

Chemically Crosslinked Isorecticular Metal-Organic Frameworks

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SUPPORTING INFORMATION

EXPERIMENTAL

General. 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 (^1H NMR) were recorded by a Varian FT-NMR spectrometer (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak. 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.

Ligand Synthesis

General Synthesis for Tetramethyl Ester. Dimethyl-2-aminoterephthalate (1.0 g, 4.6 mmol) was dissolved in 10 mL DMF. The dichloride (2.2 mmol) was added and stirred overnight. The DMF solvent was removed by rotary evaporation and the residue was washed with acetone, filtered, and dried overnight to obtain the protected ligand as a white powder. Running the reaction on a larger scale often resulted in lower yields; however, multiple batches of the protected ligand could be combined into single hydrolysis reactions to produce large quantities of the desired ligands.

General Hydrolysis to $\text{XL}_n\text{AM-BDC}$. The tetra ester was dissolved in THF (varying amounts depending on the scale of the reaction) and an equal volume of 4% KOH(aq). This was stirred for 1 h, the aqueous layer was collected and acidified to pH ~2 with 1 M HCl. A white precipitate formed, which was washed with water, filtered, and dried at

room temperature under vacuum overnight.

Tetramethyl 2,2'-(glutaroylbis(azanediyl))diterephthalate. Yield: 630 mg (57%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 2.23 (t, 2H; CH₂), 2.62 (t, 4H; CH₂), 3.93 (d, 12H; CO₂CH₃), 7.72 (d, 1H; ArH), 8.07 (d, 1H; ArH), 9.34 (s, 1H; ArH), 11.06 (s, 2H; NH). ESI-MS(+): *m/z* 514.84[M+H]⁺, 531.76[M+NH₄]⁺.

2,2'-(Glutaroylbis(azanediyl))diterephthalic acid. Yield: 7.9 g, 15.2 mmol (99%). ¹H NMR (DMSO, 400 MHz, 25°C): δ 1.95 (t, 2H; CH₂), 2.48 (t, 4H; CH₂), 7.64(d, 1H; ArH), 7.99 (d, 1H; ArH), 8.97 (s, 1H; ArH), 11.05 (s, 2H; NH). ESI-MS(-): *m/z* 457.07[M-H]⁻, 479.07[M+Na-2H]⁻, 496.07[M+K-2H]⁻.

Tetramethyl 2,2'-(adipoylbis(azanediyl))diterephthalate. Yield: 890 mg (78%). ¹H NMR (CDCl₃, 400 MHz, 25°C): δ 1.88 (t, 4H; CH₂), 2.53 (t, 4H; CH₂), 3.93 (d, 12H; CO₂CH₃), 7.72 (d, 1H; ArH), 8.06 (d, 1H; ArH), 9.33 (s, 1H; ArH), 11.05 (s, 2H; NH). ESI-MS(+): *m/z* 528.90[M+H]⁺, 545.83[M+NH₄]⁺.

2,2'-(Adipoylbis(azanediyl))diterephthalic acid. Yield: 8.23 g, 17.42 mmol (92%). ¹H NMR (DMSO, 400 MHz, 25°C): δ 1.68 (t, 4H; CH₂), 2.44 (t, 4H; CH₂), 7.63 (d, 1H; ArH), 8.01 (d, 1H; ArH), 8.99 (s, 1H; ArH), 11.04 (s, 2H; NH). ESI-MS(-): *m/z* 471.11[M-H]⁻, 493.12[M+Na-2H]⁻.

Tetramethyl 2,2'-(pimeloylbis(azanediyl))diterephthalate. Yield: 560 mg (48%). ¹H

NMR (CDCl₃, 400 MHz, 25°C): δ 1.52 (m, 2H; CH₂), 1.84 (m, 4H; CH₂), 2.49 (t, 4H; CH₂), 3.93 (d, 12H; CO₂CH₃), 7.74 (d, 1H; ArH), 8.07 (d, 1H; ArH), 9.35 (s, 1H; ArH), 11.03 (s, 2H; NH). ESI-MS(+): m/z 542.96[M+H]⁺, 559.85[M+NH₄]⁺.

2,2'-(Pimeloylbis(azanediyl))diterephthalic acid. Yield: 7.2 g, 14.8 mmol (99%). ¹H NMR (DMSO, 400 MHz, 25°C): δ 1.39 (t, 2H; CH₂), 1.66 (t, 4H; CH₂), 2.41 (t, 4H; CH₂), 7.64 (d, 1H; ArH), 8.02 (d, 1H; ArH), 8.01 (s, 1H; ArH), 11.05 (s, 2H; NH). ESI-MS(-): m/z 485.17[M-H]⁻, 507.17[M+Na-2H]⁻.

Tetramethyl 2,2'-(suberoylbis(azanediyl))diterephthalate. Yield: 100 mg (9%). ¹H NMR (CDCl₃, 400 MHz, 25°C): δ 1.46 (m, 4H; CH₂), 1.79 (t, 4H; CH₂), 2.47 (t, 4H; CH₂), 3.93 (d, 12H; CO₂CH₃), 7.73 (d, 1H; ArH), 8.07 (d, 1H; ArH), 9.35 (s, 1H; ArH), 11.01 (s, 2H; NH). ESI-MS(+): m/z 557.01[M+H]⁺, 573.89[M+NH₄]⁺.

2,2'-(Suberoylbis(azanediyl))diterephthalic acid. Yield: 7.8 g, 15.5 mmol (95%). ¹H NMR (DMSO, 400 MHz, 25°C): δ 1.37 (t, 4H; CH₂), 1.64 (t, 4H; CH₂), 2.41 (d, 4H; CH₂), 7.67 (d, 1H; ArH), 8.03 (d, 1H; ArH), 9.304(s, 1H; ArH), 11.05 (s, 2H; NH). ESI-MS(-): m/z 499.22[M-H]⁻, 521.15[M+Na-2H]⁻.

Tetramethyl 2,2'-(azelaoylbis(azanediyl))diterephthalate. Yield: 500 mg (41%). ¹H NMR (CDCl₃, 400 MHz, 25°C): δ 1.42 (m, 6H; CH₂), 1.77 (t, 4H; CH₂), 2.46 (t, 4H; CH₂), 3.93 (d, 12H; CO₂CH₃), 7.73 (d, 1H; ArH), 8.08 (d, 1H; ArH), 9.36 (s, 1H; ArH), 11.02 (s, 2H; NH). ESI-MS(+): m/z 571.04[M+H]⁺, 587.88[M+NH₄]⁺.

2,2'-(Azelaoylbis(azanediyl))diterephthalic acid. Yield: 1.7 g, 3.28 mmol (90%). ^1H NMR (DMSO, 400 MHz, 25°C): δ 1.31 (t, 6H; CH_2), 1.60 (t, 4H; CH_2), 2.37 (d, 4H; CH_2), 7.64 (d, 1H; ArH), 8.01 (d, 1H; ArH), 8.99 (s, 1H; ArH), 11.04 (s, 2H; NH). ESI-MS(-): m/z 513.14[M-H] $^-$, 535.14[M+Na-2H] $^-$.

Characterization Experiments

BET Surface Area Analysis. ~60-100 mg of MOF (stored in CHCl_3) was evacuated on a vacuum line for <1 min at room temperature. The sample was transferred to a preweighed sample tube and degassed at 105 or 150 °C (depending on chain length, see main text) for a minimum of 12 h or until the outgas rate was < 5 μmHg . The sample tube was re-weighed to obtain a consistent sample mass. BET surface area (m^2/g) measurements were collected on at least three independent samples of each MOF at 77 K using dinitrogen and the volumetric technique.

^1H NMR Analysis. ~5 mg of MOF was used immediately following BET analysis and digested in 500 μL of d^6 -DMSO and 100 μL of dilute DCl (23 μL of 35% DCl in D_2O diluted with 1.0 mL of d^6 -DMSO).

ESI-MS Analysis. Samples for analysis were prepared by taking 10 μL of the ^1H NMR solution diluted with 1 mL MeOH.

Thermal Analysis. ~10-20 mg was used immediately following BET analysis. Samples were analyzed under a dinitrogen stream from room temperature to 600 °C at a ramping rate of 5 °C/min.

PXRD Analysis. ~15 mg of MOF (soaked in DMF) was air dried prior to PXRD analysis. Powder X-ray diffraction (PXRD) data were collected at ambient temperature with a scan speed of 0.5 sec/step, step size of 0.02° in 2θ , and a 2θ range of $3-40^\circ$.

Single Crystal X-ray Diffraction. Single crystals of IRMOF-AM n XL were mounted on nylon loops with Paratone oil and placed under a nitrogen cold stream (200-250 K). Increased temperature notably improved the diffraction of the crystals as has been seen previously.¹ The resolution of the diffraction is approximately 1.1 Å and the data was collected up to 0.95 Å. All structures were assigned in $Fm-3m$ by SHELXTL however for AM5-6XL, a solution for the data could not be determined until solved in $F-43m$. A semiempirical method utilizing equivalents was employed to correct for absorption. All data collections were solved and refined using SHELXTL and treated with the “SQUEEZE” protocol in PLATON to account for electron density associated with the alkyl linkers and disordered solvent molecules (e.g. DMF, $CHCl_3$) within the framework. These structures have been deposited to the CCDC under deposition numbers 906534-906538.

Computational Methods. All molecular dynamics simulations were performed with DL_POLY2² on a MOF-5³ structure consisting of 27 unit cells with periodic boundary conditions. The MM3 force field⁴ used was specifically parameterized for MOF-5 by Schmid and co-workers,⁵ adding the missing term for the ligands from the original MM3 force field. Partial charges for the crosslinked ligands were fitted to the calculated electrostatic potential using the CHELPG scheme⁶ after a full optimization of the ligand using the B3LYP⁷ functional with the triple- ζ basis set⁸ from Ahlrichs and co-workers on all atoms, using the Gaussian09 code.⁹ The short-range interactions were truncated at an

atom-atom distance of 9.0 Å. The isorecticular MOFs were modeled from the crystallographic data on MOF-5, modifying a pair of 1,4-benzenedicarboxylate (BDC) ligands to become bounded via the amide based linkers (L3-7). The different isomers were generated in silico, and allowed to relax during a molecular dynamics simulation of 100ps in the canonical (NVT) ensemble. After the relaxation, 500ps were run in the constant stress and constant temperature (N σ T) ensemble, at 77K and 1 atm. Temperature and pressure were maintained using a Hoover thermostat with relaxation times of 1ps for both temperature and pressure. The equations of motion were propagated with a time step of 1fs.

Computational Results. To explore which of the four possible isomers (Fig. S8) are possible for any given aliphatic chain, in silico modeling of the MOF-5 unit cell was done. As expected, the crosslinked ligands with shorter chains (L3-4) can only be modeled in the isomer 1 configuration. Although both systems are stable through the MD simulations, small distortions of the unit cell can be observed due to the tension introduced by the crosslinking. This is particularly clear in the L3, which has the shortest aliphatic chain, thus introducing maximum tension in the framework. L5 is the first ligand that can be modeled in configurations for isomers 1 and 2. Again, MD simulations are stable in both isomers. It must be noted that the length between edges in the crystallographic MOF-5 structure is approximately ~ 10 Å, which is very similar to the maximum length that L5 can attain (~ 10.5 Å). Thus, although possible, isomer 2 introduces a certain degree of tension between edges that can be followed during the MD simulation. L6 can be modeled in isomers 1, 2, and 3 configurations. No substantial

differences are observed during the simulations. Finally, only L7 can be modeled in all four possible isomer configurations. Although the MD simulations provide insight in the possible configurations that can be obtained as a function of linker length, they are not able rule out more complex scenarios such as combinations of isomers within one lattice. Experiments are ongoing to elucidate the exact conformations for crosslinked ligands in a more complex model of the MOF material containing multiple crosslinks.

MOF Synthesis and Characterization

IRMOF-3-AM3XL. 2,2'-(Glutaroylbis(azanediyl))diterephthalic acid (1.88 g, 4.1 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (6.84 g, 23 mmol) were dissolved in DMF (200 mL). These were separated into 20 scintillation vials (10 mL/ea) and heated in a sand bath inside a temperature-controlled oven at 2.5 °C/min from 35 °C to 100 °C, held at 100 °C for 18 h, and then cooled to room temperature at 2.5 °C/min. The resulting colorless, block crystals were washed with DMF (3×10 mL) and CHCl_3 (10 mL). The CHCl_3 was exchanged once a day for three full days of washing. Yield: 101 mg (78%).

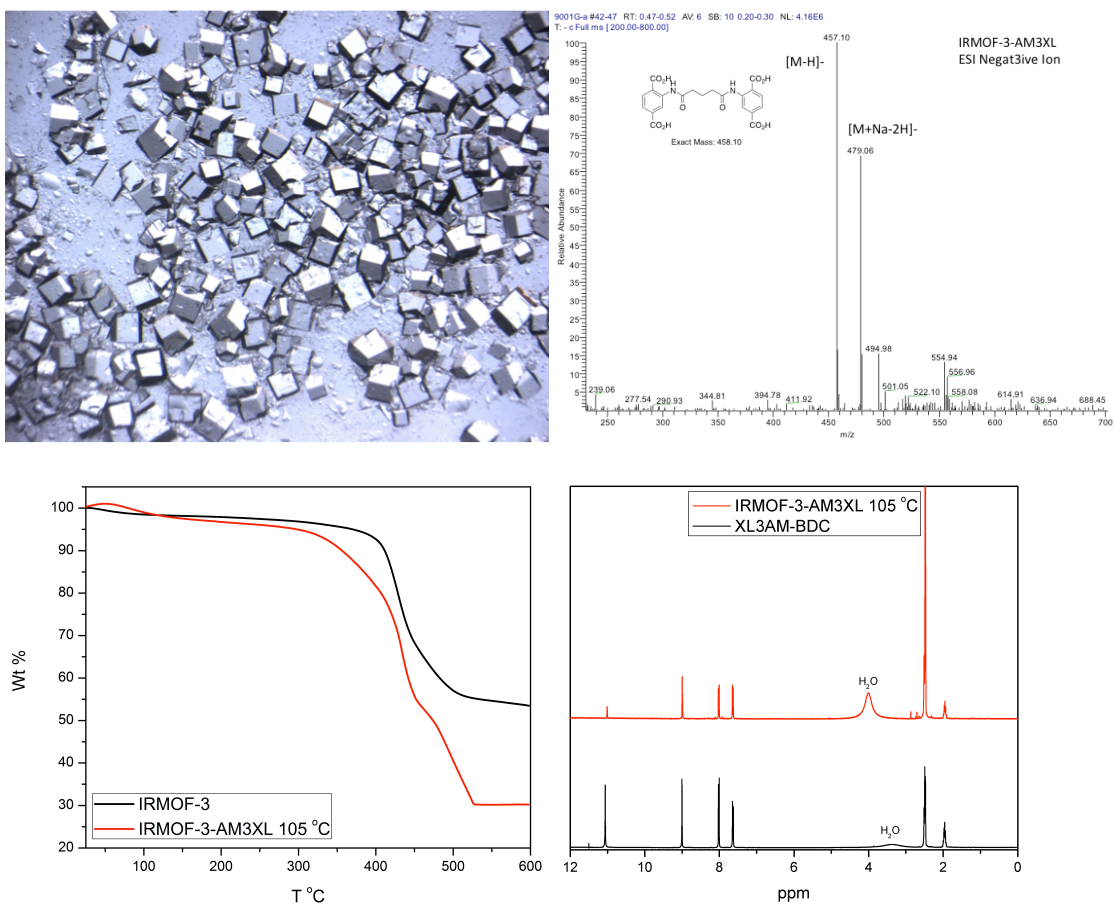


Figure S1. Characterization of IRMOF-3-AM3XL. Clockwise from top left: photograph of crystals; ESI-MS analysis of digested crystals; TGA analysis of activated crystals (compared to IRMOF-3); and ¹H NMR analysis of the parent ligand (black) and activated, digested crystals (red).

IRMOF-3-AM4XL. 2,2'-(Adipoylbis(azanediyl))diterephthalic acid (1.93 g, 4.1 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (6.84 g, 23 mmol) were dissolved in DMF (200 mL). These were separated into 20 scintillation vials (10 mL) and heated in a sand bath to 100 °C at 2.5 °C/min, left for 18 h, and cooled to room temperature at 2.5 °C/min. The colorless, block crystals were washed with DMF (3×10 mL) and CHCl_3 (10 mL). The CHCl_3 was exchanged once a day for a total of three days of soaking. Yield: 60 mg (46%).

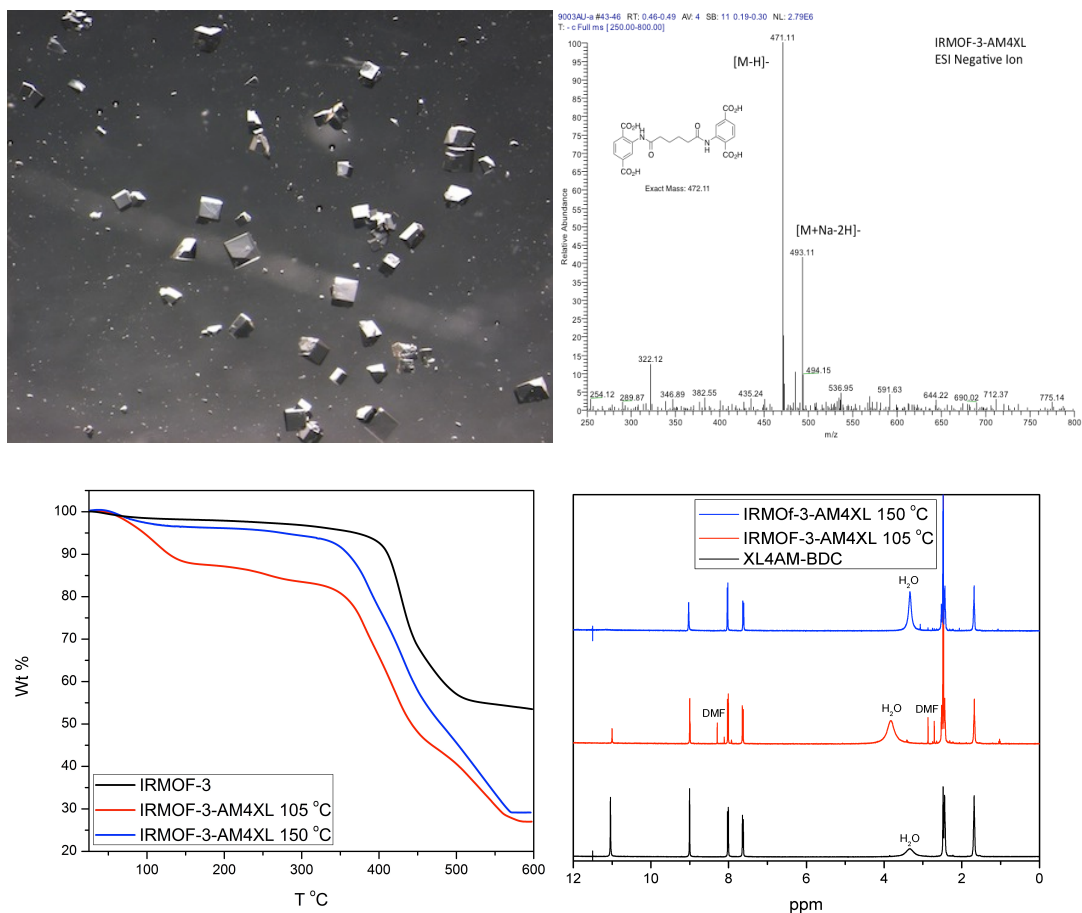


Figure S2. Characterization of IRMOF-3-AM4XL. Clockwise from top left: photograph of crystals; ESI-MS analysis of digested crystals; TGA analysis of activated crystals at both 105 and 150 °C (compared to IRMOF-3); and ¹H NMR analysis of the parent ligand (black), digested crystals after 105 °C activation (red) and activated at 150 °C, digested crystals (blue).

IRMOF-3-AM5XL. 2,2'-(Pimeloylbis(azanediyl))diterephthalic acid (0.5 g, 1.03 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.7 g, 5.74 mmol) were dissolved in DMF (50 mL). These were separated into 5 scintillation vials (10 mL) and heated in a sand bath to 100 °C at 2.5 °C/min, left for 48 h, and cooled to room temperature at 2.5 °C/min. The colorless, semi-opaque crystals were washed with DMF (3×10 mL) and CHCl_3 (10 mL). The CHCl_3 was exchanged once a day for a total of three days of soaking. Yield: 101 mg (75%).

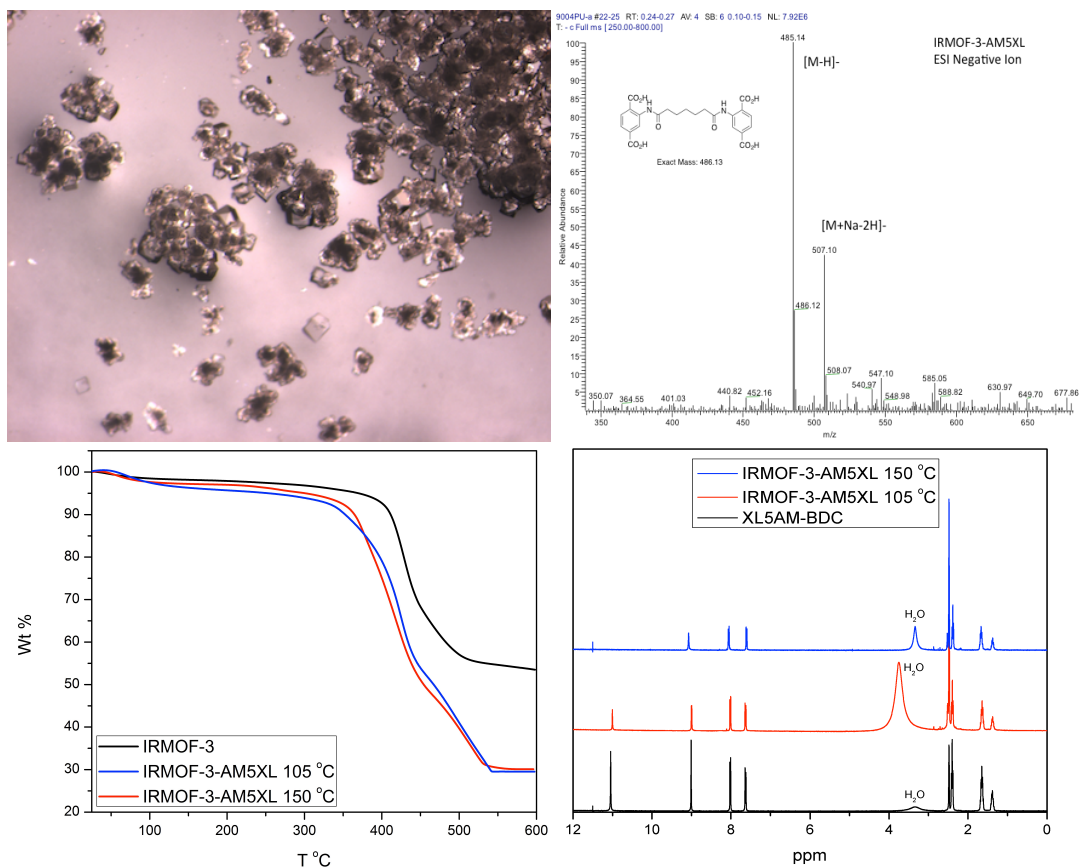


Figure S3. Characterization of IRMOF-3-AM5XL. Clockwise from top left: photograph of crystals; ESI-MS analysis of digested crystals; TGA analysis of activated crystals at both 105 and 150 °C (compared to IRMOF-3); and ¹H NMR analysis of the parent ligand (black), digested crystals after 105 °C activation (red) and activated at 150 °C, digested crystals (blue)

IRMOF-3-AM6XL. 2,2'-(Suberoylbis(azanediyl))diterephthalic acid (0.51 g, 1.03 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.7 g, 5.74 mmol) were dissolved in DMF (50 mL). These were separated into 5 scintillation vials (10 mL) and heated in a sand bath to 100 °C at 2.5 °C/min, left for 48 h, and cooled to room temperature at 2.5 °C/min. The beige, block crystals were washed with DMF (3×10 mL) and CHCl_3 (10 mL). The CHCl_3 was exchanged once a day for a total of three days of soaking. Yield: 99 mg (72%).

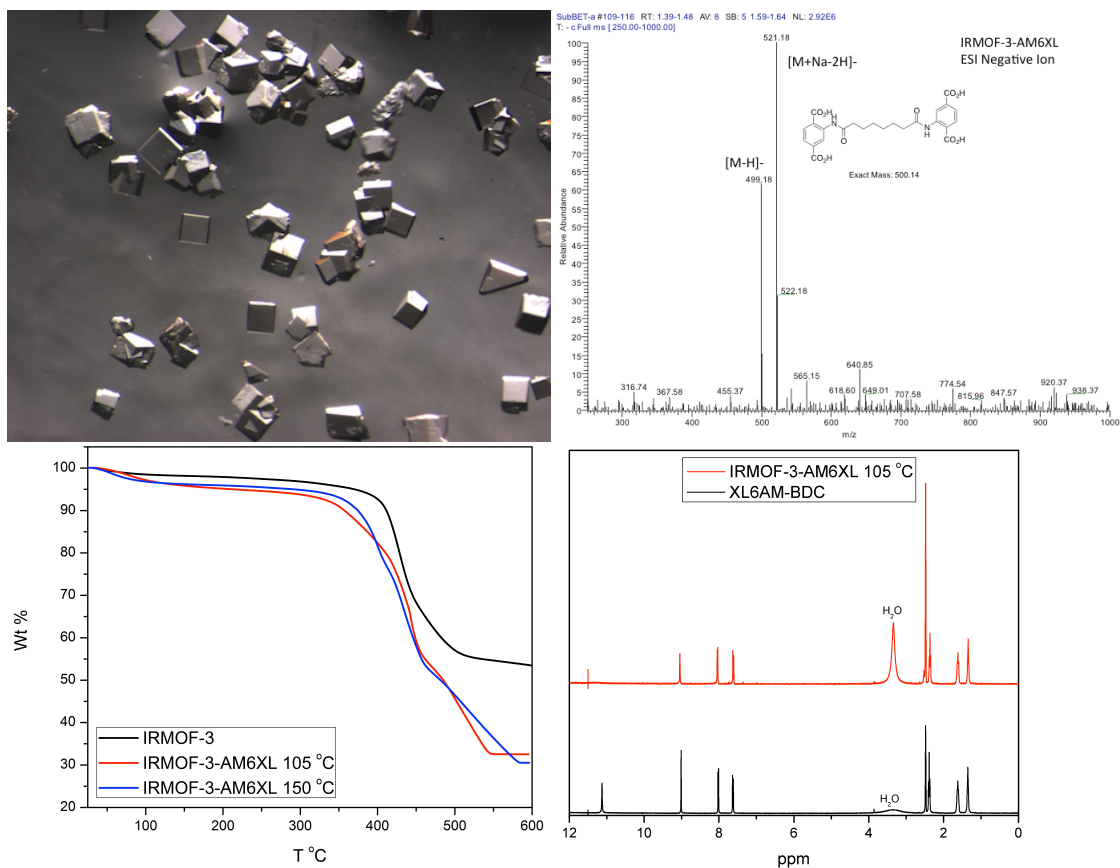


Figure S4. Characterization of IRMOF-3-AM6XL. Clockwise from top left: photograph of crystals; ESI-MS analysis of digested crystals; TGA analysis of activated crystals at both 105 and 150 °C (compared to IRMOF-3); and ¹H NMR analysis of the parent ligand (black) and digested crystals after activation (red).

IRMOF-3-AM7XL. 2,2'-(Azelaoylbis(azanediyl))diterephthalic acid (0.1 g, 0.2 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.34 g, 1.15 mmol) were dissolved in DMF (10 mL) in a scintillation vial. This was heated in a sand bath to 100 °C at 2.5 °C/min, left for 48 h, and cooled to room temperature at 2.5 °C/min. The beige, block crystals were washed with DMF (3×10 mL) and CHCl_3 (10 mL). The CHCl_3 was exchanged once a day for a total of three days of soaking. Yield: 73 mg (52%).

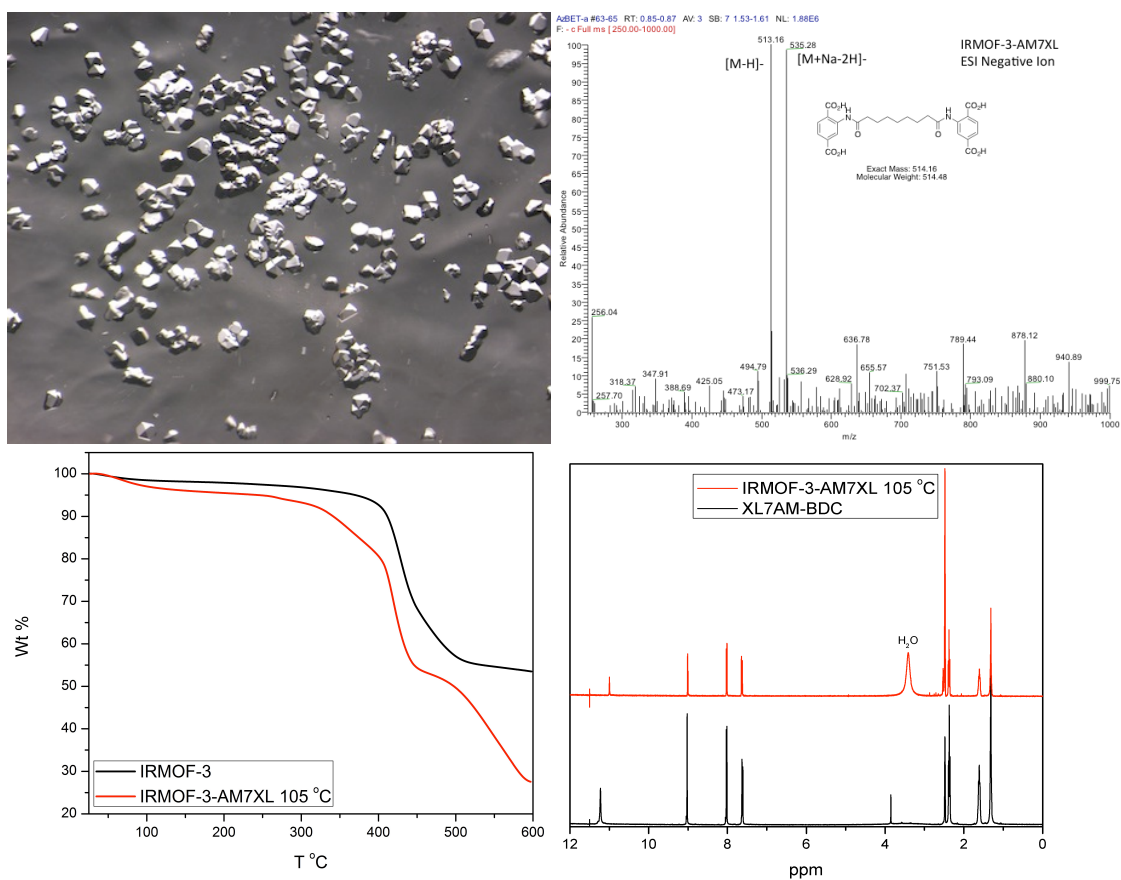


Figure S5. Characterization of IRMOF-3-AM7XL. Clockwise from top left: photograph of crystals; ESI-MS analysis of digested crystals; TGA analysis of activated crystals (compared to IRMOF-3); and ¹H NMR analysis of the parent ligand (black) and activated, digested crystals (red).

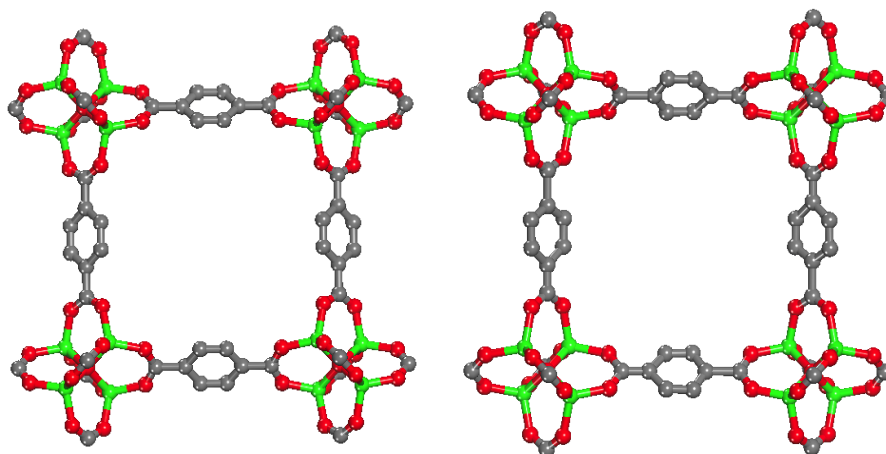


Figure S6. Representation of crystal structures for IRMOF-3-AM3XL (top) and IRMOF-3-AM6XL (bottom). All of the crosslinked MOFs showed the expected IRMOF topology; however, the chemical crosslinks could not be resolved in the electron density maps.

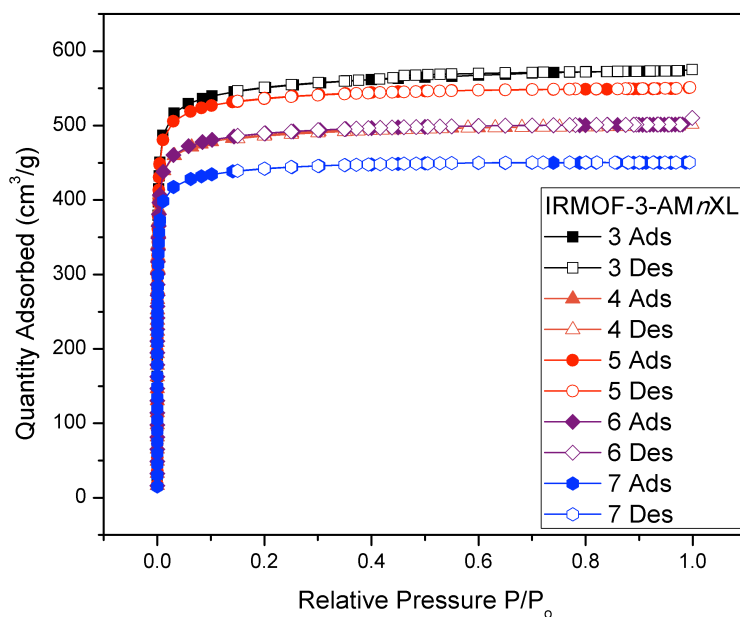


Figure S7. N₂ isotherms of IRMOF-3-AM_nXL materials activated at 105 °C. Filled and open symbols represent the absorption and desorption curves, respectively.

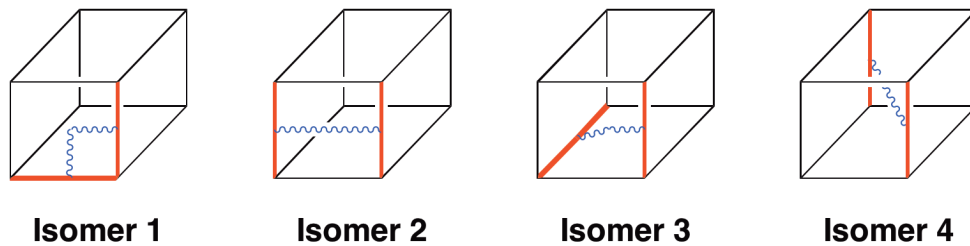


Figure S8. Possible linkage isomers for IRMOF-3-AM n XL. Curved blue lines represent the linker and bold red lines represent the crosslinked ligands.

Table S1. Crystallographic data tables for IRMOF-3-AM(3-5)XL.

Identification code	IRMOF-3-AM3XL	IRMOF-3-AM4XL	IRMOF-3-AM5XL
Empirical formula	C _{31.5} H _{25.6} N ₃ O ₁₆ Zn ₄	C ₃₃ O ₁₆ Zn ₄ H ₂₇ N ₃	C _{34.5} H ₃₀ N ₃ O ₁₆ Zn ₄
Formula weight	766.79	759.72	763.77
Temperature	200(2) K	250(2) K	250(2) K
Wavelength	1.54178 Å	0.71073 Å	1.54178 Å
Crystal system	Cubic	Cubic	Cubic
Space group	<i>Fm-3m</i>	<i>Fm-3m</i>	<i>F-43m</i>
Unit cell dimensions	$a = b = c =$ 25.5827(7) Å $\alpha = \beta = \gamma = 90^\circ$	$a = b = c =$ 25.543(2) Å $\alpha = \beta = \gamma = 90^\circ$	$a = b = c =$ 25.6341(6) Å $\alpha = \beta = \gamma = 90^\circ$
Volume	16743.2(8) Å ³	16666(3) Å ³	16844.3(7) Å ³
Z	8	8	8
Density (calculated)	0.608 Mg/m ³	0.604 Mg/m ³	0.602 Mg/m ³
Absorption coefficient	1.494 mm ⁻¹	1.159 mm ⁻¹	1.485 mm ⁻¹
F(000)	3016	2944	2992
Crystal size (mm ³)	0.20 x 0.15 x 0.15	0.10 x 0.10 x 0.05	0.08 x 0.05 x 0.05
Theta range	2.99 to 46.06°.	3.19 to 19.72°.	2.99 to 68.33°.
Reflections collected	374	2430	8625
Independent reflections	374 [<i>R</i> (int) = 0.0229]	430 [<i>R</i> (int) = 0.0326]	1489 [<i>R</i> (int) = 0.0380]
Completeness to theta = 46.06°	90.1 %	98.6 %	99.8 %
Refinement Method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	374 / 2 / 25	430 / 0 / 25	1489 / 2 / 49
Goodness-of-fit on F ²	1.329	1.132	1.225
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.1085, <i>wR</i> 2 = 0.3319	<i>R</i> 1 = 0.0900, <i>wR</i> 2 = 0.2624	<i>R</i> 1 = 0.0995, <i>wR</i> 2 = 0.2994
R indices (all data)	<i>R</i> 1 = 0.1188, <i>wR</i> 2 = 0.3420	<i>R</i> 1 = 0.1108, <i>wR</i> 2 = 0.2908	<i>R</i> 1 = 0.1087, <i>wR</i> 2 = 0.3213
Largest diff. peak and hole	0.316 and -0.290 e.Å ⁻³	0.466 and -0.540 e.Å ⁻³	1.115 and -0.288 e.Å ⁻³

Table S2. Crystallographic data tables for IRMOF-3-AM(6-7)XL.

Identification code	IRMOF-3-AM6XL	IRMOF-3-AM7XL
Empirical formula	C ₃₆ H ₃₃ N ₃ O ₁₆ Zn ₄	C _{37.5} H ₃₆ N ₃ O ₁₆ Zn ₄
Formula weight	763.77	757.72
Temperature	250(2) K	250(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Cubic	Cubic
Space group	<i>F</i> -43 <i>m</i>	<i>Fm</i> -3 <i>m</i>
Unit cell dimensions	$a = b = c = 25.741(3) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$	$a = b = c = 25.654(19) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume	17055(3) Å ³	16884(22) Å ³
Z	8	8
Density (calculated)	0.595 Mg/m ³	0.596 Mg/m ³
Absorption coefficient	1.132 mm ⁻¹	1.144 mm ⁻¹
F(000)	2992	2944
Crystal size	0.10 x 0.10 x 0.08 mm ³	0.40 x 0.40 x 0.20 mm ³
Theta range	1.58 to 21.68°.	2.63 to 19.70°.
Reflections collected	3726	1773
Independent reflections	1018 [<i>R</i> (int) = 0.0252]	418 [<i>R</i> (int) = 0.1061]
Completeness to theta = 21.68°	99.5 %	95.7 %
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	1018 / 0 / 49	418 / 1 / 21
Goodness-of-fit on <i>F</i> ²	1.100	1.107
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0668, <i>wR</i> 2 = 0.1999	<i>R</i> 1 = 0.1074, <i>wR</i> 2 = 0.2889
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0769, <i>wR</i> 2 = 0.2063	<i>R</i> 1 = 0.1454, <i>wR</i> 2 = 0.3421
Largest diff. peak and hole	0.518 and -0.753 e.Å ⁻³	0.718 and -0.744 e.Å ⁻³

Table S3. Brunauer-Emmett-Teller (BET) surface area measurements after activation at 105 °C under vacuum.

IRMOF-3-AM n XL	BET (m ² /g)	Std. Dev. (m ² /g) ^a	Pore Size (Å) ^b
3	2049	8	6.72
4 (150 °C)	1774	15	6.62
4	1618	21	6.58
5	1636	55	6.59
6	1827	23	6.49
7	1575	49	6.41

^a Standard deviations are from three independent samples.

^b Pore sizes measured using the HK model from N₂ isotherms at 77K.

Table S4. Elemental Analysis of activated IRMOF-3-AM n XL materials.

n^a	Molecular Formula ^b	Wt% Calc	Wt% Exp ^c	Difference
3	Zn ₄ O(C ₂₁ H ₁₄ N ₂ O ₁₀) _{3/2}	952.81		
	C	39.67%	39.72%	-0.05%
	H	2.22%	3.20%	-0.98%
	N	4.40%	5.34%	-0.94%
4	Zn ₄ O(C ₂₂ H ₁₆ N ₂ O ₁₀) _{3/2}	973.83		
	C	40.66%	39.98%	0.68%
	H	2.48%	3.27%	-0.79%
	N	4.31%	5.07%	-0.76%
4 (150)	Zn ₄ O(C ₂₂ H ₁₆ N ₂ O ₁₀) _{3/2}	973.83		
	C	40.66%	39.76%	0.90%
	H	2.48%	3.18%	-0.70%
	N	4.31%	4.93%	-0.62%
5	Zn ₄ O(C ₂₃ H ₁₈ N ₂ O ₁₀) _{3/2}	994.86		
	C	41.60%	41.24%	0.36%
	H	2.73%	3.24%	-0.51%
	N	4.22%	4.81%	-0.59%
6	Zn ₄ O(C ₂₄ H ₂₀ N ₂ O ₁₀) _{3/2}	1015.88		
	C	42.52%	41.78%	0.74%
	H	2.97%	3.28%	-0.31%
	N	4.13%	4.57%	-0.44%
7	Zn ₄ O(C ₂₅ H ₂₂ N ₂ O ₁₀) _{3/2}	1036.9		
	C	43.39%	42.97%	0.42%
	H	3.20%	3.64%	-0.44%
	N	4.05%	4.50%	-0.45%

^a All samples activated at 105 °C unless noted otherwise.

^b Calculated with both BDC ends structurally incorporated into the MOF.

^c Based on two independent samples in duplicate.

Table S5. Elemental Analysis of activated IRMOF-3-AM n XL materials.

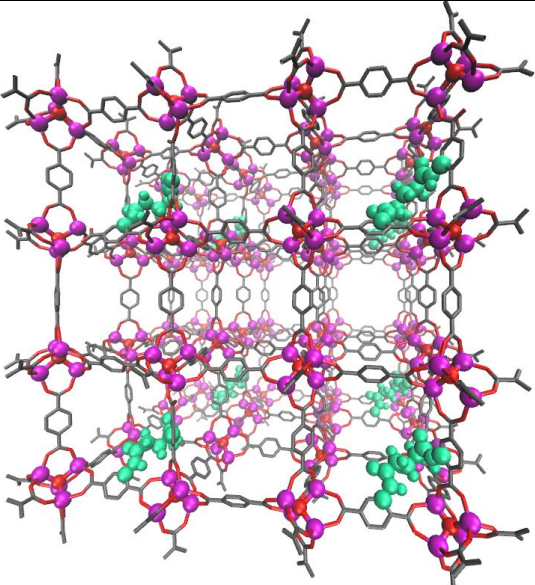
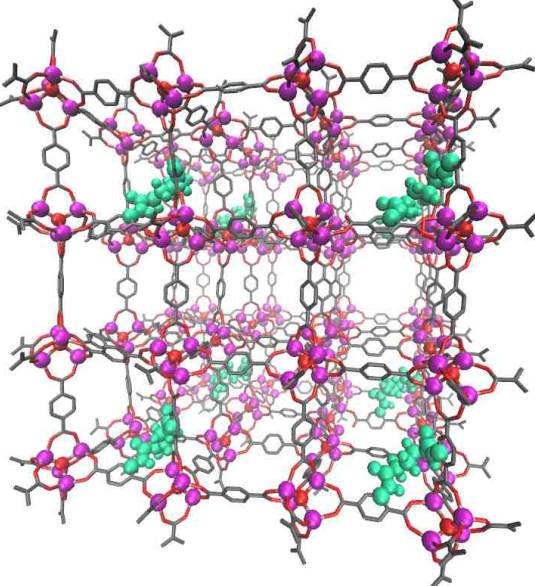
n^a	Molecular Formula ^b	Wt% Calc	Wt% Exp ^c	Difference
3	Zn ₄ O(C ₂₁ H ₁₄ N ₂ O ₁₀) ₃	1639.95		
	C	46.09%	39.72%	6.37%
	H	2.95%	3.20%	-0.25%
	N	5.12%	5.34%	-0.22%
4	Zn ₄ O(C ₂₂ H ₁₆ N ₂ O ₁₀) ₃	1682		
	C	47.08%	39.98%	7.10%
	H	3.23%	3.27%	-0.04%
	N	4.99%	5.07%	-0.08%
4 (150)	Zn ₄ O(C ₂₂ H ₁₆ N ₂ O ₁₀) ₃	1682		
	C	47.08%	39.76%	7.32%
	H	3.23%	3.18%	0.05%
	N	4.99%	4.93%	0.06%
5	Zn ₄ O(C ₂₃ H ₁₈ N ₂ O ₁₀) ₃	1724.05		
	C	48.02%	41.24%	6.78%
	H	3.50%	3.24%	0.26%
	N	4.87%	4.81%	0.06%
6	Zn ₄ O(C ₂₄ H ₂₀ N ₂ O ₁₀) ₃	1766.09		
	C	48.92%	41.78%	7.14%
	H	3.76%	3.28%	0.48%
	N	4.75%	4.57%	0.18%
7	Zn ₄ O(C ₂₅ H ₂₂ N ₂ O ₁₀) ₃	1808.14		
	C	49.77%	42.97%	6.80%
	H	4.01%	3.64%	0.37%
	N	4.64%	4.50%	0.14%

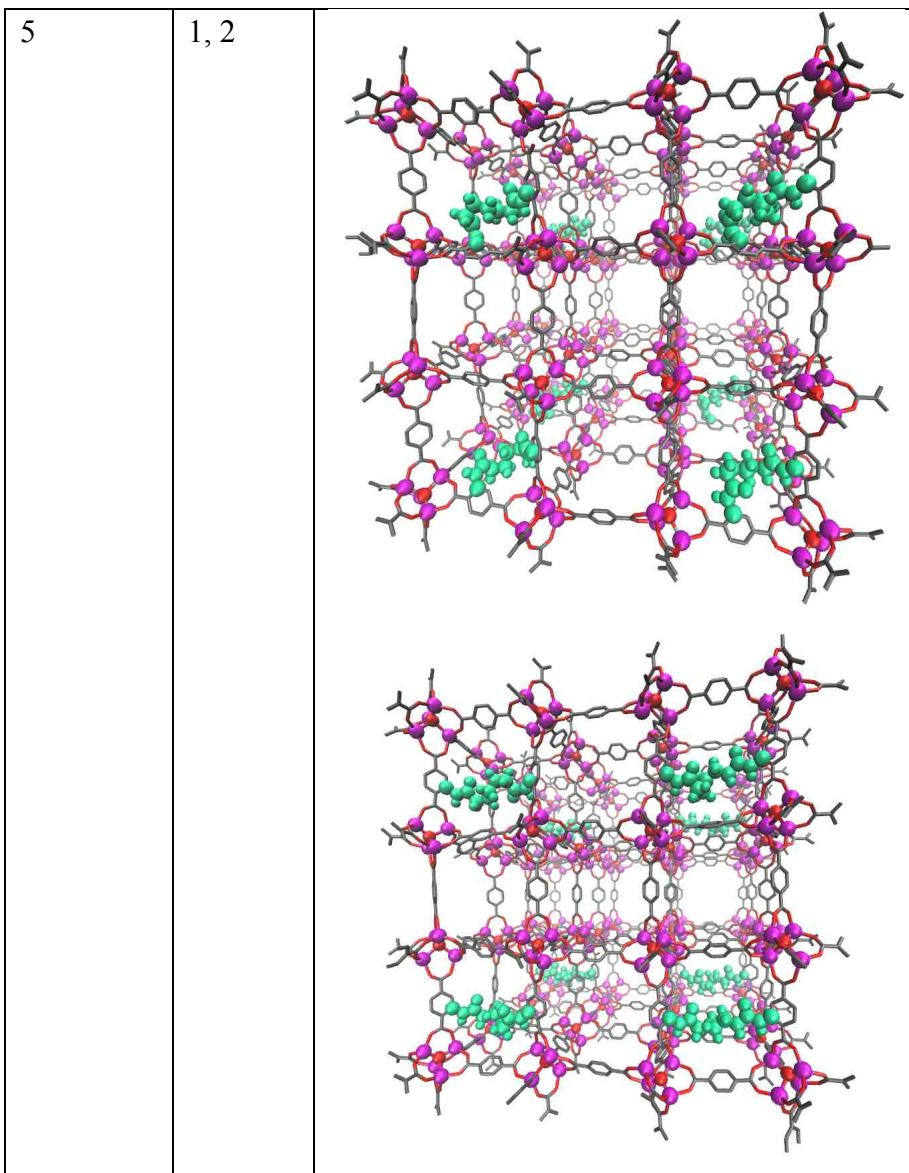
^a All samples activated at 105 °C unless noted otherwise.

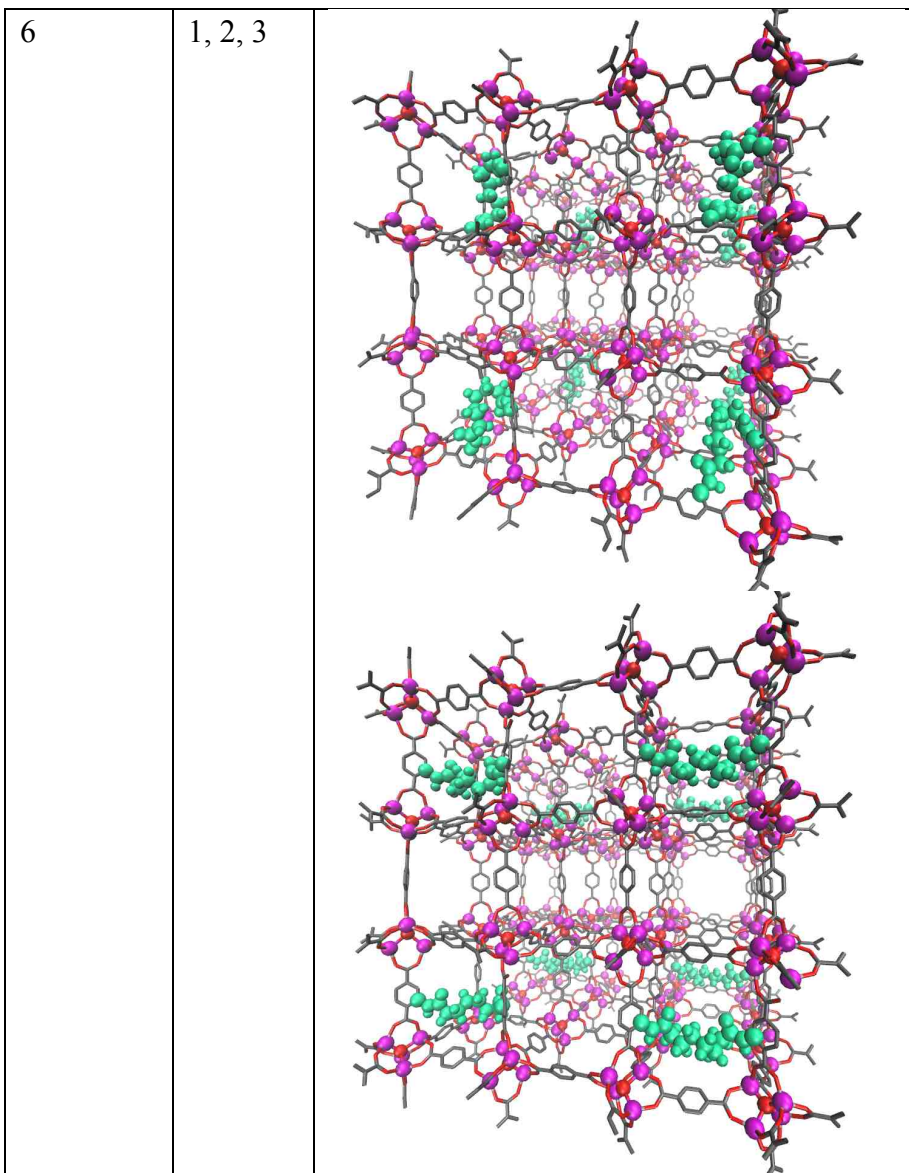
^b Calculated with only 1 BDC end structurally incorporated into the MOF and the rest part of the substituent.

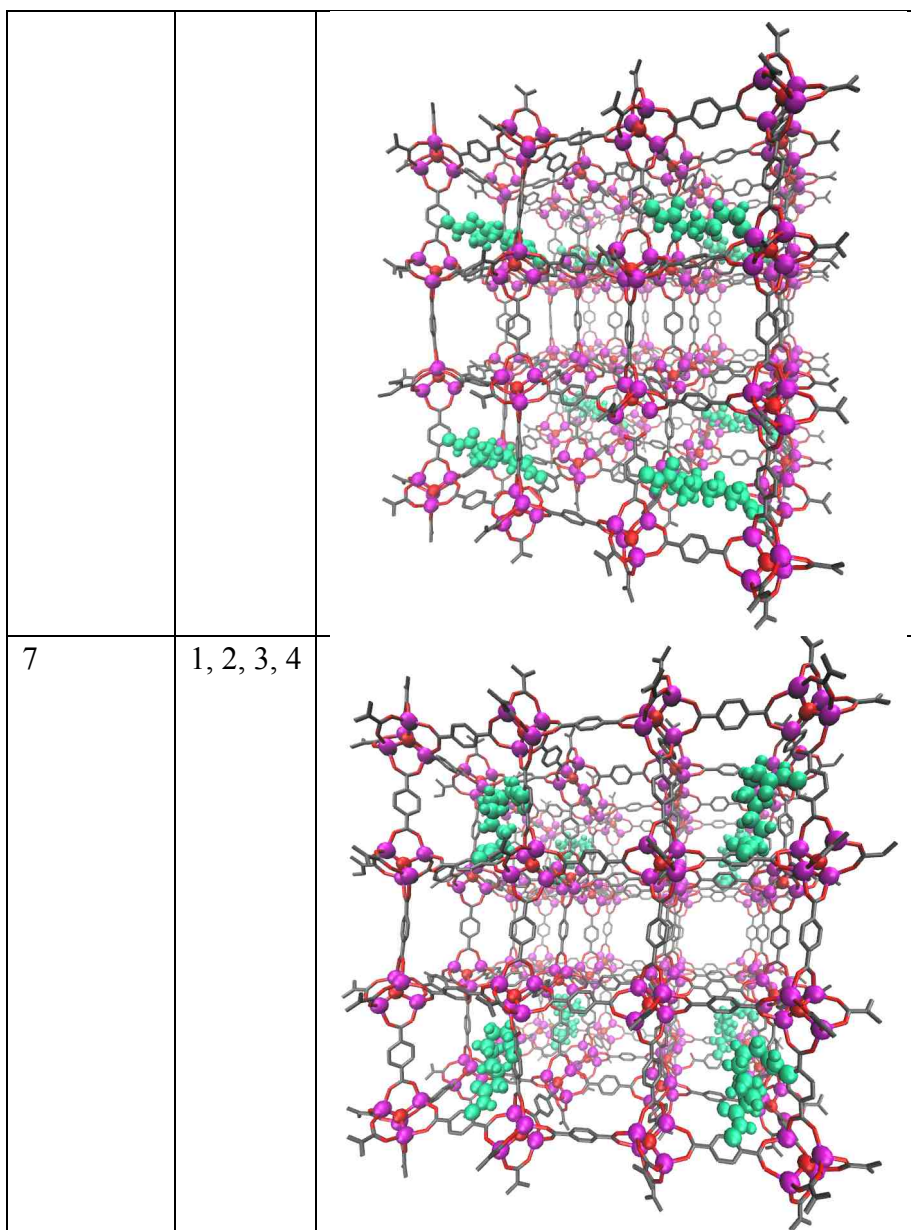
^c Based on two independent samples in duplicate.

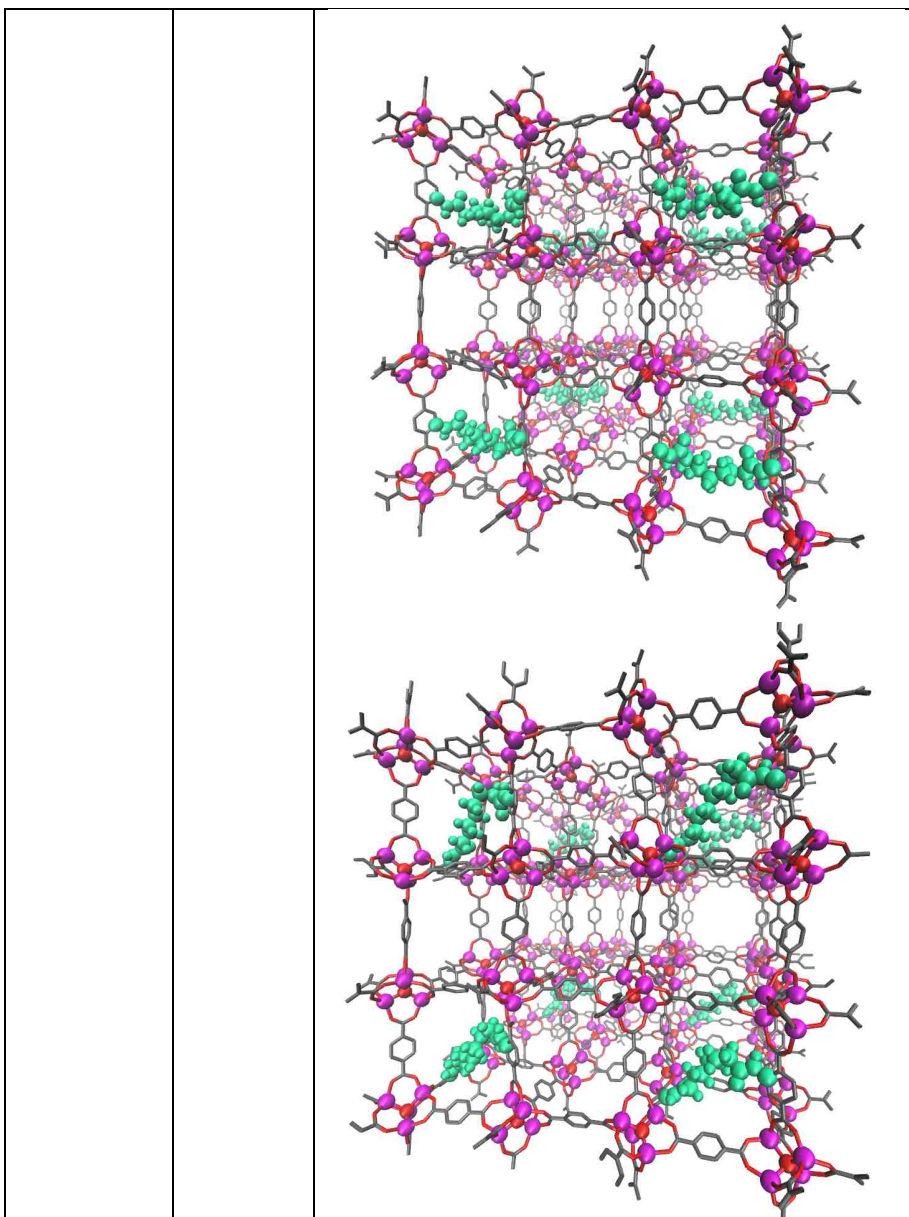
Table S6. Stable isomer conformations for all IRMOF-3-AM n XLs. Carbon atoms are grey, oxygen atoms are red, zinc ions are magenta, and the linker is shown in green spacefill.

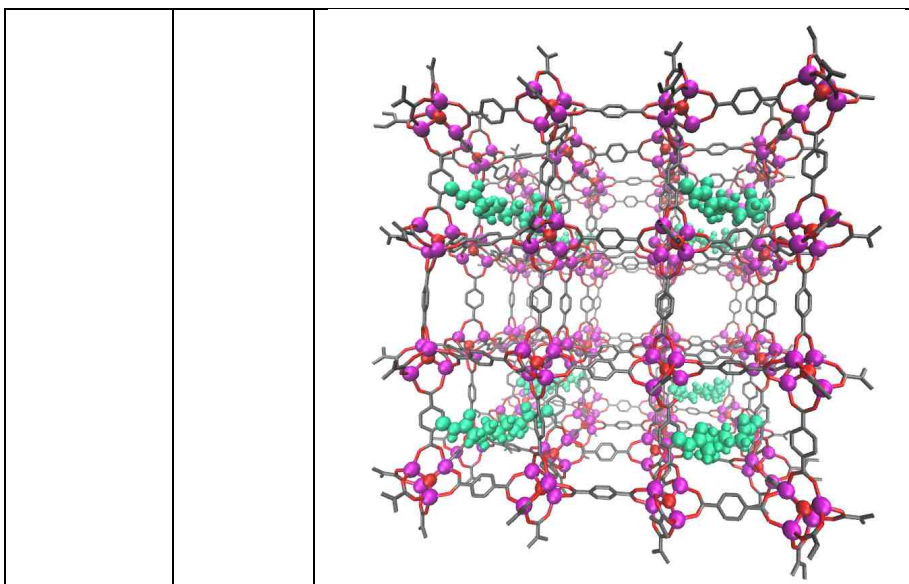
IRMOF-3-AM n XL	Stable Isomers ^a	Pictorial Representation
3	1	 A 3D ball-and-stick model of the IRMOF-3-AM3XL structure. The framework consists of zinc ions (magenta spheres) coordinated to oxygen atoms (red spheres) and carbon atoms (grey spheres). The linker is shown as a green spacefill model. The structure is a porous, layered metal-organic framework.
4	1	 A 3D ball-and-stick model of the IRMOF-3-AM4XL structure. The framework consists of zinc ions (magenta spheres) coordinated to oxygen atoms (red spheres) and carbon atoms (grey spheres). The linker is shown as a green spacefill model. The structure is a porous, layered metal-organic framework, similar to the AM3XL structure but with a different linker length.











^a Based on 500 ps MM3 molecular simulations.

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