Supporting Information

Metal-Organic Frameworks with Hexakis(4-carboxyphenyl)benzene – Extensions to Reticular Chemistry and Introducing Foldable Nets

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1. Experimental Section

1.1 Synthesis of the linker

Hexakis(4-carboxyphenyl)benzene 5 (H₆CPB) was prepared according to a literature-known procedure. The synthesis route of H₆CPB is shown in Figure S1. Methyl-4-iodobenzoate reacts in a first reaction step via Sonogashira cross coupling with trimethylsilylacetylene 2 to 1,4-bis(p-carbomethoxybenzene)-1,2-acetylene 3. Intermediate 3 reacted via cyclotrimerization reaction to ester 4, which was in a final step hydrolyzed to product 5.

Figure S1. Reaction scheme for hexakis(4-carboxyphenyl)benzene 5.

1.2 MOF syntheses

CTH-6, [Bi₂(cpb)(HOAc)₂(dmf)]₄ Bismuth (III) nitrate pentahydrate (19.44 mg, 0.020 mmol) and H₆cpb (16 mg, 0.020 mmol) in 4 mL of N-N’-dimethylformamide (dmf) were added to an 8
mL vial. This was followed by the addition of 1 mL of glacial acetic acid. The mixture was heated and stirred for few minutes. The solution was then transferred to a 10 mL Pyrex tube and heated at 120 °C for 3 days to produce colorless rectangular crystals. All preparations of CTH-6 were contaminated with a small amount of concomitantly occurring black phase interpreted as Bi(s) and we were not able to get high yields of CTH-6. PXRD also indicated the presence of another minor phase. TGA shows solvent loss between 80-200°C that is difficult to quantify due to the impurities. Both TGA and elemental analysis is consistent with a substantial amount of Bi formed. Elemental analysis: Calcd for C₆₄H₆₀Bi₃.₆N₄O₂₄ (with 0.8 eq of Bi₂O₃): C, 38.03; H, 2.99; N, 2.77. Found: C, 35.6; H, 3.6; N, 3.4).

**Synthesis of CTH-7, 2(Hdma)[Cu₂(cpdb)].** Copper nitrate trihydrate (9.683 mg, 0.020 mmol) in 4 mL dmf was added to a vial in which H₆cpb (16 mg, 0.020 mmol) was preloaded. The mixture was heated, stirred, and 1 mL glacial acetic acid and 1 mL distilled water was added. The solution was transferred to a 10 mL Pyrex tube then heated at 120 °C for 3 days. Light blue crystals were obtained. TGA shows a gradual mass loss from around 100 °C to 390 °C with final mass of 11.4% (calc; 15.7 %, with two extra dmf 13.7%) Elemental analysis: Calcd for C₅₈H₅₄Cu₂N₄O₁₄ (with two extra dmf): C, 60.15; H, 4.70; N, 4.84. Found: C, 60.1; H, 4.8; N, 5.4

**Synthesis of CTH-8, [Fe₄(cpdb)(acetato)₂(dmf)₄].** Fe(NO₃)₃·9H₂O (16.192 mg, 0.020 mmol) and (16 mg, 0.020 mmol) were placed in a 25 mL round-bottom flask. Dimethylformamide (dmf, 10 mL) and triethylamine (tea, 0.5 mL) were added. The mixture was stirred for 24h. Subsequently, 6 mL of glacial acetic acid was added, and the solution then heated at 150 °C. After 5 days yellow crystals were formed. Simulated and experimental powder X-ray diffraction (PXRD) are in good agreement, however TGA and elemental analysis indicate an impurity interpreted as co-precipitated H₆cpb. TGA shows a gradual mass loss from around 100 °C followed by a more abrupt
step at around 360° with final mass of 8.81 % (calc. 10.0% with extra two H6cpb and two dmf).
Calcd for C167H134Fe4N6O46 (with extra two H6cpb and two dmf): C, 62.99; H, 4.24; N, 2.64. Found: C, 64.3; H, 5.1; N, 2.1.

**Synthesis of CTH-9, [Co₄(cpbdacetato)₂(dmfg)].** Co(NO₃)₂·6H₂O (11.664 mg, 0.020 mmol) and H6cpb (16 mg, 0.020 mmol) were suspended in a 5 mL solution of a 4:1 dmf/glacial acetic acid using a 8 mL vial. The reaction mixture was heated and stirred for a few minutes for the solution to be cleared, then placed in a Pyrex tube for solvothermal synthesis at 120 °C. Purple crystals were observed after 3 days. TGA shows a multi-step mass loss of 28.6% from around 100° C corresponding to two acetic acid and two dmf (calc. 27.2%), followed by a more abrupt step at around 330° with a final mass of 23.08 % (calc; 23.1 %, with one extra dmf 22.0%). Calcd for C67H65Co₄N₅O₂₁ (one extra dmf added): C, 53.22; H, 4.33; N, 4.63. Found: C, 53.0; H, 4.3; N, 4.7.

**Synthesis of CTH-10, (HNEt₃)₂[Fe₂(cpbd)].** The synthesis of CTH-10 was conducted as for CTH-8, except that formic acid was used instead of glacial acetic acid. Within 5 days, orange crystals had formed. TGA show two distinct events potentially corresponding to two differently hydrogen boded NEt₃(eta) molecules leaving after proton transfer (13.9 %, calc. 18.3 %) and final mass of 19.8 % (calc; 14.4 %). Elemental analysis: Calcd for C₆₄H₅₆Fe₂N₂O₁₂: C, 64.99; H, 5.09; N, 2.53. Found: C, 65.4; H, 5.0; N, 2.1.

**Synthesis of Zn-MOF-888 and CTH-11 2(H₂NMe₂)[Zn₂(cpbd)].** Zn-MOF-888 and CTH-11 crystallized concomitantly in a one pot solvothermal synthesis. Zn(NO₃)₂·6H₂O (23.847 mg, 0.020 mmol) and H8cpb (16 mg, 0.020 mmol) were dissolved in 5 mL of N, N’-dimethylacetamide (dmac) and 1 mL of glacial acetic acid. The solution was sealed tightly and placed into an oven at 150 °C and indistinguishable colorless crystals of Zn-MOF-888 and CTH-11 were obtained. TGA shows mass loss in several steps of 11.4% (1.5 dmac cacl. 12.6%) and 7.9% (2 dma calc. 11.7%)
with a final mass of 12.8 % (calc. 14.1 %). Calcd for C_{58}H_{49}Zn_{2}N_{3}O_{13}: C, 60.77; H, 4.70; N, 4.28. Found: C, 60.99; H, 4.48; N, 3.81.

**Synthesis of CTH-12, [Cu_{2}(cph)(acetato)_{2}(dmf)_{2}]·2dmf.** The sample preparation was the same as CTH-7 but no distilled water was used, and the mixture was heated at 100 °C. Dark blue crystals were harvested after 3 days. TGA shows mass loss of 32.8 % in three gradually overlapping steps from 70°C to 280°C corresponding to four dmf and two acetic acid (calc. 30.9 %) with a final mass of 15.5 % (calc. 11.9 %). Calcd for C_{69}H_{73}Cu_{2}N_{5}O_{23} (with one extra dmf and one acetic acid) C, 56.48; H, 5.01; N, 4.77. Found: C, 56.0; H, 5.4; N, 5.3.

**Synthesis of CTH-13 yav-2(H_{2}NMe_{2})[Zn_{2}(cph)(H_{2}O)_{2}]·2dmf.** The molar ratio of 1: 2: 1 of 4,4-azopyridine, H_{6}cph and Zn(NO_{3})_{2}·6H_{2}O in 4 ml of dmf and 1 ml glacial acetic acid at 120 °C for 3 days yielded colorless crystals of CTH-13. TGA shows mass loss of first 3.0 % (2 H_{2}O, up to 170 °C calc. 4.9 %) and then 12.2 % (2 dmf up to 350 °C calc. 8.5 %) with a final mass of 12.9 % (calc. 13.6 %).

**1.3 Single Crystal X-ray Diffraction Analysis.** Single crystal x-ray diffraction data were collected on an Oxford Diffraction Xcalibur 3 system using ω-scans and Mo Kα (λ = 0.71073 Å) for **CTH-6.** Intensity data for **CTH-7** and **CTH-13** were collected with a Rigaku Synergy, Dualflex, AtlasS2 diffractometer using Cu Kα radiation (λ = 1.54184 Å) and the CrysAlis PRO 1.171.38.43 suite at -173 °C. In the three structures, CCD data were extracted and integrated using CrysAlis.\(^5\)\(^{-6}\) Single crystals of **CTH-8, CTH-9, CTH-10** and **CTH-12** were mounted on the goniometer of a Bruker APEX DUO diffractometer equipped with Mo Kα, radiation (λ = 0.71073 Å). The phi scan and omega scan techniques were utilized for collection of their intensity data. Data reduction was conducted using the SAINT-Plus\(^4\) software, and the absorption correction of the collection intensities were performed using the SADABS program.\(^5\)\(^{-6}\) Direct methods were
used for all structures, the refinements were established by full-matrix least squares with SHELX-2018/3 using the X-seed™ platform as a graphical interface. All non-hydrogen atoms in all structures were found in the difference electron density map and refined anisotropically except in case of disordered molecules and the structures having abnormal anisotropic thermal parameters (CTH-9 and CTH-10). All hydrogens except the COOH, and the hydrogen attached to the amine nitrogen were placed with geometric constraints and refined isotropically.

Table S1. Crystallographic Data and Structure Refinement. Parameters of CTH-6 to CTH-10.

| Code       | CTH-6             | CTH-7             | CTH-8             | CTH-9             | CTH-10             |
|------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Structural formula | C₃₂H₂₉N₂O₁₀Bi | C₂₆H₂₀N₂O₆Cu₁ | C₆₈H₃₈N₄O₂₈Fe₄ | C₆₄H₅₈N₄O₁₅Co₄ | C₁₂₀H₁₁₂N₄O₂₄Fe₄ |
| Molecular mass (g mol⁻¹) | 810.56           | 505.97           | 1426.54           | 1438.86           | 2217.53           |
| Data collection temp. (K) | 293 (2)          | 100 (2)          | 293 (2)          | 297 (2)          | 297 (2)          |
| Crystal system | Monoclinic       | Monoclinic       | Monoclinic       | Monoclinic       | Monoclinic       |
| Space group | P21/n            | I2/a             | P2/c             | P2/c             | P2₁              |
| a (Å)      | 8.0268(2)        | 12.8598(8)       | 29.166(1)        | 29.075(6)        | 16.696 (4)       |
| b (Å)      | 23.5350(6)       | 29.2610(14)      | 16.1141(7)       | 16.016(4)        | 21.624 (5)       |
| c (Å)      | 16.7335(5)       | 13.8247(7)       | 13.9552(6)       | 13.826(3)        | 16.696 (4)       |
| α (°)      | 90               | 90               | 90               | 90               | 90               |
| β (°)      | 97.682(3)        | 103.980(6)       | 98.847(1)        | 98.390(5)        | 120.00           |
| γ (°)      | 90               | 90               | 90               | 90               | 90               |
| Volume (Å³) | 3132.8(2)        | 5048.0(5)        | 6480.7(5)        | 6369(2)          | 5220 (2)         |
| Z          | 4                | 8                | 4                | 4                | 2                |
| Dc, calc density (g cm⁻³) | 1.721           | 1.332            | 1.462            | 1.500            | 1.411            |
| Absorption coefficient (mm⁻¹) | 5.688           | 1.556            | 0.954            | 1.102            | 0.623            |
| θ range   | 2.98-29.39       | 3.02-68.24       | 2.27-26.37       | 1.96-25.56       | 2.35-25.35       |
| Reflections collected | 34948           | 12993            | 100439           | 68796            | 61104            |
| No data I >2 sigma (I) | 5307            | 4402             | 10364            | 4857             | 6889             |
| Final R indices [I>2 sigma (I)] | 0.0491          | 0.1199           | 0.0416           | 0.1667           | 0.1765           |
| R indices (all data) | 0.0838          | 0.1225           | 0.0626           | 0.2717           | 0.2383           |
| Goodness-of-fit on F² | 1.058           | 1.090            | 1.075            | 1.107            | 1.285            |
| CCDC no.   | 1971673          | 1971674          | 1971675          | 1971676          | 1971677          |

Table S2. Crystallographic Data and Structure Refinement. Parameters of CTH-12 to CTH-13.
1.4 Electron Diffraction.  

3D electron diffraction data of Zn-MOF-888 and CTH-11 were collected using a JEOL JEM-2100 TEM, equipped with a Timepix detector from Amsterdam Scientific Instruments, while continuously rotating the crystal at 0.45° s⁻¹.¹⁻¹⁰ Data reduction was performed using XDS¹¹ and the structures were subsequently solved using ShelXT¹².

| Code    | CTH-12      | CTH-13      |
|---------|-------------|-------------|
| Structural formula | C₃₂H₃₁N₂O₁₀Cu | C₄₈H₃₉O₁₅Zn₂ |
| Molecular mass (g mol⁻¹) | 667.13 | 959.44 |
| Data collection temp. (K) | 206 (2) | 100 (2) |
| Crystal system | Triclinic | Monoclinic |
| Space group | P₁ | C₂/c |
| a (Å) | 7.9251(9) | 29.1139(9) |
| b (Å) | 12.738(1) | 16.3925(5) |
| c (Å) | 16.693(2) | 11.4361(3) |
| α (°) | 74.195(3) | 90 |
| β (°) | 86.514(3) | 99.919(2) |
| γ (°) | 82.047(3) | 90 |
| Volume (Å³) | 1605.4(3) | 5376.3(3) |
| Z | 2 | 4 |
| Dc, calc density (g cm⁻³) | 1.380 | 1.299 |
| Absorption coefficient (mm⁻¹) | 0.739 | 1.628 |
| θ range | 2.36-26.31 | 3.08-67.11 |
| Reflections collected | 36165 | 17681 |
| No data I >2 sigma (I) | 3934 | 16719 |
| Final R indices [I>2 sigma (I)] | 0.0773 | 0.0463 |
| R indices (all data) | 0.0895 | 0.0483 |
| Goodness-of-fit on F² | 1.180 | 1.144 |
| CCDC no. | 1971678 | 1996813 |

2. Transmission Electron Microscopy Images

Scanning electron microscopy images of Zn-MOF-888 and CTH-11 were collected on a JEOL JEM-2100 TEM.
**Figure S2.** TEM micrographs of (a) Zn-MOF-888 and (b) CTH-11.

3. **Crystallographic Information of Zn-MOF-888 and CTH-11**

3.1 Zn-MOF-888

**Figure S3.** Two adjacent layers of Zn-MOF-888 (shown for three different data sets). The viewing is set to be perpendicular to the individual layers.

**Table S3.** Crystallographic information for the 3D ED data of three Zn-MOF-888 crystals.

| Identification code | Zn-MOF888, crystal 1 | Zn-MOF-888, crystal 2 | Zn-MOF-888, crystal 3 |
|---------------------|----------------------|----------------------|----------------------|
| Crystal system      | Monoclinic           | Monoclinic           | Monoclinic           |
| Space group         | C2/c (No. 15)        | C2/c (No. 15)        | C2/c (No. 15)        |
| Unit cell dimensions| a = 17.12 Å          | a = 17.07 Å          | a = 17.13 Å          |
|                     | b = 30.67 Å          | b = 30.65 Å          | b = 30.65 Å          |
|                     | c = 13.31 Å          | c = 14.74 Å          | c = 14.64 Å          |
|                     | β = 124.26°          | β = 131.30°          | β = 131.13°          |
| Volume (Å³)         | 5776 Å³              | 5793 Å³              | 5793 Å³              |
3.2 CTH-11

**Figure S4.** Two adjacent layers of CTH-11 (shown for two different data sets). The viewing is set to be perpendicular to the individual layers.

**Table S4.** Crystallographic information for the 3D ED data of two CTH-11 crystals.

| Identification code | CTH-11, crystal 1 | CTH-11, crystal 2 |
|---------------------|-------------------|-------------------|
| Crystal system      | Monoclinic        | Monoclinic        |
| Space group         | C2/c (No. 15)     | C2/c (No. 15)     |
| Unit cell dimensions|                  |                   |
|                     | a = 30.94 Å       | a = 30.88 Å       |
|                     | b = 16.83 Å       | b = 16.78 Å       |
|                     | c = 11.89 Å       | c = 11.82 Å       |
|                     | β = 112.07°       | β = 112.54°       |
| Volume (Å³)         | 5739 Å³           | 5657 Å³           |
| Z                   | 8                 | 8                 |
| Rotation range      | 100.38° (-47.79° to 52.59°) | 89.07° (-32.18° to 56.89°) |
| Index ranges        | -35 ≤ h ≤ 38     | -35 ≤ h ≤ 38     |
|                     | -20 ≤ k ≤ 20     | -20 ≤ k ≤ 20     |
4. Thermal Analysis

Thermogravimetric analysis (TGA) data were collected on a Mettler Toledo TGA/DSC 3+ under a purge gas of air flow at a scan rate of 10 °C min⁻¹. TGA of all samples were performed between 30 °C and 800 °C. CTH-6 TGA trace is shown in Figure S5 and the first step illustrates a weight loss of 2.62% which is associated with half an acetic acid molecule. A further 12.87% weight loss, corresponding to half acetic acid and two dmf molecules (calc; 2dmf + acetic acid = 16.14 %, experimental; 2dmf + acetic acid = 15.49 %). CTH-6 crystals were coated with dark grey moieties which correspond to Bi₂O₃ and were difficult to separate to perform thermogravimetric analysis, so the Bi₂O₃ mass was included when calculating the percentage weight loss of the solvents (dmf and acetic acid) in the framework. In CTH-7 (Figure S6), there is a small % mass loss ranging from 100% to 90.77% (9.23%) corresponding to the loss of one dma molecule (calc; 8.91%) and a 78.42 % mass loss due to the linker (calc; 78.29 %). The CTH-8 TGA curve is illustrated in Figure S7 and the TGA trace shows a one step weight loss, (dmf and acetic acid solvents are coordinated to Fe atoms in the framework) corresponding to four dmf, two acetic acid and the linker. According to the thermogravimetric analysis of CTH-9 in Figure S8, the trace demonstrates a weight loss of 8.04 % corresponding to two acetic acid molecules (calc; 8.35 %). A further 20.56 % weight loss is observed, which is attributed to four dmf molecules (calc; 20.32 %). The rest of the mass loss in the curve is the % weight of the linker. The mass loss of 13.9 % (calc. 18.3 %) in
CTH-10 (Figure S9) is the loss of triethylamine (tea) molecules and then followed by the decomposition of the linker. The Zn-MOF-888 and CTH-11 trace is showed in Figure S10 with three weight loss steps: the first step is at 5.52%, the second at 6.32 % and the third at 7.46 % corresponding to 1.5 dmac molecules (calc; 22.35 %), all of these steps are within the 2% requirement between the calculated and experimental % weight loss. Three steps are demonstrated in the CTH-12 TGA curve (Figure S11). The first step at 22.21 % is the release of two dmf molecules (calc; 21.9 0 %). The second step at 10.55 % is attributed to the acetic acid (calc; 9.0 %) and the last step to the decomposition of the linker. Figure S12 shows the TGA trace of CTH-13, where the first weight loss is 4.83% (calc; 3.43 %) corresponding to the coordinated water molecule, the second weight loss at 6.78% (calc; 8.58%) corresponding to the protonated dimethylamine in the framework then 75.36% (calc; 75.20%) which is the loss of the linker.

![CTH-6 TGA curve](image)

**Figure S5.** TGA curve of CTH-6.
Figure S6. TGA curve of CTH-7.

Figure S7. TGA curve of CTH-8.
Figure S8. TGA curve of CTH-9.

Figure S9. TGA curve of CTH-10.
Figure S10. TGA curve of Zn-MOF-888 and CTH-11.

Figure S11. TGA curve of CTH-12.
Figure S12. TGA curve of CTH-13.

5. PXRD analyses

**Powder X-ray diffraction.** Powder X-ray diffraction patterns were recorded using a Bruker D8 Twin diffractometer (Billerica, Massachusetts, USA) with Cu-K\(\alpha\) radiation \(\lambda = 1.54\) Å at room temperature scanning between 20° and 50°. Variable temperature powder X-ray diffraction data were gathered using a Panalytical X’pert Pro diffractometer (Cu K\(\alpha_{1,2}\), \(\lambda_1 = 1.540598\) Å, \(\lambda_2 = 1.544426\) Å) using a Bragg–Brentano geometry, equipped with a Anton Paar XRK 900 High temperature chamber.
Figure S13. CTH-6 PXRD patterns. Experimental (red), simulated pattern from the single crystal data (blue) and after adsorption at 120 °C (orange).
Figure S14. CTH-7 PXRD patterns. After adsorption at 120 °C (red), simulated pattern from the single crystal data (orange) and experimental (blue).

Figure S15. CTH-8 PXRD patterns. Experimental (red), simulated pattern from the single crystal data (blue) and after adsorption at 120 °C (orange).
Figure S16. CTH-9 PXRD patterns. Experimental (red), simulated pattern from the single crystal data (blue) and after adsorption at 120 °C (orange).
Figure S17. CTH-10 PXRD patterns. Experimental (red), simulated pattern from the single crystal data (blue) and after adsorption at 120 °C (orange).

Figure S18. CTH-12 PXRD patterns. Experimental (red), simulated pattern from the single crystal data (blue) and after adsorption at 120 °C (orange).
Figure S19. Measured VTPXRD patterns CTH-9. The peak at $2\theta = 28^\circ$ is a silicon standard.
Figure S20. Measured VTPXRD patterns CTH-12. The peak at 2θ = 28° is a silicon standard.

6. Gas Adsorption Measurements

Gas adsorption isotherms were obtained using a Micromeritics ASAP2020 surface area analyzer (Atlanta, Georgia, USA). Prior to the analysis, the samples were pre-treated by heating to 120 °C for 6 hours under dynamic vacuum (1 × 10^-4 Pa) using a Micromeritics SmartVacPrep 067 instrument (Atlanta, Georgia, USA). The BET (SBET) and Langmuir surface area (SLang) values were calculated using the N\textsubscript{2} adsorption isotherms obtained at -196 °C (with data within a relative pressure between 0.05 and 0.15). CO\textsubscript{2}, and N\textsubscript{2} isotherms were also obtained at 20 °C using the same instrument.

| MOF     | A\textsubscript{BET} (m\textsuperscript{2}g\textsuperscript{-1}) | Lang (m\textsuperscript{2}g\textsuperscript{-1}) | N\textsubscript{2} uptake (mmol g\textsuperscript{-1}) | CO\textsubscript{2} uptake (mmol g\textsuperscript{-1}) |
|---------|------------------|------------------|------------------|------------------|
| CTH-6*  | 67.04            | 82.97            | 0.1083           | 0.8333           |
| CTH-7   | 125.97           | 155.17           | 0.0616           | 0.5334           |
| CTH-8*  | 210.69           | 261.05           | 0.1018           | 0.9832           |
| CTH-9   | 302.61           | 373.58           | 0.0691           | 0.7326           |
| CTH-10  | 145.15           | 177.50           | 0.0538           | 0.4943           |
| CTH-12  | 34.34            | 42.50            | 0.0638           | 1.2085           |

*Impure
**Figure S21.** \( \text{N}_2 \) isotherm curve for CTH-6.

**Figure S22.** \( \text{CO}_2 \) and \( \text{N}_2 \) isotherm curves for CTH-6.
Figure S23. The pore size distribution curve for CTH-6.

Figure S24. \( \text{N}_2 \) isotherm curve for CTH-7.
Figure S25. CO₂ and N₂ isotherm curves for CTH-7.

Figure S26. The pore size distribution curve for CTH-7.
**Figure S27.** N\(_2\) isotherm curve for CTH-8.

**Figure S28.** CO\(_2\) and N\(_2\) isotherm curves for CTH-8.
Figure S29. The pore size distribution curve for CTH-8.

Figure S30. $N_2$ isotherm curve for CTH-9.
**Figure S31.** CO₂ and N₂ isotherm curves for CTH-9.

**Figure S32.** The pore size distribution curve for CTH-9.
**Figure S33.** $\text{N}_2$ isotherm curve for CTH-10.

**Figure S34.** $\text{CO}_2$ and $\text{N}_2$ isotherm curves for CTH-10.
**Figure S35.** The pore size distribution curve for CTH-10.

**Figure S36.** N₂ isotherm curve for CTH-12.
**Figure S37.** CO$_2$ and N$_2$ isotherm curves for CTH-12.

**Figure S38.** The pore size distribution curve for CTH-12.
7. CSD analysis of the cpb core

**Figure S39.** Torsion angles between the central and peripheral benzene rings in the cpb core as searched in the CSD. Conformations with exactly 90° are non-chiral, the rest are chiral.

**Figure S40.** The cpb core as searched in the CSD in red the structures with Sohncke space groups. They all lack any enantiopure component and thus appear to be chiral and form conglomerates because the cpb adopting only one of the two propeller shaped conformations.
8. Reticular Chemistry

Systre input file for CTH-6

# Structure id (optional; ID and NAME both work)
ID    Bi-MOF-CTH6
# The space group
GROUP P21/n
# Cell parameters: a b c alpha beta gamma
CELL         13.3082 15.6219 16.4727 90.00000   90   90.00000
# Atom specification: name coordination x y z
  # (decimal numbers or fractions can be used for coordinates)
  #H6
ATOM  1 6   0.5000 0.5000 1.0000
#Bi
ATOM  2 3 0.1462 0.3090 0.4747
EDGE 1 0.8538 0.6910 1.5253
EDGE 1 0.1462 0.3090 1.4747
EDGE 1 -0.3538 0.1910 0.9747
EDGE 1 0.1462 0.3090 0.4747
EDGE 1 0.8538 0.6910 0.5253
EDGE 1 1.3538 0.8090 1.0253
# This ends the structure description
END

Systre output file for CTH-6

Structure #1 - "Bi-MOF-CTH6".  
Input structure described as 3-periodic.  
Given space group is P21/n.  
6 nodes and 12 edges in repeat unit as given.  
Given repeat unit is accurate.  
Point group has 16 elements.  
2 kinds of node.  
Coordination sequences:
  Node 1:    6 10 38 34 102 74 198 130 326 202
  Node 2:    3 14 19 62 51 144 99 254 163 400
TD10 = 1180
Wells point symbols:
  Node 1:   4^2.6^10.8^3
  Node 2:   4.6^2
Ideal space group is P42/mnm.  
Ideal group or setting differs from given (P42/mnm vs P121/n1).  
Structure was identified with RCSR symbol:
  Name:       rtl

Relaxed cell parameters:
  a = 1.74959, b = 1.74959, c = 1.50860
  alpha = 90.0000, beta = 90.0000, gamma = 90.0000
Cell volume: 4.61789
Adjusted positions:
Node 1:  0.00000  0.00000  0.00000
Node 2:  0.41860  0.58140  0.00000

Edges:
0.00000  0.00000  0.00000  <-  0.58140 -0.58140  0.00000
0.00000  0.00000  0.00000  <-  0.08140  0.08140  0.50000

Edge centers:
0.29070  -0.29070  0.00000
0.04070  0.04070  0.25000

Edge statistics: minimum = 0.78072, maximum = 1.43855, average = 1.00000
Angle statistics: minimum = 29.89982, maximum = 180.00000, average = 105.73337
Shortest non-bonded distance = 0.40281

Degrees of freedom: 3

Finished structure #1 - "Bi-MOF-CTH6".
Systre input file for the *laf*-net

```crystal
CRYSTAL
  NAME laf
  GROUP P42/mnm
  CELL 1.33390 1.33390 2.66446 90.0000 90.0000 90.0000
  NODE 2 3 0.00000 0.00000 0.37529
  NODE 1 6 0.00000 0.00000 0.00000
  EDGE 0.00000 0.00000 0.00000 0.50000 -0.50000 0.12471
  EDGE 0.00000 0.00000 0.00000 0.00000 0.00000 0.37529
# EDGE_CENTER 0.25000 -0.25000 0.06235
# EDGE_CENTER 0.00000 0.00000 0.18765
END
```

Systre output file for the *laf*-net

Input structure described as 3-periodic.
  Given space group is P42/mnm.
  6 nodes and 12 edges in repeat unit as given.
  Given repeat unit is accurate.
  Point group has 16 elements.
  2 kinds of node.
  Coordination sequences:
    Node 2: 3 14 23 88 79 228 163 426 275 676
    Node 1: 6 10 46 50 158 120 326 218 550 344
  TD10 = 1927
  Wells point symbols:
    Node 2: 4.8^2
    Node 1: 4^2.8^11.10^2
  Ideal space group is P42/mnm.
  Structure already seen in this run.
    Name: laf

Relaxed cell parameters:
  a = 1.33390, b = 1.33390, c = 2.66440
    alpha = 90.0000, beta = 90.0000, gamma = 90.0000
  Cell volume: 4.74073
Relaxed positions:
  Node 2: 0.00000 0.00000 0.37532
  Node 1: 0.00000 0.00000 0.00000
Edges:
  0.00000 0.00000 0.00000 <- 0.00000 0.00000 0.37532
  0.00000 0.00000 0.00000 <- 0.50000 -0.50000 0.12468
Edge centers:
  0.00000 0.00000 0.18766
    0.25000 -0.25000 0.06234
  Edge statistics: minimum = 1.00000, maximum = 1.00000, average = 1.00000
  Angle statistics: minimum = 38.80495, maximum = 180.00000, average = 111.42857
  Shortest non-bonded distance = 0.66440
  Degrees of freedom: 3

Finished structure #1 - "laf".

Folding of the laf-net model
Movie S1 Folding of the laf-net
9. Secondary Ion Mass Spectrometer

ToF-SIMS. ToF-SIMS analysis was performed using a TOFSIMS 5 instrument (ION-TOF GmbH, Münster, Germany). A 25 keV Bi$^{3+}$ cluster ion gun was used as the primary ion source and a 10 keV C60$^+$ gun was used for etching and depth profiling. The samples were analyzed in the delayed extraction mode using a pulsed primary ion beam (Bi$_3$$^{2+}$ 0.2 pA at 50 keV) with a focus of approximately 400 nm. The mass resolution was approximately M/ΔM = 3000 fwhm at m/z 100. Depth profile analysis was performed using a C$_{60}$$^{2+}$ beam at 20keV with a current of 0.18 nA in the non-interlaced mode with 1s of analysis, 1s of sputtering and a pause of 1s for each sputter cycle. The maximum ion dose density of Bi$_3$$^{2+}$ was kept between 1×10$^{12}$ and 5×10$^{12}$ cm$^{-2}$ over the whole depth profiling experiment, while the ion dose for C60$^{2+}$ ranged from 1x10$^{14}$ to 6x10$^{14}$ ions cm$^{-2}$. Low energy electrons were used for charge compensation during analysis. All spectra and images were analyzed using the Surface Lab software (version 6.4, ION-TOF GmbH, Münster, Germany)
Figure S41. ToF-SIMS depth profile of CTH-7 soaked in a methanol iodine mixture for a week.

Figure S42. ToF-SIMS 3D profiles surface analysis for CTH-7 after the crystals were soaked in a methanol iodine mixture for a week.
Figure S43. ToF-SIMS 3D rendered AFM images for CTH-7 after the crystals were soaked in a methanol iodine mixture for a week.
Figure S44. ToF-SIMS depth profile of CTH-7 soaked in a methanol iodine mixture for two days.

Figure S45. ToF-SIMS 3D rendered AFM images for CTH-7 after the crystals were soaked in a methanol iodine mixture for two days, where 63.03 u corresponds to Cu and 26.01 u to CN.
Figure S46. ToF-SIMS depth profile of CTH-7 after iodine gas exposure for a week.

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