluble Ni–I•OTf cube

Subcomponent A (10.0 mg, 0.014 mmol, 6 equiv), 2-formylpyridine (5.2 μL, 0.054 mmol, 24 equiv), nickel(II) triflate (6.8 mg, 0.019 mmol, 8 equiv), and 2.0 mL of DMF were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles and heated at 100°C overnight. Addition of diethyl ether to the crude solution induced precipitation of a dark purple solid that was inferred to contain cube Ni–1•OTf, the mixture was centrifuged and the supernatant DMF/Et₂O was decanted; this process was repeated two times with Et₂O. Clean Ni–1•OTf cube was recovered as a purple solid (17.9 mg, yield 84%). Next, Ni–1•OTf cage was dissolved in CH₃CN and tetrabutylammonium sulfate (TBA₂SO₄) solution 50wt % in H₂O (24 equivalents per cage) was added leading to
precipitation of a purple solid, the mixture was centrifuged and the supernatant was
decanted; this process was repeated with CH$_3$CN:H$_2$O (9:1) and with CH$_3$CN for the last
time. Cube Ni-1•SO$_4$ was obtained as a dark red to crimson solid (13.2 mg, yield 89%).
ESI-MS (5:1 H$_2$O/CH$_3$CN): m/z = 636.0 [Ni-1(OTf)$_4$]$^{+12}$, 707.3 [Ni-1(OTf)$_5$]$^{+11}$, 792.9 [Ni-
1(OTf)$_6$]$^{+10}$, 897.8 [Ni-1(OTf)$_7$]$^{+9}$, 1028.5 [Ni-1(OTf)$_8$]$^{+8}$, 1196.8 [Ni-1(OTf)$_9$]$^{+7}$, 1421.0
[Ni-1(OTf)$_{10}$]$^{+6}$, 1735.0 [Ni-1(OTf)$_{11}$]$^{+5}$. Elemental analysis (%) calcd for
C$_{408}$H$_{264}$N$_{72}$O$_{32}$S$_8$Zn$_6$•4H$_2$O•2CH$_3$CN: C 62.17, H 3.52, N 13.02; found: C 62.24, H
3.56, N 13.00.

Figure S14. ESI-MS spectrum of Ni–1•SO$_4$ (5:1 H$_2$O/CH$_3$CN).

Addition of 24 equivalents of LiOTf (1.5 equiv per sulfate) to a H$_2$O solution of Ni-1•SO$_4$
(5.0 mg in 500 μL) induced precipitation of a purple solid in quantitative yield (5.67 mg,
yield 94%); the mixture was centrifuged and the supernatant H$_2$O was decanted; this
process was repeated two times with H$_2$O. ESI-MS recorded in CH$_3$CN confirmed that this
solid corresponded to the former Ni-1•OTf complex (Figure S15); spectroscopic details as
follows: ESI-MS (CH$_3$CN): $m/z = 524.0$ [Ni-1(OTf)$_2$]$^{+14}$, 573.7 [Ni-1(OTf)$_3$]$^{+13}$, 636.0 [Ni-1(OTf)$_4$]$^{+12}$, 707.4 [Ni-1(OTf)$_5$]$^{+11}$, 792.8 [Ni-1(OTf)$_6$]$^{+10}$, 898.0 [Ni-1(OTf)$_7$]$^{+9}$, 1029.0 [Ni-1(OTf)$_8$]$^{+8}$, 1197.0 [Ni-1(OTf)$_9$]$^{+7}$, 1421.4 [Ni-1(OTf)$_{10}$]$^{+6}$. Elemental analysis (%) calcd for C$_{424}$H$_{264}$F$_{48}$N$_{72}$O$_{48}$S$_{16}$Zn$_6$·9.5H$_2$O: C 53.09, H 2.97, N 10.51; found: C 53.12, H 2.94, N 10.32. Notably, X-ray quality crystals were obtained from this solution corroborating the molecular structure of the Ni-1 framework and further confirming the reversibility of this process to regenerate the original Ni-1•OTf complex (see X-ray crystallography section, *vide infra*).

Subsequently, further addition of TBA$_2$SO$_4$ to an acetonitrile solution of this freshly regenerated Ni-1•OTf induced a precipitation of the water-soluble Ni-1•SO$_4$. The complete Ni-1•OTf→Ni-1•SO$_4$→Ni-1•OTf anion exchange cycle was carried out multiple times, with 88-94% recovery by weight per cycle.

Figure S15. ESI-MS spectrum of Ni-1•OTf (CH$_3$CN) obtained upon reversible anion exchange from Ni-1•SO$_4$. 

S24
3.2 Synthesis of the water-soluble tetrahedron Ni–2•SO₄ and its reversible conversion into the acetonitrile-soluble Ni–2•OTf cage.

Subcomponent B (5.0 mg, 0.014 mmol, 4 equiv), 2-formylpyridine (4.0 μL, 0.043 mmol, 12 equiv), nickel(II) sulfate hexahydrate (3.7 mg, 0.014 mmol, 4 equiv), and 1.5 mL of 1:1 CH₃CN/H₂O solution were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles and heated at 100°C overnight giving a dark orange solution. Afterward, the crude solution was cooled down to room temperature and excess of cold acetonitrile was added leading to precipitation of an orange solid. The mixture was centrifuged and the supernatant CH₃CN/H₂O was decanted, this process was repeated with CH₃CN:H₂O (9:1), then with CH₃CN, and the excess solvent was removed under N₂ flow. Clean Ni–2•SO₄ was recovered as a pale orange solid (9.4 mg, yield 86%). ESI-MS (H₂O):

m/z = 338.5 [Ni-2]⁺⁸, 393.4 [Ni-2(CHO)₂]⁺⁷, 467.2 [Ni-2(SO₄)]⁺⁶, 573.4 [Ni-2(SO₄)(NO₃)]⁺⁵, 734.3 [Ni-2(SO₄)(HSO₄)(CHO)₂]⁺⁴. Elemental analysis (%) calcd for C₁₆₈H₁₂₀N₂₄Ni₄O₁₆S₄•H₂O•CH₃CN: C 64.76, H 4.00, N 11.11; found: C 64.96, H 3.95, N 11.09.
Addition of 12 equivalents of LiOTf (1.5 equiv per sulfate) to an aqueous solution of Ni-2•SO₄ (5.5 mg in 500 μL) induced precipitation of a pale yellow solid, the mixture was centrifuged and the solvent decanted yielding cage Ni-2•OTf in almost quantitative yield (6.41 mg, yield 93%). ESI-MS analyses in CH₃CN confirmed that this solid corresponded to Ni-2•OTf complex (Figures S17); spectroscopic details as follows: ESI-MS (CH₃CN): m/z = 338.7 [Ni-2]⁺⁸, 408.2 [Ni-2(OTf)]⁺⁷, 501.2 [Ni-2(OTf)₂]⁺⁶, 631.8 [Ni-2(OTf)₃]⁺⁵, 826.3 [Ni-2(OTf)₄]⁺⁴, 1151.7 [Ni-2(OTf)₅]⁺³. Elemental analysis (%) calcd for C₁₇₆H₁₂₀F₂₄N₂₄Ni₄O₃₂S₈•2H₂O: C 53.68, H 3.17, N 8.54; found: C 53.78, H 3.28, N 8.80.

Addition of TBA₂SO₄ to an acetonitrile solution of this Ni-2•OTf induced precipitation of the former water-soluble Ni-2•SO₄. The complete Ni-2•SO₄→Ni-2•OTf→Ni-2•SO₄ anion exchange cycle was carried out multiple times, with 87-93% recovery by weight per cycle.
3.3 Synthesis of the water-soluble tetrahedron Ni–3•SO₄ and its reversible conversion into the acetonitrile-soluble Ni–3•OTf cage.

Subcomponent C (3.2 mg, 0.017 mmol, 6 equiv), 2-formylpyridine (3.3 μL, 0.043 mmol, 12 equiv), nickel(II) sulfate hexahydrate (2.8 mg, 0.011 mmol, 4 equiv), and 1.5 mL of 1:1 CH₃CN/H₂O solution were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles and heated at 100°C overnight giving a dark yellow solution.
Afterward, the crude solution was cooled down to room temperature and excess cold acetonitrile was added until a yellow solid precipitated out from the solution. The mixture was centrifuged and the supernatant CH$_3$CN/H$_2$O was decanted, this process was repeated with CH$_3$CN:H$_2$O (9:1), then with CH$_3$CN, and the excess solvent was removed under N$_2$ flow. Cage Ni–3•SO$_4$ was recovered as a pale yellow solid (7.1 mg, yield 88%). ESI-MS (H$_2$O): $m/z = 301.1$ [Ni-3]$^{+8}$, 417.4 [Ni-3(SO$_4$)]$^{+6}$, 650.4, [Ni-3(SO$_4$)$_2$]$^{+4}$. Elemental analysis (%) calcd for C$_{144}$H$_{108}$N$_{24}$Ni$_4$O$_{16}$S$_4$•2CH$_3$CN: C 61.82, H 4.00, N 12.66; found: C 61.98, H 4.10, N 12.76.

Figure S18. ESI-MS spectrum of Ni–3•SO$_4$ (H$_2$O).

Addition of 12 equivalents of LiOTf (1.5 equiv per sulfate) to an aqueous solution of Ni–3•SO$_4$ (6.5 mg in 500 μL) induced precipitation of a pale yellow solid, the mixture was centrifuged and the solvent decanted yielding cage Ni–3•OTf in quantitative yield (7.8 mg, yield 93%). ESI-MS analyses in CH$_3$CN confirmed that this solid corresponded to the Ni–3•OTf complex (Figure S19); spectroscopic details as follows: ESI-MS (CH$_3$CN): $m/z = 365.3$ [Ni-3(OTf)]$^{+7}$, 451.0 [Ni-3(OTf)$_2$]$^{+6}$, 571.0 [Ni-3(OTf)$_3$]$^{+5}$, 751.1 [Ni-3(OTf)$_4$]$^{+4}$, 1051.2 [Ni-3(OTf)$_5$]$^{+3}$, 1651.6 [Ni-3(OTf)$_6$]$^{+2}$. Elemental analysis (%) calcd for
C_{152}H_{108}F_{24}N_{24}Ni_{4}O_{24}S_{8}•2H_{2}O: C 50.18, H 3.10, N 9.24; found: C 50.49, H 3.28, N 9.42.

Noteworthy, X-ray quality crystals were obtained from this solution corroborating the tetrahedral structure of the Ni-3 framework and further confirming the reversibility of this process to regenerate the original Ni-3•SO_{4} complex (see X-ray crystallography section, vide infra).

Addition of TBA_{2}SO_{4} to an acetonitrile solution of this Ni-3•OTf induced precipitation of the former water-soluble Ni-3•SO_{4}. The complete Ni-3•SO_{4}→Ni-3•OTf→Ni-3•SO_{4} anion exchange cycle was carried out multiple times, with 87-93% recovery by weight per cycle.

Figure S19. ESI-MS spectrum of Ni-3•OTf (CH_{3}CN) obtained upon reversible anion exchange from Ni-3•SO_{4}. 
3.4 Synthesis of the water-soluble tetrahedron Ni–4•SO₄ and its reversible conversion into the acetonitrile-soluble Ni–4•OTf cage

Subcomponent D (4.0 mg, 0.010 mmol, 4 equiv), 4-methoxyaniline (3.7 mg, 0.031 mmol, 12 equiv), nickel(II) sulfate hexahydrate (2.7 mg, 0.010 mmol, 4 equiv), and 1.5 mL of 1:1 CH₃CN/H₂O solution were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles and heated at 100°C overnight giving a dark yellow solution. Afterward, the crude solution was cooled down to room temperature and excess of cold acetonitrile was added until a yellow solid precipitated out from the solution. The mixture was centrifuged and the supernatant CH₃CN/H₂O was decanted, this process was repeated with CH₃CN:H₂O (9:1), then with CH₃CN, and the excess of solvent was removed under N₂ flow. Cage Ni–4•SO₄ was recovered as a pale yellow solid (7.4 mg, yield 86%). ESI-MS (H₂O): m/z = 459.9 [Ni–4(OTf)]⁺⁷, 525.1 [Ni–4(CHO₂)₂]⁺⁶, 543.9 [Ni–4(CHO₂)(OTf)]⁺⁶, 560.7 [Ni–4(OTf)₂]⁺⁶, 661.5 [Ni–4(CHO₂)₂(OTf)]⁺⁵, 671.9 [Ni–4(HSO₄)₃]⁺⁵, 682.2 [Ni–4(HSO₄)₂(OTf)]⁺⁵, 851.3 [Ni–4(CHO₂)₂(HSO₄)(OTf)]⁺⁴, 864.7 [Ni–4(CHO₂)₂(OTf)₂]⁺⁴. Elemental analysis (%) calcd for C₁₈₀H₁₄₄Ni₄O₂₈S₄•CH₃CN•H₂O: C 62.22, H 4.27, N 9.97; found: C 62.59, H 4.32, N 9.92.
Addition of 12 equivalents of LiOTf (1.5 equiv per sulfate) to an aqueous solution of Ni-4•SO$_4$ (4.0 mg in 500 μL) induced precipitation of a pale yellow solid, the mixture was centrifuged and the solvent decanted yielding cage Ni-4•OTf in almost quantitative yield (4.4 mg, yield 90%). ESI-MS analyses in CH$_3$CN confirmed that this solid corresponded to the Ni-4•OTf complex (Figure S21); spectroscopic details as follows: ESI-MS (CH$_3$CN): $m/z = 459.6$ [Ni-4(OTf)]$^7^+$, 560.7 [Ni-4(OTf)$_2$]$^6^+$, 702.8 [Ni-4(OTf)$_3$]$^5^+$, 916.1 [Ni-4(OTf)$_4$]$^4^+$, 1271.3 [Ni-4(OTf)$_5$]$^3^+$. Elemental analysis (%) calcd for C$_{188}$H$_{144}$F$_{24}$N$_{24}$O$_{36}$S$_8$•3H$_2$O: C 52.31, H 3.50, N 7.79; found: C 52.44, H 3.58, N 7.84.

Addition of TBA$_2$SO$_4$ to an acetonitrile solution of this Ni-4•OTf induced precipitation of the former water-soluble Ni-4•SO$_4$. The complete Ni-4•SO$_4$→Ni-4•OTf→Ni-4•SO$_4$ anion exchange cycle was carried out multiple times, with 87-93% recovery by weight per cycle.
3.5 Attempted reaction to prepare a water-soluble Ni–5•SO₄ tetrahedron

Reactions between subcomponent E and NiSO₄ were attempted using diverse temperature and solvent conditions in order to prepare cage Ni-5•SO₄, all reactions remained unsuccessful and only led to insoluble materials.

We have previously reported that reactions of aldehyde E with nickel(II) salts containing BF₄⁻, NTf₂⁻, ClO₄⁻, or NO₃⁻ did not yield tetrahedral structure Ni-5. As previously
observed, E reacts with Ni(OTf)$_2$ to form a mixture of assemblies. When treated with TBA$_2$SO$_4$ in MeCN, this mixture gave species that were initially soluble in water, but which decomposed by precipitation within minutes.

3.6 Selected binding experiments using water-soluble Ni$^{II}$-based capsules with fluorinated guests

The $^1$H NMR spectra of complexes containing octahedrally coordinated Ni$^{II}$ produced little insight due to the long relaxation times arising from the orbitally non-degenerate ground state of these complexes. Given that we have gained knowledge into the outcome of the self-assembly reactions and anion exchange sequences solely through ESI-MS and X-ray crystallography, we carried out selected encapsulation experiments using these Ni$^{II}$-based capsules with some common fluorinated aromatics as guests including fluorobenzene, 1,3,5-trifluorobenzene, and hexafluorobenzene; the binding of each prospective guest was followed by $^{19}$F NMR. These host-guest experiments only intended to serve as further proof of the capsular nature of the Ni$^{II}$-based complexes and a full investigation into the host-guest properties of these capsules is beyond the scope of this work.

No encapsulation of prospective fluorinated guests or triflate anion in CD$_3$CN was inferred to have taken place when the triflate versions of the capsules were used. Only one signal was observed in the $^{19}$F NMR spectra, the signals for the fluorinated aromatics were identical to those in the absence of host. On the other hand, host occupation was inferred to occur in D$_2$O using sulfate derivatives of nickel(II)-capsules; shifting or broadening of the guest peaks were observed.
Figure S22. Reaction systems for investigating the Host-Guest interaction between cages Ni–2•X to Ni–4•X (X = OTf\(^{-}\), SO\(_4^{2-}\)) and fluorinated aromatic guests in water and acetonitrile.
Solutions of Ni-n\textsuperscript{•}SO\textsubscript{4} (n = 2, 3, 4) capsules (200–300 μM) in D\textsubscript{2}O were transferred to an NMR tube and the prospective fluorinated guest was added in excess due to their low solubility and miscibility in water (~10–15 equivalents per cage). The mixture was sonicated for 10 minutes and then stored at room temperature; the spectra were recorded periodically until the host-guest complex equilibrated as shown by the \textsuperscript{19}F NMR spectra; generally, equilibration times were short (t < 8 h).

Initially, the \textsuperscript{19}F NMR spectra revealed the presence of two peaks corresponding to the free and encapsulated fluorinated molecule. The peaks for the free fluorinated molecules progressively vanished likely due to separation and evaporation from the aqueous solution given their very poor solubility in water; Figures S23 and S24 exemplify such observations. As a result, only the peak of the encapsulated guest (host-guest complex) persisted in the \textsuperscript{19}F NMR spectra over the time. The free and bound guests were referenced to C\textsubscript{6}F\textsubscript{6} (as an external standard in a capillary tube at δ = −164.9 ppm). Likewise, the assignment of the free and bound guest was further aided using \textsuperscript{19}F NMR spectra of samples containing only the free guest in D\textsubscript{2}O and C\textsubscript{6}F\textsubscript{6} as an external standard in a capillary tube.

![Figure S23. \textsuperscript{19}F NMR spectra (376 MHz, D\textsubscript{2}O, 298 K) of the C\textsubscript{6}H\textsubscript{3}F\textsubscript{3}⊂Ni-3\textsuperscript{•}SO\textsubscript{4} Host-Guest complex showing signals for the free and encapsulated guest (top), and the disappearance of the resonance for the free molecule over the time (bottom).](image-url)
Figure S24. $^{19}$F NMR spectra (376 MHz, D$_2$O, 298 K) of the C$_6$H$_5$F⊂Ni–4$\cdot$SO$_4$ Host-Guest complex showing signals for the free and encapsulated guest (top), and disappearance of the free guest peak over the time (bottom).

Figure S25. $^{19}$F NMR spectra (376 MHz, D$_2$O, 298 K) of the equilibrated Host-Guest complexes derived from cages Ni–2$\cdot$SO$_4$, Ni–3$\cdot$SO$_4$, and Ni–4$\cdot$SO$_4$ showing signals for the encapsulated guest.
4. Attempted preparations of water-soluble Zn\textsuperscript{II}– and Cd\textsuperscript{II}–based capsules

Reactions of subcomponents \textbf{A} and \textbf{D} with 2-formylpyridine and anisidine respectively, yielded the corresponding acetonitrile-soluble capsules (as triflate salts) when combined with Zn\textsuperscript{II} and Cd\textsuperscript{II}. These capsules precipitated upon addition of TBA\textsubscript{2}SO\textsubscript{4} in acetonitrile suggesting the exchange of triflate for sulfate. Addition of water to these solids enabled their immediate dissolution; however, the resulting solutions became cloudy just after a few seconds leading to mostly insoluble material within the first three minutes after dissolution in the case of frameworks Zn-4•SO\textsubscript{4} and Cd-4•SO\textsubscript{4} formed by aldehyde D.

Although the cubic structures Zn-1•SO\textsubscript{4} and Cd-1•SO\textsubscript{4} also failed to survive in aqueous solution, it was possible to record initial NMR spectra and monitor the disassembly process in aqueous solution.

Dissolution of cubic structures Zn-1•SO\textsubscript{4} and Cd-1•SO\textsubscript{4} in D\textsubscript{2}O brought about cloudiness of the red brick to dark brown solutions and the eventual appearance of insoluble blue solid (free porphyrin \textbf{A}). While it was possible to observe peaks of low-intensity corresponding to cube Zn-1 within the first hour, the Cd-1 framework was almost completely hydrolysed after 20 minutes strongly indicating its lower stability.
Figure S26. Selected self-assembly reactions tested to investigate the dissolution and stability in water of Zn$^{II}$– and Cd$^{II}$–based capsules. All reactions, either via direct assembly with sulfate salts or via anion exchange, remained unsuccessful for the formation of stable cages.
Figure S27. $^1$H NMR spectrum (400 MHz, CD$_3$CN, 298 K) of Zn–1•OTf.

Figure S28. ESI-MS spectrum (CH$_3$CN) of Zn–1•OTf.
Figure S29. $^1$H NMR spectra (400 MHz, D$_2$O, 298 K) of Zn–1•SO$_4$ showing the progressive vanishing of the cube peaks over the time; blue circles denote cage peaks.

Figure S30. $^1$H NMR spectrum (400 MHz, CD$_3$CN, 298 K) of Cd–1•OTf.
Figure S31. ESI-MS spectrum (CH$_3$CN) of Cd–1•OTf.

Figure S32. $^1$H NMR spectra (400 MHz, D$_2$O, 298 K, recorded 15 min after dissolution) of Cd–1•SO$_4$ evidencing rapid disassembly in solution; yellow circles denote cage peaks.
5. Chelating amines for the synthesis of water-soluble Zn$^{II}$– and Cd$^{II}$– based architectures

The $C_2$-symmetric subcomponents E–H were combined with chelating amines TREN or TRPN for the direct self-assembly reactions with ZnSO$_4$ or CdSO$_4$ yielding a collection of water soluble self-assembled structures. Two sets of conditions for the same aldehyde-based subcomponent were used, Zn$^{II}$/TREN or Cd$^{II}$/TRPN, leading to the synthesis of helicates Zn–6SO$_4$ to Zn–9SO$_4$ and tetrahedra Cd–11SO$_4$ to Cd–14SO$_4$, respectively. Conversely, reactions of the $C_3$-symmetric subcomponent D using both sets of conditions exclusively afforded tetrahedra, cages Zn–10SO$_4$ and Cd–15SO$_4$. Similar to the Co$^{II}$– and Ni$^{II}$–based structures presented, these assemblies are robust enough to undergo anion metathesis with LiOTf and generate the corresponding acetonitrile-soluble derivatives. Crystallization of helical structures Zn–7 and Zn–8 as well as tetrahedra Cd–12 and Cd–14 from their acetonitrile solutions clearly attests to this quality; Figures S68, S69 and S78 also illustrate the dissolution in acetonitrile of these assemblies as triflate derivatives.

Although all ESI-MS spectra (obtained in pure H$_2$O) showed charged states consistent with the Zn$^{II}_2$L$_3$, Cd$^{II}_3$L$_6$, Zn$^{II}_4$L$_4$, and Cd$^{II}_4$L$_4$ formulations of the target frameworks, some peaks resulted from anion exchange under ESI-MS conditions. Hence, peaks with SO$_4^{2–}$, HSO$_4^{–}$, Cl$^–$, NTF$_2^{–}$, CHO$_2^{–}$, BF$_4^{–}$ counter anions were observed due to their residual and persistent presence in the equipment or to washing with formic acid (Figures S36, S40, S44, S49, S53, S57, S62, S67, S74 and S77).
5.1 Reactions of aldehyde \( E \) to form helicate \( \text{Zn-6•SO}_4 \) or tetrahedron \( \text{Cd-11•SO}_4 \)

Subcomponent \( E \) (10.0 mg, 0.047 mmol, 3 equiv), tris(2-aminoethyl)amine (TREN) (4.8 μL, 0.031 mmol, 2 equiv), zinc(II) sulfate heptahydrate (2.7 mg, 0.031 mmol, 2 equiv), and 1.0 mL of 1:1 CH\(_3\)CN/H\(_2\)O were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles, sonicated for 15 minutes and heated at 85°C overnight yielding a yellow solution with a small amount of fine dark yellow solid. The fine yellow solid was removed by filtration using a small column with celite, and excess of CH\(_3\)CN was added to the bright yellow liquor giving a yellow suspension. The suspension was centrifuged and the supernatant CH\(_3\)CN/H\(_2\)O was decanted. To remove the excess of unreacted aldehyde \( E \) and TREN, the solid was washed with CH\(_2\)Cl\(_2\), centrifuged and the supernatant decanted; this process was carried out a second time with Et\(_2\)O, and a two times with CH\(_3\)CN. Finally, the excess of solvents was removed by a gentle flow of N\(_2\) gas yielding helicate \( \text{Zn-6•SO}_4 \) as a microcrystalline beige solid (15.9 mg, yield 88%). \( ^1\text{H} \) NMR (400 MHz, D\(_2\)O, 298 K): \( \delta \) = 8.92 (s, 6H, imine-Ha), 8.14 (dd, \( ^3J_{1\text{H–1H}} = 7.9, 2.0 \) Hz, 6H, Py-Hb), 8.09 (d, \( ^3J_{1\text{H–1H}} = 7.9 \) Hz, 6H, Py-Hc), 6.05 (d, \( ^3J_{1\text{H–1H}} = 1.9 \) Hz, 6H, Py-Hd), 4.11 (dd, \( ^2J_{1\text{H–1H}} = 12.2, ^3J_{1\text{H–1H}} = 12.0 \) Hz, 6H, TREN-He), 3.84 (dd, \( ^2J_{1\text{H–1H}} = 12.4, ^3J_{1\text{H–1H}} = 3.2 \) Hz, 6H, TREN-He), 3.31 (dd, \( ^2J_{1\text{H–1H}} = 13.6, ^3J_{1\text{H–1H}} = 3.6 \) Hz, 6H, TREN-Hf), 3.12
(ddd, $^2J_{\text{H-H}} = 13.6$, $^3J_{\text{H-H}} = 13.4$, 3.5 Hz, 6H, TREN-Hf). $^{13}$C NMR (100 MHz, D$_2$O, 298 K): $\delta = 163.7, 148.6, 148.5, 139.9, 138.2, 129.0, 56.5, 54.1$. DOSY Diffusion coefficient = $2.98 \times 10^{-10}$ m$^2$/s. ESI-MS (H$_2$O): $m/z = 237.7$ [$\text{Zn-6}$$^4$]+, 349.4 [$\text{Zn-6(HSO}_4$)]$^3$+, 524.1 [$\text{Zn-6(SO}_4$)]$^2$. Elemental analysis (%) calcd for C$_{48}$H$_{48}$N$_{14}$O$_8$S$_2$Zn$_2$$^\cdot$H$_2$O: C 49.62, H 4.34, N 16.88; found: C 49.28, H 4.36, N 16.72.

Figure S33. $^1$H NMR spectrum (400 MHz, D$_2$O, 298 K) of helicate Zn–6$^\cdot$SO$_4$. 
**Figure S34.** $^1$H DOSY NMR spectrum (400 MHz, D$_2$O, 298 K) of helicate Zn–6$^{•}$SO$_4$.

**Figure S35.** $^1$H–$^1$H COSY NMR spectrum (400 MHz, D$_2$O, 298 K) of helicate Zn–6$^{•}$SO$_4$. 

S45
Subcomponent E (5.0 mg, 0.024 mmol, 6 equiv), tris(3-aminopropyl)amine (TRPN) (3.1 μL, 0.016 mmol, 4 equiv), cadmium(II) sulfate (3.2 mg, 0.018 mmol, 4 equiv), and 1.0 mL of 1:1 CH_3CN/H_2O were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles, sonicated for 15 minutes and heated at 80°C overnight yielding a yellow solution with a small amount of fine dark yellow solid. This yellow solid was removed by filtration using a small column with celite, and excess of CH_3CN was added to the bright yellow liquor giving a yellow suspension. The suspension was centrifuged and the supernatant CH_3CN/H_2O was decanted. To remove the excess of unreacted aldehyde E and TRPN, the solid was washed with CH_2Cl_2, centrifuged and the supernatant decanted; this process was carried out a second time with Et_2O, and a two times with CH_3CN. Finally, the excess of solvents was removed by a gentle flow of N_2 gas yielding cage Cd-11•SO_4 as a microcrystalline light yellow solid (8.5 mg, yield 82%).

^1H NMR (400 MHz, D_2O, 298 K): δ = 9.02 (s, 3^1H-113Cd = 21.4 Hz, 12H, imine-Ha), 8.19 (d, ^3J_{1H-1H} = 7.6 Hz, 12H, Py-Hb), 8.01 (d, ^3J_{1H-1H} = 7.9 Hz, 12H, Py-He), 7.32 (s, 12H, Py-Hd), 3.98 (d, ^2J_{1H-1H} = 10.6 Hz, 12H, TRPN-He), 3.40 (m, 24H, TRPN-He, Hf), 2.35 (m, 12H, TRPN-Hf), 2.23 (m, 12H, TRPN-Hg), 1.94 (d, ^2J_{1H-1H} = 13.9 Hz, 12H, TRPN-Hg).

^13C NMR (100 MHz, D_2O, 298 K): δ = 161.4, 147.9, 147.5, 140.3, 137.9, 129.1, 61.9, 58.5, 58.1.
DOSY Diffusion coefficient = $2.13 \times 10^{-10}$ m$^2$/s. ESI-MS (H$_2$O): $m/z = 282.8$ [Cd-11]$^{+8}$, 328.4 [Cd-11(Cl)]$^{+7}$, 392.7 [Cd-11(SO$_4$)]$^{+6}$, 474.0 [Cd-11(Cl)$_3$]$^{+5}$, 613.1 [Cd-11(SO$_4$)$_2$]$^{+4}$, 822.4 [Cd-11(CHO$_2$)$_3$(Cl)$_2$]$^{+3}$, 1274.5 [Cd-11(SO$_4$)$_3$]$^{+2}$. Elemental analysis (%) calcd for C$_{108}$H$_{120}$Cd$_4$N$_{28}$O$_{16}$S$_4$•3.5H$_2$O•CH$_3$CN: C 48.07, H 4.77, N 14.78; found: C 48.18, H 4.76, N 14.72.

Figure S37. $^1$H NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Cd–11•SO$_4$. 
Figure S38. $^1$H DOSY NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Cd–11•SO$_4$.

Figure S39. $^1$H–$^1$H COSY NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Cd–11•SO$_4$. 

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Figure S40. ESI-MS spectrum of tetrahedron Cd–11•SO₄ recorded in H₂O.

5.2 Reactions of aldehyde F to form helicate Zn–7•SO₄ or tetrahedron Cd–12•SO₄
Subcomponent F (8.2 mg, 0.028 mmol, 3 equiv), tris(2-aminoethyl)amine (TREN) (2.9 μL, 0.019 mmol, 2 equiv), zinc(II) sulfate heptahydrate (5.4 mg, 0.019 mmol, 2 equiv), and 1.0 mL of 1:1 CH$_3$CN/H$_2$O were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles, sonicated for 15 minutes and heated at 85°C overnight yielding a yellow solution with some yellow insoluble material. The insoluble material was removed by filtration through celite, and excess CH$_3$CN was added to the bright yellow liquor leading to precipitation of a light yellow solid. The mixture was centrifuged and the supernatant CH$_3$CN/H$_2$O was decanted. To remove excess unreacted aldehyde F and TREN, the solid was washed with CH$_2$Cl$_2$, centrifuged and the supernatant decanted; this process was carried out a second time with Et$_2$O, and two times with CH$_3$CN. Finally, the excess of solvents was removed by a gentle flow of N$_2$ gas yielding helicate Zn-7•SO$_4$ as a microcrystalline beige solid (11.7 mg, yield 90%).

$^1$H NMR (400 MHz, D$_2$O, 298 K): δ = 8.91 (s, 6H, imine-Ha), 8.63 (d, $^3$J$_{1H-1H}$ = 8.0 Hz, 6H, Py-Hb), 8.19 (d, $^3$J$_{1H-1H}$ = 8.1 Hz, 6H, Py-Hc), 7.25 (s, 12H, Ar-Hh), 6.53 (s, 6H, Py-Hd), 4.10 (dd, $^2$J$_{1H-1H}$ = 12.6, $^3$J$_{1H-1H}$ = 12.2 Hz, 6H, TREN-He), 3.81 (d, $^2$J$_{1H-1H}$ = 12.4 Hz, 6H, TREN-He), 3.32 (d, $^2$J$_{1H-1H}$ = 11.9 Hz, 6H, TREN-Hf), 3.11 (dd, $^2$J$_{1H-1H}$ = 12.1, $^3$J$_{1H-1H}$ = 12.0 Hz, 6H, TREN-Hf). $^{13}$C NMR (100 MHz, D$_2$O, 298 K): δ = 163.5, 147.2, 147.0, 138.1, 135.7, 129.6, 128.1, 57.1, 54.3. DOSY Diffusion coefficient = $2.70 \times 10^{-10}$ m$^2$/s. ESI-MS (H$_2$O): $m/z$ = 294.7 [Zn-7]$^{4+}$, 408.2 [Zn-7(CHO$_2$)]$^{3+}$, 425.6 [Zn-7(HSO$_4$)]$^{3+}$, 635.1 [Zn-7(CHO$_2$)$_2$]$^{2+}$, 661.2 [Zn-7(CHO$_2$)$_2$]$^{2+}$, 687.3 [Zn-7(HSO$_4$)$_2$]$^{2+}$. Elemental analysis (%) calcd for C$_{60}$H$_{60}$N$_{14}$O$_8$S$_2$Zn$_2$•2.5H$_2$O: C 53.57, H 4.87, N 14.58; found: C 53.86, H 4.91, N 14.72.
**Figure S41.** $^1$H NMR spectrum (400 MHz, D$_2$O, 298 K) of helicate Zn–7•SO$_4$.

**Figure S42.** $^1$H DOSY NMR spectrum (400 MHz, D$_2$O, 298 K) of helicate Zn–7•SO$_4$.
Figure S43. $^1$H–$^1$H COSY NMR spectrum (400 MHz, D$_2$O, 298 K) of helicate Zn–7•SO$_4$.

Figure S44. ESI-MS spectrum of helicate Zn–7•SO$_4$ recorded in H$_2$O.
The products of the reactions between aldehyde F and CdSO₄ aimed to prepare tetrahedron Cd-12•SO₄ were dependent on the concentration. It was observed that higher concentration of subcomponents yielded a mixture of two species, the target Cd₄L₆ capsule and a Cd₂L₃ helicate. While the self-assembly reaction using aldehyde F with a concentration of 17.4 mM (5.0 mg in 1000 μL of solvent) yielded a water-soluble mixture of helicate/tetrahedron, reaction at a concentration of 5.7 mM (5.0 mg in 3000 μL of solvent) assured the formation of the target tetrahedron Cd-12•SO₄ as the pure product in good yield (Figure S45).

**Figure S45.** Aromatic region of the ¹H NMR spectra (400 MHz, D₂O, 298 K) of products obtained from three different self-assembly reactions of aldehyde F with CdSO₄ and TRPN at varied concentrations; such variations may yield either a mixture of helicate/tetrahedron or only tetrahedron Cd–12•SO₄ as products. Blue circles (●) denote helicate peaks and red triangles (▲) the tetrahedron signals.

Details of the preparation of pure tetrahedron are given as follows: Subcomponent F (5.0 mg, 0.017 mmol, 6 equiv), tris(3-aminopropyl)amine (TRPN) (2.1 μL, 0.012 mmol, 4 equiv), cadmium(II) sulfate (2.4 mg, 0.012 mmol, 4 equiv), and 3.0 mL of 1:1 CH₃CN/H₂O.
were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles, sonicated for 15 minutes and heated at 80°C overnight yielding a yellow solution with a small amount of beige insoluble material. This solid was removed by filtration through celite, and excess CH$_3$CN was added to the bright yellow liquor leading to precipitation of a light yellow solid. The mixture was centrifuged and the supernatant CH$_3$CN/H$_2$O was decanted. To remove the excess of unreacted aldehyde F and TRPN, the solid was washed with CH$_2$Cl$_2$, centrifuged and the supernatant decanted; this process was carried out a second time with Et$_2$O, and a two times with CH$_3$CN. Finally, the excess of solvents was removed by a gentle flow of N$_2$ gas yielding cage Cd-$\text{12}\cdot\text{SO}_4$ as a microcrystalline light yellow solid (7.1 mg, yield 80%).

$^1$H NMR (400 MHz, D$_2$O, 298 K): $\delta = 8.98$ (s, $^3J_{1H-113Cd} = 21.0$ Hz, 12H, imine-$H_a$), 8.56 (d, $^3J_{1H-1H} = 8.1$ Hz, 12H, Py-$H_b$), 8.27 (d, $^3J_{1H-1H} = 8.0$ Hz, 12H, Py-$H_c$), 7.70 (s, 12H, Py-$D$), 7.36 (s, 24H, Ar-$H$), 4.04 (d, $^2J_{1H-1H} = 10.8$ Hz, 12H, TRPN-$He$), 3.64 (m, 24H, TRPN-$He$, $H_f$), 2.50 (m, 12H, TRPN-$H_f$), 2.37 (m, 12H, TRPN-$H_g$), 2.06 (d, $^2J_{1H-1H} = 13.9$ Hz, 12H, TRPN-$H_g$). $^{13}$C NMR (100 MHz, D$_2$O, 298 K): $\delta = 162.0$, 147.4, 147.0, 140.6, 138.8, 136.7, 129.0, 128.3, 62.3, 58.9, 26.2. DOSY Diffusion coefficient $= 1.82 \times 10^{-10}$ m$^2$/s. ESI-MS (H$_2$O): $m/z = 339.5$ [Cd-$\text{12}$]$^{8+}$, 394.3 [Cd-$\text{12}$($\text{CHO}_2$)]$^{7+}$, 468.0 [Cd-$\text{12}$($\text{SO}_4$)]$^{6+}$, 476.4 [Cd-$\text{12}$($\text{CHO}_2$)($\text{HSO}_4$)]$^{5+}$, 571.4 [Cd-$\text{12}$($\text{SO}_4$)]$^{5+}$, 580.9 [Cd-$\text{12}$($\text{HSO}_4$)($\text{SO}_4$)]$^{4+}$, 725.7 [Cd-$\text{12}$($\text{SO}_4$)$_2$]$^{4+}$, 737.2 [Cd-$\text{12}$($\text{CHO}_2$)($\text{HSO}_4$)($\text{SO}_4$)]$^{4+}$. Elemental analysis (%) calcd for C$_{144}$H$_{144}$Cd$_4$N$_{28}$O$_{16}$S$_4$•4.5H$_2$O: C 54.36, H 4.85, N 12.33; found: C 54.28, H 4.76, N 12.25.
Figure S46. $^1$H NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Cd–12•SO$_4$.

Figure S47. $^1$H DOSY NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Cd–12•SO$_4$. 

Diff. Coeff. ($D$) | $1.82 \times 10^{-10}$ m/s$^2$

Hydrodynamic Radius ($R_H$) | 13.5 Å
Figure S48. $^1$H–$^1$H COSY NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Cd–12$\cdot$SO$_4$.

Figure S49. ESI-MS spectrum of tetrahedron Cd–12$\cdot$SO$_4$ recorded in H$_2$O.
Subcomponent G (7.5 mg, 0.024 mmol, 3 equiv), tris(2-aminoethyl)amine (TREN) (2.4 μL, 0.016 mmol, 2 equiv), zinc(II) sulfate heptahydrate (4.5 mg, 0.016 mmol, 2 equiv), and 1.5 mL of 1:1 CH$_3$CN/H$_2$O were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles, sonicated for 15 minutes and heated at 85°C overnight yielding a yellow solution with a minor amount of insoluble material, which was removed by filtration using a small column with celite. Excess of CH$_3$CN was added to the bright yellow liquor leading to precipitation of a cream-colored solid. The mixture was centrifuged and the supernatant CH$_3$CN/H$_2$O was decanted. To remove excess unreacted aldehyde G and TREN, the precipitate was washed with CH$_2$Cl$_2$, centrifuged and the supernatant decanted; this process was carried out a second time with Et$_2$O, and two times more with CH$_3$CN. Finally, the excess of solvents was removed by a gentle flow of N$_2$ gas yielding helicate Zn–8•SO$_4$ as a microcrystalline white solid (10.2 mg, yield 88%). $^1$H NMR (400 MHz, D$_2$O, 298 K): δ = 8.87 (s, 6H, imine-Ha), 8.48 (d, $^3$J$_{1H-1H}$ = 8.0 Hz, 6H, Py-Hb), 8.19 (d, $^3$J$_{1H-1H}$ = 7.9 Hz, 6H, Py-Hc), 7.23 (s, 6H, Ar-Hh), 7.21 (s, 6H, Py-Hd), 4.01 (dd, $^2$J$_{1H-1H}$ = 12.4, $^2$J$_{1H-1H}$ = 11.8 Hz, 6H, TREN-He), 3.74 (d, $^2$J$_{1H-1H}$ = 11.2 Hz, 6H, TREN-He), 3.34 (d, $^2$J$_{1H-1H}$ = 12.9 Hz, 6H, TREN-Hf), 3.06 (dd, $^2$J$_{1H-1H}$ = 13.6, $^3$J$_{1H-1H}$ =
12.9 Hz, 6H, TREN-Hf), 1.70 (s, 18H, –CH3-Hi). $^{13}$C NMR (100 MHz, D$_2$O, 298 K): $\delta =$
163.8, 148.4, 146.4, 141.5, 140.9, 135.9, 134.2, 133.2, 130.2, 57.6, 54.9, 19.0. DOSY Diffusion coefficient = 2.45 $\times$ 10$^{-10}$ m$^2$/s. ESI-MS (H$_2$O): $m/z = 316.1$ [Zn-8]$^{4+}$, 436.4 [Zn-8(CHO$_2$)]$^{3+}$, 453.8 [Zn-8(HSO$_4$)]$^{+3}$, 679.0 [Zn-8(SO$_4$)]$^{+2}$, 729.3 [Zn-8(HSO$_4$)$_2$]$^{+2}$. Elemental analysis (%) calcd for C$_{72}$H$_{72}$N$_{14}$O$_8$S$_2$Zn$_2$•4H$_2$O: C 56.58, H 5.28, N 12.83; found: C 56.86, H 5.56, N 12.78.

**Figure S50.** $^1$H NMR spectrum (400 MHz, D$_2$O, 298 K) of helicate Zn–8•SO$_4$.
Figure S51. $^1$H DOSY NMR spectrum (400 MHz, D$_2$O, 298 K) of helicate Zn–8•SO$_4$.

Figure S52. $^1$H–$^1$H COSY NMR spectrum (400 MHz, D$_2$O, 298 K) of helicate Zn–8•SO$_4$. 

Diff. Coeff. ($D$) $2.45 \times 10^{-10}$ m/s$^2$

Hydrodynamic Radius ($R_H$) 10.0 Å
Subcomponent G (5.2 mg, 0.016 mmol, 6 equiv), tris(3-aminopropyl)amine (TRPN) (2.1 μL, 0.011 mmol, 4 equiv), cadmium(II) sulfate (2.3 mg, 0.011 mmol, 4 equiv), and 1.5 mL of 1:1 CH$_3$CN/H$_2$O were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles, sonicated for 15 minutes and heated at 80°C overnight yielding a yellow solution with a small amount of pale yellow insoluble material. This solid was removed by filtration using a small column with celite, and excess of CH$_3$CN was added to the bright yellow liquor leading to precipitation of a creamy solid. The mixture was centrifuged and the supernatant CH$_3$CN/H$_2$O was decanted. To remove the excess of unreacted aldehyde G and TRPN, the solid was washed with CH$_2$Cl$_2$, centrifuged and the supernatant decanted; this process was carried out a second time with Et$_2$O, and two times more with CH$_3$CN. Finally, the excess of solvents was removed by a gentle flow of N$_2$ gas yielding cage Cd-13•SO$_4$ as a microcrystalline white solid (6.3 mg, yield 80%). $^1$H NMR (400 MHz, D$_2$O, 298 K): δ = 8.97 (s, $^3$J$_{1H-113Cd}$ = 20.5 Hz, 12H, imine-Ha), 8.25 (d, $^3$J$_{1H-1H}$ = 7.2 Hz, 12H, Py-Hc), 8.20 (d, $^3$J$_{1H-1H}$ = 7.6 Hz, 12H, Py-Hb), 7.42 (s, 12H, Py-Hd), 7.09
(s, 12H, Ar-Hh), 4.09 (d, $^2J_{1H-1H} = 10.0$ Hz, 12H, TRPN-He), 3.81–3.61 (m, 24H, TRPN-He, Hf), 2.54 (m, 12H, TRPN-Hf), 2.43 (d, $^2J_{1H-1H} = 10.5$ Hz, 12H, TRPN-Hg), 2.11 (d, $^2J_{1H-1H} = 13.2$ Hz, 12H, TRPN-Hg), 1.76 (s, 36H, –CH$_3$-Hi). $^{13}$C NMR (100 MHz, D$_2$O, 298 K): δ = 161.8, 148.7, 147.0, 141.9, 141.6, 137.2, 133.9, 132.6, 129.1, 62.2, 59.0, 26.2, 19.1. DOSY Diffusion coefficient = $1.79 \times 10^{-10}$ m$^2$/s. ESI-MS (H$_2$O): $m/z = 360.5\text{[Cd-13]}^{+8}$, 420.7 $\text{[Cd-13(NO$_3$)]}^{+7}$, 452.1 $\text{[Cd-13(NTF$_2$)]}^{+7}$, 496.9 $\text{[Cd-13(SO}_4^1\text{)]}^{+6}$, 504.6 $\text{[Cd-13(CHO}_2\text{)(HSO}_4\text{)]}^{+6}$, 607.9 $\text{[Cd-13(CHO}_2\text{(NO}_3\text{)]}^{+5}$, 769.2 $\text{[Cd-13(SO}_4^2\text{)]}^{+4}$ Elementual analysis (%) calcd for C$_{156}$H$_{156}$Cd$_4$N$_{28}$O$_{16}$S$_4$•5.5H$_2$O: C 55.83, H 5.02, N 11.69; found: C 55.98, H 5.16, N 11.35.

Figure S54. $^1$H NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Cd–13•SO$_4$. 
Figure S55. $^1$H DOSY NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Cd–13•SO$_4$.

Figure S56. $^1$H–$^1$H COSY NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Cd–13•SO$_4$. 
Figure S57. ESI-MS spectrum of tetrahedron Cd–13•SO₄ recorded in H₂O.

5.4 Reactions of aldehyde H to form helicate Zn–9•SO₄ or tetrahedron Cd–14•SO₄
Subcomponent H (4.8 mg, 0.013 mmol, 3.6 equiv), tris(2-aminoethyl)amine (TREN) (1.1 μL, 0.007 mmol, 2 equiv), zinc(II) sulfate heptahydrate (2.1 mg, 0.007 mmol, 2 equiv), and 1.5 mL of 2:1 CH₃CN/H₂O were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles, sonicated for 20 minutes and heated at 85°C for 24h yielding a yellow suspension. The solid (likely unreacted aldehyde H and oligomeric material) was removed by filtration using a small column with celite. Excess of CH₃CN was added to the bright yellow liquor leading to precipitation of yellow solid. The mixture was centrifuged and the supernatant CH₃CN/H₂O was removed. The precipitate was washed with CH₂Cl₂, centrifuged and the supernatant decanted; this process was repeated with Et₂O, and carried out two times with CH₃CN. Finally, the excess of solvents was removed by a gentle flow of N₂ gas yielding helicate Zn-9•SO₄ as a microcrystalline yellow solid (4.5 mg, yield 75%).

^1H NMR (400 MHz, D₂O, 298 K): δ = 8.93 (s, 6H, imine-Ha), 8.56 (d, J¹H-¹H = 8.0 Hz, 6H, Py-Hb), 8.24 (d, J²H-¹H = 7.9 Hz, 6H, Py-Hc), 7.22 (s, 6H, Py-Hd), 4.09 (dd, J²H-¹H = 11.2, J²H-¹H = 10.5 Hz, 6H, TREN-He), 3.80 (d, J²H-¹H = 11.2 Hz, 6H, TREN-He), 3.34 (d, J²H-¹H = 13.6 Hz, 6H, TREN-Hf), 3.09 (dd, J²H-¹H = 13.4, J²H-¹H = 12.5 Hz, 6H, TREN-Hf). ^13C NMR (100 MHz, D₂O, 298 K): δ = 165.1, 151.2, 150.3, 143.8, 138.2, 128.0, 122.2, 118.0, 57.9, 54.6. ^19F NMR (376 MHz, D₂O): δ = −145.3. DOSY Diffusion coefficient = 2.54 × 10⁻¹⁰ m²/s. ESI-MS (H₂O): m/z = 348.8 [Zn-9]⁺⁺, 480.0 [Zn-9(CHO₂)]⁺⁺, 497.4 [Zn-9(HSO₄)]⁺⁺, 745.8 [Zn-9(SO₄)]⁺⁺, 794.9 [Zn-9(HSO₄)₂]⁺⁺. Elemental analysis (%) calcd for C₆₀H₄₈F₁₂N₁₄O₈S₂Zn₂•3.5H₂O•0.5CH₃CN: C 45.80, H 3.56, N 12.70; found: C 45.86, H 3.48, N 12.66.
Figure S58. $^1$H NMR spectrum (400 MHz, D$_2$O, 298 K) of helicate Zn$^{9}$SO$_4$.

Figure S59. $^1$H DOSY NMR spectrum (400 MHz, D$_2$O, 298 K) of helicate Zn$^{9}$SO$_4$. 

Diffusion Units

Diff. Coeff. ($D$) $2.54 \times 10^{-10}$ m/s$^2$
Hydrodynamic Radius ($R_H$) 9.7 Å

S65
Figure S60. $^1$H–$^1$H COSY NMR spectrum (400 MHz, D$_2$O, 298 K) of helicate Zn–9•SO$_4$.

Figure S61. $^{19}$F NMR spectrum (376 MHz, D$_2$O, 298 K) of helicate Zn–9•SO$_4$. 
Figure S62. ESI-MS spectrum of helicate Zn–9 SO₄ recorded in H₂O.

Subcomponent H (5.4 mg, 0.016 mmol, 7.2 equiv), tris(3-aminopropyl)amine (TRPN) (1.6 µL, 0.008 mmol, 4 equiv), cadmium(II) sulfate (1.7 mg, 0.008 mmol, 4 equiv), and 2.0 mL of 3:1 CH₃CN/H₂O were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles, sonicated for 20 minutes and heated at 80°C for 36 h yielding a yellow-mustard suspension. The solid (likely unreacted aldehyde H and oligomeric material) was removed by filtration using a small column with celite. Excess of CH₃CN was added to the bright yellow liquor leading to precipitation of yellow solid. The mixture was centrifuged and the supernatant CH₃CN/H₂O was removed. The precipitate was washed with CH₂Cl₂, centrifuged and the supernatant decanted; this process was repeated with Et₂O, and carried out two times with CH₃CN. Finally, the excess of solvents was removed by a gentle flow of N₂ gas yielding cage Cd-14•SO₄ as a microcrystalline yellow solid (5.1 mg, yield 69%). 1H NMR (400 MHz, D₂O, 298 K): δ = 8.93 (s, 3J₁H-113Cd = 21.1 Hz, 12H, imine-Hₐ), 8.40 (br, 12H, Py-Hc), 8.19 (d, 3J₁H-1H = 7.7 Hz, 12H, Py-Hb), 7.43 (s, 12H, Py-Hd), 4.00 (d, 3J₁H-1H = 11.9 Hz, 12H, TRPN-He), 3.58 (m, 24H, TRPN-He, Hf), 2.43 (m, 12H, TRPN-Hf), 2.32 (d, 3J₁H-1H = 10.5 Hz, 12H, TRPN-Hg), 2.00 (d,
\(^2J_{^1H-^1H} = 14.2 \text{ Hz}, 12 \text{H}, \text{TRPN-Hg})\). \(^{13}\text{C}\) NMR (100 MHz, D\(_2\)O, 298 K): \(\delta = 163.8, 151.7, 151.3, 143.1, 138.6, 128.2, 121.7, 118.1, 63.7, 58.2, 25.9\). \(^{19}\text{F}\) NMR (376 MHz, D\(_2\)O, 298 K): \(\delta = -142.9\). DOSY Diffusion coefficient = \(1.80 \times 10^{-10} \text{ m}^2/\text{s}\). ESI-MS (H\(_2\)O): \(m/z = 393.3 \ [\text{Cd-14}]^{+8}, 539.8 \ [\text{Cd-14}(\text{CHO}_2)]^{+6}, 548.6 \ [\text{Cd-14}(\text{CHO}_2)(\text{HSO}_4)]^{+6}, 658.6 \ [\text{Cd-14}(\text{CHO}_2)_2(\text{HSO}_4)]^{+5}, 667.1 \ [\text{Cd-14}(\text{CHO}_2)_2(\text{HSO}_4)]^{+5}, 677.7 \ [\text{Cd-14}(\text{CHO}_2)(\text{HSO}_4)_2]^{+5}, 845.3 \ [\text{Cd-14}(\text{CHO}_2)_3(\text{HSO}_4)]^{+4}, 858.3 \ [\text{Cd-14}(\text{CHO}_2)_2(\text{HSO}_4)_2]^{+4}\). Elemental analysis (\%) calcd for C\(_{144}\)H\(_{120}\)Cd\(_4\)F\(_{24}\)N\(_{28}\)O\(_{16}\)S\(_4\)•8H\(_2\)O: C 47.04, H 3.73, N 10.67; found: C 46.96, H 3.58, N 10.45.

**Figure S63.** \(^1\text{H}\) NMR spectrum (400 MHz, D\(_2\)O, 298 K) of tetrahedron Cd–14•SO\(_4\).
Figure S64. $^1$H DOSY NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Cd–14•SO$_4$.

Figure S65. $^1$H–$^1$H COSY NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Cd–14•SO$_4$. 

Diff. Coeff. ($D$) $1.80 \times 10^{-10}$ m/s$^2$

Hydrodynamic Radius ($R_H$) 13.6 Å
Figure S66. $^{19}$F NMR spectrum (376 MHz, D$_2$O, 298 K) of tetrahedron Cd–14•SO$_4$.

Figure S67. ESI-MS spectrum of tetrahedron Cd–14•SO$_4$ recorded in H$_2$O.
Figure S68. $^1$H NMR spectrum (400 MHz, CD$_3$CN, 298 K) of tetrahedron Cd–14•OTf, sample obtained upon anion exchange with LiOTf from water-soluble cage Cd–14•SO$_4$.

Figure S69. ESI-MS spectrum of tetrahedron Cd–14•OTf recorded in CH$_3$CN; sample obtained upon anion exchange with LiOTf from water-soluble cage Cd–14•SO$_4$. 
5.5 Reactions of aldehyde D to form tetrahedra Zn–10•SO₄ and Cd–15•SO₄

Subcomponent D (7.2 mg, 0.018 mmol, 4 equiv), tris(2-aminoethyl)amine (TREN) (2.8 μL, 0.018 mmol, 4 equiv), zinc(II) sulfate heptahydrate (5.2 mg, 0.018 mmol, 4 equiv), and 1.8 mL of 1:1 CH₃CN/H₂O were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles, sonicated for 20 minutes and heated at 85°C overnight yielding a light yellow solution mixed with a small amount of insoluble material. This solid was removed by filtration using a small column with celite, and excess of CH₃CN was added to the bright yellow liquor leading to precipitation of a creamy solid. The mixture was centrifuged and the supernatant CH₃CN/H₂O was decanted. To remove the excess of unreacted aldehyde D and TREN, the solid was washed with CH₂Cl₂, centrifuged and the supernatant decanted; this process was carried out a second time with Et₂O, and a two times more with CH₃CN. Finally, the excess of solvents was removed by a gentle flow of N₂ gas yielding cage Zn-10•SO₄ as a microcrystalline white solid (10.8 mg, yield 91%).

**¹H NMR** (400 MHz, D₂O, 298 K): δ = 9.01 (s, 12H, imine-Ηα), 8.47 (m, 12H, Py-Ηc), 8.46 (m, 12H, Py-Ηb), 7.37 (s, 12H, Py-Ηh), 7.26 (s, 12H, Py-Ηc), 4.03 (m, 12H, TREN-Ηe), 3.82 (d, 2JΗ-Η = 10.1 Hz, 12H, TREN-Ηe), 3.36 (d, 2JΗ-Η = 12.3 Hz, 12H, TREN-Ηf), 3.09 (m, 12H, TREN-Ηf).

**¹³C NMR** (100 MHz, D₂O, 298 K): δ = 163.1, 148.0, 145.6, 137.6, 137.5, 131.5.
136.7, 129.7, 124.7, 56.9, 54.9. DOSY Diffusion coefficient = $1.85 \times 10^{-10}$ m$^2$/s. ESI-MS (H$_2$O): $m/z = 275.5$ [Zn-10]$^{+8}$, 336.1 [Zn-10(OTf)$]^+7$, 383.2 [Zn-10(SO$_4$)]$^{+6}$, 428.3 [Zn-10(BF$_4$)(NTf$_2$)]$^{+6}$, 502.9 [Zn-10(BF$_4$)(TFA)$_2$]$^{+5}$, 598.9 [Zn-10(SO$_4$)$_2$]$^{+4}$, 665.1 [Zn-10(TFA)$_4$]$^{+4}$. Elemental analysis (%) calcd for C$_{120}$H$_{108}$N$_{28}$O$_{16}$S$_4$Zn$_4$•4H$_2$O•CH$_3$CN: C 54.25, H 4.44, N 15.04; found: C 54.38, H 4.56, N 15.12.

Figure S70. $^1$H NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Zn–10•SO$_4$. 
Figure S71. $^1$H DOSY NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Zn–10•SO$_4$.

Figure S72. $^1$H–$^1$H COSY NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Zn–10•SO$_4$.  

Diff. Coeff. ($D$) $1.85 \times 10^{-10}$ m/s$^2$

Hydrodynamic Radius ($R_H$) 13.3 Å
Subcomponent D (6.0 mg, 0.015 mmol, 4 equiv), tris(3-aminopropyl)amine (TRPN) (2.9 μL, 0.015 mmol, 4 equiv), cadmium(II) sulfate (3.2 mg, 0.015 mmol, 4 equiv), and 2.0 mL of 1:1 CH₃CN/H₂O were placed in a Schlenk flask. The mixture was degassed by three evacuation/nitrogen fill cycles, sonicated for 20 minutes and heated at 80°C overnight yielding a light yellow solution mixed with a small amount of insoluble material. This solid was removed by filtration using a small column with celite, and excess of CH₃CN was added to the bright yellow liquor leading to precipitation of a yellow solid. The mixture was centrifuged and the supernatant CH₃CN/H₂O was decanted. To remove the excess of unreacted aldehyde D and TRPN, the solid was washed with CH₂Cl₂, centrifuged and the supernatant decanted; this process was carried out a second time with Et₂O, and two times more with CH₃CN. Finally, the excess of solvents was removed by a gentle flow of N₂ gas yielding cage Cd-15•SO₄ as a microcrystalline yellow solid (9.5 mg, yield 85%). ¹H NMR (400 MHz, D₂O, 298 K): δ = 8.97 (s, 3 J₁H–₁₁₃Cd = 21.1 Hz, 12H, imine-Hₐ), 8.48 (m, 12H, Py-Hc), 8.43 (m, 12H, Py-Hb), 7.39 (s, 12H, Py-Hd), 7.21 (s, 12H, Py-Hh), 4.01 (d, 2 J₁H–₁H = 10.9 Hz, 12H, TRPN-He), 3.71–3.55 (m, 24H, TRPN-He, Hf), 2.46 (m, 12H, TRPN-Hf), 2.31 (d, 2 J₁H–₁H = 12.4 Hz, 12H, TRPN-Hg), 2.02 (d, 2 J₁H–₁H = 12.7 Hz, 12H, TRPN-Hg).
$^{13}$C NMR (100 MHz, D$_2$O, 298 K): δ = 162.5, 148.2, 145.7, 137.3, 137.0, 129.5, 123.8, 62.8, 59.0, 26.1. DOSY Diffusion coefficient = $1.67 \times 10^{-10}$ m$^2$/s. ESI-MS (H$_2$O): $m/z = 319.8$ [Cd-15]$^{+8}$, 371.0 [Cd-15(Cl)]$^{+7}$, 442.6 [Cd-15(SO$_4$))$^{+6}$, 532.4 [Cd-15(Cl)$_3$]$^{+5}$, 668.1 [Cd-15 (SO$_4$)$_2$]$^{+4}$. Elemental analysis (%) calcd for C$_{132}$H$_{132}$Cd$_4$N$_{28}$O$_{16}$S$_4$•5.5H$_2$O: C 52.09, H 4.74, N 12.89; found: C 52.19, H 4.68, N 12.70.

Figure S74. $^1$H NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Cd–15•SO$_4$. 
Figure S75. $^1$H DOSY NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Cd–15•SO$_4$.

Figure S76. $^1$H–$^1$H COSY NMR spectrum (400 MHz, D$_2$O, 298 K) of tetrahedron Cd–15•SO$_4$.
**Figure S77.** ESI-MS spectrum of tetrahedron Cd–15•SO₄ recorded in H₂O.

**Figure S78.** ESI-MS spectrum of tetrahedron Cd–15•OTf recorded in CH₃CN. Sample obtained upon anion exchange with LiOTf from water-soluble cage Cd–15•SO₄.
6. X–ray Crystallography

All attempts to obtain suitable crystals for X-ray diffraction studies from aqueous solutions of the water-soluble sulfate capsules were unsuccessful; all crystalline samples were obtained from acetonitrile solutions of cages. Generally, sulfate cages were dissolved in pure water and subjected to anion metathesis reactions with LiOTf, the resulting triflate coordination capsules were purified, dried and dissolved and these solutions were used to grow crystals. Notably, the obtained crystallographic evidence confirms the presence of the diverse self-assembled frameworks within the original sulfate compounds and the robustness of the structures prepared that can travel through solution–solid phases within a system.

Data were collected either using a Bruker D8 VENTURE equipped with high-brilliance IµS Cu-Kα radiation (1.54178 Å), with ω and ψ scans at 180(2) K or at Beamline I19 of Diamond Light Source employing silicon double crystal monochromated synchrotron radiation (0.6889 Å) with ω scans at 100(2) K.\(^\text{13}\) Data integration and reduction were undertaken with SAINT and XPREP\(^\text{14}\) or Xia2.\(^\text{15}\) Subsequent computations were carried out using the WinGX-32 graphical user interface.\(^\text{16}\) Multi-scan empirical absorption corrections were applied to the data using SADABS\(^\text{14}\) or the AIMLESS tool in the CCP4 suite. Structures were solved by direct methods using SHELXT-2016\(^\text{17}\) then refined and extended with SHELXL-2016.\(^\text{18}\) In general, non-hydrogen atoms with occupancies greater than 0.5 were refined anisotropically. Carbon-bound hydrogen atoms were included in idealized positions and refined using a riding model. Disorder was modelled using standard crystallographic methods including constraints, restraints and rigid bodies where necessary. Crystallographic data along with specific details pertaining to the refinement follow. Crystallographic data have been deposited with the CCDC (1837541-1837547).
6.1 Crystallographic data and refinement details for cube Co–I

**[Co₈L₆]·16OTf·11.5MeCN·16C₆H₆·5.75H₂O**

Formula | $\text{C}_{543}\text{H}_{406}\text{Co}_{8}\text{F}_{48}\text{N}_{83.50}\text{O}_{53.75}\text{S}_{16}\text{Zn}_{6}$ | $M = 11249.11$, Tetragonal, space group $\text{P 4/n (}\#85\text{)}$, $a = 34.300(5)$, $b = 34.300(5)$, $c = 27.428(6)$ Å, $V = 32269(11)$ Å$^3$, $\Delta c$ 1.158 g cm$^{-3}$, $Z = 2$, crystal size 0.050 by 0.050 by 0.010 mm, colour brown, habit block, temperature 100(2) K, $\lambda$(Synchrotron) 0.6889 Å, $\mu$(Synchrotron) 0.500 mm$^{-1}$, $T$(Analytical)$_{\text{min,max}}$ 0.952391076963, 1.0, $2\theta$$_{\text{max}}$ 45.00, $hkl$ range -38 38, -36 36, -30 27, $N$ 130101, $N_{\text{ind}}$ 22840($R_{\text{merge}}$ 0.0341), $N_{\text{obs}}$ 16227($I > 2\sigma(I)$), $N_{\text{var}}$ 2077, residuals $^*$ $R1(F)$ 0.1019, $wR2(F^2)$ 0.3215, GoF(all) 1.078, $\Delta\rho_{\text{min,max}}$ -1.698, 1.678 e$^-\text{Å}^{-3}$.

$^*R1 = \Sigma||F_O|| - |F_C||/\Sigma|F_O|$ for $F_O > 2\sigma(F_O)$; $wR2 = (\Sigma w(F_O^2 - F_C^2)^2/\Sigma(wF_C^2)^2)^{1/2}$ all reflections

\[w=1/[\sigma^2(F_O^2)+(0.2000P)^2+35.0000P]\] where P=$\left(F_O^2+2F_C^2\right)/3$

**Refinement details** The crystals of [Co₈L₆]·16OTf·11.5MeCN·16C₆H₆·5.75H₂O were grown by diffusion of benzene into an acetonitrile solution of [Co₈L₆]·16OTf. The crystals immediately lost solvent after removal from the mother liquor and rapid handling prior to flash cooling in the cryostream was required to collect data. Despite these measures and the use of synchrotron radiation few reflections at greater than 0.9 Å resolution were observed. The asymmetric unit was found to contain one quarter of a Co₈L₆ assembly and associated counterions and solvent molecules. The anions within the structure show evidence of substantial disorder. All triflate anions were modelled as disordered over up to four locations and some anions were modelled with partial occupancy. The occupancies of these partial occupancy anions were allowed to refine freely and then fixed at the obtained values. Any additional minor occupancy positions of these anions could not be located in the electron density map due to the limited resolution of the data. Many of the solvent molecules were also modelled as disordered and/or with partial occupancy. Substantial
bond length and thermal parameter restraints were applied to facilitate a reasonable refinement of the disordered triflate anions and solvent molecules and most low occupancy disordered groups were modelled with isotropic thermal parameters. Thermal parameter restraints (SIMU, RIGU) were also applied to all atoms except for cobalt and zinc. The hydrogen atoms of some water molecules could not be located in the electron density map and were therefore not included in the model.

Further reflecting the solvent loss and poor diffraction properties there is a significant amount of void volume in the lattice containing smeared electron density from disordered solvent. Consequently the SQUEEZE\textsuperscript{19} function of PLATON\textsuperscript{20} was employed to remove the contribution of the electron density associated with this highly disordered solvent, which gave a potential solvent accessible void of 5547 Å\textsuperscript{3} per unit cell (a total of approximately 1621 electrons). Since the diffuse solvent molecules could not be assigned conclusively to acetonitrile or benzene only those solvent molecules that could be modelled with discrete atom positions were included in the formula. Consequently, the molecular weight and density given above are likely to be underestimated. The remaining electron density peaks and holes (up to 1.678 e\textsuperscript{−} Å\textsuperscript{3}) are close to the zinc centres reflecting absorption effects or a small amount of unresolved disorder.

CheckCIF gives one A and five B level alerts. The A level alert arises from irregular bond lengths in a benzene molecule located on a special position for which some additional minor disorder was not modelled. The B level alerts arise from the limited resolution of the data, further disorder in some solvent molecules and formula discrepancies arising from minor occupancy positions of disordered anions that could not be modelled as described above.
Figure S79. Cationic part of the crystal structure of cube Co–1, as viewed down a face. Counterions, solvents and disordered fragments are omitted for clarity. Co$^{II}$ and Zn$^{II}$ centres are coloured dark orange and cyan respectively.

Figure S80. View of the cationic part of the crystal structure of cube Co–1, as viewed down a Co$^{II}$ corner (left) and space-filling view of Co–1, as viewed down an edge (right). Counterions, solvents and disordered fragments are omitted for clarity. Co$^{II}$ and Zn$^{II}$ centres are coloured dark orange and light blue respectively.
6.2 Crystallographic data and refinement details for cube Ni–I

[Ni₈L₆]·16OTf·10.25MeCN·14.5C₆H₆·5.25H₂O

Formula $C_{531.50}H_{392.25}F_{48}N_{82.25}O_{53.25}S_{16}Zn_{6}$, $M$ 11069.86, Tetragonal, space group P 4/n (#85), $a$ 34.210(5), $b$ 34.210(5), $c$ 27.215(5) Å, $V = 31852(11)$ Å$^3$, $D_c$ 1.154 g cm$^{-3}$, $Z$ 2, crystal size 0.040 by 0.020 by 0.020 mm, colour green brown, habit block, temperature 100(2) K, $\lambda$(Synchrotron) 0.6889 Å, $\mu$(Synchrotron) 0.531 mm$^{-1}$, $T$(Analytical)$_{\text{min,max}}$ 0.952391076963, 1.0, $2\theta_{\text{max}}$ 40.72, $hkl$ range -34 34, -34 34, -27 27, $N$ 109166, $N_{\text{ind}}$ 17157 ($R_{\text{merge}}$ 0.0428), $N_{\text{obs}}$ 11538 ($I > 2\sigma(I)$), $N_{\text{var}}$ 2025, residuals

$R1(F) = 0.1211$, $wR2(F^2) = 0.3533$, GoF(all) 1.054, $\Delta\rho_{\text{min,max}}$ -0.743, 0.832 e$^{-}$ Å$^{-3}$. 

$R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections

$w = 1/[(\sigma^2(F_o^2) + (0.2000P)^2 + 50.0000P)]$ where $P = (F_o^2 + 2F_c^2)/3$

Refinement details] The crystals of [Ni₈L₆]·16OTf·10.25MeCN·14.5C₆H₆·5.25H₂O were grown by diffusion of benzene into an acetonitrile solution of [Ni₈L₆]·16OTf. The crystals immediately lost solvent after removal from the mother liquor and rapid handling prior to flash cooling in the cryostream was required to collect data. Despite these measures and the use of synchrotron radiation few reflections at greater than 0.99 Å resolution were observed. The asymmetric unit was found to contain one quarter of a Ni₈L₆ assembly and associated counterions and solvent molecules. The crystals were isomorphous to those of [Co₈L₆]·16OTf·11.5MeCN·16C₆H₆·5.75H₂O except for the occupancies of some disordered anions and solvent molecules. The anions within the structure show evidence of substantial disorder. All triflate anions were modelled as disordered over up to four locations and some anions were modelled with partial occupancy. The occupancies of these partial occupancy anions were allowed to refine freely and then fixed at the obtained values. Any additional minor occupancy positions of these anions could not be located in
the electron density map due to the limited resolution of the data. Many of the solvent molecules were also modelled as disordered and/or with partial occupancy. Substantial bond length and thermal parameter restraints were applied to facilitate a reasonable refinement of the disordered triflate anions and solvent molecules and most low occupancy disordered groups were modelled with isotropic thermal parameters. Thermal parameter restraints (SIMU, RIGU) were also applied to all atoms except for nickel and zinc. The hydrogen atoms of some water molecules could not be located in the electron density map and were therefore not included in the model.

Further reflecting the solvent loss and poor diffraction properties there is a significant amount of void volume in the lattice containing smeared electron density from disordered solvent. Consequently the SQUEEZE\textsuperscript{19} function of PLATON\textsuperscript{20} was employed to remove the contribution of the electron density associated with this highly disordered solvent, which gave a potential solvent accessible void of 5222 Å\textsuperscript{3} per unit cell (a total of approximately 1148 electrons). Since the diffuse solvent molecules could not be assigned conclusively to acetonitrile or benzene only those solvent molecules that could be modelled with discrete atom positions were included in the formula. Consequently, the molecular weight and density given above are likely to be underestimated.

CheckCIF gives three A and fourteen B level alerts. These alerts (both A and B level) result from the limited data resolution and thermal motion and/or unresolved disorder of some anions and solvent molecules as described above.
Figure S81. Cationic part of the crystal structure of cube Ni–1, as viewed down a face. Counterions, solvents and disorder are omitted for clarity. Ni\textsuperscript{II} and Zn\textsuperscript{II} centres are coloured green and light blue respectively.

Figure S82. View of the cationic part of the crystal structure of cube Ni–1, as viewed down a Ni\textsuperscript{II} corner (left) and space-filling view of Ni–1, as viewed down an edge (right). Counterions, solvents and disordered fragments are omitted for clarity. Ni\textsuperscript{II} and Zn\textsuperscript{II} centres are coloured green and light blue respectively.
6.3 Crystallographic data and refinement details for tetrahedron Ni–3

\[ \text{[Ni}_4\text{L}_6\text{]}\cdot5\text{OTf}\cdot3\text{BF}_4\cdot5.25\text{MeCN}\cdot0.25\text{Et}_2\text{O} \]

Formula \( \text{C}_{160.50}\text{H}_{126.25}\text{B}_3\text{F}_{27}\text{N}_{29.25}\text{Ni}_4\text{O}_{15.25}\text{S}_5 \), \( M = 3649.22 \), Monoclinic, space group \( \text{C 2/c (} \#15 \) ), \( a 34.257(7) \), \( b 18.552(4) \), \( c 54.149(11) \) Å, \( \beta 97.09(3) \), \( V = 34150(12) \) Å\(^3\), \( D_c 1.420 \text{ g cm}^{-3} \), \( Z 8 \), crystal size 0.005 by 0.001 by 0.001 mm, colour pale yellow, habit plate, temperature 100(2) K, \( \lambda \text{(Synchrotron)} 0.6889 \) Å, \( \mu \text{(Synchrotron)} 0.543 \text{ mm}^{-1} \), \( T \text{(Analytical)} \) min,max 0.98254939378, 1.0, \( 2\theta \text{max} 47.22 \), \( hkl \) range -39 38, -21 21, -56 62, \( N 113743 \), \( N_{\text{ind}} 27632(R_{\text{merge}} 0.0445) \), \( N_{\text{obs}} 18606(I > 2\sigma(I)) \), \( N_{\text{var}} 2489 \), residuals \(* R1(F) 0.0817, wR2(F^2) 0.2765, \text{GoF(all) 1.075, } \Delta\rho_{\text{min,max}} -0.741, 0.899 \text{ e}^- \text{ Å}^{-3} \).

\( \ast \) \( R1 = \Sigma||F_o|| - |F_c||/\Sigma|F_o|| \) for \( F_o > 2\sigma(F_o) \); \( wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2} \) all reflections

\( w=1/[\sigma^2(F_o^2)+(0.2000P)^2] \) where \( P=(F_o^2+2F_c^2)/3 \)

**Refinement details** The crystals of [Ni\(_4\)L\(_6\)]\cdot5OTf\cdot3BF\(_4\)\cdot5.25MeCN\cdot0.25Et\(_2\)O were grown by diffusion of diethyl ether into an acetonitrile solution of [Ni\(_4\)L\(_6\)]\cdot8OTf containing LiBF\(_4\). The crystals immediately lost solvent after removal from the mother liquor and rapid handling prior to flash cooling in the cryostream was required to collect data. The asymmetric unit was found to contain one complete Ni\(_4\)L\(_6\) assembly and associated counterions and solvent molecules.

The triflate anions within the structure show evidence of substantial disorder. Four triflate anions were modelled as disordered over multiple locations and/or with partial occupancy; one of these anions was also further disordered over a special position. Two acetonitrile molecules were modelled as disordered over three locations each and a further partial occupancy solvent molecule was modelled as a mixture of acetonitrile and diethyl ether. Substantial bond length and thermal parameter restraints were applied to facilitate a
reasonable refinement of the disordered triflate anions and solvent molecules and most low occupancy disordered groups were modelled with isotropic thermal parameters. Thermal parameter restraints (SIMU, RIGU) were also applied to all atoms except for nickel.

CheckCIF gives five B level alerts. These alerts all result from thermal motion and/or minor unresolved disorder of some anions.

Figure S83. View of the cationic part of the crystal structure of tetrahedron Ni–3 showing an encapsulated BF$_4^-$ anion, as viewed down an edge (left) and as space-filling representation viewed down a face (right). Counterions, solvents and disorder are omitted for clarity.
6.4 Crystallographic data and refinement details for helicate Zn–7

\([\text{Zn}_2\text{L}_3] \cdot 2.5\text{SbF}_6 \cdot 1.5\text{OTf} \cdot 1.5\text{MeCN}\)

Formula \(\text{C}_{70.50}\text{H}_{64.50}\text{F}_{19.50}\text{N}_{15.50}\text{O}_{4.50}\text{S}_{1.50}\text{Sb}_{2.50}\text{Zn}_2\), \(M = 2054.58\), Monoclinic, space group \(\text{C} 2\) (#5), \(a\ 32.3977(13), b\ 31.6390(13), c\ 22.0583(9) \text{ Å}, \beta 123.314(2), V = 18894.9(14) \text{ Å}^3, D_c 1.444 \text{ g cm}^{-3}, Z 8\), crystal size 0.390 by 0.300 by 0.030 mm, colourless, habit plate, temperature 180(2) K, \(\lambda\text{(CuK}\alpha)\ 1.54178 \text{ Å}, \mu\text{(CuK}\alpha)\ 7.258 \text{ mm}^{-1}\), \(T(\text{SADABS})_{\text{min,max}}\ 0.3713, 0.7522, 2\theta_{\text{max}} 117.86, hkl\ range -34 35, -34 35, -24 21, N 56673, \(N_{\text{ind}}\ 25343(\text{R}_{\text{merge}}\ 0.0533), N_{\text{obs}}\ 19795(I > 2\sigma(I)), N_{\text{var}}\ 2229, \) residuals \(*R1(F)\ 0.0751, wR2(F^2)\ 0.2177, \text{GoF(all)}\ 1.036, \Delta\rho_{\text{min,max}}\ -1.348, 0.898 \text{ e}^{-} \text{ Å}^{-3}\).

\(*R1 = \Sigma ||F_o|| - |F_c|/\Sigma |F_o|\ for\ F_o > 2\sigma(F_o);\ wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma (wF_c^2)^2)^{1/2}\ all\ reflections\)

\(w=1/[\sigma^2(F_o^2)+0.1277P]^2+64.5576P]\) where \(P=(F_o^2+2F_c^2)/3\)

Refinement details The crystals of \([\text{Zn}_2\text{L}_3] \cdot 2.5\text{SbF}_6 \cdot 1.5\text{OTf} \cdot 1.5\text{MeCN}\) were grown by diffusion of diisopropyl ether into an acetonitrile solution of \([\text{Zn}_2\text{L}_3] \cdot 4\text{OTf}\) containing excess K\text{SbF}_6. The crystals immediately lost solvent after removal from the mother liquor and rapid handling prior to flash cooling in the cryostream was required to collect data. Despite these measures and the use of a high intensity laboratory source few reflections at greater than 0.9 \text{ Å} resolution were observed. Nevertheless, the quality of the data is far more than sufficient to establish the connectivity of the structure. The asymmetric unit was found to contain two complete \text{Zn}_2\text{L}_3\ assemblies and associated counterions and solvent molecules. Due to the limited resolution bond lengths and angles within pairs of chemically identical organic ligands were restrained to be similar to each other and thermal parameter restraints (SIMU, RIGU) were applied to all atoms except for zinc and antimony.

The anions within the structure show evidence of substantial disorder. All anions were modeled as disordered over up to four locations and some anions were modelled with partial occupancy. Some anion lattice sites were modelled as a disordered mixture of S88
hexafluoroantimonate and triflate. The occupancies of partial occupancy anions were allowed to refine freely and then fixed at the obtained values. Any additional minor occupancy positions of these anions could not be located in the electron density map due to the limited resolution of the data and high levels of disorder. The acetonitrile solvent molecules were also modelled as disordered over two or three locations. Substantial bond length and thermal parameter restraints were applied to facilitate a reasonable refinement of the disordered anions and solvent molecules and most low occupancy disordered groups were modelled with isotropic thermal parameters.

Further reflecting the solvent loss and poor diffraction properties there is a significant amount of void volume in the lattice containing smeared electron density from disordered solvent. Consequently the SQUEEZE\textsuperscript{19} function of PLATON\textsuperscript{20} was employed to remove the contribution of the electron density associated with this highly disordered solvent, which gave a potential solvent accessible void of 3156 \AA\textsuperscript{3} per unit cell (a total of approximately 1127 electrons). Since the diffuse solvent molecules could not be assigned conclusively to acetonitrile or diisopropyl ether only those solvent molecules that could be modelled with discrete atom positions were included in the formula. Consequently, the molecular weight and density given above are likely to be underestimated.

CheckCIF gives one A and four B level alerts. These alerts (both A and B level) result from the limited data resolution and thermal motion and/or unresolved disorder of some anions and solvent molecules as described above.
**Figure S84.** Two views of the cationic part of the crystal structure of helicate Zn–7, stick (left) and space-filling (right) representations. Counterions, solvents and disorder are omitted for clarity.

### 6.5 Crystallographic data and refinement details for helicate Zn–8

\([\text{Zn}_2\text{L}_3]\cdot\text{SbF}_6\cdot3.833\text{OTf}\cdot1.5\text{MeCN}\cdot0.833\text{K}\)

Formula \(C_{78.83}H_{76.50}F_{17.50}K_{0.83}N_{15.50}O_{11.50}S_{3.83}\text{SbZn}_2\), \(M = 2165.52\), Trigonal, space group R\(-3\) (#148), \(a\ 14.930(2), b\ 14.930(2), c\ 68.868(14) \text{Å}, \gamma 120^\circ, V = 13294(5) \text{Å}^3\), \(D_c\ 1.623 \text{ g cm}^{-3}\), \(Z\ 6\), crystal size 0.005 by 0.003 by 0.002 mm, colour colourless, habit prism, temperature 100(2) K, \(\lambda\) (Synchrotron) 0.6889 Å, \(\mu\) (Synchrotron) 0.980 mm\(^{-1}\), \(T\) (Analytical)\(\text{min,max}\) 0.987425612782, 1.0, \(2\theta_{\text{max}}\) 58.94, \(hkl\) range \(-21 16, -16 21, -97 94\), \(N\ 38333, N\text{ind} 8890(R_{\text{merge}} 0.0688), N_{\text{obs}} 7682(I > 2\sigma(I)), N_{\text{var}} 539, \text{residuals}^* R1(F) 0.0516, wR2(F^2) 0.1639, \text{GoF(all)} 1.132, \Delta\rho_{\text{min,max}} -0.636, 1.271 e^- \text{Å}^{-3}\).
Refinement details] The crystals of [Zn$_2$L$_3$]·SbF$_6$·3.833OTf·1.5MeCN·0.833K were grown by diffusion of diisopropyl ether into an acetonitrile solution of [Zn$_2$L$_3$]·4OTf containing excess K$_2$SbF$_6$. The crystals immediately lost solvent after removal from the mother liquor and rapid handling prior to flash cooling in the cryostream was required to collect data. The asymmetric unit was found to contain one third of a Zn$_2$L$_3$ assembly and associated counterions and solvent molecules.

The anions and solvent molecules within the structure show evidence of substantial disorder. All anions were modelled as disordered over up to three locations and two anion lattice sites show further disorder around symmetry positions. Two anion lattice sites were modelled as a disordered mixture of hexafluoroantimonate and triflate. The occupancies of partial occupancy anions and potassium cations were allowed to refine freely. The additional minor occupancy positions of the anions required for charge balance could not be located in the electron density map due to their low occupancy and high levels of disorder resulting in a small discrepancy between the calculated and reported molecular weights. Substantial bond length and thermal parameter restraints were applied to facilitate a reasonable refinement of the disordered anions and solvent molecules and most low occupancy disordered groups were modelled with isotropic thermal parameters.

CheckCIF gives two A and one B level alerts. These alerts (both A and B level) result from anion disorder and formula discrepancies arising from minor occupancy positions of disordered anions that could not be modelled as described above.
Figure S85. Two views of the cationic part of the crystal structure of helicate Zn–8, stick (left) and space-filling (right) representations. Counterions, solvents and disorder are omitted for clarity.

6.6 Crystallographic data and refinement details for tetrahedron Cd–12

[Cd₄L₆]·8OTf

Formula C₁₅₂H₁₄₄Cd₄F₂₅N₂₈O₂₄S₈, M = 3909.02, Cubic, space group F -4 3 c (#219), a 34.3297(7), b 34.3297(7), c 34.3297(7) Å, V = 40459(2) Å³, D_c 1.284 g cm⁻³, Z 8, crystal size 0.170 by 0.160 by 0.160 mm, colour colourless, habit prism, temperature 180(2) K, λ(CuKα) 1.54178 Å, μ(CuKα) 4.817 mm⁻¹, T(SADABS)min,max 0.6306, 0.7528, 2θmax 133.57, hkl range -40 40, -38 40, -40 28, N 29643, N_ind 2961(R_merge 0.0287), N_obs 2668(I > 2σ(I)), N_var 149, residuals* R1(F) 0.0400, wR2(F²) 0.1103, GoF(all) 1.043, Δρ_min,max -0.553, 0.254 e⁻ Å⁻³.
\[ R1 = \frac{\sum |F_o| - |F_c|/\Sigma|F_o|}{2\sigma(F_o)} \] for \( F_o > 2\sigma(F_o); \)

\[ wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2} \]

all reflections

\[ w = 1/\left[ \sigma^2(F_o^2) + (0.0543P)^2 + 105.4221P \right] \]

where \( P = (F_o^2 + 2F_c^2)/3 \)

**Refinement details** The crystals of \([Cd_4L_6]^-8OTf\) were grown by diffusion of diisopropyl ether into an acetonitrile solution of the complex. The crystals immediately lost solvent after removal from the mother liquor and rapid handling prior to flash cooling in the cryostream was required to collect data. The asymmetric unit was found to contain one twelfth of a \(Cd_4L_4\) assembly. The central phenyl ring of the ligand was modelled as disordered over a special position with the occupancy of each part fixed at 0.5 by symmetry. Some bond length restraints (DFIX) were required in order to obtain a reasonable model for the organic portion of the structure and thermal parameter restraints (SIMU, RIGU) were applied to all atoms except for cadmium. The anions and solvent within the lattice were significantly disordered and despite numerous attempts at modelling, including with rigid bodies no satisfactory model for the electron-density associated with them could be found. Therefore the SQUEEZE\(^{19}\) function of PLATON\(^{20}\) was employed to account for these highly disordered solvent and anions, which gave a potential solvent accessible void of 17857 Å\(^3\) per unit cell (a total of approximately 3768 electrons). Since the diffuse solvent molecules could not be assigned conclusively to acetonitrile or diisopropyl ether they were not included in the formula. Consequently, the molecular weight and density given above are likely to be underestimated.
**Figure S86.** View of the cationic part of the crystal structure of tetrahedron Cd–12, as viewed down an edge. Counterions, solvents and disorder are omitted for clarity.

**Figure S87.** Two views of the cationic part of the crystal structure of tetrahedron Cd–12, as viewed down a face in stick (left) and space-filling (right) representations. Counterions, solvents and disorder are omitted for clarity.
6.7 Crystallographic data and refinement details for tetrahedron Cd–14

\[ \text{[Cd}_4\text{L}_6]\text{·7SbF}_6\text{·OTf·4MeCN} \]

Formula \( \text{C}_{153}\text{H}_{132}\text{Cd}_4\text{F}_{69}\text{N}_{32}\text{O}_{3}\text{Sb}_7 \), \( M = 5111.81 \), Cubic, space group \( \text{P 21 3} \) (#198), \( a 26.441(3) \), \( b 26.441(3) \), \( c 26.441(3) \) Å, \( V = 18487(6) \) Å\(^3\), \( D_c 1.837 \) g cm\(^{-3}\), \( Z 4 \), crystal size 0.006 by 0.005 by 0.004 mm, colour colourless, habit prism, temperature 100(2) K, \( \lambda(\text{Synchrotron}) 0.6889 \) Å, \( \mu(\text{Synchrotron}) 1.448 \) mm\(^{-1}\), \( T(\text{Analytical})_{\min,\max} 0.9594\text{11743808} \), 1.0, \( 2\theta_{\max} 54.66 \), \( hkl \) range -34 35, -35 31, -35 28, \( N 148304 \), \( N_{\text{ind}} 15319(R_{\text{merge}} 0.1187) \), \( N_{\text{obs}} 13422(I > 2\sigma(I)) \), \( N_{\text{var}} 819 \), residuals* \( R_1(F) 0.0654, \)
\( wR_2(F^2) 0.1983 \), GoF(all) 1.024, \( \Delta \rho_{\min,\max} -2.718, 2.272 \text{ e}^{-}\text{Å}^{-3} \).

* \( R_1 = \sum |F_o| - |F_c|/\sum |F_o| \) for \( F_o > 2\sigma(F_o) \); \( wR_2 = (\sum w(F_o^2 - F_c^2)^2/\sum (wF_c^2)^2)^{1/2} \) all reflections
\( w=1/[(\sigma^2(F_o^2)+(0.1637P)^2)] \) where \( P=(F_o^2+2F_c^2)/3 \)

**Refinement details**| The crystals of \([\text{Cd}_4\text{L}_6]\text{·7SbF}_6\text{·OTf·4MeCN} \) were grown by diffusion of diethyl ether into an acetonitrile solution of \([\text{Cd}_4\text{L}_6]\text{·8OTf} \) containing excess K\text{SbF}_6. The crystals immediately lost solvent after removal from the mother liquor and rapid handling prior to flash cooling in the cryostream was required to collect data. The asymmetric unit was found to contain one third of a \( \text{Cd}_4\text{L}_4 \) assembly and associated counterions and solvent molecules. One anion lattice site was modelled as a disordered mixture of triflate and hexafluoroantimonate with bond length and thermal parameter restraints applied to the disordered moieties in order to facilitate a reasonable refinement. Thermal parameter restraints (SIMU, RIGU) were also applied to all atoms except for cadmium and antimony.

CheckCIF gives three B level alerts. These alerts all result from thermal motion and/or minor unresolved disorder of some anions.
Figure S88. View of the cationic part of the crystal structure of tetrahedron Cd–14, as viewed down an edge. Counterions, solvents and disorder are omitted for clarity.

Figure S89. Two views of the cationic part of the crystal structure of tetrahedron Cd–14, as viewed down a face in stick (left) and space-filling (right) representations. Counterions, solvents and disorder are omitted for clarity.

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7. Volume calculations

In order to determine the available void space within the water-soluble cubes, VOIDOO calculations based on their crystal structures were performed. We only carried out calculations\textsuperscript{21} on the Co-1 and Ni-1 cubes since these systems remain intact in water solution unlike the Zn-1 and Cd-1 cubes. A virtual probe of 1.4 Å (set by default, water-sized) was employed, and the standard parameters tabulated below were used.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum number of volume-refinement cycles</td>
<td>30</td>
</tr>
<tr>
<td>Minimum size of secondary grid</td>
<td>3</td>
</tr>
<tr>
<td>Grid for plot files</td>
<td>0.1</td>
</tr>
<tr>
<td>Primary grid spacing</td>
<td>0.1</td>
</tr>
<tr>
<td>Plot grid spacing</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The volume was thus calculated to be 1331 and 1324 Å\textsuperscript{3} for the Co-1 and Ni-1 cubes, respectively. The void volume for the Fe-1 cube was previously informed by our group.\textsuperscript{3}

![VOIDOO calculated void space](image)

**Figure S90.** VOIDOO calculated void space (shown in mesh) within the Co-1 (*left*) and Ni-1 (*right*) cubes obtained from the corresponding crystal structures.
8. References


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