Modulating H₂ Sorption in Metal-organic Frameworks via Ordered Functional Groups

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Supplementary Information

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General Methods for Metal-Organic Frameworks Experiments

Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). Proton nuclear magnetic resonance spectra (\(^{1}\)H NMR) were recorded by a Varian FT-NMR spectrometer (400 MHz). Chemical shifts are quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants, \(J\), were reported in Hertz unit (Hz). Column chromatography was performed using a CombiFlash automated chromatography system.

Ligand Synthesis

Figure S1. General synthesis of aromatic functionalized bdc ligands.

General procedure for the 2 steps synthesis of aromatic functionalized bdc ligands.

For the first step, dimethyl 2-aminoterephthalate (10 mmol) was dissolved in CHCl_3 (150 mL). Several drops of Et_3N were added to the reaction. The acid chloride (11 mmol) was then added to the reaction. The reaction was heated to 55 °C overnight. The reaction was cooled to room temperature. The product was purified via column chromatography (CH_2Cl_2) to afford a white product (yields are between 60-80%).
In the second step, the amide product of the first step (~10 mmol) was dissolved in a mixture of THF and 4%KOH (50:50 v/v, 200 mL total). The reaction was stirred at room temperature overnight. The aqueous layer was separated and acidified with concentrated HCl to yield a white solid as final product. The white solid was collected via vacuum filtration and washed with plenty of water (yields are between 70-99%).

Figure S2. Chemical structures of the ester intermediates and aromatic functionalized bdc ligands.

1. $^1$H NMR (CDCl$_3$): $\delta$ 12.02 (br, 1H), 9.57 (s, 1H), 8.16 (d, 1H, $J = 8$Hz), 8.07 (d, 2H, $J = 8$Hz), 7.79 (d, 1H, $J = 8$Hz), 7.61 ppm (m, 3H), 4.00 (s, 3H), 3.96 (s, 3H). MS: Cald 313.10, Found [M+H]$^+$ 313.98 [M+NH$_4$]$^+$ 330.80.
2. $^1$H NMR (CDCl$_3$): δ 12.04 (br, 1H), 9.53 (s, 1H), 8.16 (d, 1H, $J$ = 8Hz), 8.00 (d, 2H, $J$ = 8Hz), 7.80 (d, 1H, $J$ = 8Hz), 7.51 (d, 2H, $J$ = 8Hz), 4.00 (s, 3H), 3.96 (s, 3H). MS: Cald 347.06, Found [M+H]$^+$ 348.02 [M+NH$_4$]$^+$ 364.87.

3. $^1$H NMR (CDCl$_3$): δ 12.03 (br, 1H), 9.51 (s, 1H), 8.16 (d, 1H, $J$ = 8Hz), 8.05 (s, 1H), 7.91 (d, 1H, $J$ = 8Hz), 7.80 (d, 1H, $J$ = 8Hz), 7.55 (d, 1H, $J$ = 8Hz), 7.48 (t, 1H, $J$ = 16Hz), 4.01 (s, 3H), 3.97 (s, 3H). MS: Cald 347.06, Found [M+H]$^+$ 348.02 [M+NH$_4$]$^+$ 364.87.

4. $^1$H NMR (CDCl$_3$): δ 11.49 (br, 1H), 9.51 (s, 1H), 8.14 (d, 1H, $J$ = 8Hz), 7.80 (d, 1H, $J$ = 8Hz), 7.67 (d, 1H, $J$ = 8Hz), 7.45 (m, 3H), 3.96 (s, 3H), 3.93 (s, 3H). MS: Cald 347.06, Found [M+H]$^+$ 348.02 [M+NH$_4$]$^+$ 364.87.

5. $^1$H NMR (DMSO-$d_6$): δ 12.12 (br, 1H), 9.27 (s, 1H), 8.14 (d, 1H, $J$ = 8Hz), 7.97 (d, 2H, $J$ = 8Hz), 7.74 (dd, 1H, $J$ = 12Hz), 7.63 (m, 3H). MS: Cald 285.06, Found [M-H]$^-$ 284.13.

6. $^1$H NMR (DMSO-$d_6$): δ 12.08 (br, 1H), 9.20 (s, 1H), 8.13 (d, 1H, $J$ = 8Hz), 7.97 (d, 2H, $J$ = 8Hz), 7.75 (d, 1H, $J$ = 8Hz), 7.69 (d, 2H, $J$ = 8Hz). MS: Cald 319.02, Found [M-H]$^-$ 318.11.

7. $^1$H NMR (DMSO-$d_6$): δ 12.09 (br, 1H), 9.16 (s, 1H), 8.12 (d, 1H, $J$ = 8Hz), 7.97 (s, 1H), 7.91 (d, 1H, $J$ = 8Hz), 7.74 (m, 2H), 7.64 (t, 1H, $J$ = 16Hz). MS: Cald 319.02, Found [M-H]$^-$ 318.28.
8. \(^1\)H NMR (DMSO-\(d_6\)): \( \delta \) 11.59 (br, 1H), 9.13 (s, 1H), 8.11 (d, 1H, \( J = 8\)Hz), 7.77 (d, 1H, \( J = 8\)Hz), 7.73 (d, 1H, \( J = 8\)Hz), 7.56 (m, 4H). MS: Cald 319.02, Found [M-H]⁻ 318.28.

Figure S3. Synthesis of AMCy-bdc (10).

*Synthesis of 9.* Dimethyl 2-aminoterephthalate (6.5 g, 31.0 mmol) was dissolved in CHCl₃ (100 mL). Several drops of Et₃N were added to the solution. Cyclohexanecarbonyl chloride (5.0 g, 34.1 mmol) was added to the reaction mixture. The reaction was heated to 55 °C overnight. The reaction is cooled to room temperature. 9 was isolated via column chromatography (CH₂Cl₂) to afford a white solid (7.7 g, 24.2 mmol, 78%). \(^1\)H NMR (CDCl₃): \( \delta \) 11.06 (br, 1H), 9.39 (s, 1H), 8.09 (d, 1H, \( J = 8\)Hz), 7.72 (d, 1H, \( J = 8\)Hz), 2.35 (t, 1H, \( J = 20 \)Hz), 1.73 (m, 10 H). MS: Cald. 319.35, Found [M+H]⁺: 320.15.

*Synthesis of 10.* 9 (3.0 g, 9.4 mmol) was dissolved in a 50:50 v/v mixture of THF (100 mL) and 4% KOH (100 mL). The mixture was stirred at room temperature overnight. The aqueous layer was separated and acidified with concentrated HCl to yield a white solid as the product. The white solid was washed with plenty of water (2.4 g, 8.4 mmol, 89%). \(^1\)H NMR (DMSO-\(d_6\)): \( \delta \) 11.12 (s, 1H), 9.05 (s, 1H), 8.05 (d, 1H, \( J = 8\)Hz), 7.65 (d, 1H, \( J = 8\)Hz), 2.30 (m, 1H), 1.90 (d, 2H, \( J = 8\)Hz), 1.64 (d, 1H, \( J = 12 \)Hz), 1.32 (m, 7H). MS: Cald. 291.11, Found [M-H]⁻: 290.18.
**MOFs Synthesis.**

*Synthesis of IRMOF-3.* IRMOF-3 was synthesized as previously reported.¹

*Synthesis of α-IRMOF-3-AMPb.* AMP-bdc (113 mg, 0.4 mmol) and Zn(NO₃)₂•6H₂O (341 mg, 1.1 mmol) were dissolved in \textit{N,N’}-diethylformamide (DEF, 10 mL) via sonication in a scintillation vial. The vial was transferred to and kept in a preheated oven at 120 °C for 24 h. The vial was cooled down to room temperature. Large, dark red cubic crystals were obtained. The crystals were rinsed with DEF (3×10 mL) and CHCl₃ (3×10 mL). Fresh CHCl₃ was replace every day for 3 days. The MOFs were kept in CHCl₃ until further characterization.

*Synthesis of IRMOF-3-AM4Clb.* AM4Cl-bdc (126 mg, 0.4 mmol) and Zn(NO₃)₂•6H₂O (341 mg, 1.1 mmol) were dissolved in DEF (10 mL) via sonication in a scintillation vial. The vial was transferred to and kept in a preheated oven at 120 °C for 48 h. The vial was cooled down to room temperature. Large, dark red cubic crystals were obtained. The crystals were rinsed with DEF (3×10 mL) and CHCl₃ (3×10 mL). Fresh CHCl₃ was replace every day for 3 days. The MOFs were kept in CHCl₃ until further characterization.

*Synthesis of IRMOF-3-AM3Clb.* AM3Cl-bdc (126 mg, 0.4 mmol) and Zn(NO₃)₂•6H₂O (341 mg, 1.1 mmol) were dissolved in DEF (10 mL) via sonication in a scintillation vial. The vial was transferred to and kept in a preheated oven at 120 °C for 24 h. The vial was cooled down to room temperature. Large, dark red cubic crystals were obtained. The crystals were rinsed with DEF (3×10 mL) and CHCl₃ (3×10 mL).
Fresh CHCl₃ was replace every day for 3 days. The MOFs were kept in CHCl₃ until further characterization.

*Synthesis of IRMOF-3-AM2ClPh.* AM2ClPh-bdc (126 mg, 0.4 mmol) and Zn(NO₃)₂•6H₂O (341 mg, 1.1 mmol) were dissolved in DEF (10 mL) via sonication in a scintillation vial. The vial was transferred to and kept in a preheated oven at 120 °C for 24 h. The vial was cooled down to room temperature. Large, dark red cubic crystals were obtained. The crystals were rinsed with DEF (3×10 mL) and CHCl₃ (3×10 mL). Fresh CHCl₃ was replace every day for 3 days. The MOFs were kept in CHCl₃ until further characterization.

*Synthesis of IRMOF-3-AMCy.* AMCy-bdc (115 mg, 0.4 mmol) and Zn(NO₃)•6H₂O (341 mg, 1.1 mmol) were dissolved in DMF (10 mL) in a scintillation vial via sonication. The vial was transferred to a pre-heated oven at 120 °C for 24 h. The vial was transferred to and kept in a preheated oven at 120 °C for 24 h. The vial was cooled down to room temperature. Large, colorless cubic crystals were obtained. The crystals were rinsed with DMF (3×10 mL) and CHCl₃ (3×10 mL). Fresh CHCl₃ was replace every day for 3 days. The MOFs were kept in CHCl₃ until further characterization.

*Postsynthetic modification (PSM) to transform IRMOF-3 to β-IRMOF-3-AMPh.* β-IRMOF-3-AMPh was prepared by combining IRMOF-3 (~120 mg, ~0.4 mmol equiv of –NH₂) with benzoic anhydride (90 mg, 0.4 mmol) dissolved in CHCl₃ (4 mL) in a scintillation vial. The vial was transferred to and kept in a preheated oven at 55 °C for 17 d. A fresh benzoic anhydride solution was used to replace the reaction solution every
day. The MOF crystals were rinsed with CHCl$_3$ (3×10 mL) every day for 3 d before further characterization.

**MOFs Characterization.**

*Powder X-ray Diffraction Analysis.* Approximately 20-30 mg of MOF material was dried in air for ~30 second and polarized to become a homogeneous powder prior to PXRD analysis. PXRD data was collected at ambient temperature on a Bruker D8 Advance diffractometer using a LynxEye detector at 40 kV, 40 mA for Cu K$_\alpha$ ($\lambda$ = 1.5418 Å), with a scan speed of 1 sec/step, a step size of 0.02°, 2θ range of 5-45°.

*BET Surface Area and Gas Sorption Analysis.* A common activation process was applied for all MOFs reported in this study. Briefly, ~30-100 mg of MOF material was evacuated under vacuum for ~1 min at room temperature to remove residual CHCl$_3$ storage solvent. Samples were then transferred to a pre-weighed sample tube and degassed at 150 °C on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mmHg/min. The sample tube was re-weighed to obtain a consistent mass for the degassed MOF. Brunauer-Emmett-Teller (BET) surface area (m$^2$/g) measurements were collected at 77 K with N$_2$ on a Micromeritics ASAP 2020 Adsorption Analyzer using a volumetric technique. The samples were then manually degassed at 150 °C for at least 12 h prior to H$_2$ isotherm at 77 K.

*Single Crystal X-ray Diffraction.* Single crystal of IRMOFs taken from CHCl$_3$ were mounted on nylon loops with paratone oil and placed under a nitrogen cold stream at 100
K and 280 K. Data was collected on a Bruker Apex diffractometer using Cu Kα (λ = 1.5418 Å) or Mo Kα (λ = 0.71073 Å) radiation controlled using the APEX 2010 software package. A multi-scan method utilizing equivalents was employed to correct for absorption. All data collections were solved and refined using the SHELXTL software suite. Structures of IRMOFs were treated with the “SQUEEZE” protocol in PLATON to account for partially occupied or disordered solvent (e.g. DEF, CHCl₃) within the porous framework.

Attempts to solve and refine disordered IRMOF-3-AM3ClPh, IRMOF-3-AM2ClPh, and IRMOF-3AMCy have been tried in Cubic P system. However, the outcomes are the same whether the disordered structures were solved and refined in Cubic F or Cubic P systems.

Digestion and Analysis by $^1$H NMR. MOF materials (~10 mg) were dried under vacuum at room temperature overnight. MOF materials were then digested with DMSO-d$_6$ (800 uL) and 35% DCl in D$_2$O (5 uL).

Mass Spectrometry Analysis. Electrospray ionization mass spectrometry (ESI-MS) was performed using a ThermoFinnigan LCQ-DECA mass spectrometer and the data was analyzed using the Xcalibur software suite. MOFs digested for $^1$H NMR analysis were used for MS experiments.
Thermalgravimetric Analysis. Approximately 10-15 mg of MOF materials were used for thermogravimetric analysis (TGA) measurements, immediately after collection of gas sorption data (i.e. activated samples). Samples were analyzed under a stream of N\textsubscript{2} (10 ml/min) using a TA Instrument Q600 SDT running from room temperature to 600 °C with a ramping rate of 5 °C/min.
Figure S4. Digestion and $^1$H NMR analysis of IRMOFs.
Figure S5. Thermal gravimetric analysis (TGA) of IRMOFs.
Figure S6. Crystal structures of α-IRMOF-3-AMPh (left), highlighting a unit with 6 different –AMPh groups (red cubes) and a unit without any –AMPh group (black cube). Expand of the alternating packing structure of α-IRMOF-3-AMPh (middle). Schematic representation of the long range order of α-IRMOF-3-AMPh, showing alternative packing between units with 6 different –AMPh groups (red cubes), and units without any –AMPh group (black cube). Color scheme: carbon (grey), chlorine (pale green), nitrogen (blue), oxygen (red), zinc (green).
Figure S7. Digestion and $^1$H NMR analysis of IRMOF-3 (blue) and $\beta$-IRMOF-3-AMPh (red).
The free AMPh-bdc is represented in the black line for comparison, showing the quantitative PSM to transform IRMOF-3 to $\beta$-IRMOF-3-AMPh.
Figure S8. ESI-MS analysis of β-IRMOF-3-AMPh showing no trace of free NH$_2$-bdc.
Figure S9. Crystal structure of disordered β-IRMOF-3-AMPh. Structure of one cubic unit of IRMOF-3-AMPh (left), showing the –AMPh group is disordered over 4 positions and cannot be located or refined. The overall structure of β-IRMOF-3-AMPh (right), showing the irregular, unorganized –AMPh groups (only nitrogen atom shown) throughout the infinite lattice. Color scheme: carbon (grey), nitrogen (blue), oxygen (red), zinc (green). Hydrogen atoms are omitted for clarity.
Figure S10. Crystal structure of IRMOF-3-AM4ClPh, highlighting the interatomic distance between the –AM4ClPh group and neighboring groups. Color scheme: carbon (grey), chlorine (pale green), nitrogen (blue), oxygen (red), zinc (green). Hydrogen atoms are omitted for clarity.
Figure S11. Crystal structure of IRMOF-3-AM3ClPh (left) and IRMOF-3-AM2ClPh (right). The overall structures show that the disordered functional groups cannot be located and are distributed randomly in the infinite lattice. Color scheme: carbon (grey), nitrogen (blue), oxygen (red), zinc (green). Hydrogen atoms are omitted for clarity.
Figure S12. Crystal structure of IRMOF-3-AMCy, indicating unorganized –AMCy groups throughout the infinite lattice. Color scheme: carbon (grey), nitrogen (blue), oxygen (red), zinc (green). Hydrogen atoms are omitted for clarity.
**Figure S13.** PXRD analysis of IRMOF-3-AM2ClPh (black), IRMOF-3-AM3ClPh (red), and IRMOF-3-AMCy (blue).
Figure S14. $\text{H}_2$ sorption isotherms at 77 K of $\alpha$-IRMOF-3-AMPh (red, top) and $\beta$-IRMOF-3-AMPh (black, bottom). Filled symbols represent adsorption process, and emptied symbols represent desorption process.
Figure S15. $\text{H}_2$ sorption isotherms at 77 K of IRMOF-3-AMCy (green), IRMOF-3-AM4ClPh (magenta), IRMOF-3-AM2ClPh (black), and IRMOF-3-AM3ClPh (blue). Filled symbols represent adsorption process, and emptied symbols represent desorption process.
**Table S1.** Summary BET surface areas of IRMOFs.

<table>
<thead>
<tr>
<th>MOFs</th>
<th>BET surface area (m² g⁻¹) a</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-IRMOF-3-AMPPh</td>
<td>7±6</td>
</tr>
<tr>
<td>β-IRMOF-3-AMPPh</td>
<td>1521±28</td>
</tr>
<tr>
<td>IRMOF-3-AM4ClPh</td>
<td>66±4</td>
</tr>
<tr>
<td>IRMOF-3-AM3ClPh</td>
<td>169±14</td>
</tr>
<tr>
<td>IRMOF-3-AM2ClPh</td>
<td>229±42</td>
</tr>
<tr>
<td>IRMOF-3-AMCy</td>
<td>436±31</td>
</tr>
</tbody>
</table>

a The results and standard deviation were calculated from either 2 or 3 independent measurements from different samples.

**Table S2.** Crystal system of IRMOFs at different temperature (100 K and 280 K), showing that the frameworks are disordered or ordered at both low temperature and high temperature.

<table>
<thead>
<tr>
<th>MOFs</th>
<th>100 K</th>
<th>280 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-IRMOF-3-AMPPh (α-)</td>
<td>Cubic P</td>
<td>Cubic F</td>
</tr>
<tr>
<td>β-IRMOF-3-AMPPh (β-)</td>
<td>Cubic P</td>
<td>Cubic F</td>
</tr>
<tr>
<td>IRMOF-3-AM4ClPh</td>
<td>Cubic F</td>
<td>Cubic F</td>
</tr>
<tr>
<td>IRMOF-3-AM3ClPh</td>
<td>Cubic F</td>
<td>Cubic F</td>
</tr>
<tr>
<td>IRMOF-3-AM2ClPh</td>
<td>Cubic F</td>
<td>Cubic F</td>
</tr>
<tr>
<td>IRMOF-3-AMCy</td>
<td>Cubic F</td>
<td>Cubic F</td>
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</tbody>
</table>
Table S3. Crystal data and structure refinement for α-IRMOF-3-AMPh.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Identification code</td>
<td>α-IRMOF-3-AMPh</td>
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<tr>
<td>Empirical formula</td>
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</tr>
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<tr>
<td>Wavelength</td>
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<tr>
<td>Crystal system</td>
<td>Cubic</td>
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<tr>
<td>Space group</td>
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</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = b = c = 25.5775(18) Å, α = β = γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
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</tr>
<tr>
<td>Z</td>
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<tr>
<td>Density (calculated)</td>
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<tr>
<td>Absorption coefficient</td>
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<tr>
<td>F(000)</td>
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<tr>
<td>Crystal size</td>
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<tr>
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</tr>
<tr>
<td>Index ranges</td>
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<tr>
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<tr>
<td>Independent reflections</td>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1271, wR2 = 0.2881</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.605 and -1.133 e.Å⁻³</td>
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Table S4. Crystal data and structure refinement for β-IRMOF-3-AMPh.

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<tr>
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<tr>
<td>Empirical formula</td>
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<td>Unit cell dimensions</td>
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<tr>
<td>Z</td>
<td>8</td>
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<tr>
<td>Density (calculated)</td>
<td>0.659 Mg/m&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Absorption coefficient</td>
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<tr>
<td>F(000)</td>
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<tr>
<td>Crystal size</td>
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<tr>
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<tr>
<td>Independent reflections</td>
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<td>Completeness to theta = 67.96°</td>
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<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F&lt;sup&gt;2&lt;/sup&gt;</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
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<tr>
<td>R indices (all data)</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.427 and -0.636 e.Å&lt;sup&gt;-3&lt;/sup&gt;</td>
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**Table S5.** Crystal data and structure refinement for IRMOF-3-AM4ClPh.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tr>
<td>Identification code</td>
<td>IRMOF-3-AM4ClPh</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{45}H_{24}Cl_{3}N_{3}O_{16}Zn_{4}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1230.50</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pa-3</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = b = c = 25.3840(10) Å  α = β = γ =90°</td>
</tr>
<tr>
<td>Volume</td>
<td>16356.1(11) Å</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>0.997 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.300 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>4888</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.50 x 0.50 x 0.40 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.79 to 25.33°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>0&lt;=h&lt;=21, 0&lt;=k&lt;=21, 2&lt;=l&lt;=30</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>4997</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>4997 [R(int) = 0.0000]</td>
</tr>
<tr>
<td>Completeness to theta = 25.33°</td>
<td>99.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.8856 and 0.8657</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>4997 / 15 / 99</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.576</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R₁ = 0.1544, wR₂ = 0.4234</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.1882, wR₂ = 0.4419</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.678 and -0.874 e.Å⁻³</td>
</tr>
</tbody>
</table>
Table S6. Crystal data and structure refinement for IRMOF-3-AM3ClPh.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>IRMOF-3-AM3ClPh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{24} N_{6} O_{13} Zn_{4}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>841.78</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>Fm-3m</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = b = c = 25.6910(17) Å,  α = β = γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>16956.8(19) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>0.659 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.524 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>3280</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.30 x 0.30 x 0.30 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>6.89 to 68.02°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>0&lt;=h&lt;=17, 0&lt;=k&lt;=21, 3&lt;=l&lt;=30</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>814</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>814 [R(int) = 0.0368]</td>
</tr>
<tr>
<td>Completeness to theta</td>
<td>97.4 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.8972 and 0.8729</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>814 / 0 / 31</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.425</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R₁ = 0.0930, wR₂ = 0.3115</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.1035, wR₂ = 0.3386</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.454 and -0.615 e.Å⁻³</td>
</tr>
</tbody>
</table>
Table S7. Crystal data and structure refinement for IRMOF-3-AM2ClPh.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>IRMOF-3-AM2ClPh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{24}O_{13}Zn_{4}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>757.72</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>F-43m</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = b = c = 25.6590(13) Å  α = β = γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>16893.5(15) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>0.596 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.481 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>2944</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.40 x 0.40 x 0.40 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.87 to 69.42°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-16&lt;=h&lt;=17, 0&lt;=k&lt;=21, 2&lt;=l&lt;=31</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>1528</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>1528 [R(int) = 0.0586]</td>
</tr>
<tr>
<td>Completeness to theta = 69.42°</td>
<td>97.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9120 and 0.8972</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>1528 / 2 / 45</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.038</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R₁ = 0.0832, wR₂ = 0.2490</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.1053, wR₂ = 0.2783</td>
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Table S8. Crystal data and structure refinement for IRMOF-3-AMCy.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Identification code</td>
<td>IRMOF-3-AMCy</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{24} O_{13} Zn_{4}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>757.72</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>F-43m</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = b = c = 25.6177(9) Å</td>
</tr>
<tr>
<td>Volume</td>
<td>16812.0(10) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>0.599 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.488 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>2944</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.40 x 0.40 x 0.10 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>6.91 to 68.43°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-16&lt;=h&lt;=12, 0&lt;=k&lt;=21, 3&lt;=l&lt;=30</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>1391</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>1391 [R(int) = 0.0405]</td>
</tr>
<tr>
<td>Completeness to theta = 68.43°</td>
<td>96.2 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9324 and 0.9123</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>1391 / 0 / 46</td>
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<td>Goodness-of-fit on F²</td>
<td>1.359</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R₁ = 0.1331, wR₂ = 0.3197</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.1489, wR₂ = 0.3407</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.2(4)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.442 and -1.040 e.Å⁻³</td>
</tr>
</tbody>
</table>
References.