Electronic Supplementary Material (ESI) for ChemComm.

Modulating H_2 Sorption in Metal-organic Frameworks via Ordered Functional Groups

Phuong V. Dau and Seth M. Cohen*

Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman

Drive, La Jolla, California 92093-0358

Supplementary Information

* To whom correspondence should be addressed. E-mail: scohen@ucsd.edu. Telephone: (858)822-5596. Fax: (858) 822-559

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

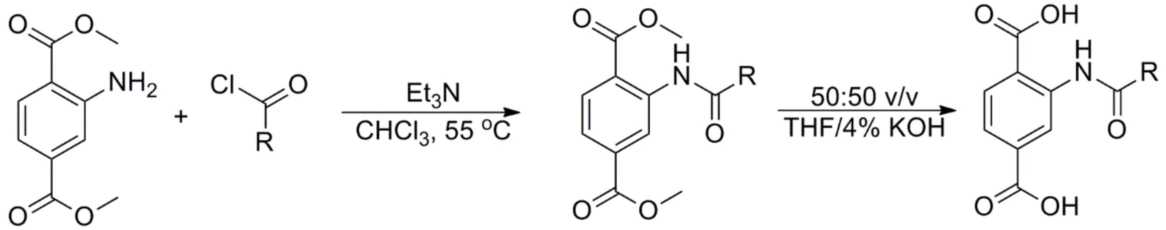
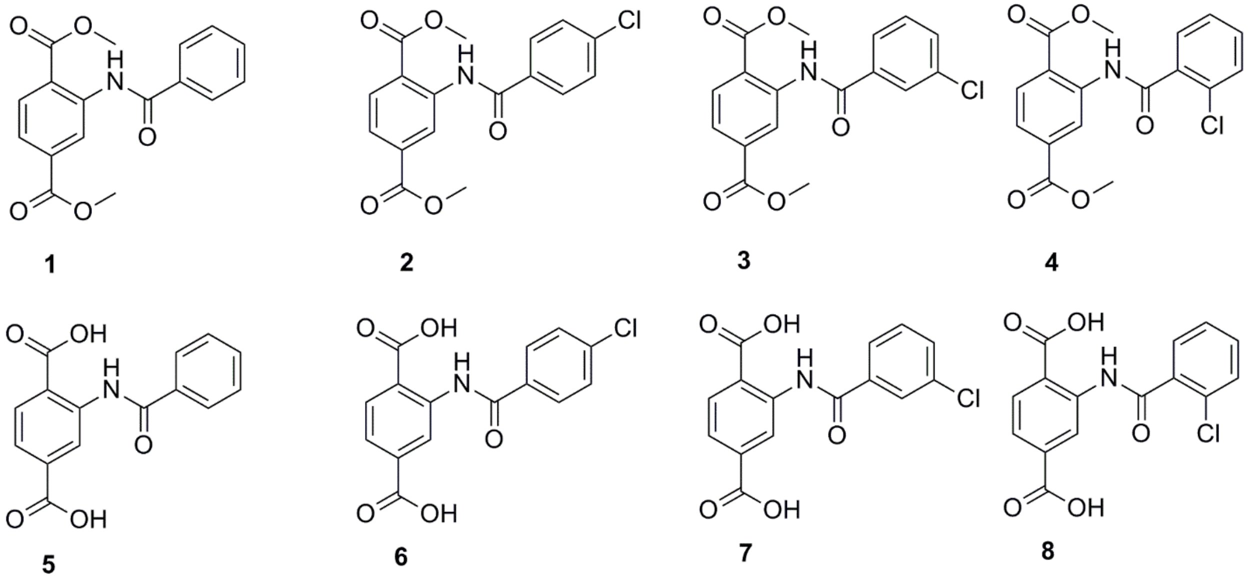


Figure S1. General synthesis of aromatic functionalized bdc ligands.

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%).


1 2 3 4

5 6 7 8

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

1. ^{1}H NMR (CDCl$_3$): δ 12.02 (br, 1H), 9.57 (s, 1H), 8.16 (d, 1H, J = 8Hz), 8.07 (d, 2H, J = 8Hz), 7.79 (d, 1H, J = 8Hz), 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): δ 11.59 (br, 1H), 9.13 (s, 1H), 8.11 (d, 1H, J = 8Hz), 7.77 (d, 1H, J = 8Hz), 7.73 (d, 1H, J = 8Hz), 7.56 (m, 4H). MS: Cald 319.02, Found [M-H]$^-$ 318.28.

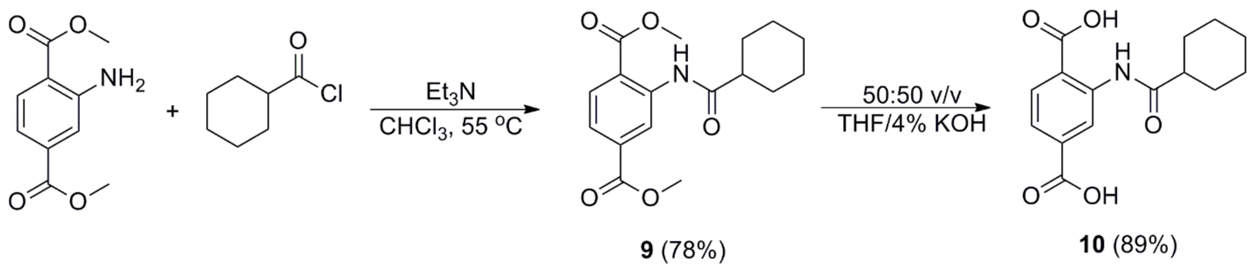


Figure S3. Synthesis of AMCy-bdc (**10**).

*Synthesis of **9***. Dimethyl 2-aminoterephthalate (6.5 g, 31.0 mmol) was dissolved in $CHCl_3$ (100 mL). Several drops of Et_3N 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 (CH_2Cl_2) to afford a white solid (7.7 g, 24.2 mmol, 78%). ^{1}H NMR ($CDCl_3$): δ 11.06 (br, 1H), 9.39 (s, 1H), 8.09 (d, 1H, J = 8Hz), 7.72 (d, 1H, J = 8Hz), 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): δ 11.12 (s, 1H), 9.05 (s, 1H), 8.05 (d, 1H, J = 8Hz), 7.65 (d, 1H, J = 8Hz), 2.30 (m, 1H), 1.90 (d, 2H, J = 8Hz), 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-AMPh. AMPh-bdc (113 mg, 0.4 mmol) and $Zn(NO_3)_2{\bullet}6H_2O$ (341 mg, 1.1 mmol) were dissolved in *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 ^{o}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 $CHCl_3$ (3×10 mL). Fresh $CHCl_3$ was replace every day for 3 days. The MOFs were kept in $CHCl_3$ until further characterization.

Synthesis of IRMOF-3-AM4ClPh. AM4ClPh-bdc (126 mg, 0.4 mmol) and $Zn(NO_3)_2{\bullet}6H_2O$ (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 ^{o}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 $CHCl_3$ (3×10 mL). Fresh $CHCl_3$ was replace every day for 3 days. The MOFs were kept in $CHCl_3$ until further characterization.

Synthesis of IRMOF-3-AM3ClPh. AM3ClPh-bdc (126 mg, 0.4 mmol) and $Zn(NO_3)_2{\bullet}6H_2O$ (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 ^{o}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 $CHCl_3$ (3×10 mL).

Fresh $CHCl_3$ was replace every day for 3 days. The MOFs were kept in $CHCl_3$ until further characterization.

Synthesis of IRMOF-3-AM2ClPh. AM2ClPh-bdc (126 mg, 0.4 mmol) and $Zn(NO_3)_2$•$6H_2O$ (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 ^oC 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 $CHCl_3$ (3×10 mL). Fresh $CHCl_3$ was replace every day for 3 days. The MOFs were kept in $CHCl_3$ until further characterization.

Synthesis of IRMOF-3-AMCy. AMCy-bdc (115 mg, 0.4 mmol) and $Zn(NO_3)$•$6H_2O$ (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 ^oC for 24 h. The vial was transferred to and kept in a preheated oven at 120 ^oC 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 $CHCl_3$ (3×10 mL). Fresh $CHCl_3$ was replace every day for 3 days. The MOFs were kept in $CHCl_3$ 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 $-NH_2$) with benzoic anhydride (90 mg, 0.4 mmol) dissolved in $CHCl_3$ (4 mL) in a scintillation vial. The vial was transferred to and kept in a preheated oven at 55 ^oC 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 Kα (λ= 1.5418 Å), with a scan speed of 1 sec/step, a step size of 0.02^{o}, 2θ range of 5-45^{o}.

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.[2] Structures of IRMOFs were treated with the "SQUEEZE" protocol in PLATON[3] to account for partially occupied or disordered solvent (e.g. DEF, $CHCl_3$) 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 ^1H 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_2O (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 ^1H 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_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.

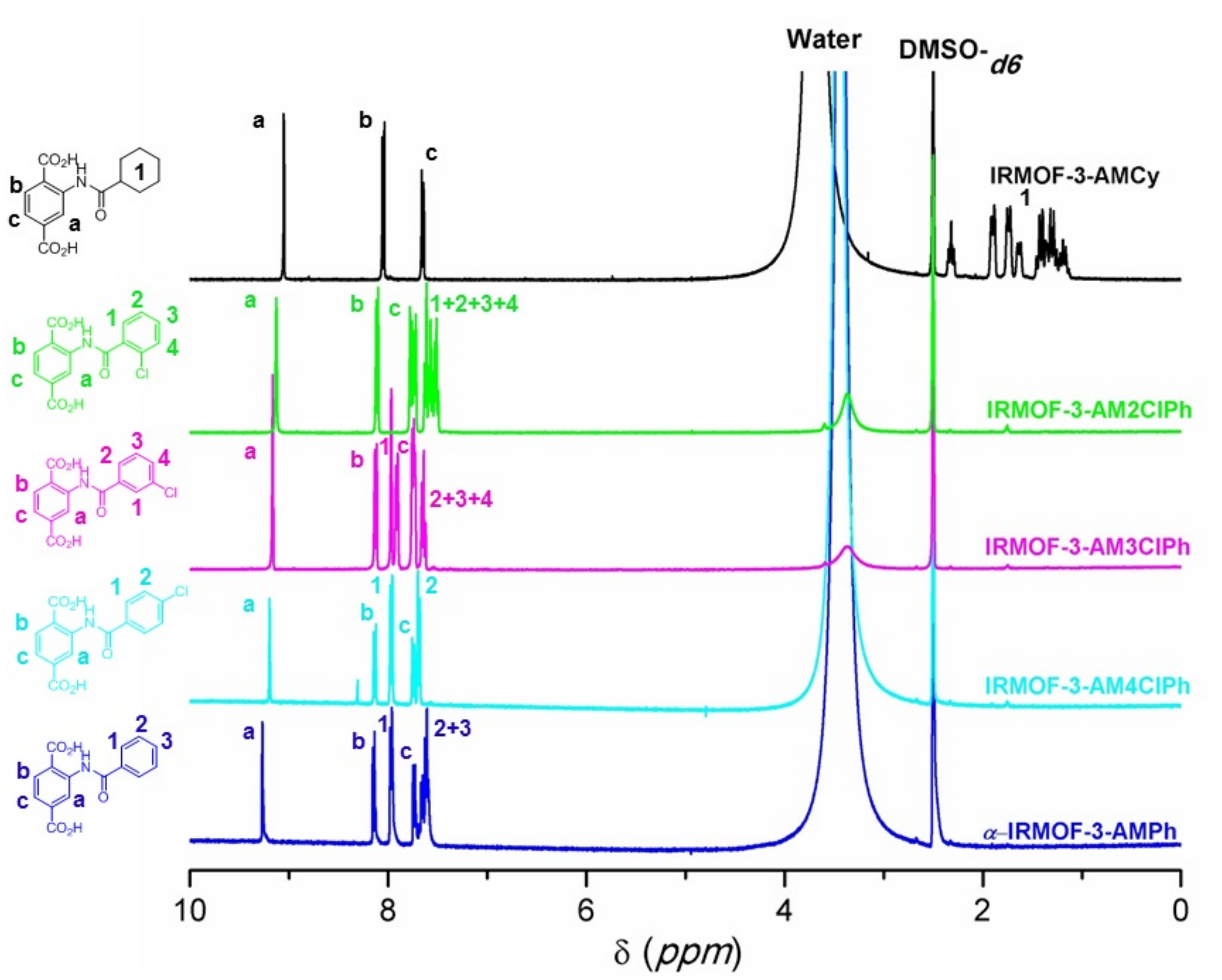


Figure S4. Digestion and ^{1}H NMR analysis of IRMOFs.

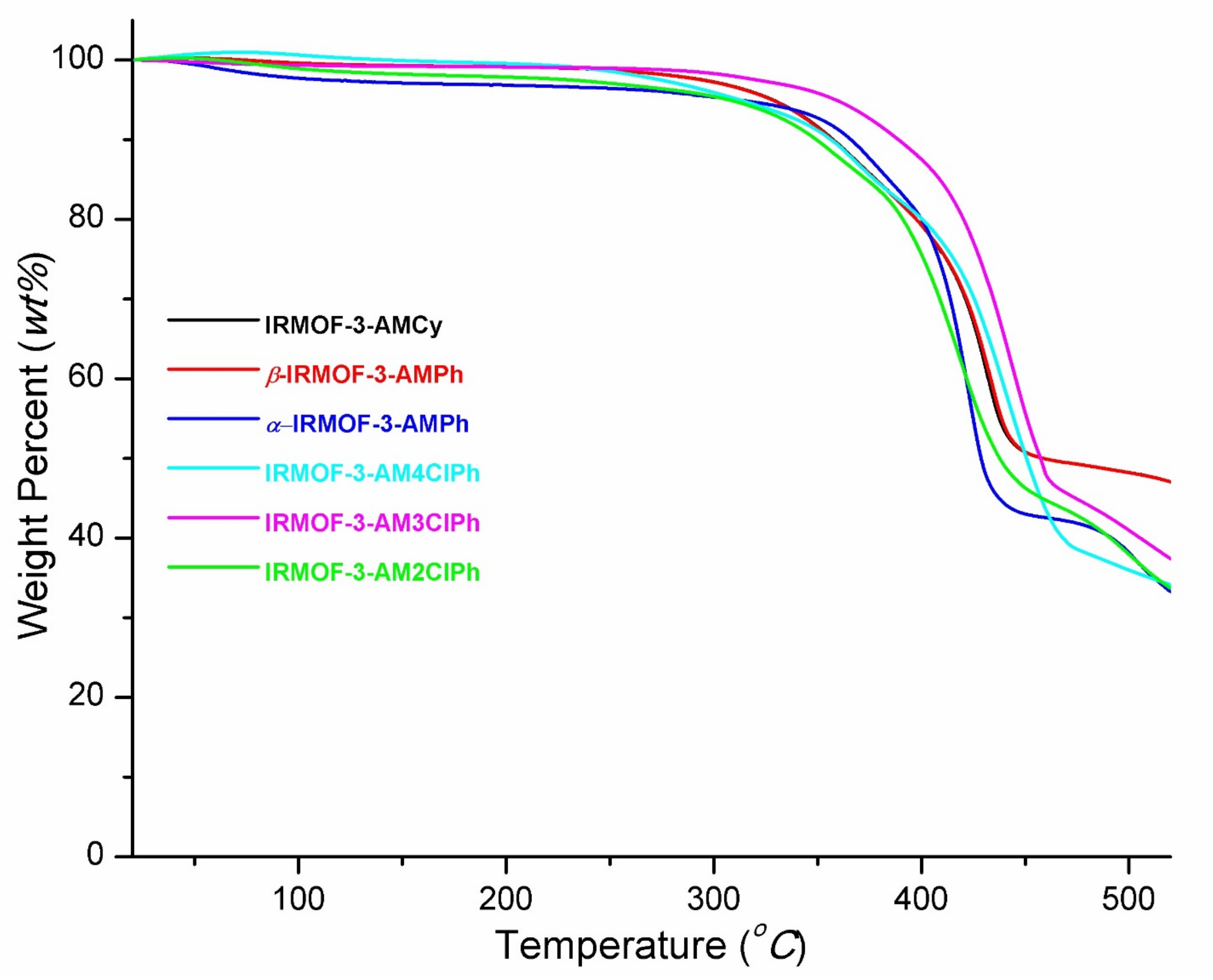


Figure S5. Thermal gravimetric analysis (TGA) of IRMOFs.

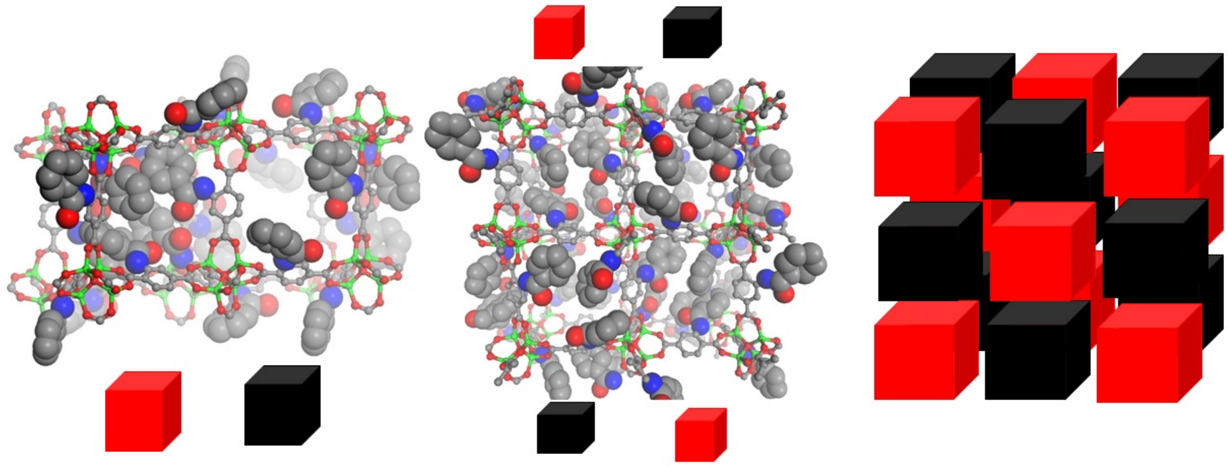


Figure S6. Crystal structures of α-IRMOF-3-AMPh (left), highlighting a unit with 6 different –AMPh groups (red cubes) and a unit without any –AMPh group (black cube). Expand of the alternating packing structure of α-IRMOF-3-AMPh (middle). Schematic representation of the long range order of α-IRMOF-3-AMPh, 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).

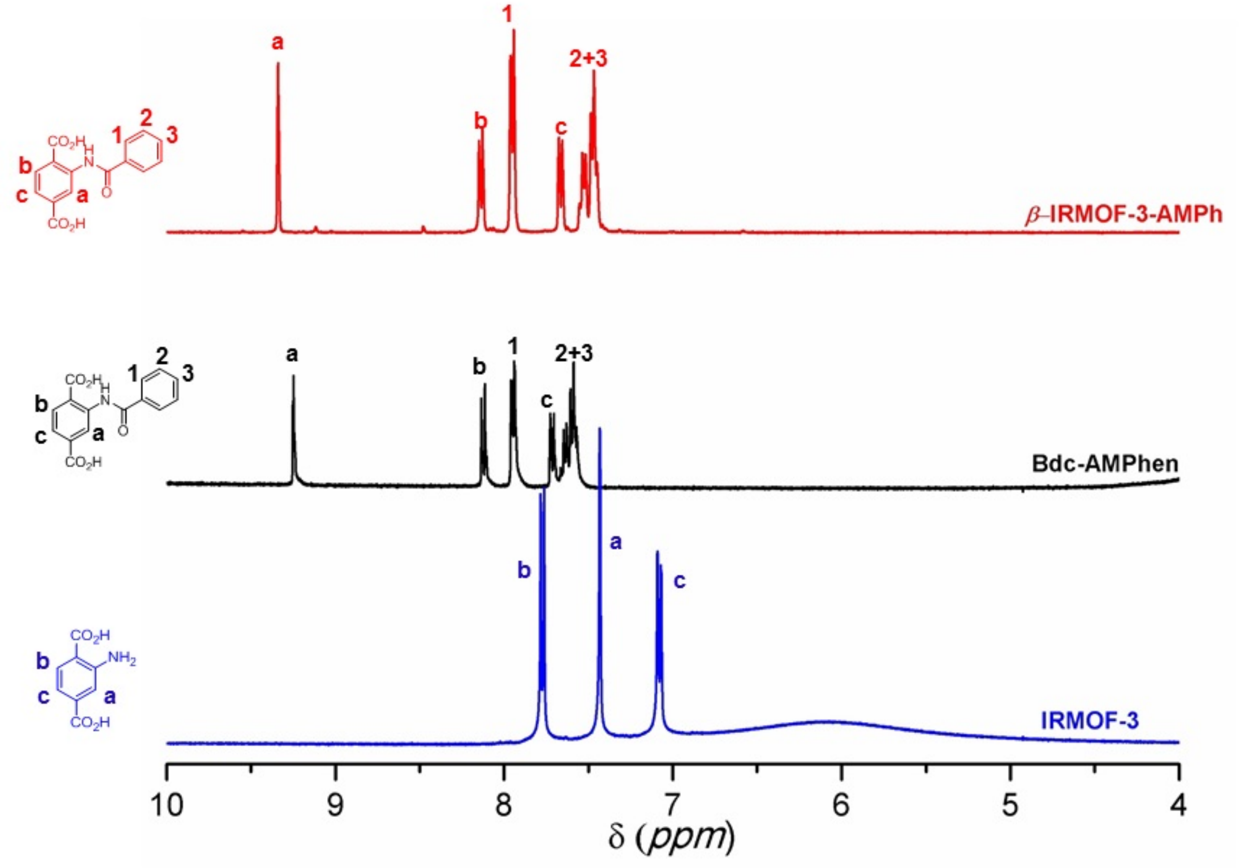


Figure S7. Digestion and ^{1}H NMR analysis of IRMOF-3 (blue) and *β*-IRMOF-3-AMPh (red). The free AMPh-bdc is represented in the black line for comparison, showing the quantitative PSM to transform IRMOF-3 to *β*-IRMOF-3-AMPh.

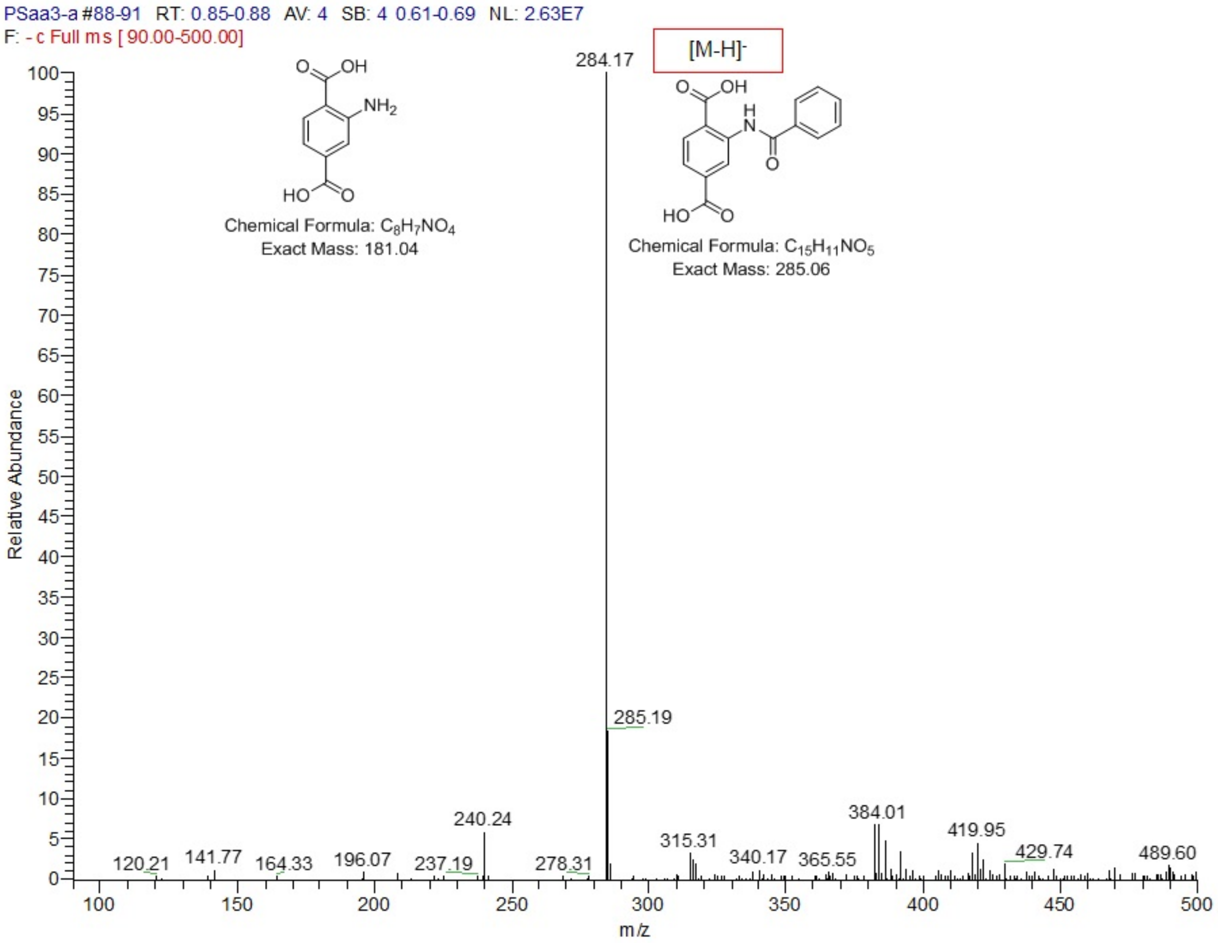


Figure S8. ESI-MS analysis of β-IRMOF-3-AMPh showing no trace of free NH_2-bdc.

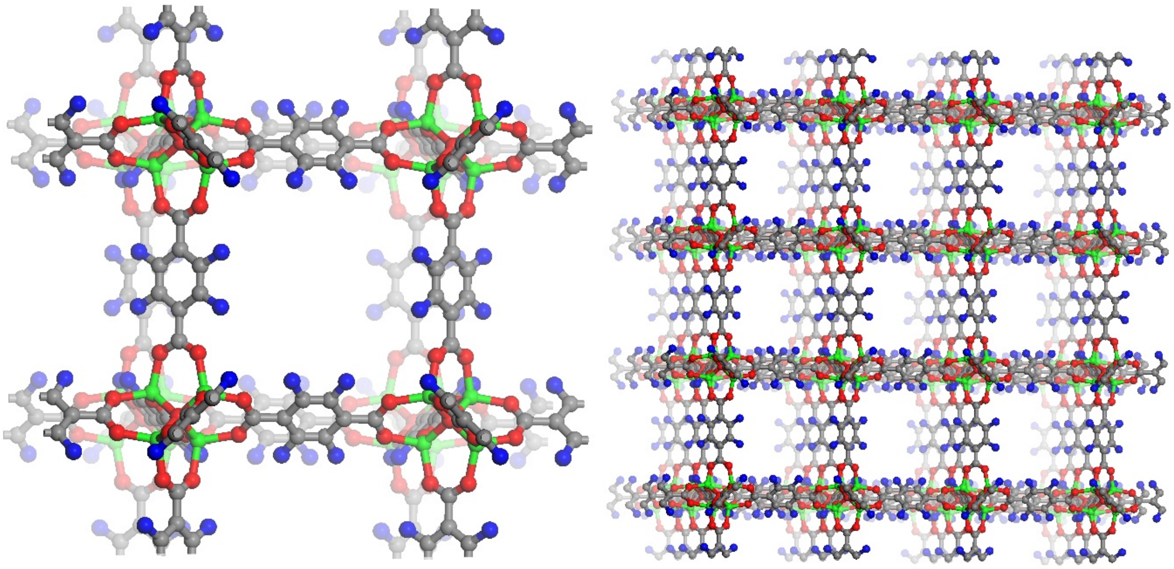


Figure S9. Crystal structure of disordered *β*-IRMOF-3-AMPh. Structure of one cubic unit of IRMOF-3-AMPh (left), showing the –AMPh group is disordered over 4 positions and cannot be located or refined. The overall structure of *β*-IRMOF-3-AMPh (right), showing the irregular, unorganized –AMPh groups (only nitrogen atom shown) throughout the infinite lattice. Color scheme: carbon (grey), nitrogen (blue), oxygen (red), zinc (green). Hydrogen atoms are omitted for clarity.

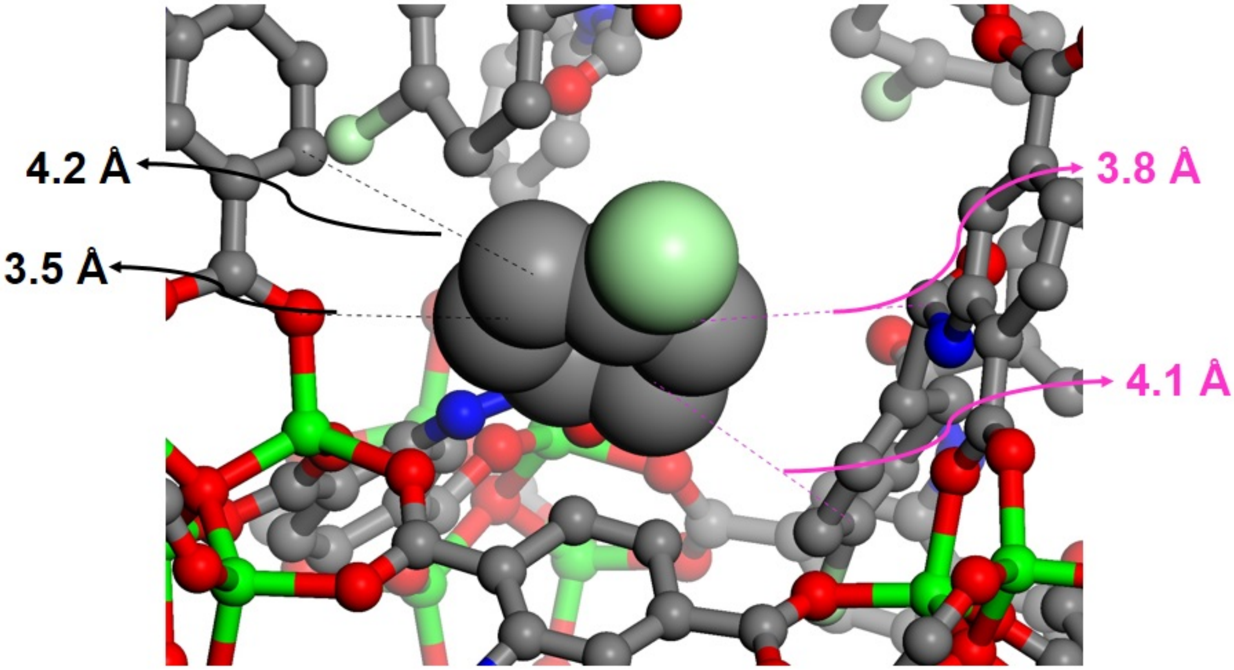


Figure S10. Crystal structure of IRMOF-3-AM4ClPh, highlighting the interatomic distance between the –AM4ClPh group and neighboring groups. Color scheme: carbon (grey), chlorine (pale green), nitrogen (blue), oxygen (red), zinc (green). Hydrogen atoms are omitted for clarity.

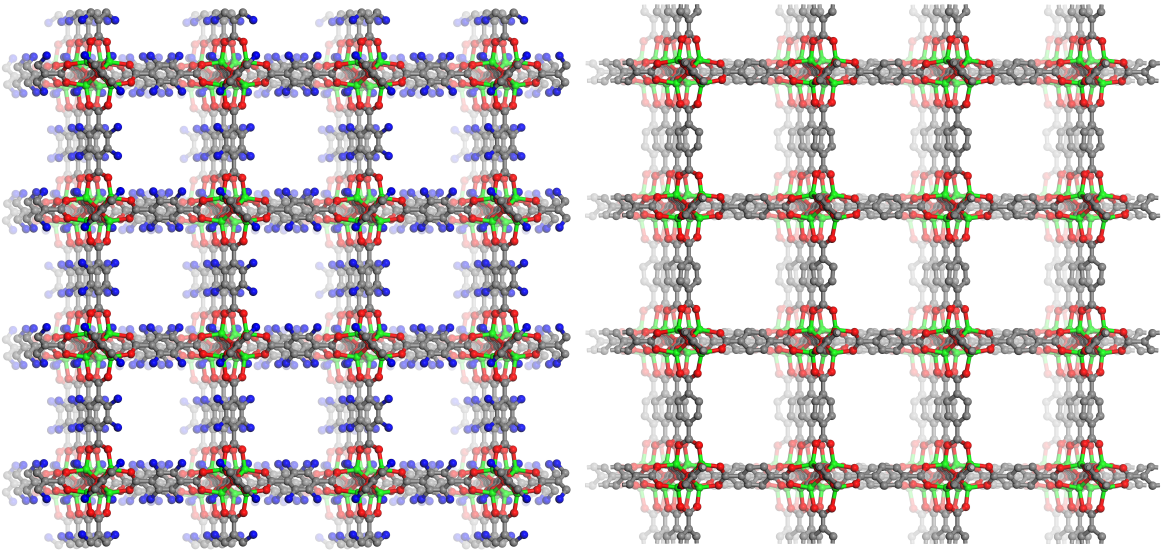


Figure S11. Crystal structure of IRMOF-3-AM3ClPh (left) and IRMOF-3-AM2ClPh (right). The overall structures show that the disordered functional groups cannot be located and are distributed randomly in the infinite lattice. Color scheme: carbon (grey), nitrogen (blue), oxygen (red), zinc (green). Hydrogen atoms are omitted for clarity.

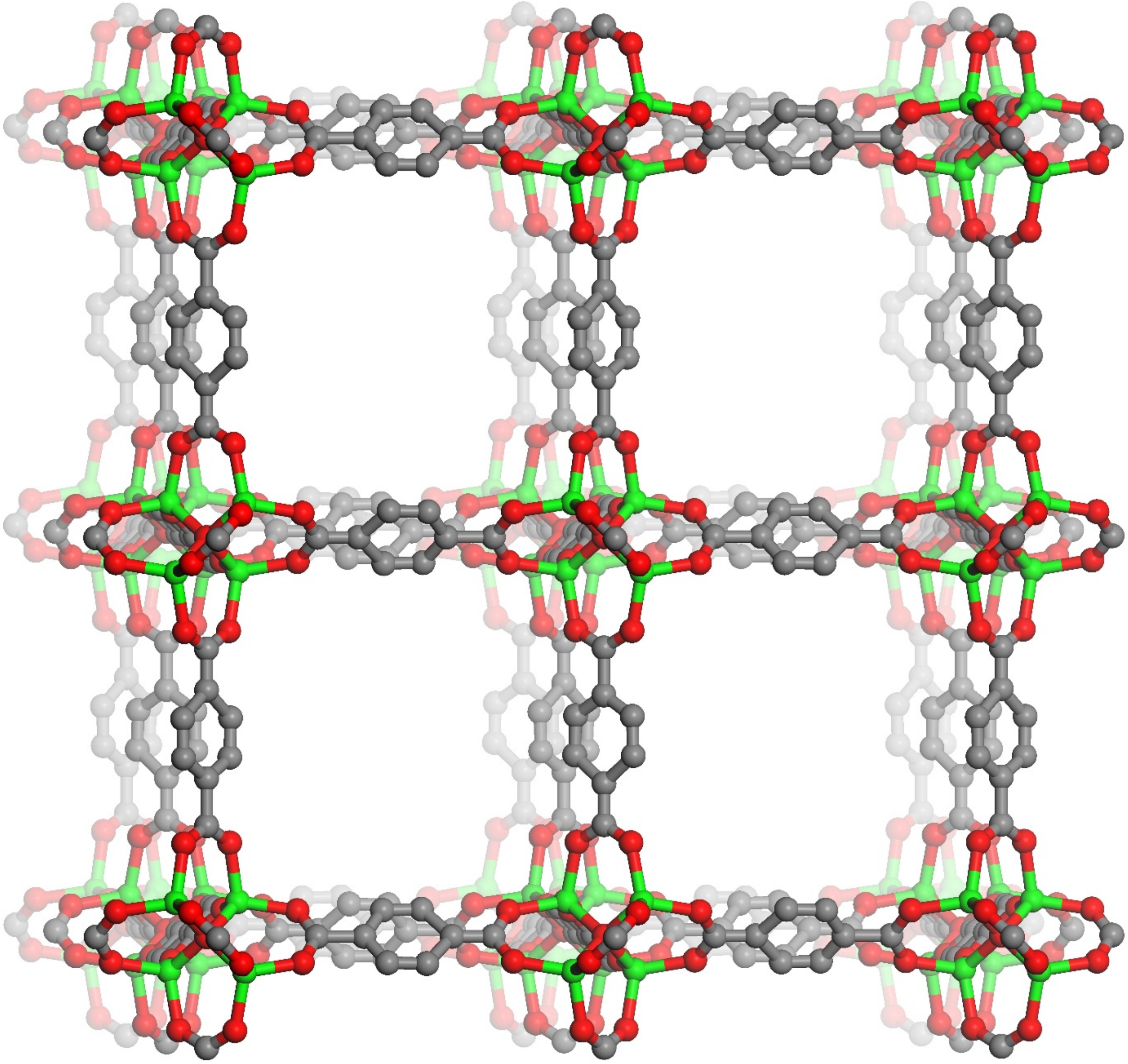


Figure S12. Crystal structure of IRMOF-3-AMCy, indicating unorganized –AMCy groups throughout the infinite lattice. Color scheme: carbon (grey), nitrogen (blue), oxygen (red), zinc (green). Hydrogen atoms are omitted for clarity.

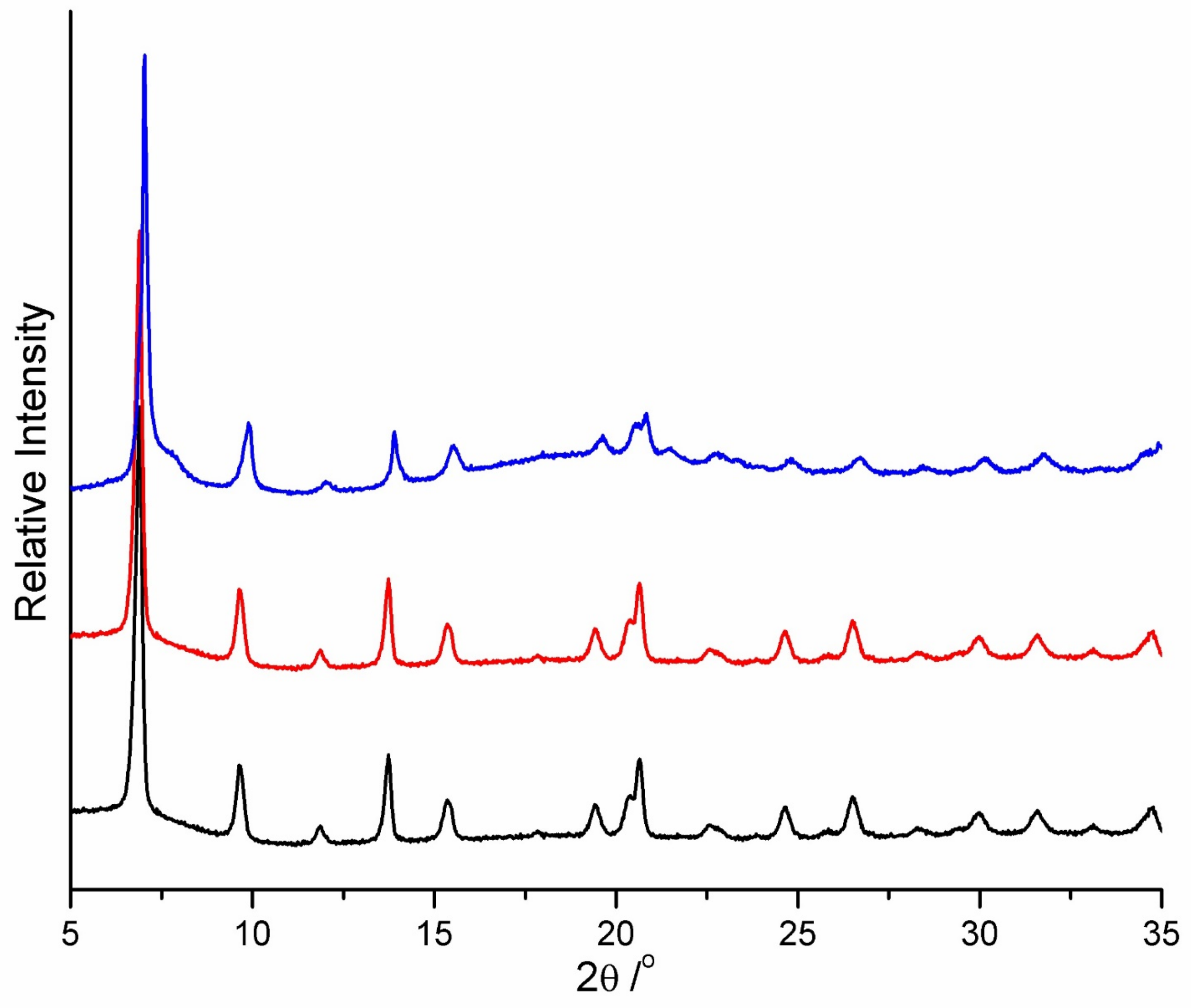


Figure S13. PXRD analysis of IRMOF-3-AM2ClPh (black), IRMOF-3-AM3ClPh (red), and IRMOF-3-AMCy (blue).

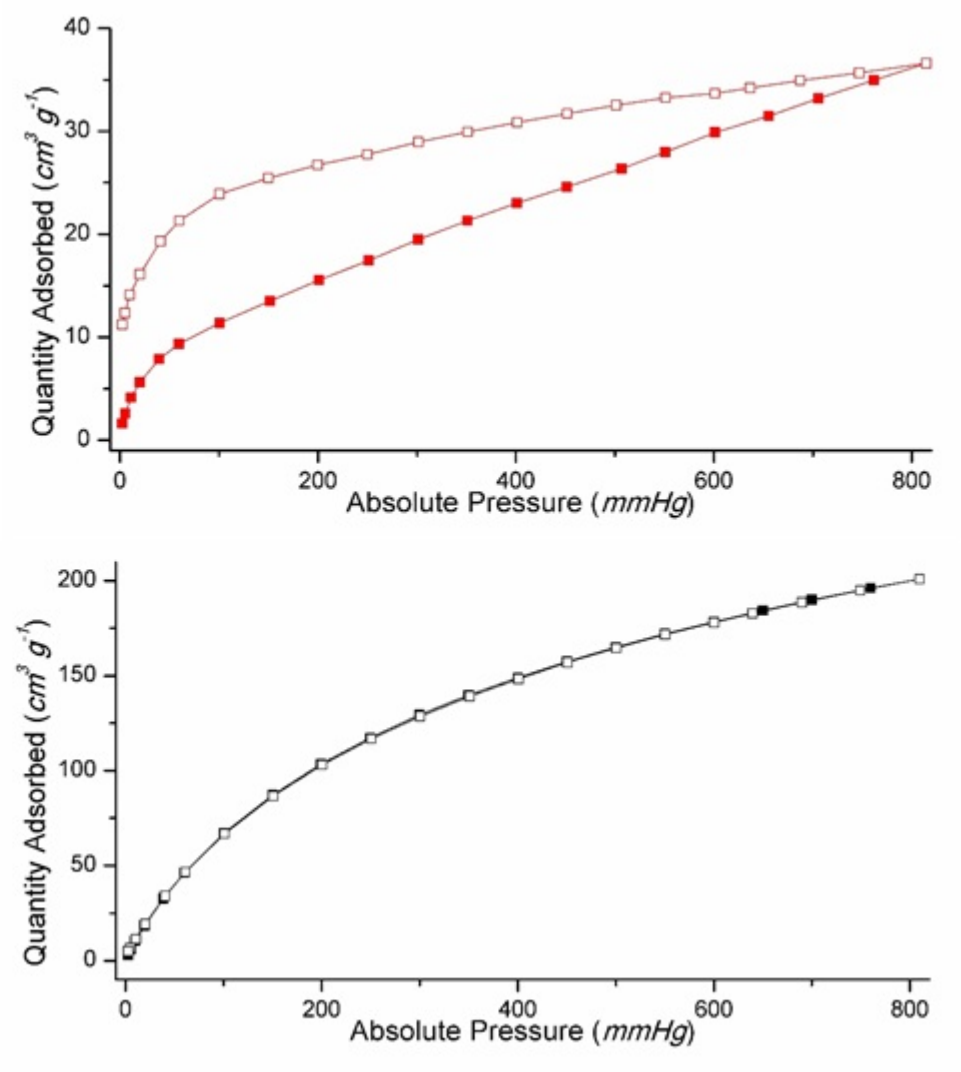


Figure S14. H_2 sorption isotherms at 77 K of α-IRMOF-3-AMPh (red, top) and β-IRMOF-3-AMPh (black, bottom). Filled symbols represent adsorption process, and emptied symbols represent desorption process.

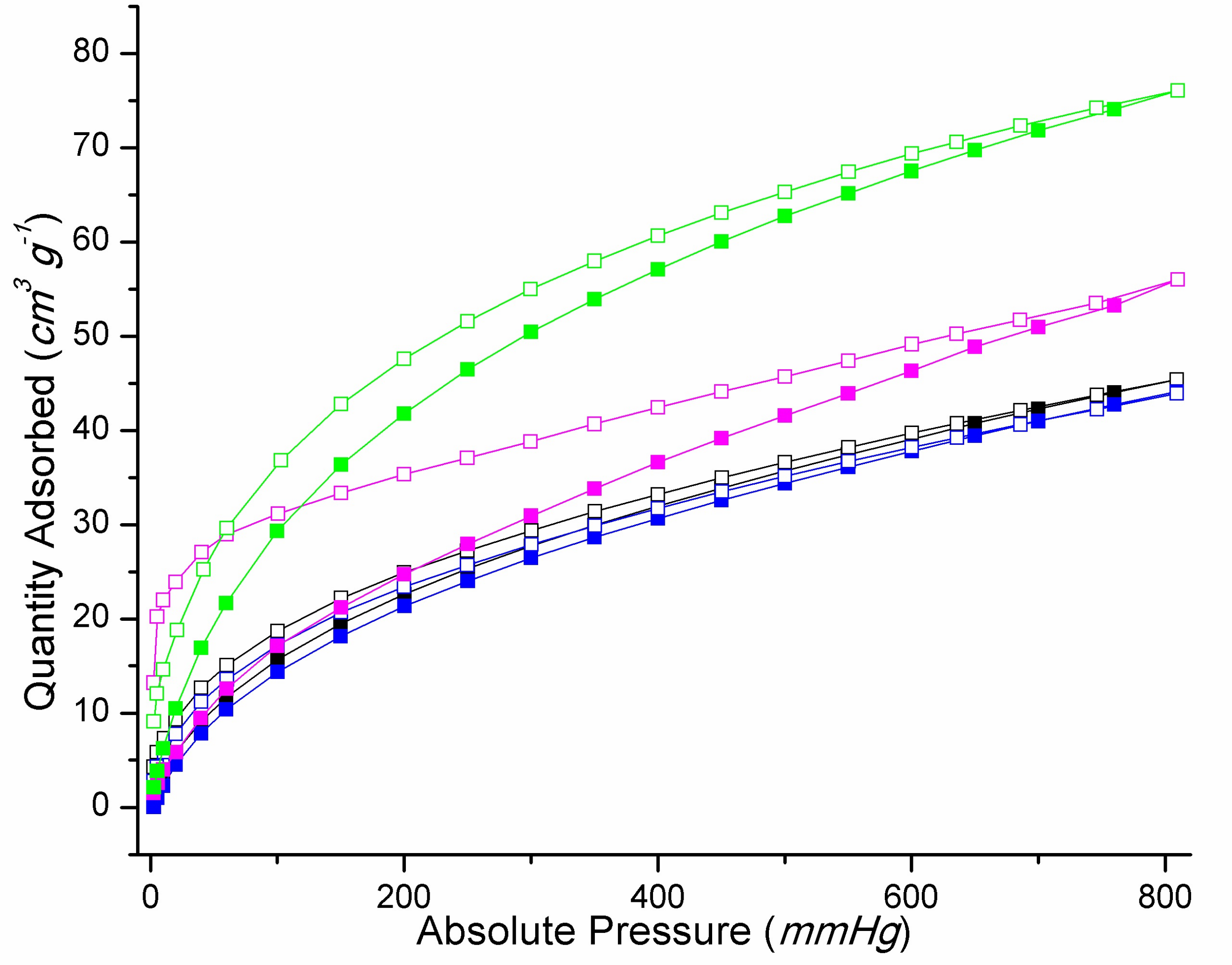


Figure S15. H_2 sorption isotherms at 77 K of IRMOF-3-AMCy (green), IRMOF-3-AM4ClPh (magenta), IRMOF-3-AM2ClPh (black), and IRMOF-3-AM3ClPh (blue). Filled symbols represent adsorption process, and emptied symbols represent desorption process.

Table S1. Summary BET surface areas of IRMOFs.

MOFs	**BET surface area (m^2 g^{-1})** [a]
α-IRMOF-3-AMPh	7±6
β-IRMOF-3-AMPh	1521±28
IRMOF-3-AM4ClPh	66±4
IRMOF-3-AM3ClPh	169±14
IRMOF-3-AM2ClPh	229±42
IRMOF-3-AMCy	436±31

[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.

IRMOF-3-	AMPh (α-)	AMPh (β-)	AM4ClPh	AM3ClPh	AM2ClPh	AMCy
100 K	Cubic *P*	Cubic *F*	Cubic *P*	Cubic *F*	Cubic *F*	Cubic *F*
280 K	Cubic *P*	Cubic *F*	Cubic *P*	Cubic *F*	Cubic *F*	Cubic *F*

Table S3. Crystal data and structure refinement for *α*-IRMOF-3-AMPh.

Identification code	*α*-IRMOF-3-AMPh
Empirical formula	$C_{45} H_{27} N_3 O_{13} Zn_4$
Formula weight	1127.18
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	Pa-3
Unit cell dimensions	a = b = c = 25.5775(18) Å α = β = γ = 90°
Volume	16733(2) $Å^3$
Z	8
Density (calculated)	0.835 Mg/m^3
Absorption coefficient	1.168 mm^{-1}
F(000)	4528
Crystal size	0.20 x 0.10 x 0.10 mm^3
Theta range for data collection	1.59 to 23.26°.
Index ranges	0<=h<=19, 0<=k<=20, 2<=l<=28
Reflections collected	4009
Independent reflections	4009 [R(int) = 0.0545]
Completeness to theta = 23.26°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9111 and 0.8910
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4009 / 15 / 136
Goodness-of-fit on F^2	1.008
Final R indices [I>2sigma(I)]	R1 = 0.0947, wR2 = 0.2677
R indices (all data)	R1 = 0.1271, wR2 = 0.2881
Largest diff. peak and hole	0.605 and -1.133 $e.Å^{-3}$

Table S4. Crystal data and structure refinement for *β*-IRMOF-3-AMPh.

Identification code	*β*-IRMOF-3-AMPh
Empirical formula	$C_{24} N_6 O_{13} Zn_4$
Formula weight	841.78
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Cubic
Space group	Fm-3m
Unit cell dimensions	a = b = c = 25.7009(9) Å α = β = γ = 90°.
Volume	16976.4(10) $Å^3$
Z	8
Density (calculated)	0.659 Mg/m^3
Absorption coefficient	1.522 mm^{-1}
F(000)	3280
Crystal size	0.40 x 0.40 x 0.30 mm^3
Theta range for data collection	2.98 to 67.96°.
Index ranges	0<=h<=17, 0<=k<=21, 1<=l<=30
Reflections collected	836
Independent reflections	836 [R(int) = 0.0000]
Completeness to theta = 67.96°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9364 and 0.9153
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	836 / 0 / 31
Goodness-of-fit on F^2	1.274
Final R indices [I>2sigma(I)]	R_1 = 0.0749, wR_2 = 0.2656
R indices (all data)	R_1 = 0.0780, wR_2 = 0.2699
Largest diff. peak and hole	0.427 and -0.636 e.$Å^{-3}$

Table S5. Crystal data and structure refinement for IRMOF-3-AM4ClPh.

Identification code	IRMOF-3-AM4ClPh
Empirical formula	$C_{45} H_{24} Cl_3 N_3 O_{16} Zn_4$
Formula weight	1230.50
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	Pa-3
Unit cell dimensions	a = b = c = 25.3840(10) Å α = β = γ =90°
Volume	16356.1(11) Å^3
Z	8
Density (calculated)	0.997 Mg/m^3
Absorption coefficient	1.300 mm^{-1}
F(000)	4888
Crystal size	0.50 x 0.50 x 0.40 mm^3
Theta range for data collection	1.79 to 25.33°.
Index ranges	0<=h<=21, 0<=k<=21, 2<=l<=30
Reflections collected	4997
Independent reflections	4997 [R(int) = 0.0000]
Completeness to theta = 25.33°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8856 and 0.8657
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4997 / 15 / 99
Goodness-of-fit on F^2	1.576
Final R indices [I>2sigma(I)]	R_1 = 0.1544, wR_2 = 0.4234
R indices (all data)	R_1 = 0.1882, wR_2 = 0.4419
Largest diff. peak and hole	1.678 and -0.874 e.Å^{-3}

Table S6. Crystal data and structure refinement for IRMOF-3-AM3ClPh.

Identification code	IRMOF-3-AM3ClPh
Empirical formula	$C_{24} N_6 O_{13} Zn_4$
Formula weight	841.78
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Cubic
Space group	Fm-3m
Unit cell dimensions	a = b = c = 25.6910(17) Å α = β = γ = 90°
Volume	16956.8(19) $Å^3$
Z	8
Density (calculated)	0.659 Mg/m^3
Absorption coefficient	1.524 mm^{-1}
F(000)	3280
Crystal size	0.30 x 0.30 x 0.30 mm^3
Theta range for data collection	6.89 to 68.02°.
Index ranges	0<=h<=17, 0<=k<=21, 3<=l<=30
Reflections collected	814
Independent reflections	814 [R(int) = 0.0368]
Completeness to theta = 68.02°	97.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8972 and 0.8729
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	814 / 0 / 31
Goodness-of-fit on F^2	1.425
Final R indices [I>2sigma(I)]	R_1 = 0.0930, wR_2 = 0.3115
R indices (all data)	R_1 = 0.1035, wR_2 = 0.3386
Largest diff. peak and hole	0.454 and -0.615 e.$Å^{-3}$

Table S7. Crystal data and structure refinement for IRMOF-3-AM2ClPh.

Identification code	IRMOF-3-AM2ClPh
Empirical formula	$C_{24} O_{13} Zn_4$
Formula weight	757.72
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Cubic
Space group	F-43m
Unit cell dimensions	a = b = c = 25.6590(13) Å α = β = γ = 90°
Volume	16893.5(15) $Å^3$
Z	8
Density (calculated)	0.596 Mg/m^3
Absorption coefficient	1.481 mm^{-1}
F(000)	2944
Crystal size	0.40 x 0.40 x 0.40 mm^3
Theta range for data collection	4.87 to 69.42°.
Index ranges	-16<=h<=17, 0<=k<=21, 2<=l<=31
Reflections collected	1528
Independent reflections	1528 [R(int) = 0.0586]
Completeness to theta = 69.42°	97.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9120 and 0.8972
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1528 / 2 / 45
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R_1 = 0.0832, wR_2 = 0.2490
R indices (all data)	R_1 = 0.1053, wR_2 = 0.2783

Table S8. Crystal data and structure refinement for IRMOF-3-AMCy.

Identification code	IRMOF-3-AMCy
Empirical formula	$C_{24} O_{13} Zn_4$
Formula weight	757.72
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Cubic
Space group	F-43m
Unit cell dimensions	a = b = c = 25.6177(9) Å α = β = γ = 90°
Volume	16812.0(10) $Å^3$
Z	8
Density (calculated)	0.599 Mg/m^3
Absorption coefficient	1.488 mm^{-1}
F(000)	2944
Crystal size	0.40 x 0.40 x 0.10 mm^3
Theta range for data collection	6.91 to 68.43°.
Index ranges	-16<=h<=12, 0<=k<=21, 3<=l<=30
Reflections collected	1391
Independent reflections	1391 [R(int) = 0.0405]
Completeness to theta = 68.43°	96.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9324 and 0.9123
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1391 / 0 / 46
Goodness-of-fit on F^2	1.359
Final R indices [I>2sigma(I)]	R_1 = 0.1331, wR_2 = 0.3197
R indices (all data)	R_1 = 0.1489, wR_2 = 0.3407
Absolute structure parameter	0.2(4)
Largest diff. peak and hole	1.442 and -1.040 e.$Å^{-3}$

References.

(1) Wang, Z.; Tanabe, K. K.; Cohen, S. M. *Chem. Eur. J.* **2010**, *16*, 212.
(2) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 122.
(3) Spek, A. L. *Acta Cryst.* **2009**, *D65*, 148.