

Supporting Information (41 pages)

Hydrogen Storage in New Metal-Organic Frameworks

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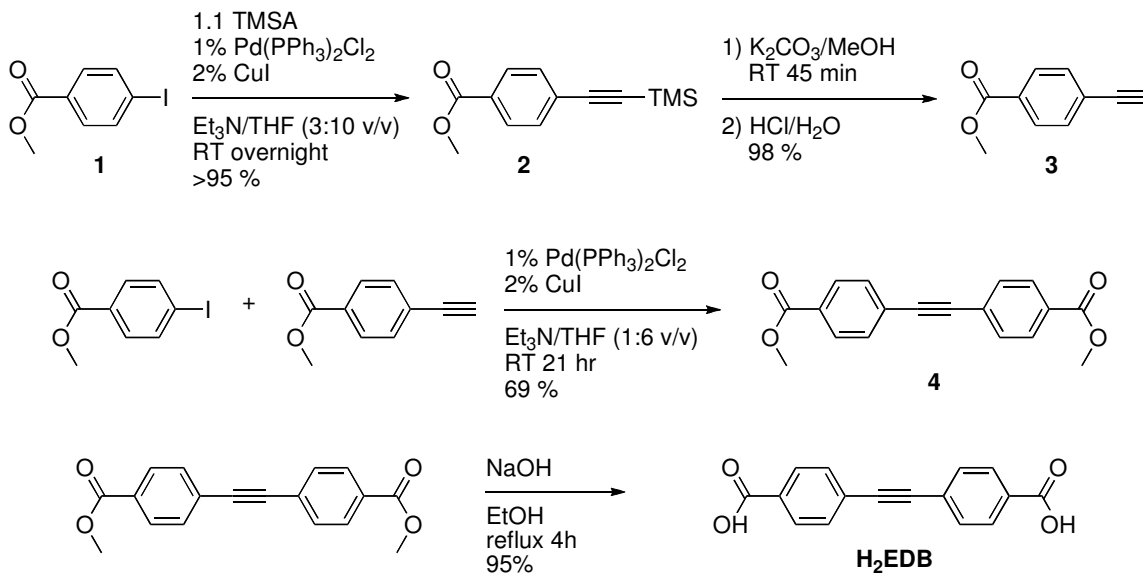
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Section S1: Synthesis of Organic Compounds

1.1 Synthesis of 4,4'-(ethyne-1,2-diyl)dibenzoic acid (H₂EDB)



Scheme S1. The synthesis of H₂EDB.

Methyl 4-(trimethylsilyl)ethynylbenzoate (2). Methyl 4-iodobenzoate (50.3 g, 193 mmol), bis(triphenylphosphine)palladium (II) chloride (1.37 g, 1.95 mmol), and copper (I) iodide (0.740 g, 3.88 mmol) were stirred in a mixture of freshly distilled tetrahydrofuran (Na/benzophenone, 230 mL) and triethylamine (60 mL), and degassed for 10 minutes with N₂. Trimethylsilylacetylene (30 mL) was added under N₂ flow, and the reaction mixture was stirred under N₂ overnight, after which time the mixture was concentrated by rotary evaporation. The solid was mixed and washed thoroughly with ethyl acetate (500 mL in 4 portions), and the combined solution was concentrated by rotary evaporation. The solid was taken up in benzene and passed through a short column of silica 60 (800 mL total benzene). The product was concentrated by rotary evaporation and purified by Kugelrohr distillation (20 mTorr, 100 °C) as an off-white solid (43.9 g, 98 %). ¹H NMR (CDCl₃, 400 MHz), δ 0.26 (s, 9H, Si(CH₃)₃), 3.91 (s, 3H, CH₃), 7.52 (d,

$J = 8.4$ Hz, 2H), 7.97 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 0.14, 52.23, 97.70, 104.08, 127.79, 129.38, 129.70, 131.88, 166.50; IR (KBr) 3002 (w), 2966 (m), 2900 (w), 2854 (w), 2162 (m), 1943 (w), 1724 (s), 1612 (m) cm^{-1} ; MS (GCMS) m/z 232 (M^+), 217.

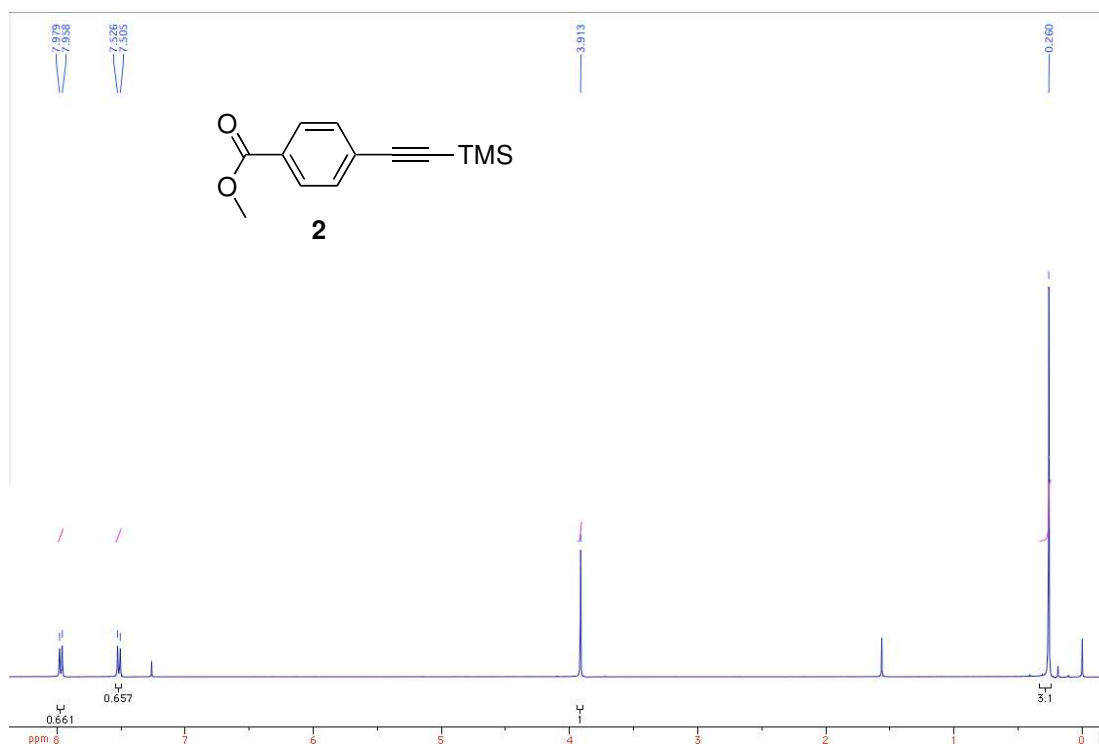


Figure S1. ^1H NMR spectrum of compound **2** in CDCl_3 , 400 MHz.

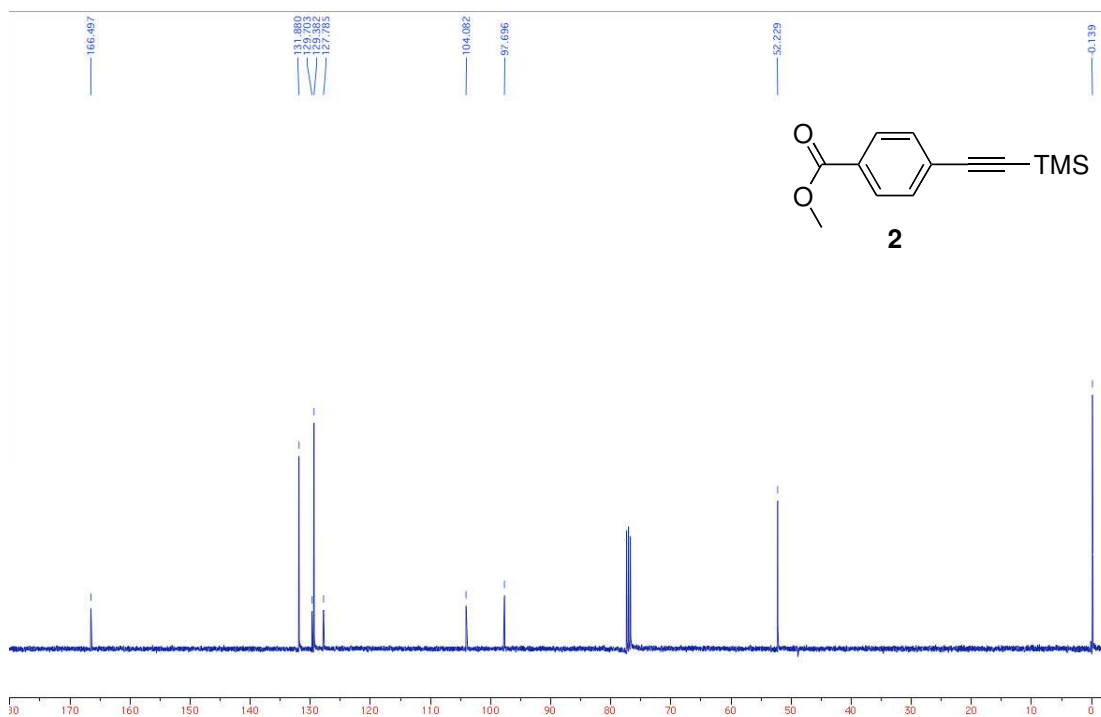


Figure S2. ¹³C NMR spectrum of compound **2** in CDCl₃, 100 MHz.

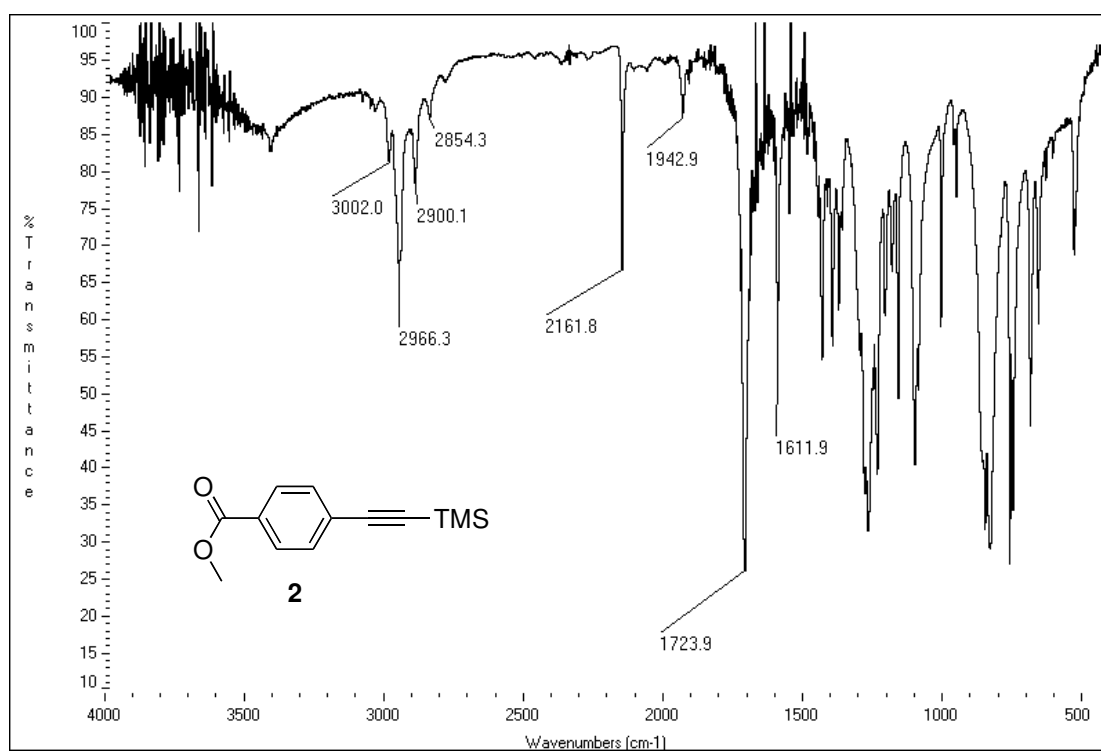


Figure S3. FT-IR spectrum of compound **2**, KBr pellet.

Methyl 4-ethynylbenzoate (3). Methyl 4-((trimethylsilyl)ethynyl)benzoate (43.9 g, 188 mmol) was stirred in methanol (375 mL), and potassium carbonate (10.0 g, 73.0 mmol) was added. The mixture was stirred for 1.5 hours, at which point the solvent was removed by rotary evaporation. Aqueous HCl (1 N, 500 mL) was slowly added, and the product was extracted with dichloromethane, dried over sodium sulfate, and concentrated by rotary evaporation to yield the ester (29.4 g, 98 %). ^1H NMR (CDCl_3 , 400 MHz), δ 3.23 (s, 1H, $\text{C}\equiv\text{C}-\text{H}$), 3.92 (s, 3H, CH_3), 7.55 (d, $J = 8.4$ Hz, 2H), 7.99 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 52.30, 80.06, 82.81, 126.76, 129.47, 130.16, 132.09, 166.42; IR (KBr) 3302 (m), 3246 (s), 2951 (m), 2106 (m), 1704 (s) cm^{-1} ; MS (GCMS) m/z 160 (M^+), 129, 101, 75.

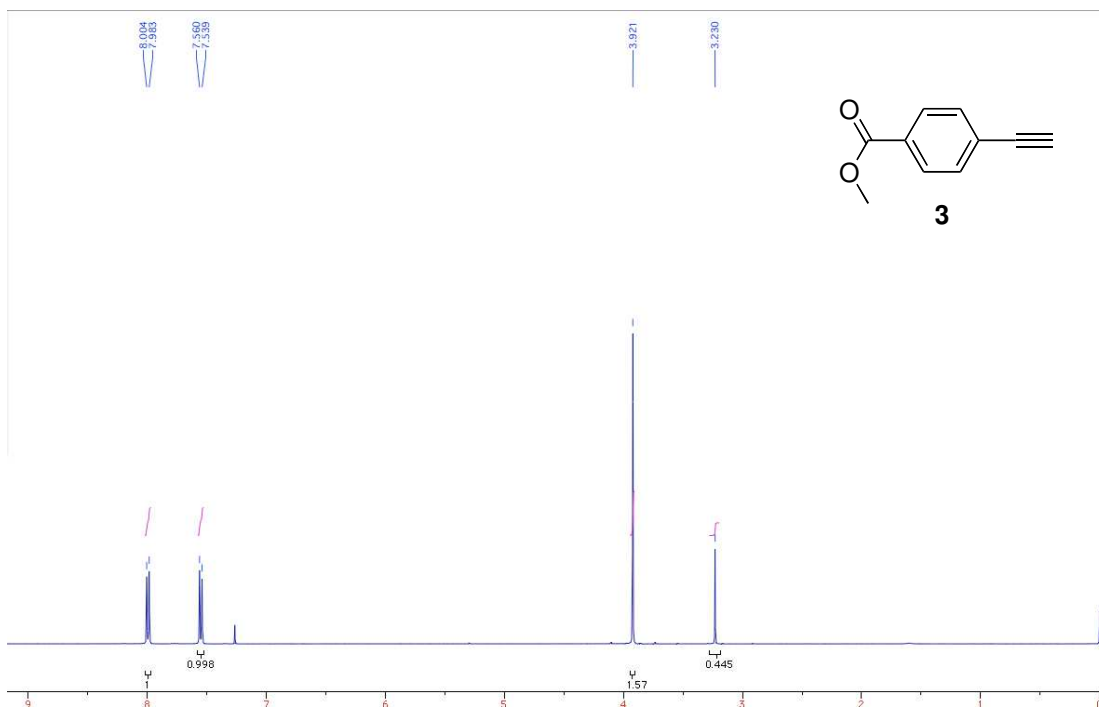


Figure S4. ^1H NMR spectrum of compound **3** in CDCl_3 , 400 MHz.

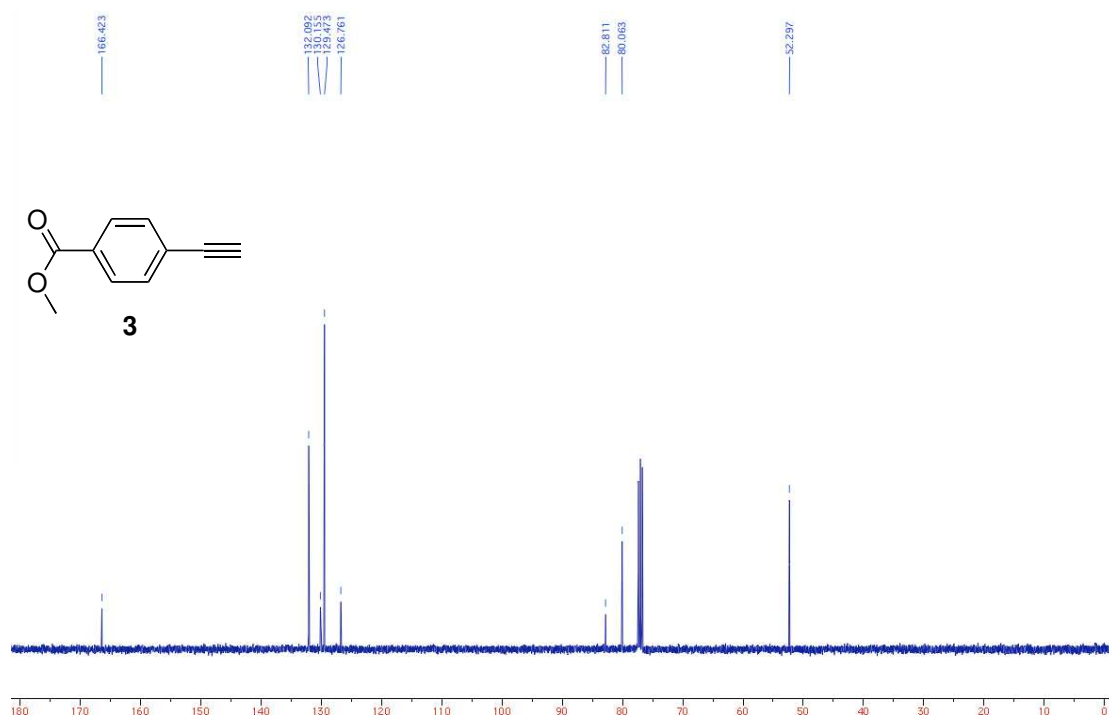


Figure S5. ¹³C NMR spectrum of compound **3** in CDCl₃.

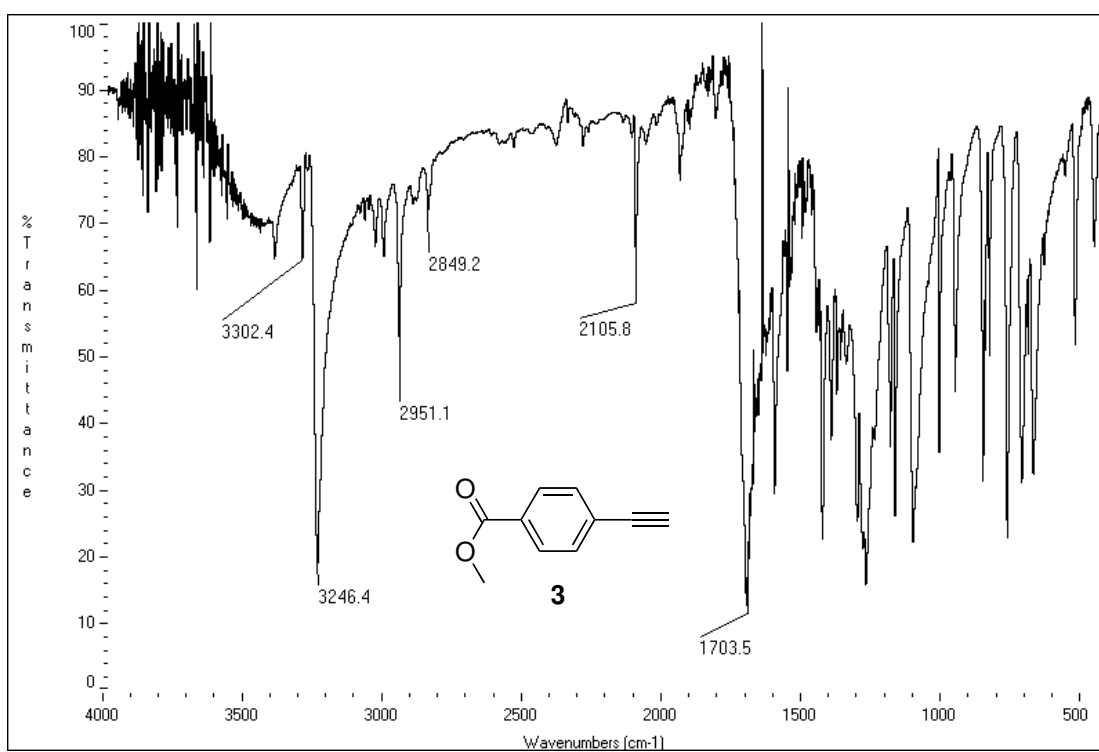


Figure S6. FT-IR Spectrum of compound **3**, KBr pellet.

1,4-bis(*p*-carbomethoxybenzene)-1,2-acetylene (4). Methyl 4-iodobenzoate (19.2 g, 73.4 mmol) and **6** (10.8 g, 67.3 mmol) were stirred in a mixture of THF (distilled over Na/benzophenone, 150 mL) and triethylamine (25 mL), and degassed with N₂ for 6 minutes. Bis(triphenylphosphine)palladium (II) chloride (0.470 g, 0.690 mmol), and copper (I) iodide (0.256 g, 1.34 mmol) were added under a N₂ blanket, and the reaction mixture was stirred under N₂ for 21.5 hours. The solid was washed with chloroform and filtered, and then Soxhlet extracted with toluene. The precipitate that formed upon cooling was filtered and recrystallized from toluene with hot filtration, giving white crystalline alkyne (13.6 g, 69%). ¹H NMR (CDCl₃, 400 MHz), δ 3.93 (s, 6H CH₃), 7.60 (d, *J* = 8.4 Hz, 4H), 8.04 (d, *J* = 8.4 Hz, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 52.43, 91.51, 127.49, 129.71, 130.08, 131.78, 166.58; IR 3022 (w), 2966 (w), 1714 (s) cm⁻¹; MS (MALDI-MS) *m/z* 294 (M⁺).

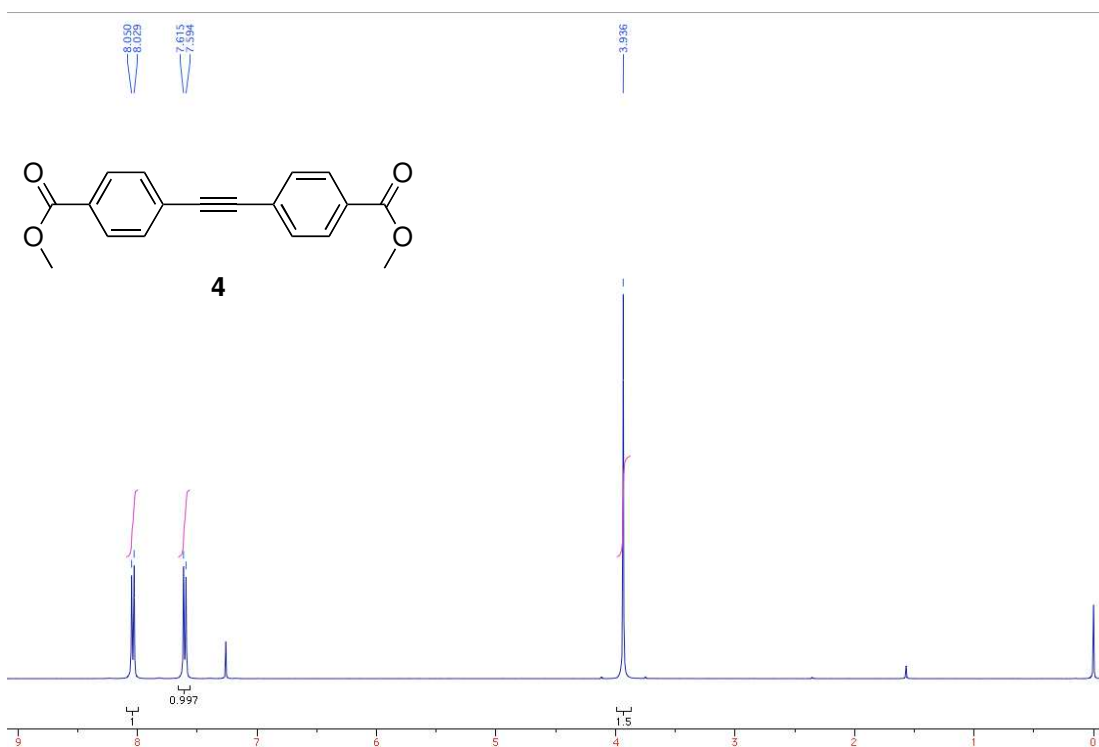


Figure S7. ¹H NMR spectrum of compound **4** in CDCl₃, 400 MHz.

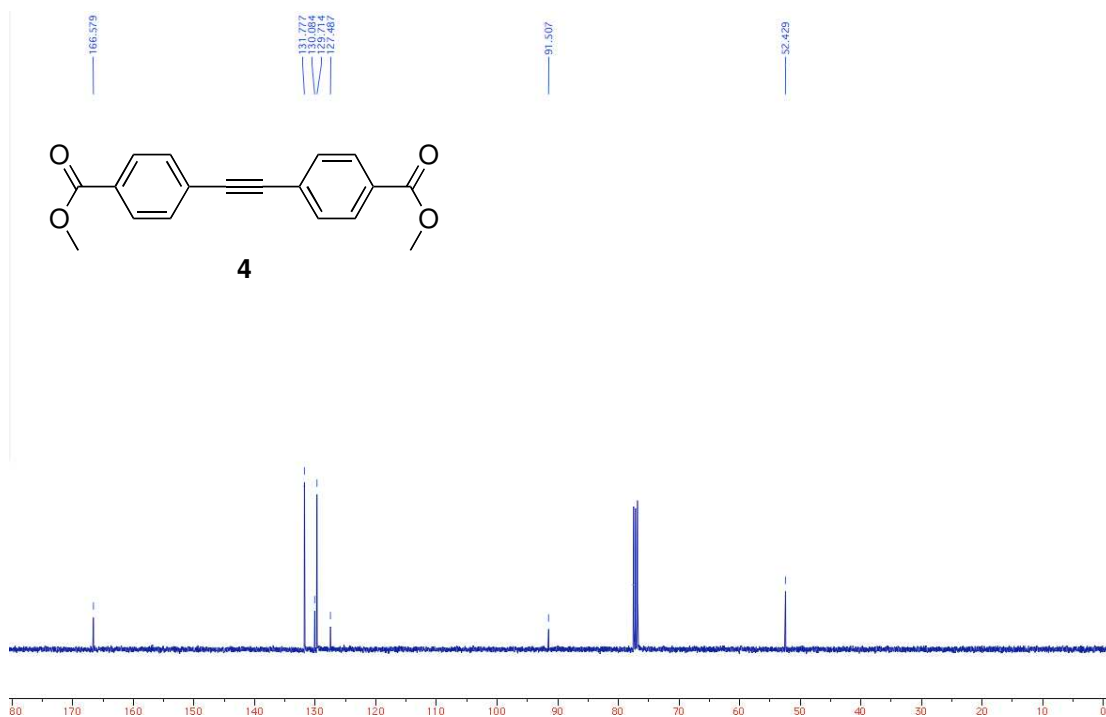


Figure S8. ¹³C NMR spectrum of compound **4** in CDCl₃, 100 MHz.

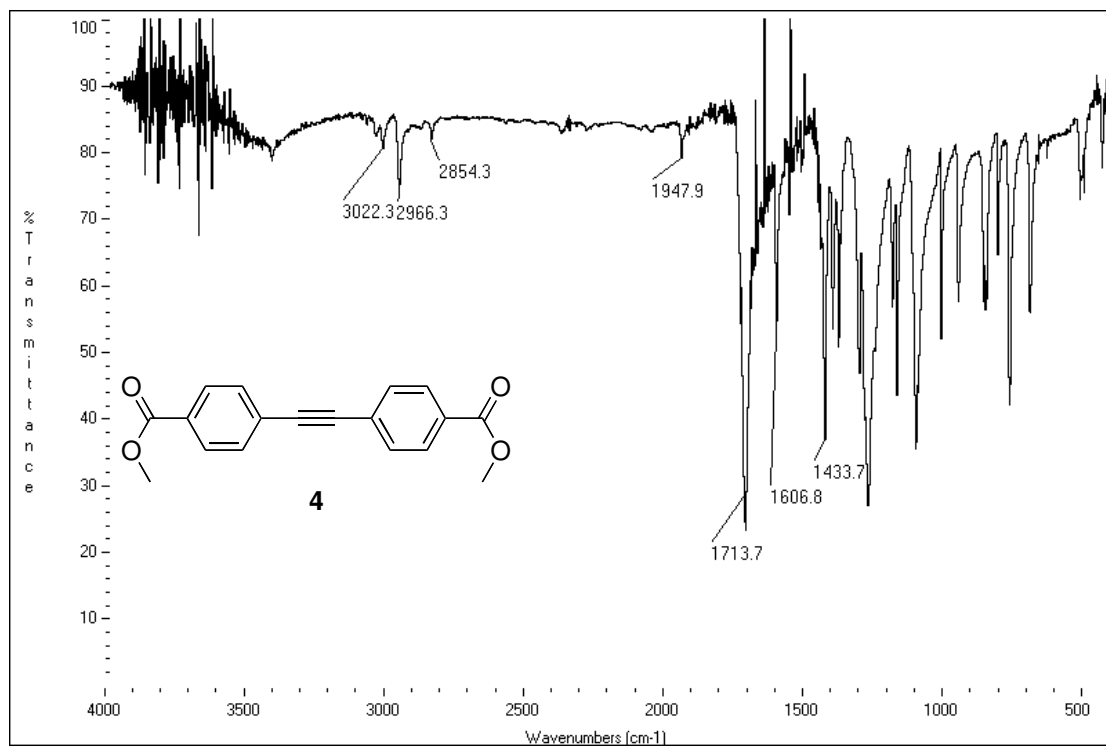


Figure S9. FT-IR spectrum of compound **4**, KBr pellet.

4,4'-(ethyne-1,2-diyl)dibenzoic acid (H₂EDB). Sodium hydroxide (7.36 g, 184 mmol) and (1,4-bis(*p*-carbomethoxybenzene)-1,2-acetylene (9.00 g, 30.6 mmol) were stirred in ethanol (95%, 200 mL) and refluxed for 18 hours. The solvent was removed by rotary evaporation, and the solid was dissolved in water, and the pH was reduced to 1 with HCl (12 M). The product was collected by filtration, washed with water (2 × 50 mL), and dried at 120 °C overnight, yielding the diacid (7.67 g, 94%). Triethylamine was added to the NMR solution to improve the solubility of **1**. ¹H NMR (CDCl₃, 400 MHz), δ 7.52 (d, J = 8.0 Hz, 4H), 7.93 (d, J = 8.4 Hz, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 90.29, 123.35, 129.25, 130.61, 138.24, 169.12; IR (KBr) 1688 (s), 1607 (s) cm⁻¹; MS (ESI, negative mode) -265 ((*m* – H)⁻/*z*), -221 (*m* – CO₂H).

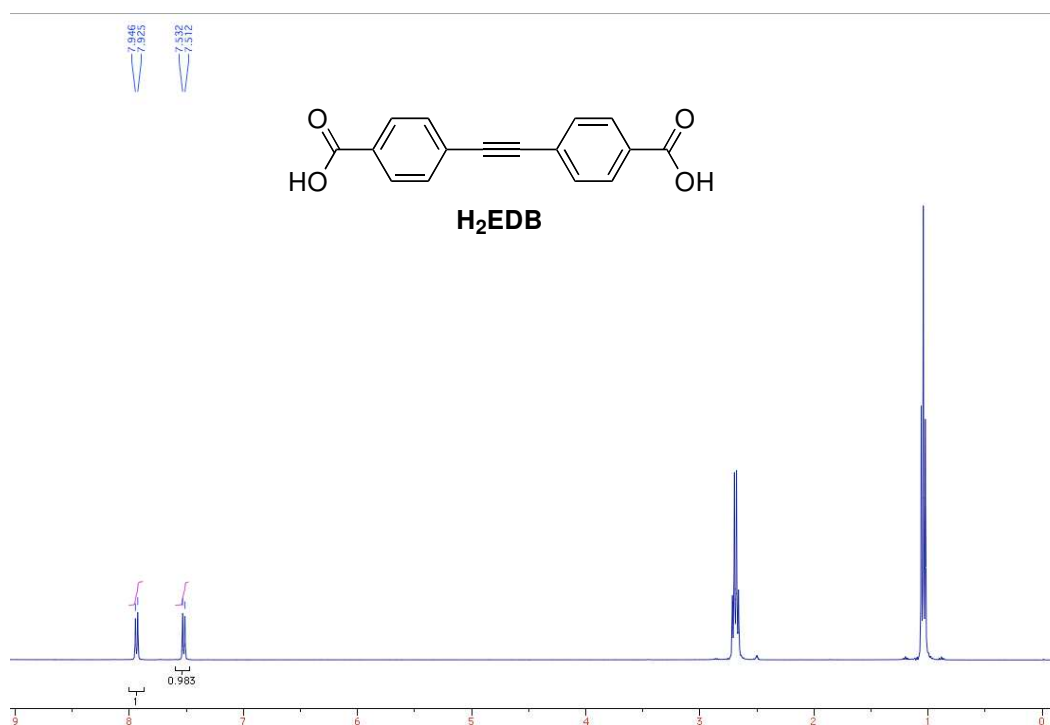


Figure S10. ¹H NMR spectrum of H₂EDB in DMSO-*d*₆, 400 MHz; triethylamine added for solubility.

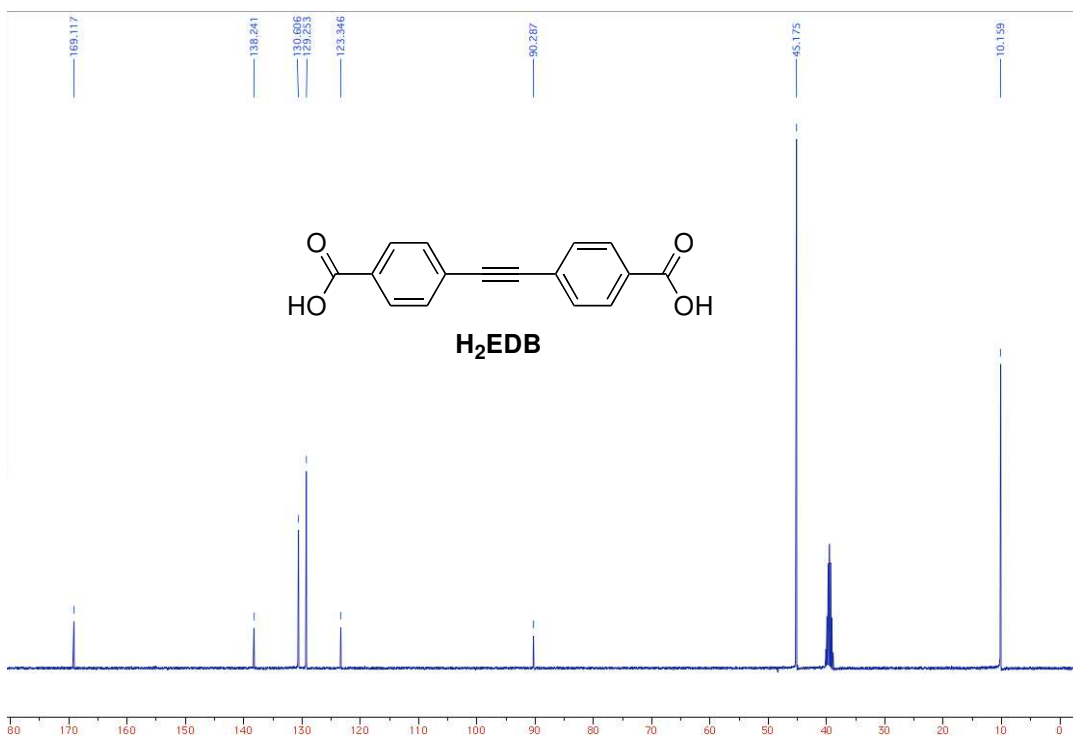


Figure S11. ¹³C NMR spectrum of H₂EDB in DMSO-*d*₆, 100 MHz; triethylamine added for solubility.

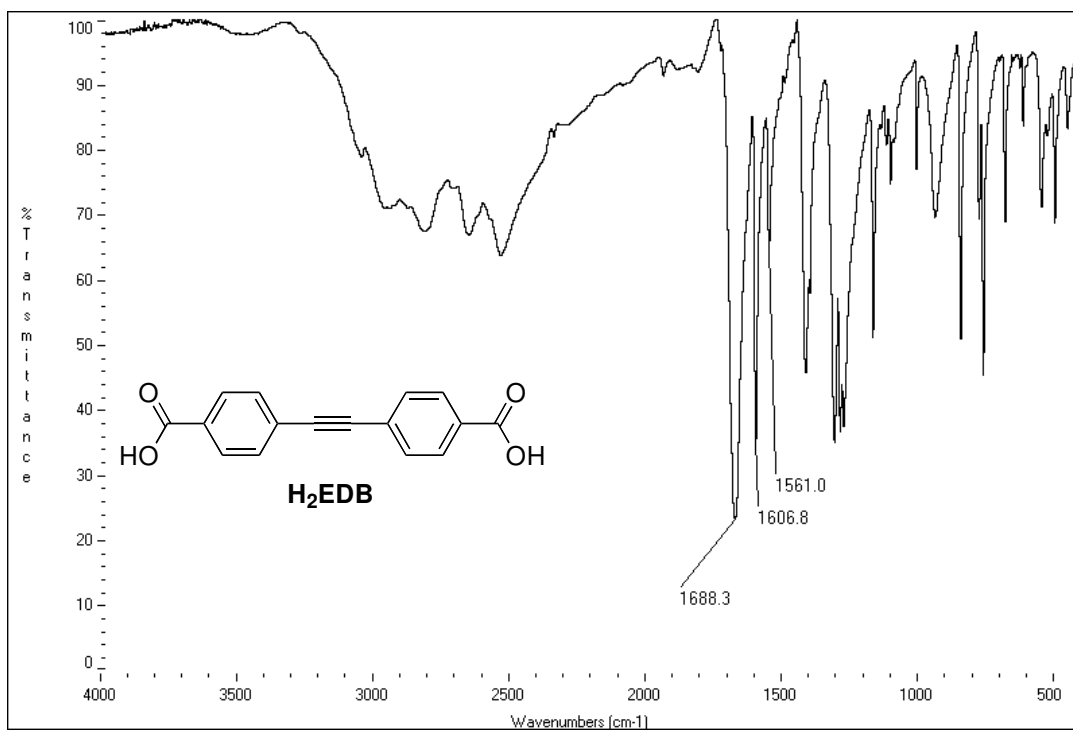
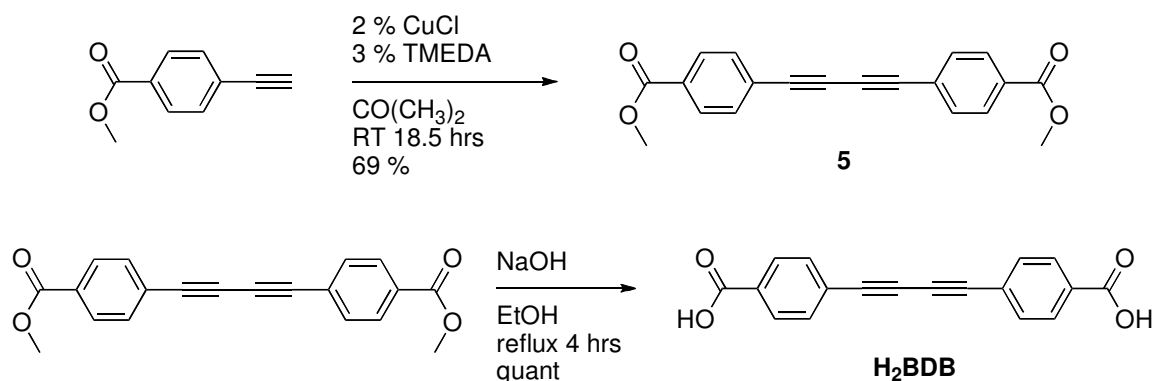


Figure S12. FT-IR spectrum of H₂EDB, KBr pellet.

1.2 Synthesis of 4,4'-(buta-1,3-diyne-1,4-diyl)dibenzoic acid (H₂BDB)



Scheme S2. The synthesis of H₂BDB.

1,4-bis(*p*-carbomethoxybenzene)-1,3-butadiyne (5). Methyl 4-ethynylbenzoate (60.2 g, 376 mmol) was dissolved in acetone (600 mL). Copper (I) chloride (0.762 g, 7.70 mmol) and TMEDA (1.34 g, 11.6 mmol) were added, and the mixture was stirred, open to air, for 20 hours. The precipitate was filtered and washed with additional acetone and then washed with chloroform (400 mL). The undissolved solid was Soxhlet extracted with chloroform. The two solutions were combined, and solvent was removed by rotary evaporation to give the butadiyne (41.0 g, 69%). ¹H NMR (CDCl₃, 400 MHz), δ 3.93 (s, 6H, CH₃), 7.59 (d, *J* = 8.4 Hz, 4H), 8.01 (d, *J* = 8.4 Hz, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 52.49, 76.39, 81.99, 126.22, 129.69, 130.66, 132.59, 166.35; IR (KBr) 3022 (w), 2961 (w), 2096 (w), 2065 (w), 1729 (s) cm⁻¹; MS (MALDI) *m/z* 318 (M⁺).

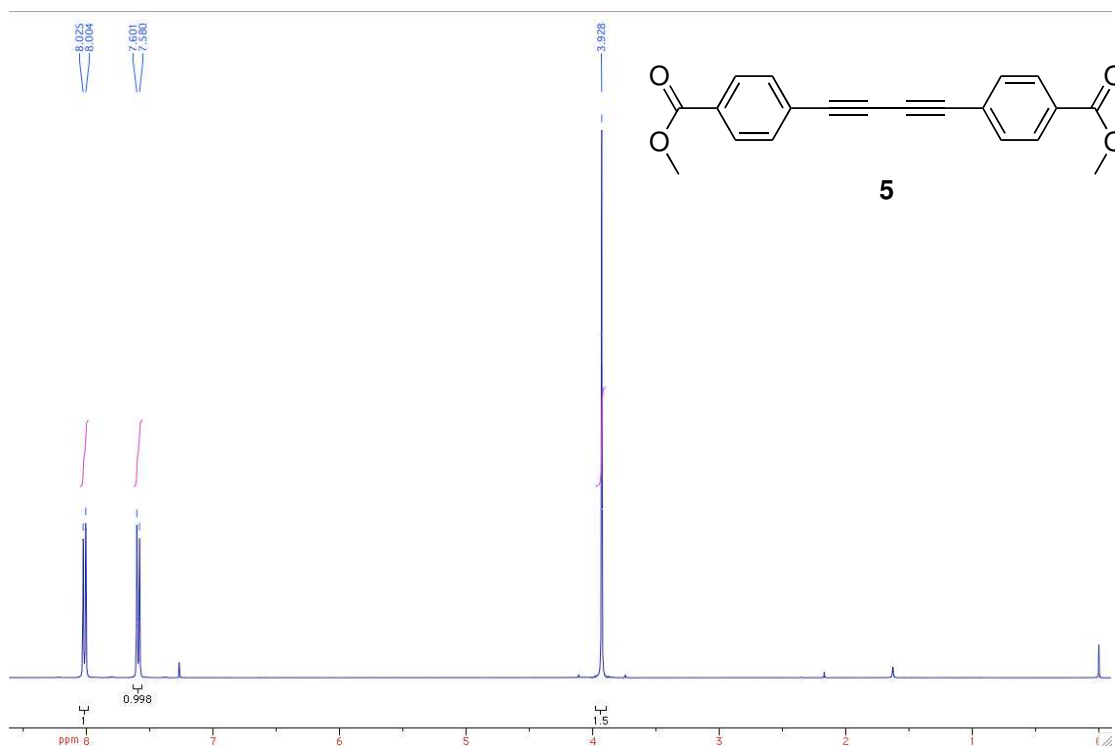


Figure S13. ¹H NMR spectrum of compound **5** in CDCl₃, 400 MHz.

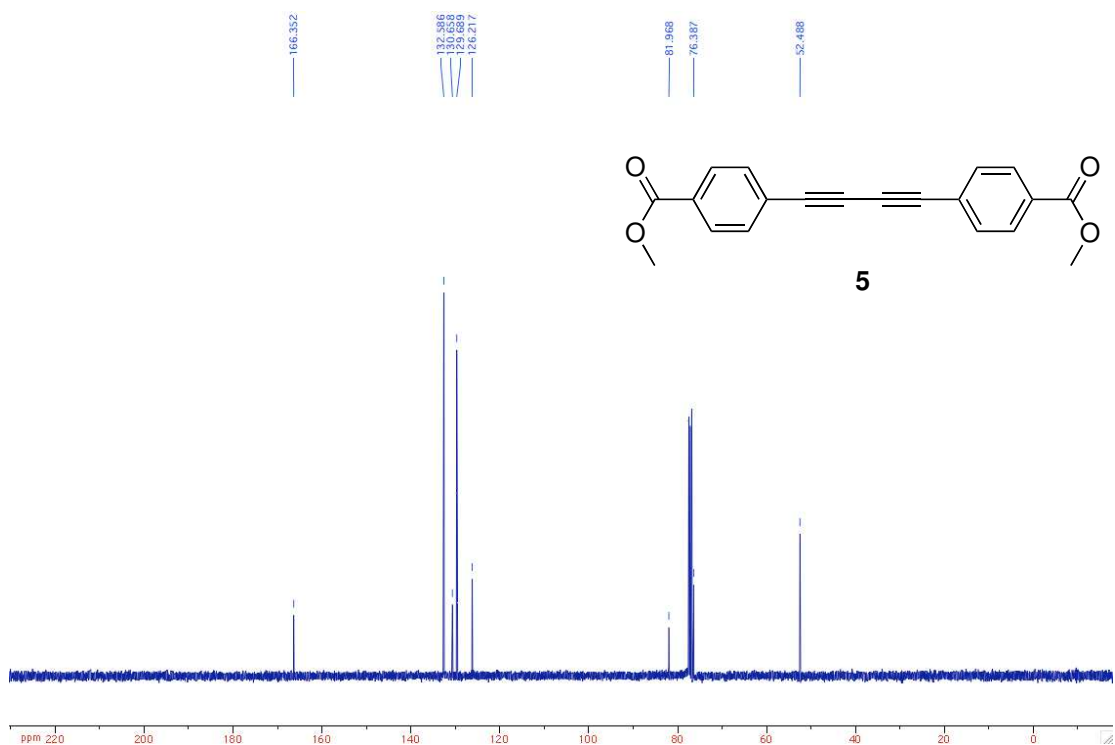


Figure S14. ¹³C NMR spectrum of compound **5** in CDCl₃, 100 MHz.

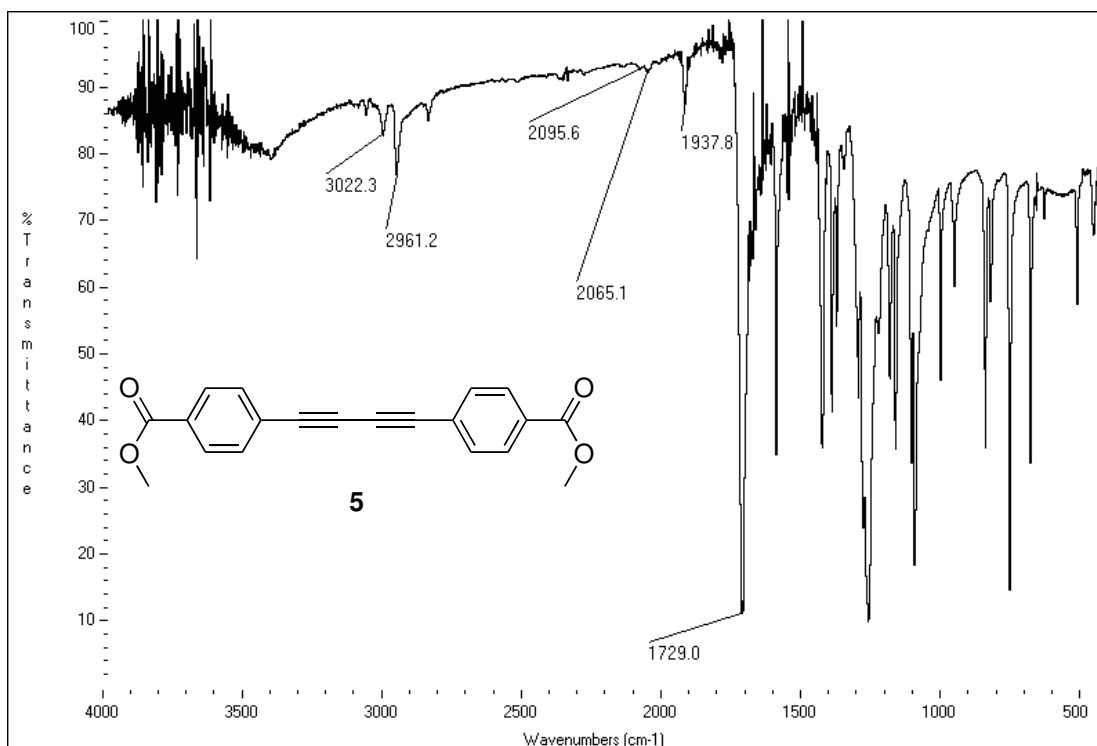


Figure S15. FT-IR spectrum of compound **5**, KBr pellet.

4,4'-(buta-1,3-diyne-1,4-diyl)dibenzoic acid (H₂BDB). Sodium hydroxide (26.1 g, 652 mmol) was dissolved in ethanol (95%, 1.5 L). The diester **8** (41.0 g, 129 mmol) was added and the mixture was stirred and refluxed for 4 hours. The mixture was cooled and filtered, and the solid was dissolved in water. The solution pH was adjusted to 1 with HCl (12 M), and the product was filtered in two funnels. Each portion was washed with water, THF (dried in a solvent purification column, 250 mL), then diethyl ether (dried in a solvent purification column, 250 mL), and dried *in vacuo* (38.6 g, *quant.*). The product exhibited low solubility in DMSO-*d*₆ for NMR characterization; triethylamine was added to the NMR solution to improve the solubility of **2**. ¹H NMR (CDCl₃, 400 MHz), δ 7.55 (d, *J* = 8.4 Hz, 4H), 7.92 (d, *J* = 8.0 Hz, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 74.19, 82.19, 121.29, 129.27, 131.63, 139.65, 168.87; IR (KBr) 1688 (s), 1603 (m) cm⁻¹; MS (ESI, negative mode) -289 ((*m* - H)⁻/*z*).

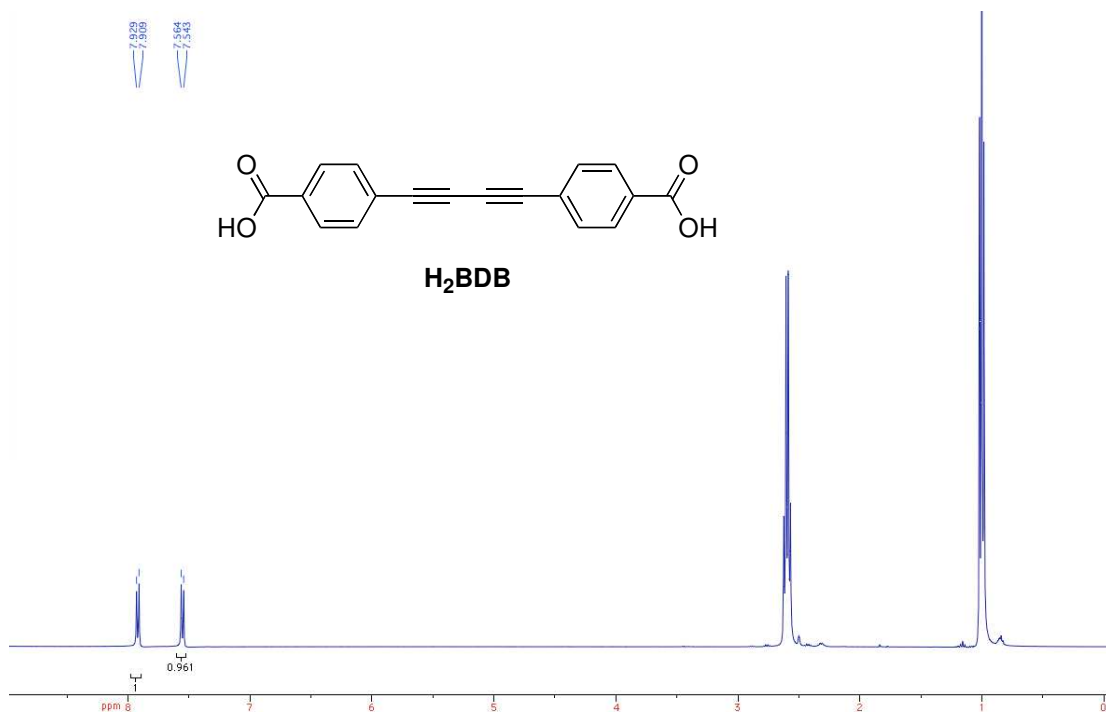


Figure S16. ¹H NMR spectrum of H₂BDB in DMSO-*d*₆, 100 MHz; triethylamine added for solubility.

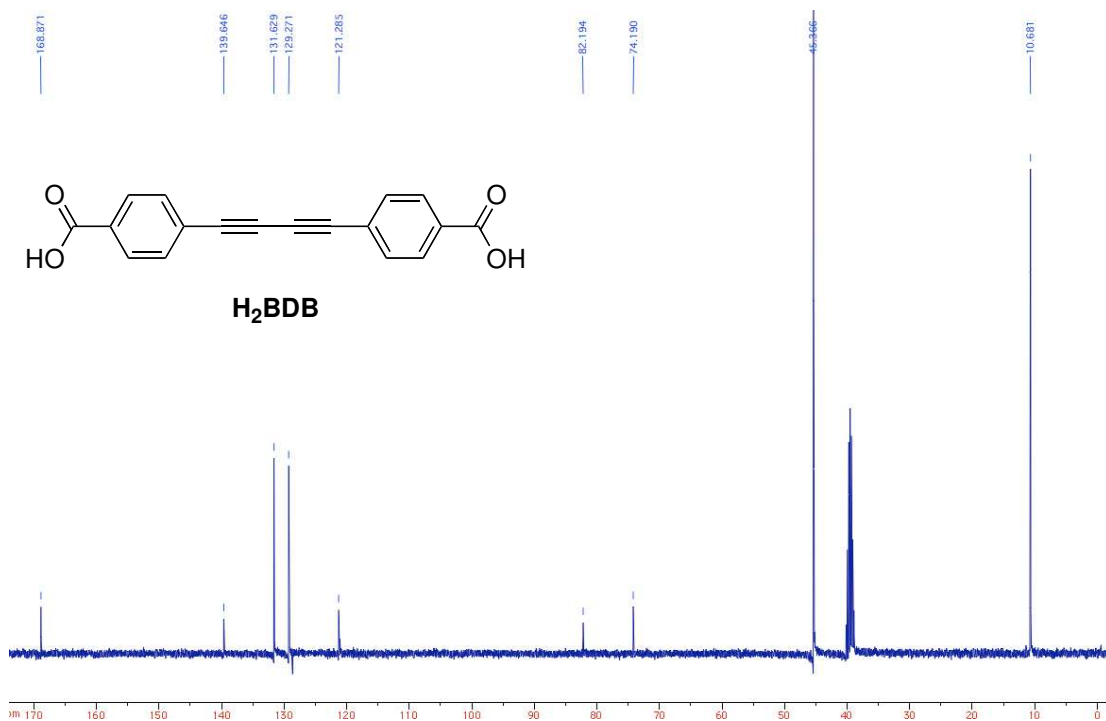


Figure S17. ¹³C NMR spectrum of H₂BDB in DMSO-*d*₆, 100 MHz; triethylamine added for solubility.

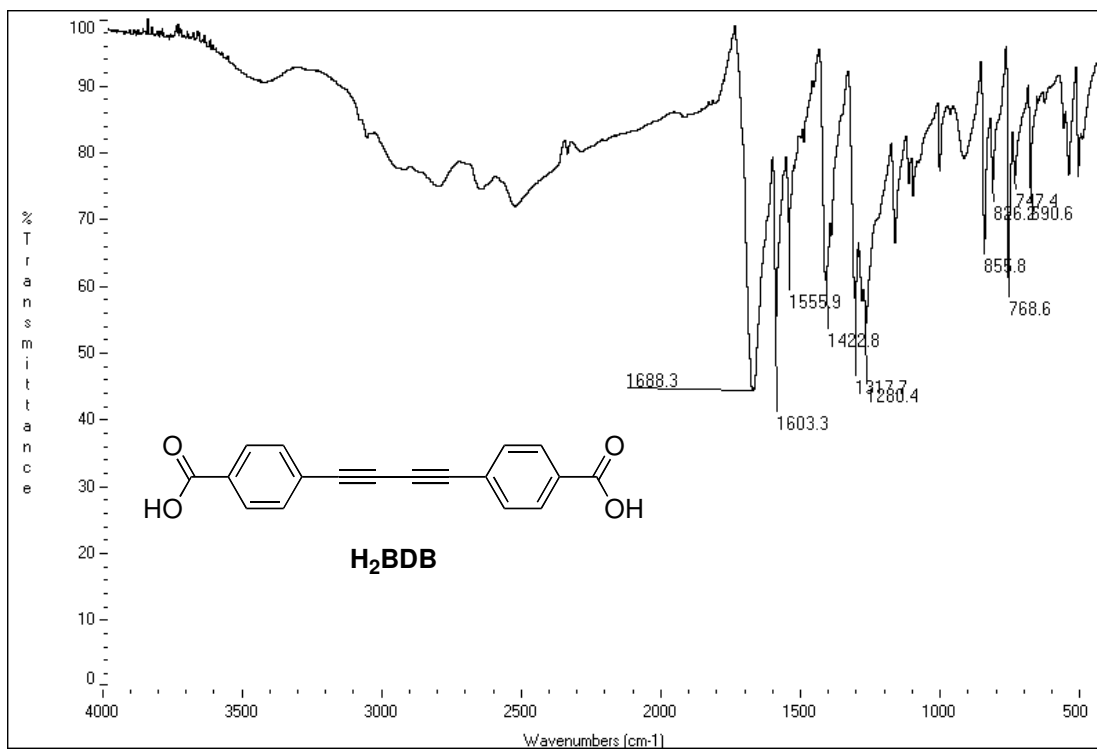


Figure S18. FT-IR spectrum of H₂BDB, KBr pellet.

Section S2: Single Crystal X-ray Diffraction Analyses

MOF-324. The diffraction data set from a colorless crystalline parallelepiped sealed in a capillary was collected at 258 K on a Bruker SMART APEX CCD diffractometer with (graphite monochromated) MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The Bruker SMART program^{S1} was used for analysis of the data collection, and SAINT^{S2} was used for the cell refinement and reduction. An absorption correction was applied using SADABS.^{S3} The crystal structure was solved using the SHELX-TL software package^{S4} in the cubic space group, $Pa\bar{3}$ (No. 205). An initial model for MOF-324 was obtained by direct methods using the Bruker program XS, and was improved by subsequent refinements using XL. With the exception of “solvent” atoms, all non-hydrogen atoms were refined anisotropically. The two hydrogen atoms of the pyrazole linker were placed in idealized positions. The PLATON SQUEEZE^{S5} routine was applied to modify the reflection data because of the amount of disordered solvent present in the pores of the MOF. With modified reflection data excluding the solvent contribution, the final refinement process converged to $R1 = 0.0841$, $wR2 = 0.2550$ ($I > 2\sigma(I)$). An asymmetric unit of MOF-324 is shown in Figure S19, and crystal and refinement data are given in Table S1.

Table S1. Crystal data and structure refinement for MOF-324.

Empirical formula	C ₂₄ H ₁₂ N ₁₂ O ₂₅ Zn ₆	
Formula weight	1260.68	
Temperature	258(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	<i>Pa</i> $\bar{3}$ (No. 205)	
Unit cell dimensions	<i>a</i> = 20.123(2) Å	α = 90°.
	<i>b</i> = 20.123(2) Å	β = 90°.
	<i>c</i> = 20.123(2) Å	γ = 90°.
Volume	8148.5(15) Å ³	
Z	4	
Density (calculated)	1.028 Mg/m ³	
Absorption coefficient	1.791 mm ⁻¹	
F(000)	2480	
Crystal size	0.3 x 0.29 x 0.18 mm ³	
Theta range for data collection	1.75 to 29.57°.	
Index ranges	-27 ≤ <i>h</i> ≤ 13, -18 ≤ <i>k</i> ≤ 25, -27 ≤ <i>l</i> ≤ 23	
Reflections collected	28521	
Independent reflections	3823 [R(int) = 0.0456]	
Completeness to theta = 29.57°	99.9%	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3823 / 0 / 96	
Goodness-of-fit on F ²	1.176	
Final R indices [I > 2σ(I)]	R1 = 0.0841, wR2 = 0.2550	
R indices (all data)	R1 = 0.1024, wR2 = 0.2651	
Largest diff. peak and hole	1,537 and -0.810 e.Å ⁻³	

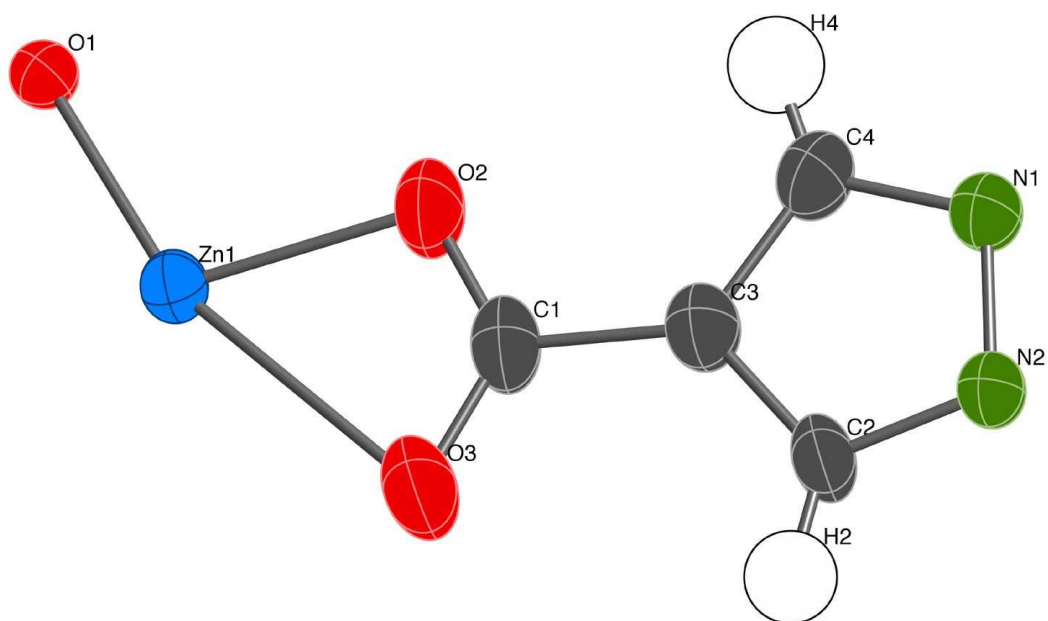


Figure S19. ORTEP drawing (50% probability) of the asymmetric unit in MOF-324.

MOF-325. The diffraction data set from a blue crystalline parallelepiped sealed in a capillary was collected at 258 K on a Bruker SMART APEX CCD diffractometer with (graphite monochromated) MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The Bruker SMART program^{S1} was used to analyze the data collection, and SAINT^{S2} was used for cell refinement and reduction. An absorption correction was applied using SADABS.^{S3} The crystal structure was solved using the Bruker SHELX-TL software package^{S4} in the cubic space group, $Fm\bar{3}m$ (No. 225). An initial model for MOF-325 was obtained by direct methods using XS, and was improved by subsequent refinements using XL. All non-hydrogen atoms of the framework were refined anisotropically. The hydrogen atom of the pyrazole linker was placed in an idealized position. The crystal structure of MOF-325 has substantial residual electron density located within the pores of the material, and these peaks could not be fit to a chemically reasonable model of either a guest or a counter-ion. The structural model of MOF-325 was refined with the guest and counter-ion contributions removed from the diffraction data using the SQUEEZE^{S5} routine in PLATON. Therefore, the formula given for MOF-325 corresponds only to the anionic truncated tetrahedral fragments. With modified reflection data excluding the solvent contribution, the final refinement process converged to $R1 = 0.0573$, $wR2 = 0.1566$ ($I > 2\sigma(I)$). An asymmetric unit of MOF-325 is shown in Figure S20, and crystal and refinement data are given in Table S2.

Table S2. Crystal data and structure refinement for MOF-325.

Empirical formula	C ₂₄ H ₁₂ N ₁₂ O ₂₃ Cu ₉	
Formula weight	1408.41	
Temperature	258(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	<i>Fm</i> $\bar{3}$ <i>m</i> (No. 225)	
Unit cell dimensions	<i>a</i> = 42.606(3) Å	α = 90°.
	<i>b</i> = 42.606(3) Å	β = 90°.
	<i>c</i> = 42.606(3) Å	γ = 90°.
Volume	77342(9) Å ³	
Z	16	
Density (calculated)	0.484 Mg/m ³	
Absorption coefficient	0.991 mm ⁻¹	
F(000)	10960.0	
Crystal size	0.28 x 0.26 x 0.23 mm ³	
Theta range for data collection	0.83 to 20.82°.	
Index ranges	-28 ≤ <i>h</i> ≤ 38, -42 ≤ <i>k</i> ≤ 35, -42 ≤ <i>l</i> ≤ 27	
Reflections collected	33974	
Independent reflections	2053 [R(int) = 0.2083]	
Completeness to theta = 20.82°	100.0%	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2053 / 0 / 71	
Goodness-of-fit on F ²	0.670	
Final R indices [I > 2σ(I)]	R1 = 0.0573, wR2 = 0.1566	
R indices (all data)	R1 = 0.1251, wR2 = 0.2157	
Largest diff. peak and hole	0.364 and -0.849 e.Å ⁻³	

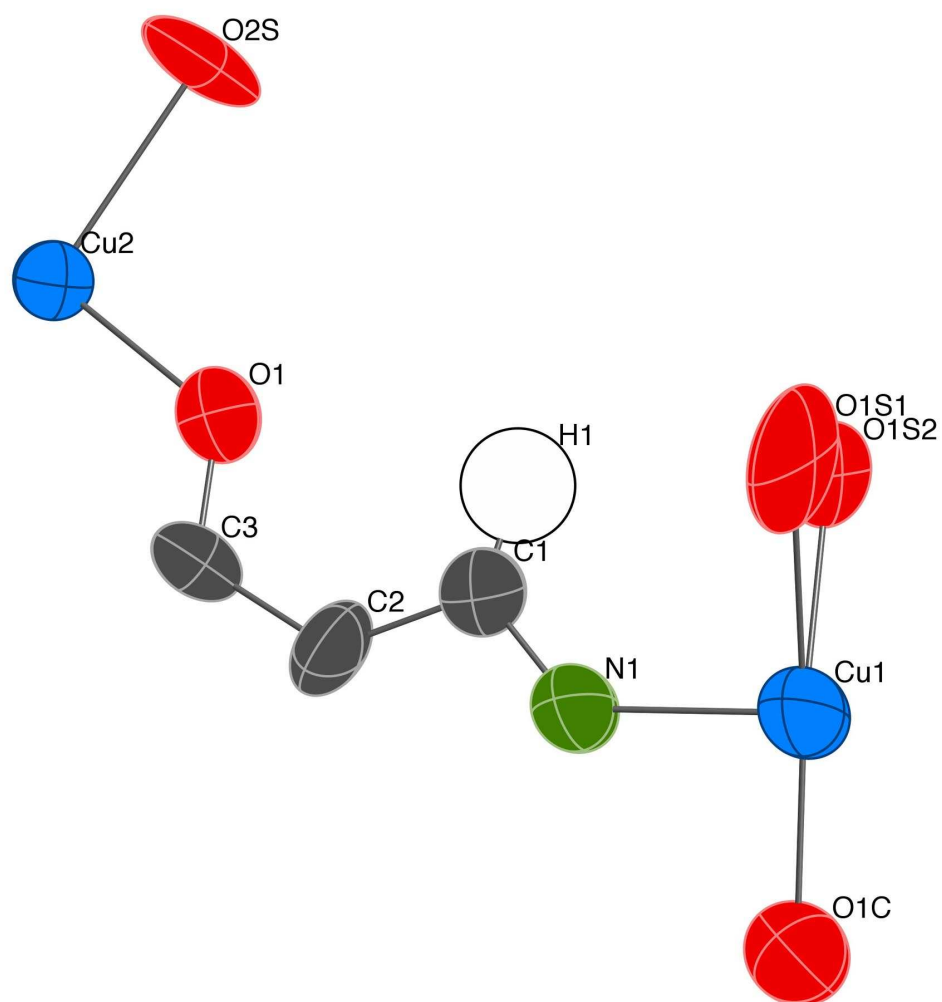


Figure S20. ORTEP drawing (50% probability) of the asymmetric unit in MOF-325.

MOF-326. The diffraction data set from a colorless crystalline parallelepiped sealed in a capillary was collected at 258 K on a Bruker SMART APEX CCD diffractometer with (graphite monochromated) MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The Bruker SMART program^{S1} was used for analysis of the data collection, and SAINT^{S2} was used for the cell refinement, and reduction. An absorption correction was applied using SADABS.^{S3} The crystal structure was solved using the Bruker SHELX-TL software package^{S4} in the cubic space group, $Fm\bar{3}m$ (No. 225). An initial model for MOF-326 was obtained by direct methods using XS, and improved by subsequent refinements using XL. All non-hydrogen atoms were refined anisotropically. The PLATON SQUEEZE^{S5} routine was applied to the data to remove the contributions of the disordered solvents. With modified reflection data excluding the solvent contribution, the final refinement process converged to $R1 = 0.0829$, $wR2 = 0.2551$ ($I > 2\sigma(I)$). An asymmetric unit of MOF-326 is shown in Figure S21, and crystal and refinement data are given in Table S3.

Table S3. Crystal data and structure refinement for MOF-326.

Empirical formula	C ₄₈ H ₇₂ B ₆ N ₁₂ O ₁₃ Zn ₄	
Formula weight	1351.52	
Temperature	258(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	<i>Fm</i> $\bar{3}$ <i>m</i> (No. 225)	
Unit cell dimensions	<i>a</i> = 33.410(4) Å	α = 90°.
	<i>b</i> = 33.410(4) Å	β = 90°.
	<i>c</i> = 33.410(4) Å	γ = 90°.
Volume	37294(7) Å ³	
Z	8	
Density (calculated)	0.481 Mg/m ³	
Absorption coefficient	0.531 mm ⁻¹	
F(000)	5584	
Crystal size	0.3 x 0.2 x 0.2 mm ³	
Theta range for data collection	1.06 to 18.85°.	
Index ranges	-15 ≤ <i>h</i> ≤ 30, -30 ≤ <i>k</i> ≤ 30, -30 ≤ <i>l</i> ≤ 28	
Reflections collected	15524	
Independent reflections	804 [R(int) = 0.1188]	
Completeness to theta = 18.85°	100.0%	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	804 / 4 / 44	
Goodness-of-fit on F ²	0.974	
Final R indices [I > 2σ(I)]	R1 = 0.0829, wR2 = 0.2551	
R indices (all data)	R1 = 0.1335, wR2 = 0.2846	
Largest diff. peak and hole	0.389 and -0.525 e.Å ⁻³	

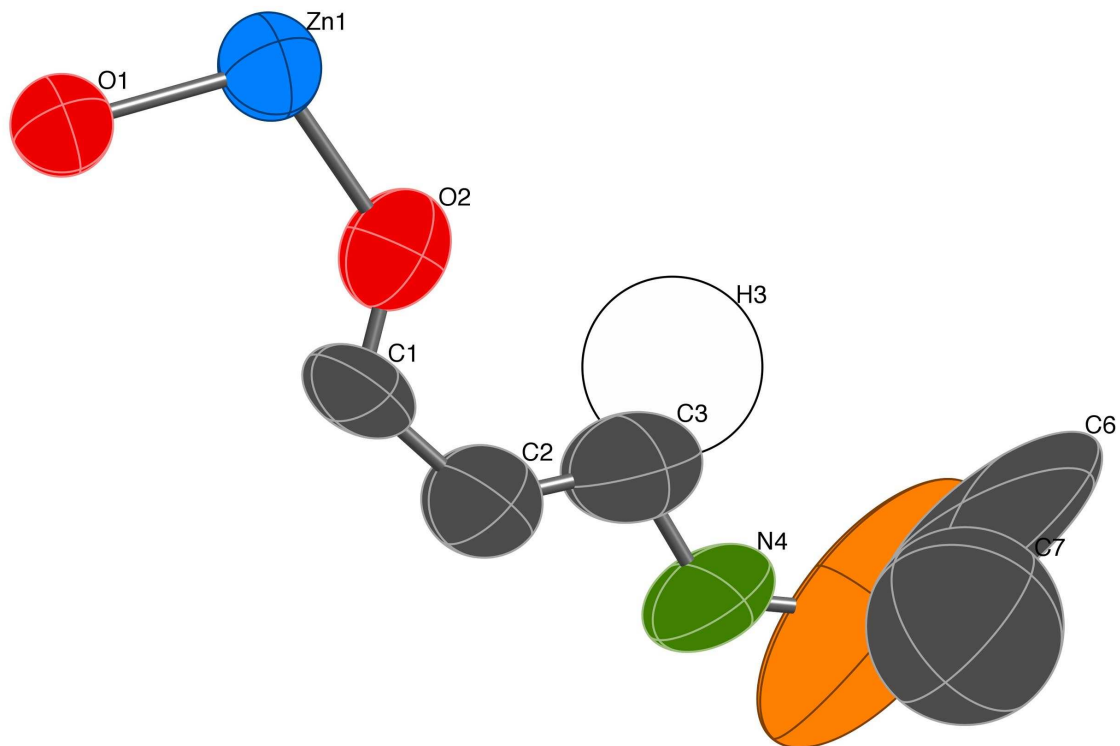


Figure S21. ORTEP drawing (50% probability) of the asymmetric unit in MOF-326.

IRMOF-61. The diffraction data set from a colorless crystalline parallelepiped sealed in a capillary was collected at 258 K on a Bruker SMART APEX CCD diffractometer with (graphite monochromated) MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The Bruker SMART program^{S1} was used for analysis of the data collection, and SAINT^{S2} was used for cell refinement and reduction. An absorption correction was applied using SADABS.^{S3} The crystal structure was solved using the Bruker SHELX-TL software package^{S4} in the tetragonal space group, $P4_2/ncm$ (No. 138). An initial model for IRMOF-61 was obtained by direct methods using XS, and was improved by subsequent refinements using XL. All non-hydrogen atoms were refined anisotropically. The PLATON SQUEEZE^{S5} routine was applied to remove contributions of the disordered solvents. With modified reflection data excluding the solvent contribution, the final refinement process converged to $R1 = 0.0526$, $wR2 = 0.1336$ ($I > 2\sigma(I)$). An asymmetric unit of IRMOF-61 is shown in Figure S22, and crystal and refinement data are given in Table S4.

Table S4. Crystal data and structure refinement for IRMOF-61.

Empirical formula	C ₄₈ H ₂₄ O ₁₃ Zn ₄	
Formula weight	1070.15	
Temperature	258(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	<i>P</i> 4 ₂ / <i>ncm</i> (No. 138)	
Unit cell dimensions	<i>a</i> = 19.7213(13) Å	$\alpha = 90^\circ$.
	<i>b</i> = 19.7213(13) Å	$\beta = 90^\circ$.
	<i>c</i> = 39.411(3) Å	$\gamma = 90^\circ$.
Volume	15328.0(18) Å ³	
Z	4	
Density (calculated)	0.464 Mg/m ³	
Absorption coefficient	0.638 mm ⁻¹	
F(000)	2144	
Crystal size	0.44 x 0.28 x 0.15 mm ³	
Theta range for data collection	1.46 to 21.99°.	
Index ranges	-20 ≤ <i>h</i> ≤ 20, -20 ≤ <i>k</i> ≤ 20, -41 ≤ <i>l</i> ≤ 41	
Reflections collected	94159	
Independent reflections	4944 [R(int) = 0.0629]	
Completeness to theta = 21.99°	100.0%	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4944 / 0 / 175	
Goodness-of-fit on F ²	1.023	
Final R indices [I > 2σ(I)]	R1 = 0.0526, wR2 = 0.1336	
R indices (all data)	R1 = 0.0951, wR2 = 0.1554	
Largest diff. peak and hole	0.655 and -0.377 e.Å ⁻³	

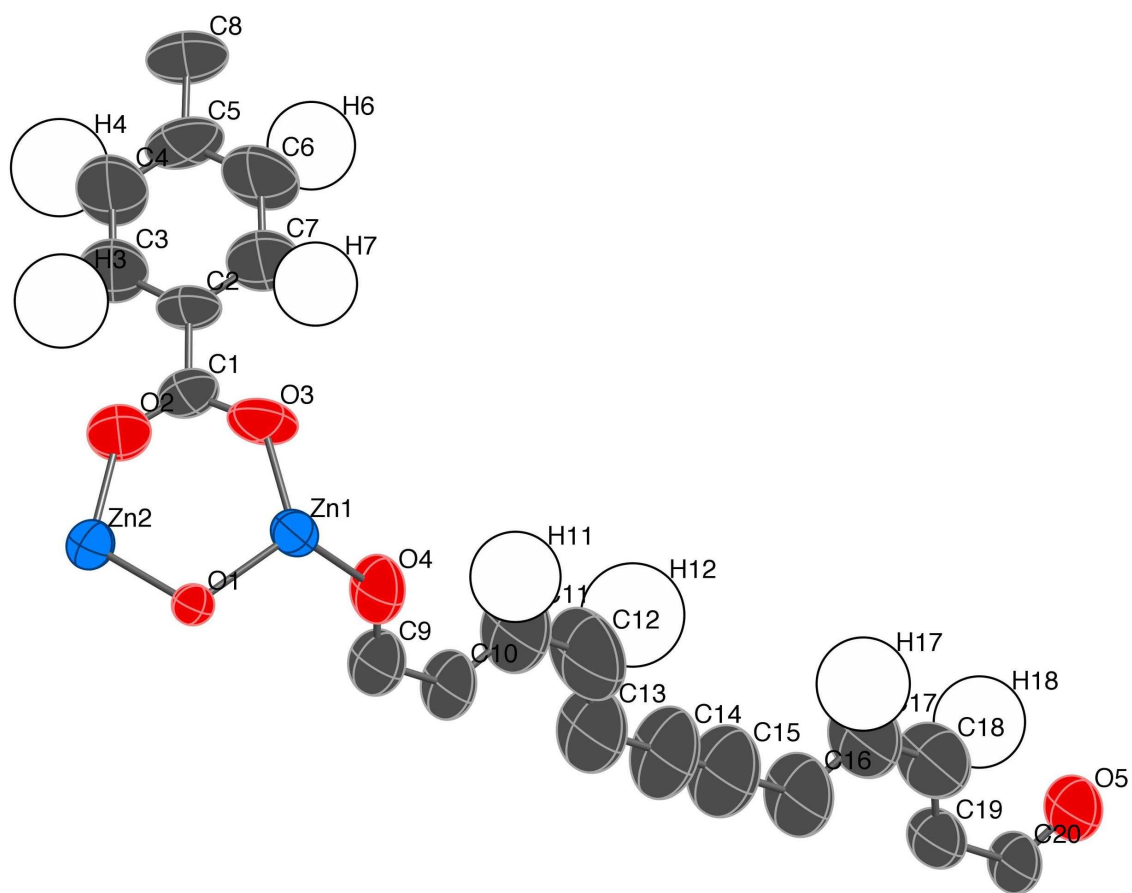


Figure S22. ORTEP drawing (50% probability) of the asymmetric unit in IRMOF-61.

IRMOF-62. The diffraction data set from a translucent orange crystalline polyhedron sealed in a capillary was collected at 258 K on a Bruker SMART APEX CCD diffractometer with (graphite monochromated) MoK α radiation ($\lambda = 0.71073$ Å). The Bruker SMART program^{S1} was used for analysis of raw data, and SAINT^{S2} was used for cell refinement and reduction. No absorption correction was applied. The crystal structure was solved using the Bruker SHELX-TL software package^{S4} in the trigonal space group, *P*3₂12 (No. 153). An initial model for IRMOF-62 was obtained by direct methods using XS, and was improved by subsequent refinements using XL. All non-hydrogen atoms were refined anisotropically. The PLATON SQUEEZE^{S5} routine was applied to the data to remove the contributions of the disordered solvents. With modified reflection data excluding the solvent contribution, the final refinement process converged to R1 = 0.0782, wR2 = 0.2221 ($I > 2\sigma(I)$). An asymmetric unit of IRMOF-62 is shown in Figure S23, and crystal and refinement data are given in Table S5.

Table S5. Crystal data and structure refinement for IRMOF-62.

Empirical formula	C ₅₄ H ₂₄ O ₁₃ Zn ₄	
Formula weight	1142.21	
Temperature	258(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	<i>P</i> 3 ₂ 12 (No. 153)	
Unit cell dimensions	<i>a</i> = 31.114(2) Å	$\alpha = 90^\circ$.
	<i>b</i> = 31.114(2) Å	$\beta = 90^\circ$.
	<i>c</i> = 39.280(3) Å	$\gamma = 120^\circ$.
Volume	32931(4) Å ³	
Z	12	
Density (calculated)	0.691 Mg/m ³	
Absorption coefficient	0.893 mm ⁻¹	
F(000)	6864	
Crystal size	0.30 x 0.30 x 0.30 mm ³	
Theta range for data collection	0.76 to 24.71°.	
Index ranges	-36 ≤ <i>h</i> ≤ 36, -36 ≤ <i>k</i> ≤ 36, -46 ≤ <i>l</i> ≤ 44	
Reflections collected	231155	
Independent reflections	37455 [R(int) = 0.0760]	
Completeness to theta = 24.71°	100.0%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	37455 / 0 / 1281	
Goodness-of-fit on F ²	0.997	
Final R indices [I > 2σ(I)]	R1 = 0.0782, wR2 = 0.2221	
R indices (all data)	R1 = 0.0978, wR2 = 0.2338	
Largest diff. peak and hole	0.642 and -0.917 e.Å ⁻³	

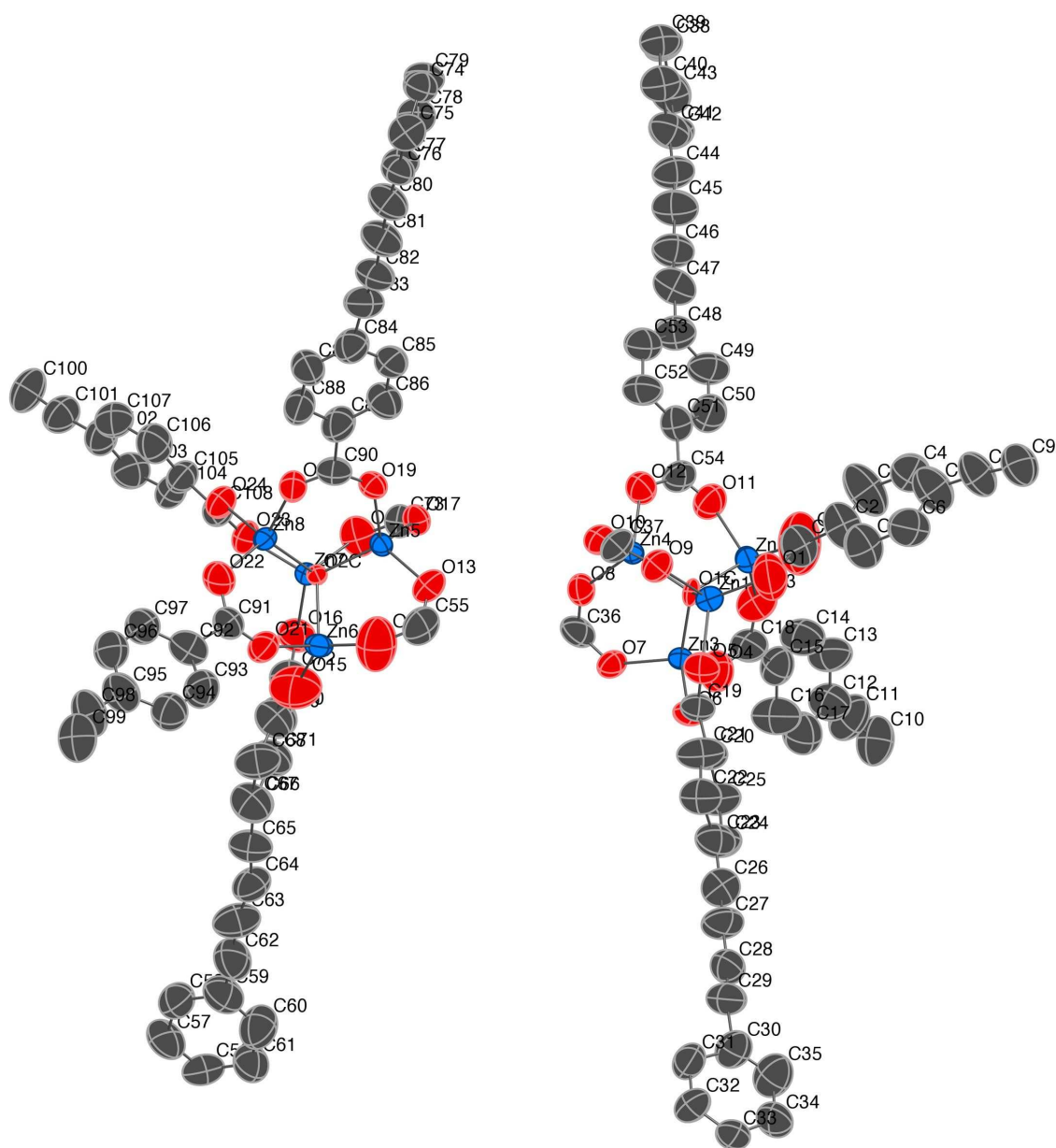


Figure S23. ORTEP drawing (50% probability) of the asymmetric unit in IRMOF-62. Hydrogen atoms have been removed for clarity.

Section S3: Powder X-Ray Diffraction Patterns

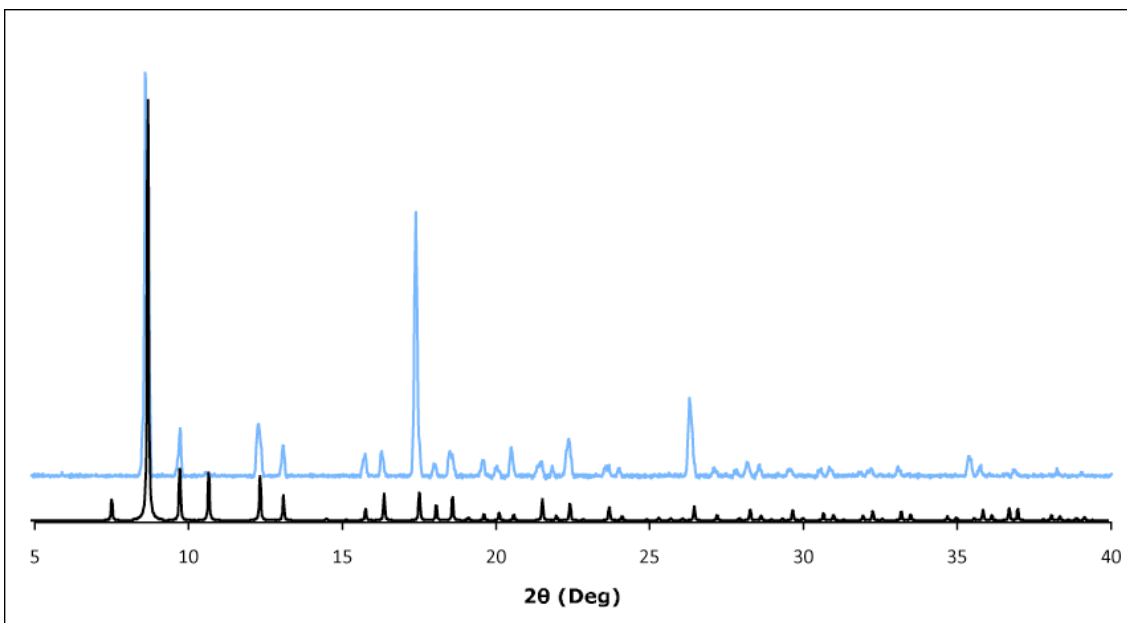


Figure S24. Powder diffraction data for MOF-324. The pattern simulated from SXRD data is black; the experimental pattern is in blue.

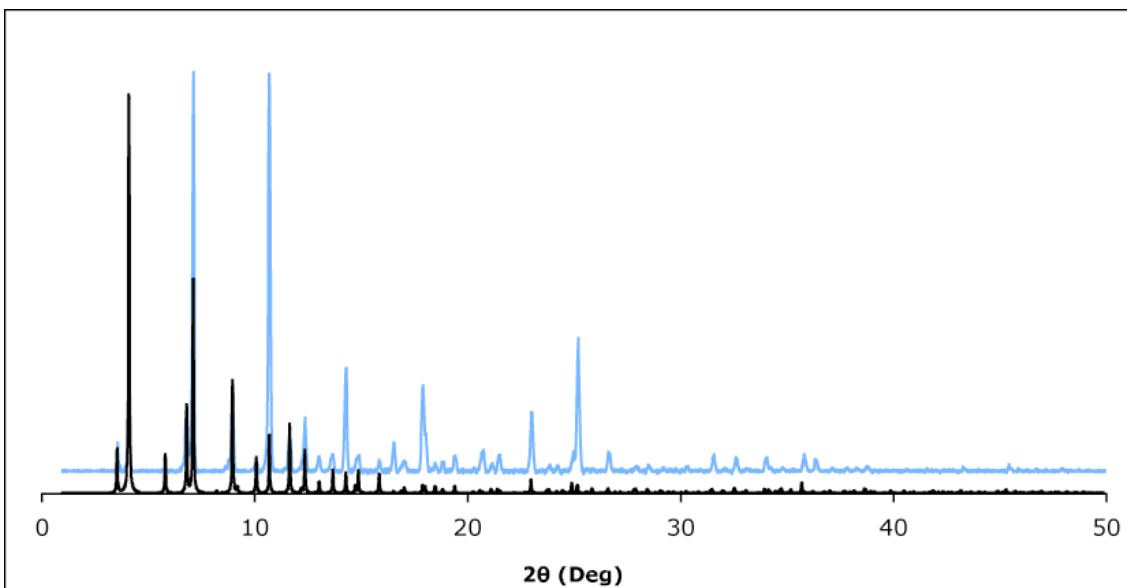


Figure S25. Powder diffraction data for MOF-325. The pattern simulated from SXRD data is black; the experimental pattern is in blue.

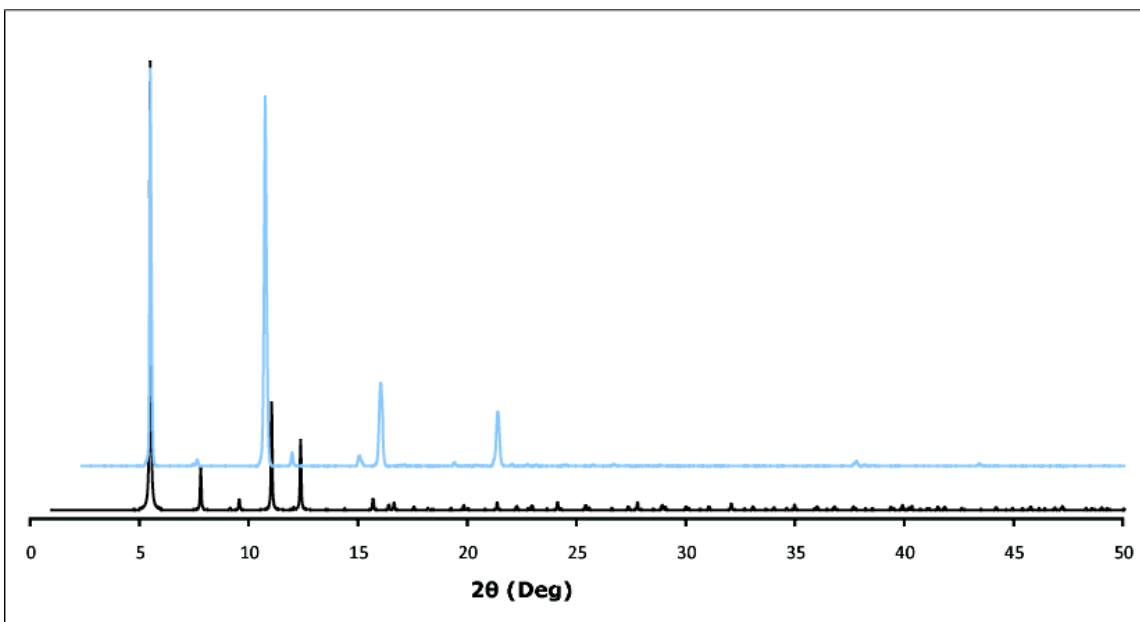


Figure S26. Powder diffraction data for MOF-326. The pattern simulated from SXRD data is black; the experimental pattern is in blue.

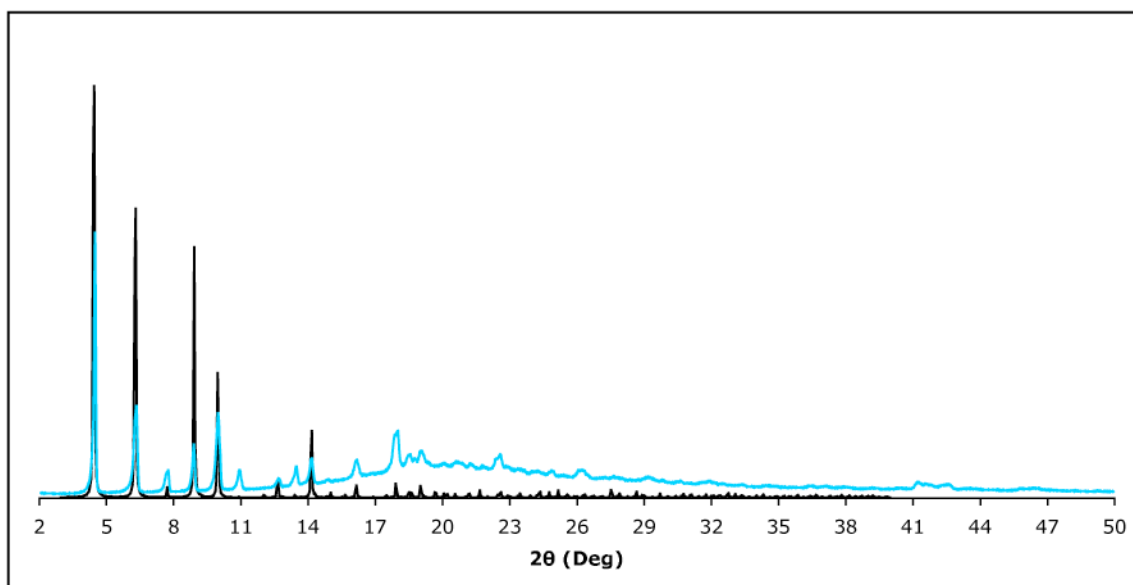


Figure S27. Powder diffraction data for IRMOF-61. The pattern simulated from SXRD data is black; the experimental pattern is in blue.

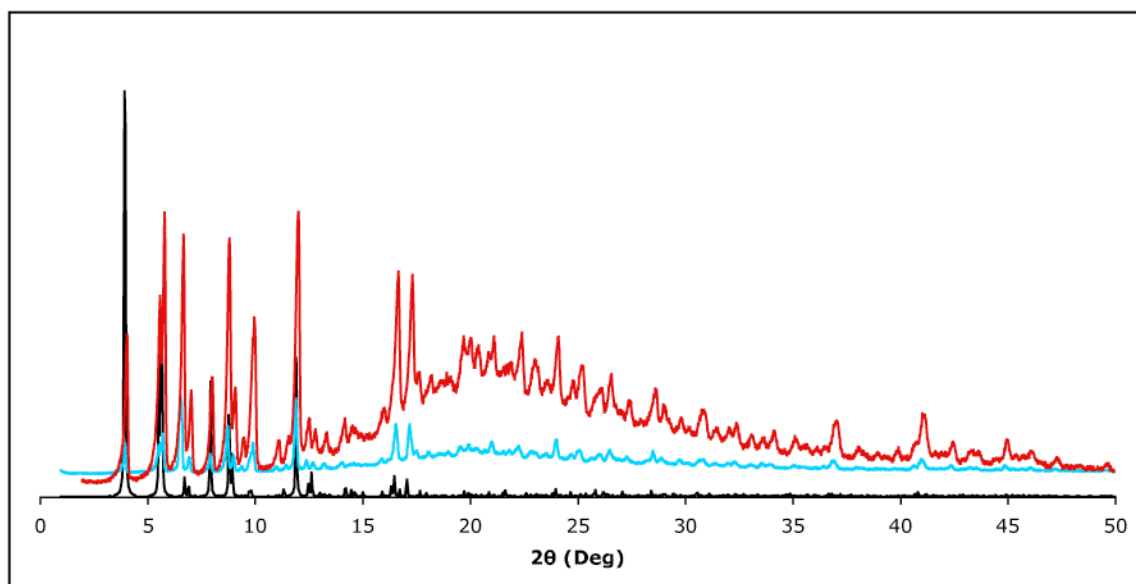


Figure S28. Powder diffraction data for IRMOF-62. The pattern simulated from SXRD data is black; the experimental patterns are in blue (solvothermal bulk synthesis) and red (room temperature bulk synthesis).

Section S4: Thermal Gravimetric Analyses

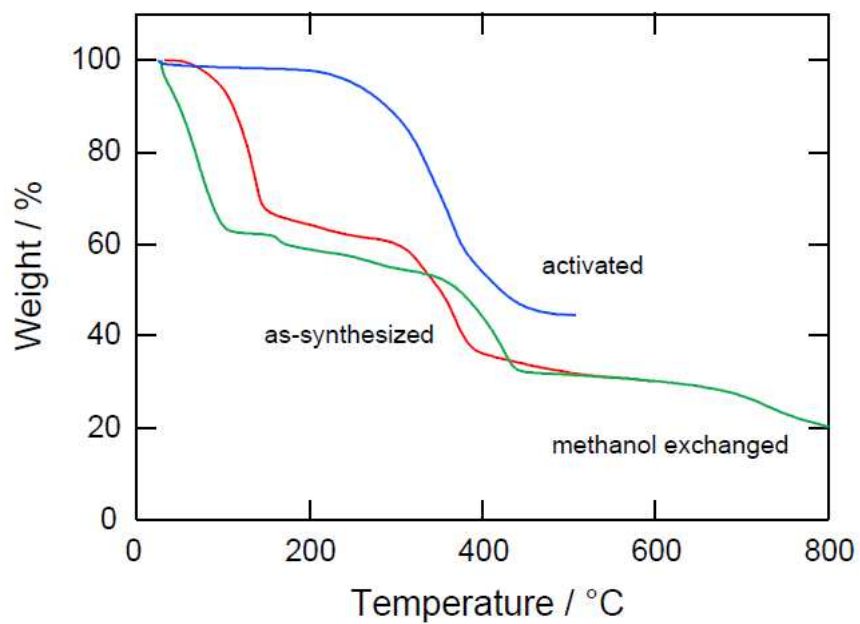


Figure S29. TGA of MOF-324 as-synthesized material (red), after exchange with methanol (green), and after activation (blue).

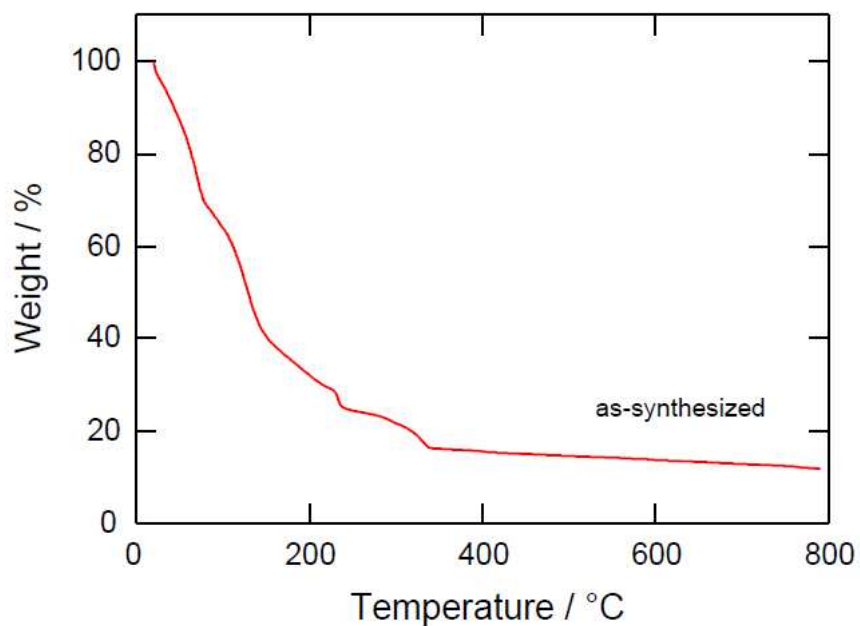


Figure S30. TGA of MOF-325 as-synthesized material.

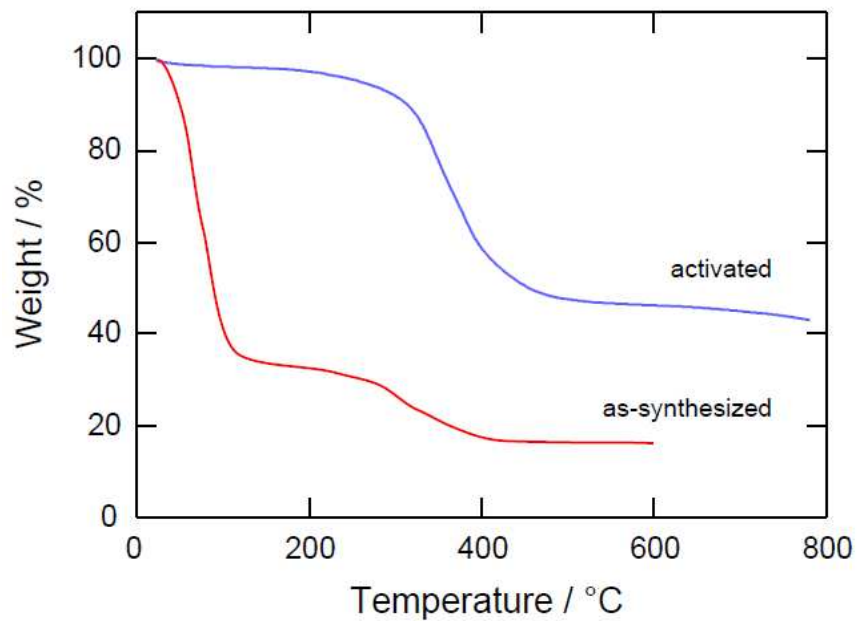


Figure S31. TGA of MOF-326 as-synthesized material (red) and after activation (blue).

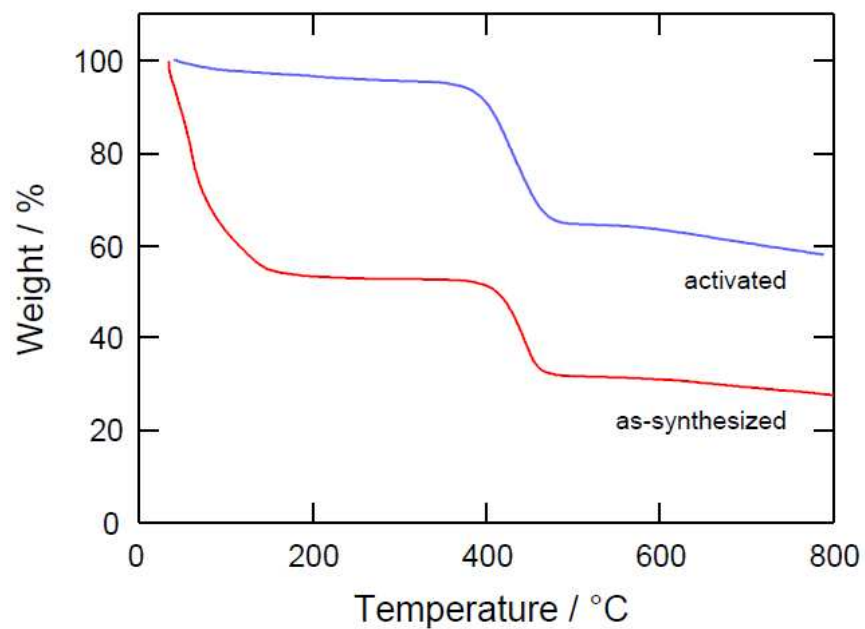


Figure S32. TGA of IRMOF-61 as-synthesized material (red) and after activation (blue). Thermal decomposition occurs at approximately 400 °C after activation.

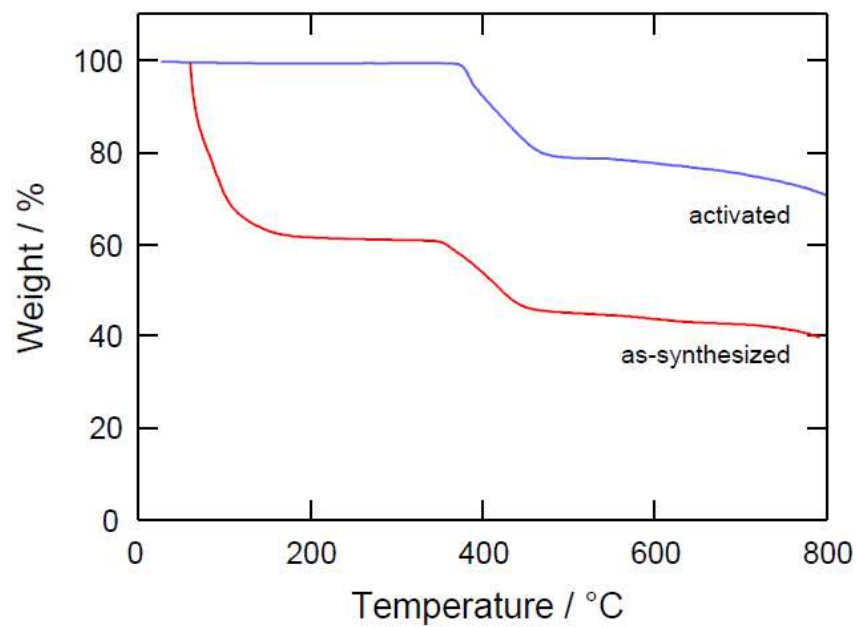


Figure S33. TGA of IRMOF-62 as-synthesized material (red) and after activation (blue). Thermal decomposition occurs at approximately 380 °C after activation.

Section S5: Gas Adsorption Measurements

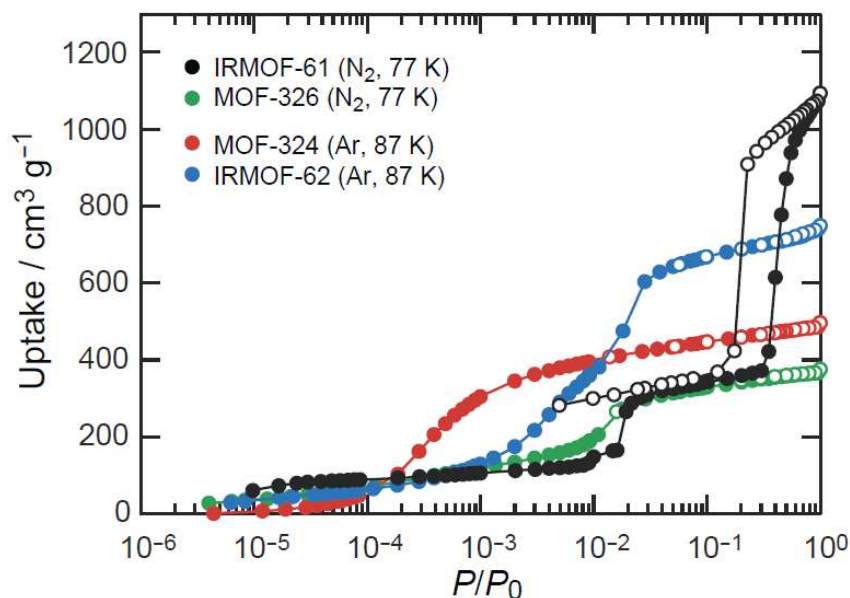


Figure S34. Ar adsorption isotherms of MOF-324 (red) and IRMOF-62 (blue) at 87 K and N₂ isotherms of MOF-326 (green) and IRMOF-61 (black) at 77 K. Filled and open circles represent adsorption and desorption branches. Connecting lines are guides for the eye..

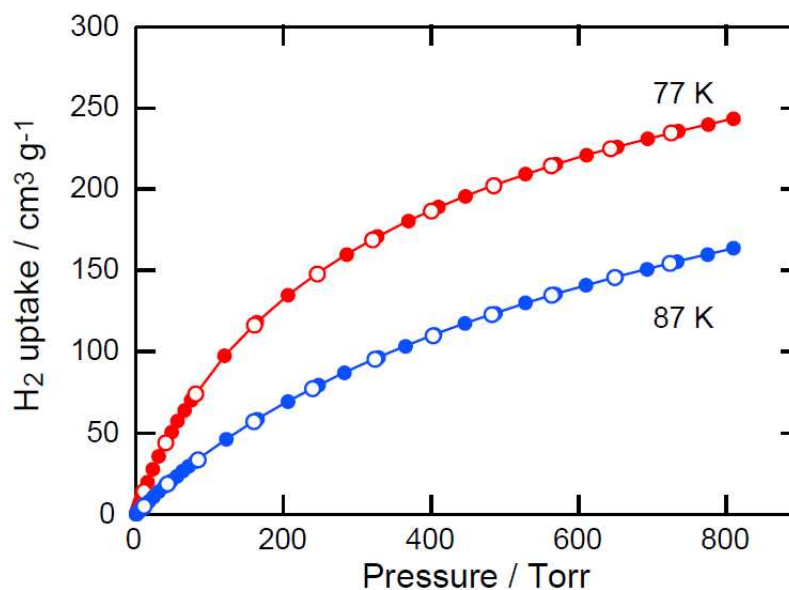


Figure S35. H₂ isotherms for MOF-324 measured at 77 (red) and 87 K (blue). Filled and open symbols represent adsorption and desorption branches.

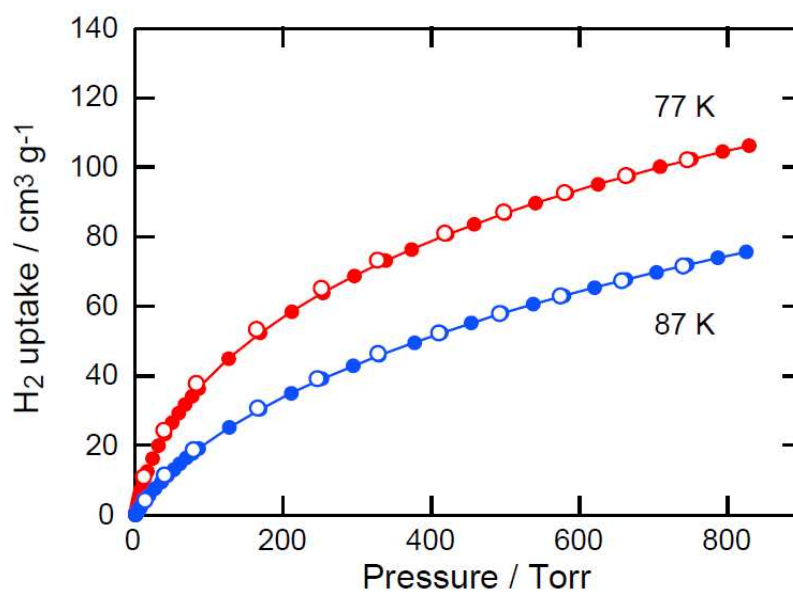


Figure S36. H₂ isotherms for MOF-326 measured at 77 (red) and 87 K (blue). Filled and open symbols represent adsorption and desorption branches.

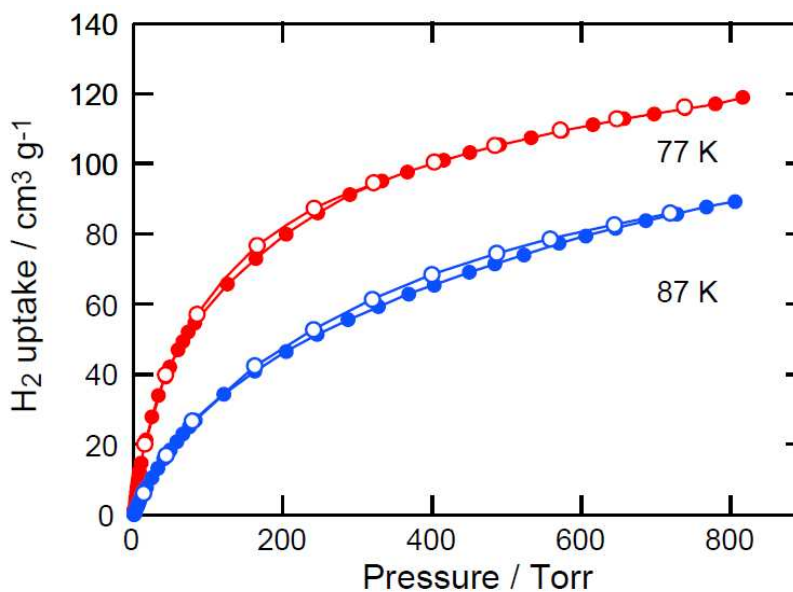


Figure S37. H₂ isotherms for IRMOF-61 measured at 77 (red) and 87 K (blue). Filled and open symbols represent adsorption and desorption branches.

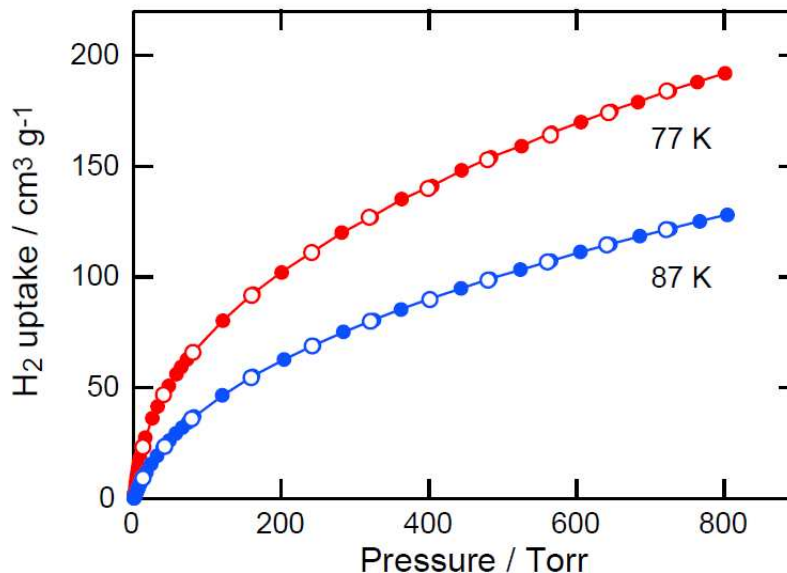


Figure S38. H₂ isotherms for IRMOF-62 measured at 77 (red) and 87 K (blue). Filled and open symbols represent adsorption and desorption branches.

Estimation of Isostatic Heat of H₂ Adsorption. The isosteric heats of H₂ adsorption were estimated for activated (IR)MOFs from the H₂ sorption data measured at 77 K and 87 K. A virial-type expression was used (eq 1), which is composed of parameters a_i and b_i that are independent of temperature.^{S6-S8} In eq 1, P is the pressure (Torr), N is the amount of adsorbed H₂ gas (mg g⁻¹), T is the temperature (K), and m and n represent the number of coefficients required to adequately describe the isotherms.

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad (1)$$

To estimate the values of the isosteric heat of H₂ adsorption, eq 2 was applied, where R is the universal gas constant.

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (2)$$

Time-course H₂ uptake profile for IRMOF-62

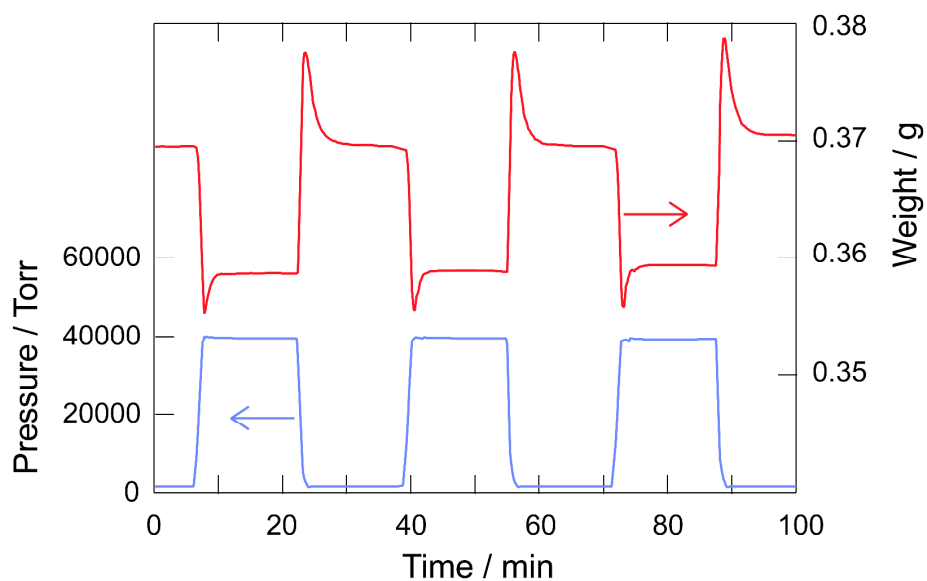


Figure S39. Time-course H₂ uptake profile for IRMOF-62 at 77 K. The red curve represents weight change as H₂ pressure is changed on the sample, uncorrected for buoyancy. The blue curve represents the H₂ pressure applied to the chamber during the experiment.

Section S6: Complete Ref. 3i

Furukawa, H.; Ko, N.; Go, Y. B.; Aratani, N.; Choi, S. B.; Choi, E.; Yazaydin, A. Ö.; Snurr, R. Q.; O’Keeffe, M.; Kim, J.; Yaghi, O. M. *Science* **2010**, 329, 424-428.

Section S7: References

- (S1) Bruker SMART version 5.625, Area-Detector Software Package; Bruker AXS 1997-2001. Madison, WI, USA.
- (S2) Bruker SAINT+ version 6.04. SAX Area-Detector Integration Program. Bruker AXS 1997-2001. Madison, WI, USA.
- (S3) Sheldrick, G. M. SADABS version 2.03, a Program for Empirical Absorption Correction; Universität Göttingen, 1997-2001.
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- (S5) A. L. Spek, (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.
- (S6) Furukawa, H.; Miller, M. A.; Yaghi, O. M. *J. Mater. Chem.* **2007**, 17, 3197.
- (S7) Czepirski, L.; Jagiełło, J. *Chem. Eng. Sci.* **1989**, 44, 797.
- (S8) Jagiello, J.; Bandosz, T. J.; Putyera, K.; Schwarz, J. A. *J. Chem. Eng. Data* **1995**, 40, 1288.