Supplementary Information

Optimal Binding of Acetylene to a Nitro-Decorated Metal-Organic Framework

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1. Synthesis and Characterization

1.1 Experimental Methods and Equipment

Chemicals and reagents were purchased from Fischer Scientific, Sigma Aldrich or Fluorochem and used as received without further purification. $^1$H NMR and $^{13}$C NMR spectra were measured on a Bruker AV400 or AV500 spectrometer. High-resolution electrospray mass spectra were measured on a Bruker MicroTOF spectrometer with samples dissolved in MeOH as the solvent. Scanning was carried out in both positive and negative modes. Infrared (IR) spectra were recorded in the 400-4000 cm$^{-1}$ range in ATR sampling mode with a Thermo Scientific iD5 diamond ATR on a Nicolet iS5 FT-IR spectrometer, and elemental analysis was carried out on a CE-440 elemental analyser (EAI Company). TGA measurements were performed using a Perkin Elmer TGA 7 Gravimetric Analyser under a flow of N$_2$ (20 ml min$^{-1}$) at a heating rate of 5 °C min$^{-1}$. Powder X-ray diffraction (PXRD) patterns were obtained on a PANalytical X’Pert Pro MPD diffractometer in Bragg-Brentano geometry with Cu-K$_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å) at 40 kV and 30 mA over 20 range 3-40°. Samples were evenly dispersed on zero-background silicon plates with a cavity depth of 0.3 mm.

1.2 Ligand Synthesis

The ligands were synthesized by Suzuki-coupling reaction between benzene-1,3-dicarboxylethylester-5-boronic acid and dibromo species followed by hydrolysis and acidification. The synthesis of H$_4$L$^1$ and H$_4$L$^2$ have been reported previously, and the detailed synthesis of H$_4$L$^3$ and H$_4$L$^4$ is described below.

![Scheme S1. Synthesis of H$_4$L$^3$ and H$_4$L$^4$.](image-url)
Synthesis of 4,4'-dibromo-2,2'-dinitrobiphenyl

To a mixture of 2,5-dibromonitrobenzene (25.0 g, 89 mmol) and activated copper powder (14 g; 220 mmol) was added dry DMF (90 mL). The resulting mixture was stirred for 3 h at 120 °C under Ar. After cooling to room temperature, the reaction mixture was dissolved in toluene (120 ml) and stirred for several minutes. Unreacted copper and insoluble materials were removed by filtration, the organic layer was washed with water and brine, dried over MgSO₄ and the solvent was evaporated in vacuo. Recrystallization of the product from EtOH yielded 4,4'-dibromo-2,2'-dinitro-1,1'-biphenyl as pale yellow prisms (12.6 g, 70% yield).

1H NMR δH (CDCl₃, 300MHz) 7.18 (2H, d, J = 2.0 Hz) 7.85 (2H, dd, J = 8.2, 2 Hz) 8.40 (2H, d, J = 2.0 Hz) ppm. 13C NMR δC (CDCl₃, 75 MHz) 122.90 (2C), 128.06 (2C), 131.96 (2C), 132.02 (2C), 136.62 (2C), 147.38 (2C) ppm. MS (ESI) m/z (M-H) + found 400.9. Calc. (%) for C₁₂H₆Br₂N₂O₄: C, 35.9; H, 1.5; N, 7.0. Found (%): C, 35.6; H, 1.5; N, 6.6.

Synthesis of 4,4'-dibromo-[1,1'-biphenyl]-2,2'-diamine

A mixture of 4,4'-dibromo-2,2'-dinitro-1,1'-biphenyl (6 g, 14.9 mmol) and anhydrous SnCl₂ (24 g, 126 mmol) in EtOH (100 mL) and concentrated HCl (37 %, 60 mL) were stirred and heated under reflux for 12h under N₂. The reaction mixture was allowed to cool and was then poured into large amount of ice. The resulting mixture was basified to pH 8 by slowly adding aqueous solution of NaOH (2M). The product was extracted several times with diethyl ether, and the organic fractions were combined, thoroughly washed with water, brine, treated with charcoal and dried over MgSO₄. The solvent was removed under reduced pressure, and the residue recrystallized from EtOH to give pure 4,4'-dibromo-[1,1'-biphenyl]-2,2'-diamine as a light yellow powder (4.45 g, 87% yield). 1H NMR δH (CDCl₃, 300 MHz) 3.76 (4H, br.s), 6.95 (6H, s) ppm. 13C NMR (CDCl₃, 75 MHz) δC 118.11 (2C), 121.68 (2C), 122.03 (2C), 122.70 (2C), 132.23 (2C), 145.36 (2C) ppm. IR (selected for Ar-NH₂): ν = 3393, 1636, 1556 cm⁻¹. Calc. (%) for C₁₂H₁₀Br₂N₂: C, 42.2; H, 3.0; N, 8.2. Found (%): C, 42.0; H, 3.0; N, 8.0.

Synthesis of 2'',3'-dinitro-[1,1':4',1''-quaterphenyl]-3,3'',5,5''-tetraethylcarboxylate ester.

A mixture of 1,3-dicarboxylethylester-5-boronic acid (3.129 g, 12 mmol), 4,4'-dibromo-2,2'-dinitrobiphenyl (2.01 g, 5 mmol), K₂CO₃ (3.36 g, 24.3 mmol), toluene (400 mL) and water (80 mL) was degassed at 60 °C for 30 min, followed by the addition of tri(tert-butyl)phosphine in toluene (2.52 ml, 0.1M) and Pd₂dba₃ (0.84 g, 0.91 mmol). After heating at 85 °C for 18h under Ar, the reaction mixture was extracted twice with CH₂Cl₂ (200 ml x2), washed with brine and dried over MgSO₄. After filtration, the solvent was removed under reduced pressure and the residue purified by column chromatography over silica gel using petroleum ether/ethyl acetate (4:1) as eluent to afford the pure product (2.33 g, 73 %). 1H NMR (500 MHz, CDCl₃) δ ppm 1.40 (t, J=7.10 Hz, 12 H) 4.41 (dd, J=7.00 Hz, 8 H) 7.41 (d, J=7.93 Hz, 2 H) 7.95 (dd, J=7.93, 1.68 Hz, 2 H) 8.45 - 8.51 (m, 6 H) 8.70 (s, 2 H). Calc. (%) for C₃₆H₃₂N₂O₁₂: C, 63.2; H, 4.7; N, 4.1. Found (%): C, 63.0; H, 4.6; N, 4.0.
Synthesis of 2''''-dinitro-[1,1':4',1''':4'',1''''-quaterphenyl]-3,3'',5,5'''-tetraacarboxylic acid.

A mixture of 2''''-dinitro-[1,1':4',1''':4'',1''''-quaterphenyl]-3,3'',5,5'''-tetraethylcarboxylate ester (1.37 g, 2 mmol), aqueous NaOH (100 mL, 2M), EtOH (100 mL) and tetrahydrofuran (100 mL) was heated at 85 °C overnight. The volatile solvents were removed by evaporation and the remaining solution acidified with concentrated HCl (pH ~3) to give a yellow precipitate. The solid was collected by filtration, washed with a copious amount of H2O, dried at 90 °C to give pure ligand H4L3. 

1H NMR (500 MHz, DMSO-d6) δ ppm 7.70 (d, J=7.93 Hz, 2H) 8.31 (dd, J=8.09, 1.83 Hz, 2H) 8.54 - 8.59 (m, 6H) 8.61 (d, J=1.83 Hz, 2H) 13.28 - 13.83 (m, 4H). HRMS (ESI): m/z calcd for C28H16N2O14: 572.07 ([M-H]-); found 571.2. Calc. (%) for C28H16N2O12: C, 63.2; H, 4.7; N, 4.1. Found (%): C, 63.0; H, 4.6; N, 4.0.

Synthesis of 2'',3' -diamino-[1,1':4',1''':4'',1''''-quaterphenyl]-3,3'',5,5'''-tetraethylcarboxylate ester.

4,4'-Dibromo-[1,1'-biphenyl]-2,2'-diamine (1.71 g, 5 mmol), 1,3-dicarboxylethylester-5-boronic acid (3.129 g, 12 mmol) and potassium triphosphate (6.23 g, 29.3 mmol) were dissolved in 1,4 dioxane (120 mL) and water (5 mL) under Ar at 60 °C. [1,1'-'Bis(diphenylphosphino) ferrocene dichloropalladium(II)], Pd(dppf)Cl2 (80 mg, 0.11 mmol) was added to the mixture, which was heated up to 85 °C for 2 days. The resulting mixture was evaporated under reduced pressure, and CHCl3 (100 mL) and H2O (100 mL) was added to re-dissolve the solid. The solution was separated and the aqueous solution extracted with CHCl3 several times. The organic phases were combined and washed with brine, and dried over MgSO4. The solution was purified by flash chromatography on silica gel eluted with CHCl3. After removing solvents, the cream colored powder was yielded as a pure product H4L4 (2.66 g, 83 %). 1H NMR δH (CDCl3, 300MHz) 1.47 (12H, t, J = 7.2 Hz), 3.97 (4H, s) 4.47 (8H, q, J = 7.2 Hz), 7.13 (2H, d, J = 1.6 Hz), 7.17 (1H, d, J = 1.6 Hz), 7.19 (1H, d, J = 1.7 Hz), 7.29 (1H, s), 7.32 (1H, s), 8.5 (4H, d, J = 1.6 Hz), 8.68 (2H, t, J = 1.6 Hz) ppm. Calc. (%) for C36H36N2O8: C, 69.2; H, 5.8; N, 4.5. Found (%): C, 69.0; H, 5.6; N, 4.5.

Synthesis of 2'',3'-diamino-[1,1':4',1''':4'',1''''-quaterphenyl]-3,3'',5,5'''-tetracarboxylic acid

Tetraethyl-2'',3'-diamino-[1,1':4',1''':4'',1''''-quaterphenyl]-3,3'',5,5'''-tetracarboxylic acid (2.5 g, 4 mmol) was suspended with NaOH solution (2M, 80 mL) and EtOH/THF (1:1 v/v, 160 mL) and the mixture refluxed in 12 h. After hydrolysis completed, volatile solvent and water were removed under reduced pressure. The residue was mixed with a little water and acidified to pH 6-7 by slowly adding HCl 3M to give precipitate of crude product. The solid was filtered and carefully washed with distilled water. Hot DMF and water were used in recrystallization with two solvent to give pure white H4L4. Yield: 1.66 g, 81 %. 1H NMR δH (DMSO-d6, 400MHz) 4.94 (4H, s), 7.02 (2H, dd), 7.14 (2H, d), 7.22 (2H, d), 8.3
(4H, s), 8.44 (2H, t) ppm. MS (EI) m/z (M-H) found 511.41. Calc. (%) for C_{28}H_{30}N_{2}O_{6}: C, 65.6; H, 3.9; N, 5.5. Found (%): C, 65.5; H, 3.6; N, 5.3.

1.3 MOF Synthesis

The preparations of MFM-102 and MFM-111 were synthesized as previously reported.1 MFM-111, MFM-102, MFM-102-NH$_2$ were synthesized via solvothermal reaction using DMF, while DMSO was added to the reaction mixture to obtain MFM-102-NO$_2$. The structure of the MOFs were obtained by single crystal X-ray diffraction, and the phase purity of the bulk crystalline materials was confirmed by powder X-ray diffraction.

**Preparation of MFM-102-NO$_2$: [Cu$_2$(H$_2$O)$_2$(L$_3$)]·7DMF·6H$_2$O**

H$_2$L$_3$ (20 mg, 0.04 mmol) and Cu(NO$_3$)$_2$·2.5H$_2$O (36.2 mg, 0.156 mmol) were dissolved in N,N’-dimethylformamide (DMF, 3.5 mL) and dimethyl sulfoxide (DMSO, 0.5 mL) acidified with a solution of HCl in DMF (2M, 0.075 mL). The solution was sealed in a pressure tube (15 mL) and heated at 90 °C for 24 h. After cooling to room temperature, a large amount of microcrystalline product precipitated. The deep green block crystals were filtered, wash with warm DMF and dried in air. FTIR (cm$^{-1}$): 3359 (br,w), 1698 (s), 1614 (s), 1556 (m), 1493 (s), 1417 (s), 1370 (s), 1228 (s), 1073 (s), 887 (s), 825 (s), 773 (s), 750 (s), 674 (s), 628 (s). Calc. (%) for C$_{28}$H$_{16}$Cu$_2$N$_2$O$_{14}$: C, 46.0; H, 2.0; N, 3.8. Found (%): C, 45.6; H, 2.6; N, 3.5.

**Preparation of MFM-102-NH$_2$: [Cu$_2$(H$_2$O)$_2$(L$_4$)]·6DMF·5H$_2$O**

H$_2$L$_4$ (20 mg, 0.04 mmol) and Cu(NO$_3$)$_2$·2.5H$_2$O (36.2 mg, 0.156 mmol) were dissolved in N,N’-dimethylformamide (DMF, 4 mL) with a solution of HCl in DMF (2M, 0.075 mL). Work up and isolation were the same as for MFM-102-NO$_2$. Yield: 20.5 mg (70 % based on H$_4$L$_3$). FTIR (cm$^{-1}$): 3348 (br,w), 1173 (s), 1647 (s), 1633 (s), 1591 (s), 1557 (s), 1446 (s), 1410 (s), 1367 (s), 1223 (s), 1089 (m), 1004 (s), 775 (s), 729 (m), 689 (s). Calc. (%) for C$_{28}$H$_{20}$Cu$_2$N$_2$O$_{10}$: C, 50.0; H, 3.0; N, 4.2. Found (%): C, 49.6; H, 2.6; N, 3.8.

2. Single Crystal X-ray Analysis

Diffraction data for the single crystals of compounds MFM-102-NO$_2$ and MFM-102-NH$_2$ were obtained at 120 K on an automated Rigaku SuperNova X-ray Diffraction system equipped with a CCD AtlasS2 detector (Mo-Kα, graphite monochromator, ω-scans). Integration, absorption correction, and determination of unit cell parameters were performed using the CrysAlisPro program package (CrysAlisPro 1.171.38.41. Rigaku Oxford Diffraction 2015). The structures were solved by dual space algorithm$^2$ and refined by the full-matrix least squares technique$^3$ in the anisotropic approximation (except hydrogen atoms). Positions of hydrogen atoms of organic
ligands were calculated geometrically and refined in the riding model. Due to heavy disorder of the NO$_2$-groups in MFM-102-NO$_2$ the corresponding atoms were refined isotropically. However, the refined model is in full agreement with other experimental data including the structure obtained by neutron powder diffraction. The SQUEEZE$^4$ procedure was applied to account the electron density within the pores. The crystallographic data and details of the structure refinements are summarized in Table S1.

Table S1. Summary of crystallographic data of MFM-102-NO$_2$ and MFM-102-NH$_2$.

|                  | MFM-102-NO$_2$                  | MFM-102-NH$_2$                  |
|------------------|---------------------------------|---------------------------------|
| Formula          | Cu$_2$C$_{28}$H$_{14}$N$_2$O$_{14}$ | Cu$_2$C$_{28}$H$_{14}$N$_2$O$_{10}$ |
| Formula Weight   | 728.48                          | 665.49                          |
| Crystal System   | Trigonal                        | Trigonal                        |
| Space group      | R-3m                            | R-3m                            |
| $a$, Å           | 18.3933(6)                      | 18.3453(8)                      |
| $c$, Å           | 52.3346(18)                     | 52.3638(16)                     |
| $V$, Å$^3$       | 15333.4(13)                     | 15262.0(16)                     |
| $Z$              | 9                               | 9                               |
| $D_c$, g cm$^{-3}$ | 0.710                          | 0.652                           |
| $\mu$, mm$^{-1}$ | 1.060                           | 0.994                           |
| Crystal size, mm | 0.15 x 0.20 x 0.29              | 0.06 x 0.10 x 0.15              |
| Temperature, K   | 120                             | 120                             |
| Radiation type CuK$_\alpha$ | Cu K$\alpha$             | Cu K$\alpha$                 |
| $\theta$ range, $^\circ$ | 3.2 – 74.5                     | 4.4 – 74.7                     |
| Reflections collected/ unique | 40584/3817,                 | 13519/3764,                    |
| Reflections with $I > 2\sigma(I)$ | 3292                         | 3155                           |
| $R_{int}$        | 0.037                           | 0.044                           |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.0857, 0.3301, 1.52          | 0.0836, 0.2895, 1.28           |
| Number of reflections | 3817                          | 3764                           |
| Number of parameters | 143                           | 125                            |
| $\Delta\rho_{max}/\Delta\rho_{min},$eÅ$^{-3}$ | -0.39, 1.17                   | -0.46, 1.56                    |

Crystallographic data for the reported structures have been deposited to the Cambridge Crystallographic Data Centre, CCDC 1857304 and 1857305 for MFM-102-NO$_2$ and MFM-102-NH$_2$, respectively.
3. Powder X-ray Diffraction (PXRD)

Figure S1. PXRD patterns for MFM-102, MFM-102-NO$_2$ and MFM-102-NH$_2$.

Figure S2. PXRD pattern for as-synthesized MFM-102-NH$_2$ and the simulated pattern derived from single crystal X-ray data. Calculated PXRD patterns were generated using Mercury 3.10.
Figure S3. (a) PXRD pattern for the as-synthesized MFM-102-NO$_2$ and the simulated pattern derived from single crystal X-ray data. Calculated PXRD patterns were generated using Mercury 3.10. (b) Comparison of the PXRD patterns for simulated and desolvated MFM-102-NO$_2$ [data collected at Beamline I11 at Diamond Light Source, $\lambda = 0.82488(4)$ Å]. The activated sample was prepared by heating the as-synthesised sample at 110 °C under high vacuum ($1 \times 10^{-6}$ mbar) for 6 h.

4. Thermogravimetric Analysis

Figure S4. TGA plots for as-synthesized samples of MFM-102-NO$_2$ and MFM-102-NH$_2$ measured under a flow of N$_2$ at a rate of 20 mL min$^{-1}$.

As-synthesized samples of MFM-102-NO$_2$ and MFM-102-NH$_2$ were analyzed by TGA (Figure S4). In general, they show very similar thermal stability. The samples were removed from their mother liquor and dried by filtration before being analyzed. A small amount of surface solvent is lost (~8%) at the
beginning of the temperature ramp (~80 °C), corresponding to uncoordinated water molecules. The following ~40% weight loss up to 280 – 300 °C is attributed to the removal of uncoordinated and coordinated DMF molecules. At 300 °C, there is a steep and sharp mass loss in both samples assigned to the decomposition of the organic linker leading to the collapse of the frameworks.

5. Gas Adsorption Data

MFM-102-NO$_2$ was stored under DMF before activation. Solvent exchanged samples were prepared by immersing as-synthesized samples in anhydrous acetone for 3 days replacing the acetone 3 times a day. The activated samples were prepared by heating the acetone-exchanged samples at 110 °C under high vacuum in 24 h. On activation, the dark green crystals of MFM-102-NO$_2$ changed to deep purple.

Volumetric cryogenic N$_2$ isotherms were performed on a Micromeritics 3-flex apparatus using ultra-high purity (99.999 %), CP grade N$_2$ at 77 K for void volumetric determination. The BET surface areas were calculated using the software integrated into the instrument. CH$_4$ and C$_2$H$_2$ gravimetric sorption isotherms were carried out at 273 – 298 K (maintained using a temperature programmed water-ethylene glycol bath) on a Hiden Isochema IGA system under ultra-high vacuum produced by a turbo pumping system. All gases used were ultra-pure CP grade (99.9999%) purchased from BOC or Air Liquide. In a typical gas adsorption experiment, around 120 mg of acetone-exchanged MFM-102-NO$_2$ was transferred into the IGA system and outgassed at 110 °C under dynamic high vacuum (10$^{-6}$ mbar measured at pump) overnight to give fully desolvated MFM-102-NO$_2$. For acetylene isotherms, the gas was filtered through 4Å molecular sieves and activated carbon to remove traces of acetone.

N$_2$ adsorption at 77 K

![BET fitting plot](image)

Figure S5. BET fitting plot for (a) MFM-102-NO$_2$ and (b) MFM-102-NH$_2$. 
Table S2. BET parameters for MFM-102-NO$_2$ and MFM-102-NH$_2$

| Parameter                  | MFM-102-NO$_2$          | MFM-102-NH$_2$          |
|----------------------------|-------------------------|-------------------------|
| BET surface area           | 2893 ± 1 m$^2$.g$^{-1}$  | 2928 ± 1 m$^2$.g$^{-1}$  |
| Slope                      | 0.001504 ± 0.00 g.cm$^{-3}$ STP | 0.001486 ± 0.00 g.cm$^{-3}$ STP |
| Y-intercept                | 0.000001 ± 0.00 g.cm$^{-3}$ STP | 0.000001 ± 0.00 g.cm$^{-3}$ STP |
| C                          | 2807                    | 2085                    |
| Q$_m$                      | 664.7 cm$^3$.g$^{-1}$ STP | 672.7 cm$^3$.g$^{-1}$ STP |
| Correlation coefficient    | 0.9999998               | 0.9999999               |
| Molecular cross-sectional area | 0.1620 nm$^2$           | 0.1620 nm$^2$           |

Figure S6. Pore size distribution for MFM-102-NO$_2$ and MFM-102-NH$_2$ determined by analyzing the N$_2$ isotherm at 77 K using non-local density functional theory (NLDFT). The data for MFM-102-NO$_2$ and MFM-102-NH$_2$ reveal similar distributions of pores with estimated diameters of 7-8 Å, 11-13 Å and 15 Å.
**CH₄ adsorption at 273 K**

![CH₄ adsorption isotherms](image1)

Figure S7. Adsorption isotherms of CH₄ in the MFM-102 series up to 20 bar at 273 K. Adsorption (filled symbols) and desorption (empty symbols).

**C₂H₂ adsorption at 273 K**

![C₂H₂ adsorption isotherms](image2)

Figure S8. Adsorption isotherms of C₂H₂ in the MFM-102 series at 273 K. Adsorption (filled symbols) and desorption (empty symbols).
Table S3. Comparison of acetylene uptake for a variety of MOFs at 298 K.

| MOF      | C₂H₂  | C₂H₂  | BET  | Total pore volume | Qₛₜ | Ref.   |
|----------|-------|-------|------|-------------------|------|--------|
|          | 273 K | 298 K |      |                   |      |        |
| MFM-102 | 251   | 150   | 3412 | 1.29              | 31.2 | This work |
| MFM-111 | 241   | 132   | 2930 | 1.19              | 32.0 | This work |
| MFM-102-NH₂ | 292  | 192   | 2893 | 1.12              | 31.5 | This work |
| ZJU-8   | 272   | 195   | 2501 | 1.02              | 29.6 | 5      |
| ZJU-40  | 286   | 216   | 2858 | 1.06              | 34.5 | 6      |
| FJI-H8  | 277   | 224   | 2025 | 0.82              | 32.0 | 7      |
| MFM-188 | 297   | 232   | 2568 | 1.12              | 32.5 | 8      |
| MOF-505 | 177   | 148   | 1139 | 0.67              | 24.7 | 9      |
| ZJU-5   | 290   | 193   | 2823 | 1.07              | 35.8 | 10     |
| HKUST-1 | 250   | 201   | 1401 | 0.76              | 34.0 | 11     |
| NJU-Bai 17 | 295 | 222   | 2423 | 0.91              | 38.0 | 12     |
| MFM-101 | 274   | 184   | 2805 | 1.08              | 32.4 | 13     |
| PCN-16  | 252   | 160   | 2604 | -                 | 35.0 | 12     |
| ZJU-7   | 245   | 180   | 2198 | 0.89              | 28.8 | 14     |
| ZJU-10  | 258   | 174   | 2392 | 0.96              | 39.0 | 15     |

*a* C₂H₂ uptake data were collected at 295 K and 1 atm.

*b* C₂H₂ uptake data were collected at 296 K and 1 atm.

**Heat of Adsorption**

The presence of a relatively strong interaction between gas molecules and the frameworks was revealed by analysis of the coverage-dependent isosteric heats of adsorption (Qₛₜ). The virial-type expression comprising the temperature-independent parameters aᵢ and bⱼ was employed to calculate the Qₛₜ for all the gases measured at 273 K and 298 K. In each case, the data were fitted using the equation below:

\[
\ln(P) = \ln(N) + \left(\frac{1}{T}\right) \sum_{i=0}^{m} a_i N_i + \sum_{j=0}^{n} b_j N^j
\]

where the pressure P is expressed in bar, N is the amount of adsorbed in mmol.g⁻¹, T is the temperature in K, aᵢ and bⱼ are virial coefficients, and m, n represent the number of parameters required to sufficiently describe the isotherms (in this case, m and n were fixed at 5 and 4, respectively). The values of virial coefficients a₀ – aₜ were then used to estimate the Qₛₜ using the following expression with the universal gas constant R:

\[
Qₛₜ = -R \sum_{i=0}^{m} a_i N_i
\]
Figure S9. Virial fitting for C$_2$H$_2$ adsorption in the MFM-102 series at 273 and 298 K.

Figure S10. Isosteric heats of adsorption for C$_2$H$_2$ in the MFM-102 series MOFs.
Figure S11. (a) Langmuir fitting of the C₂H₂ isotherms of MFM-102-NO₂; (b) $Q_{st}$ plot based upon the fitting of results derived from Langmuir fitting. The latter commonly overestimates $Q_{st}$ at low coverage.
6. Inelastic Neutron Scattering

INS spectra were recorded on the VISION spectrometer at Spallation Neutron Source, Oak Ridge National Laboratory (USA). VISION is an indirect geometry crystal analyser instrument that provides a wide dynamic range with high resolution. A sample of desolvated MFM-102-NO₂ was loaded into an 11 mm cylindrical vanadium sample container, sealed with an indium vacuum seal and connected to a gas handling system. The sample was degassed at 10⁻⁷ mbar and 373 K for 2 days prior to the experiment to remove any remaining trace guest molecules. Gas loading was performed by a volumetric method at 293 K in order to ensure that the adsorbent was available in the gas phase and to ensure sufficient mobility within the crystalline structure of MFM-102-NO₂. The sample was then slowly cooled to 10 K to ensure the guest molecule of interest was completely adsorbed with no condensation in the cell. Sufficient time was allowed to achieve thermal equilibrium before inelastic neutron spectra were collected to allow for full thermal equilibrium before data collection.

DFT Calculations and Modelling of INS Spectra

Vibrational frequencies and polarization vectors were calculated using CP2K (http://www.cp2k.org),¹⁶ based on the mixed Gaussian and plane-wave scheme¹⁷ and the Quickstep module.¹⁸ The calculation used molecularly optimized Double-Zeta-Valence plus Polarization (DZVP) basis set,¹⁹ Goedecker-Teter-Hutter pseudopotentials,²⁰ and the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional.²¹ The plane-wave energy cutoff was 400 Ry. The DFT-D2 level correction for dispersion interactions, as implemented by Grimme et al.,²² was applied, with a cutoff distance of 24 Å. The calculation was performed on Gamma point only, with no symmetry constraint. Structural optimization was performed using the Broyden-Fletcher-Goldfarb-Shannon (BFGS) optimizer, until the maximum force is below 0.00045 Ry/Bohr (0.011 eV/Å). Finite displacement method was used for the phonon calculation, with incremental displacement of 0.01 Bohr (0.0053 Å). The INS spectrum was then simulated using the OClimax software.²³
Figure S12. (a) Comparison of the experimental and DFT calculated INS spectra for MFM-102-NO₂; (b) comparison of the INS spectra of bare and C₂H₂-loaded MFM-102-NO₂; (c) detailed INS spectra displaying the internal vibrational modes for adsorbed and free C₂H₂ molecules in solid state.

7. Neutron powder diffraction.

NPD experiments were conducted at WISH, a long wavelength powder and single crystal diffractometer at the ISIS facility (DOI: 10.5286/ISIS.E.82420531). Acetone-exchanged MFM-102-NO₂ was loaded into a 6 mm diameter vanadium sample can and out gas at 1 x 10⁻⁷ mbar and 110 °C for 1 day. The sample stick was then placed into a liquid helium cryostat and cooled to 7K for data collection of the activated framework. C₂D₂ gas was introduced sequentially into the framework by warming the sample to 290 K, and the gas was dosed volumetrically from a calibrated volume. The gas containing sample was then gradually cooled to 7 K over 2 h to ensure good diffusion of adsorbed gases within the crystalline structure of MFM-102-NO₂ and to minimize the presence of free gas or condensation inside the cell. The sample was kept at 7 K for sufficient time to achieve thermal equilibrium before collecting data. The locations of adsorbed C₂D₂ molecules within MFM-102-NO₂ were determined as a function
of gas loading by sequential Fourier difference map analysis followed by Rietveld refinement using the Topas software package. Analysis of the Fourier map of the outgassed data indicated no residual nuclear density in the voids. The structure from the single crystal X-ray diffraction experiment was used as a starting point for the framework model which was geometrically restrained and refined against the NPD data. The framework atom coordinates were subsequently fixed before the models of guest molecules were developed. All binding sites were checked carefully for their unambiguous presence in the final structural model; i.e., a parallel refinement without each of the binding sites was carried out to confirm the presence of each site by comparing the R factors and the residual peaks. Common C-D bond distances and isotropic thermal factors were included for the guest molecules. Final refinements comprised all free structural variables from both the framework and guest molecules.

Table S4. Summary of NPD Rietveld refinement statistics.

|                      | Activated MOF | C$_2$D$_2$ loading MOF |
|----------------------|---------------|-------------------------|
| $R_{exp}$/%          | 0.26          | 0.26                    |
| $R_{wp}$/%           | 1.45          | 1.52                    |
| $R_p$/%              | 1.24          | 1.33                    |
| GoF                  | 5.43          | 5.88                    |
| CCDC Deposit         | 1857873       | 1857872                 |
Figure S13. Observed (blue), calculated (red) and difference (grey) profiles of neutron powder diffraction Rietveld refinements (detector banks 2-5) for activated MFM-102-NO₂.
Figure S14. Observed (blue), calculated (red) and difference (grey) profiles of neutron powder diffraction Rietveld refinements (detector banks 2-5) for MFM-102-NO₂ loaded with C₂D₂.
8. Mass spectrometric and NMR spectroscopic data for H$_4$L$^3$ and H$_3$L$^4$.

Figure S15. Mass spectrum of H$_4$L$^4$. 
Figure S16. $^1$H NMR spectra of H$_4$L$^4$. 
Figure S17. Mass spectrum of H$_4$L$^3$. 

$C_{28}H_{16}N_2O_{14}$, $M_w$: 572.07
Figure S18. $^1$H NMR spectra of $\text{H}_2\text{L}^3$. 
9. Air and water stability test

Figure S19. PXRD study on the stability of MFM-102-NO₂ in contact with air. Overall, MFM-102-NO₂ shows moderate stability to air.

Figure S20. The stability of MFM-102-NO₂ in contact with water. Acetone exchanged sample was decanted and submerged into water. The PXRD pattern was collected after soaking in water for 15 mins.
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