Electronic Supporting Information

Porosity in metal-organic frameworks following thermolytic postsynthetic deprotection: Gas sorption, dye uptake and covalent derivatisation.

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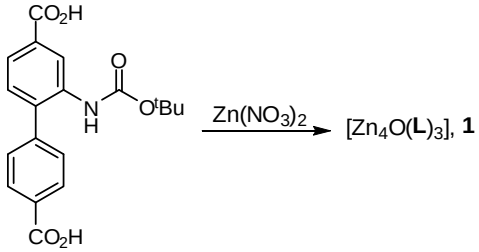
1. Synthesis of MOF 1[1]

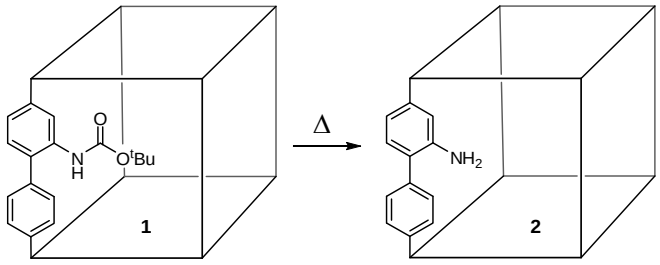


Ligand **L** (20.0 mg, 0.056 mmol) and $Zn(NO_3)_2 \cdot 4H_2O$ (87.2 mg, 0.337 mmol) were combined in dry DEF (1.5 mL) in a 20 mL scintillation vial and heated at 85 °C for at least 16 hours or until transparent cubic crystals of **1** had formed. The crystals were washed with dry DMF and stored in dry DMF for further use.

2. Activation of MOF 1 by s-CO_2

The occluded DMF in **1** was exchanged with dry acetone over a period of 24 h (solvent replenished multiple times). The sample was then placed in a Tousimis Samdri PVT-3D supercritical CO_2 dryer taking care to keep it damp with acetone at all times. The crystals were then washed with liquid CO_2 over a period of 7 h before the chamber was heated and the CO_2 held at the supercritical point for a further 7 h. The CO_2 was then bled off over a period of ~45 mins. The crystals of **1a** were either used immediately or stored in a dessicator for further use. Elemental analysis: Calcd (Found) for $[Zn_4O(\mathbf{L})_3] \cdot 6H_2O$: C, 47.16 (47.07); H, 4.37 (4.26); N, 2.89 (2.81).

3. Conversion of MOF 1 to MOF 2[1]



MOF **2** was prepared by suspending a sample of MOF **1** (~50 mg) in ~ =2 mL of dry DMF and heating in a microwave synthesizer to 150 °C for 4 h. The resultant pale yellow crystals were washed with dry DMF and stored under dry DMF for further use.

4. Activation of MOF 2 by s-CO_2

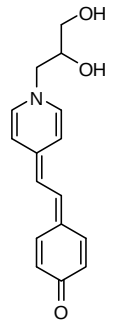
MOF **2** was activated by s-CO_2 to give MOF **2a** using the protocol described above for the activation of MOF **1**.

5. Conversion of MOF 1a to MOF 2b

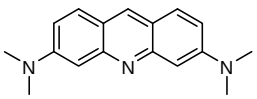
A sample of MOF **1a** was placed under vacuum in a vacuum oven and heated to 160 °C for 16 hours. Complete conversion of **1a** to **2b** was confirmed by IR spectroscopy and ^{1}H NMR spectroscopy on a digested sample.

6. Dye uptake by MOFs

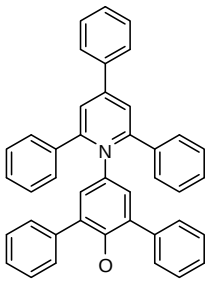
The following dyes were used as a qualitative screen of MOF porosity:



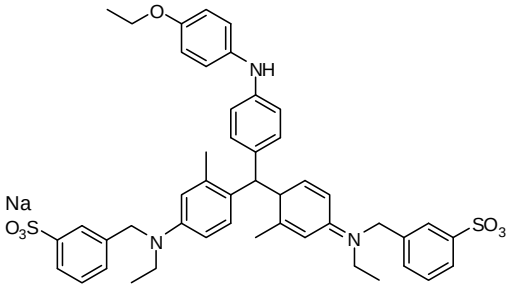
merocyanine



acridine orange



Reichardt's dye



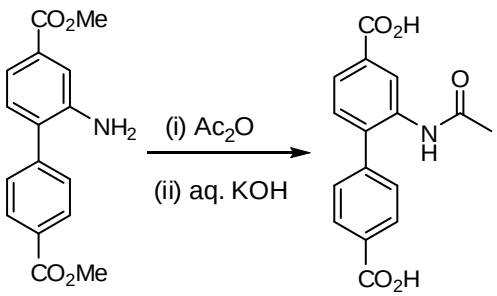
Brilliant blue G250

*Quantification of AO uptake by **1***

MOF crystals (~10 mg) were suspended in 1-2 mL of a 240 mM solution of acridine orange (AO) in CH_2Cl_2 for between ~24 h. The solution was then removed and the crystals were quickly washed with fresh CH_2Cl_2, dried on filter paper then weighed. The crystals were subsequently digested in ~150 μL of a solution prepared by combining 23 μL of 36% HCl and 1 mL of DMSO. The resulting solution was then diluted with a known amount of DMSO and the absorption spectrum of the solution was recorded. The amount of AO in the solution was quantified by a using $\varepsilon_{495nm} = 34160\ M^{-1}cm^{-1}$.

7. Acetylation of MOFs 2, 2a and 2b

Ca. 20 mg of MOF crystals was washed with dry CH_2Cl_2 and suspended in a mixture of dry CH_2Cl_2 (1 mL) and of acetic anhydride (20 μL). The reaction was capped and left at room temperature for 60 h. The crystals were then washed with dry CH_2Cl_2 and were exchanged with fresh CH_2Cl_2 over a period of 48 h (solvent replenished frequently). The crystals were then placed under vacuum before being digested for ^{1}H NMR spectroscopy using the following protocol: 23 μL of a 35% DCl solution in D_2O was mixed with 1 mL of DMSO-d_6 to give a DCl/DMSO-d_6 stock solution. Around 5 mg of MOF was digested in 71 μL of this stock solution and 0.45 mL of DMSO-d_6. Spectra were acquired immediately following dissolution of the framework. Formation of the acetylated ligands was confirmed by comparison of the ^{1} H NMR spectrum with an independently-prepared sample (see below) as well as by ESI-MS where a peak at m/z = 289.6 in negative ion mode was observed following basification of the digested solution with NEt_3 and dilution with CH_3OH.



An independent sample of the acetylated ligand, 2-acetamidobiphenyl-4,4'-dicarboxylic acid, was prepared according to the following method: Dimethyl 2-aminobiphenyl-4,4'-dicarboxylate (100 mg, 0.366 mmol), dry THF (4 mL), and acetic anhydride (370 μL, 0.392 mmol) were combined and stirred at room temperature for 20 hours. The solvent was then removed *in vacuo* and the solid material taken up in THF (6 mL). An aqueous solution of KOH (1M, 6 mL) was then added and the mixture was refluxed for 25 h. The THF was removed *in vacuo* and the resultant solution was acidified with 0.2 M HCl until precipitation of a white solid occurred. 2-Acetamidobiphenyl-4,4'-dicarboxylic acid was filtered off and washed well with water before being dried under vacuum. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.91 (s, 3H), 7.47 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.5 Hz, 2H), 7.84 (dd, J = 5.0 Hz, 1.5 Hz, 1H), 8.01 (d, J = 8.5 Hz, 2H), 8.06 (s, 1H), 9.46 (s, 1H). ES-MS (negative mode, CH_3OH/NEt_3): m/z = 298.6.

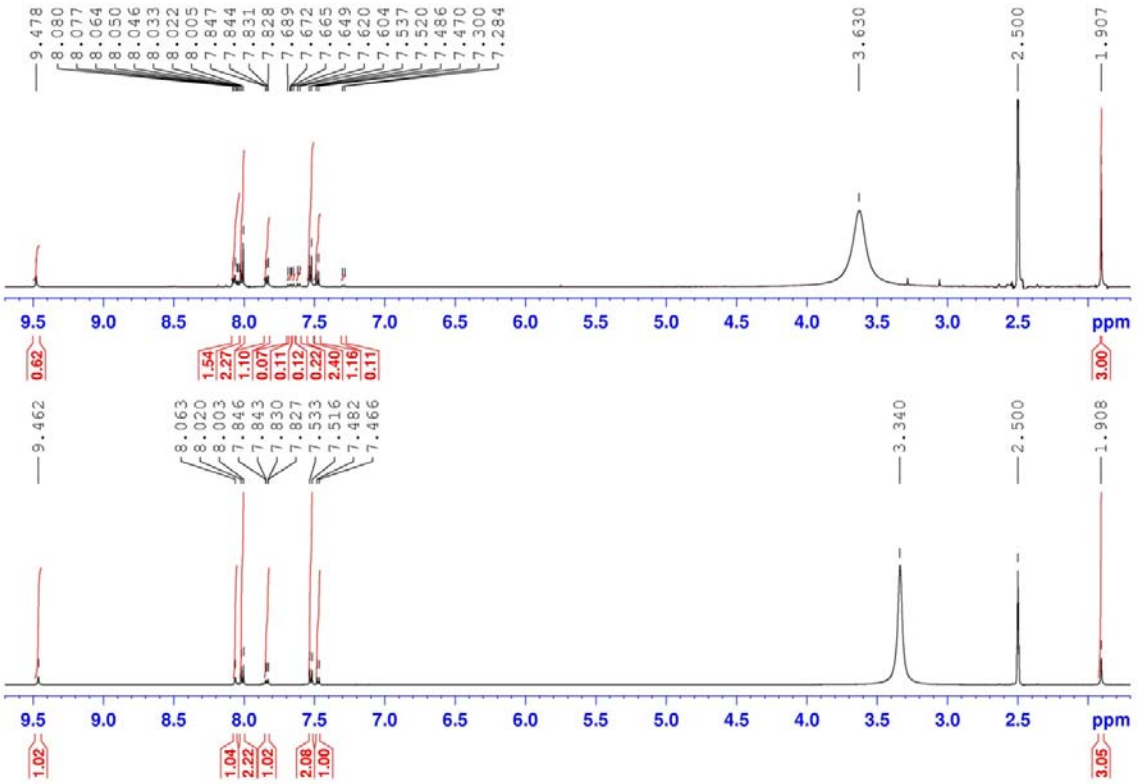


Figure S1. ^{1}H NMR spectra of 2-acetamidobiphenyl-4,4'-dicarboxylic acid (in DMSO-d_6, lower spectrum) and the digested product of the acetylation of MOF **2a** (in DMSO-d_6/D_2O/DCl, upper spectrum).

8. Measurement of N_2 sorption isotherms

Samples were activated immediately prior to N_2 physisorption measurements at 70 °C for 6 h under vacuum in a Hereaus vacuum oven (Thermo Scientific). Isotherms were determined at liquid nitrogen temperature (77 K) using a Micromeritics Tristar 3000 instrument. Specific surfaces areas were calculated according to the Brunauer-Emmett-Teller (BET) method using P/P_o values in the range 0.01-0.08. MOF **2a** gave a linear fit in this pressure region as well as a positive C constant, leading to a reproducible estimate of the BET surface area of this MOF of 1381 $m^2 g^{-1}$.

9. Powder X-ray diffraction

All powder X-ray diffraction experiments were carried out on a Rigaku Spider X-ray diffractometer with Cu K_α radiation (Rigaku MM007 microfocus rotating-anode generator), monochromated and focused with high-flux Osmic multilayer mirror optics, and a curved image plate detector. The best data were obtained from freshly prepared MOF samples that were damp with DMF. The two-dimensional images of the Debye rings were integrated with AreaMax[2] to give 2θ vs I diffractograms. If necessary, the diffractograms were baseline-corrected using PowderX.[3]

Second phase of MOF 1a

Occasionally an alternative phase of MOF **1a** following s-CO_2 activation of MOF **1** when the bleed time of the supercritical CO_2 dryer was extended (Fig. S2). MOF **2a**, which exhibited the expected PXRD pattern, was still produced upon thermolysis of this material in DMF.

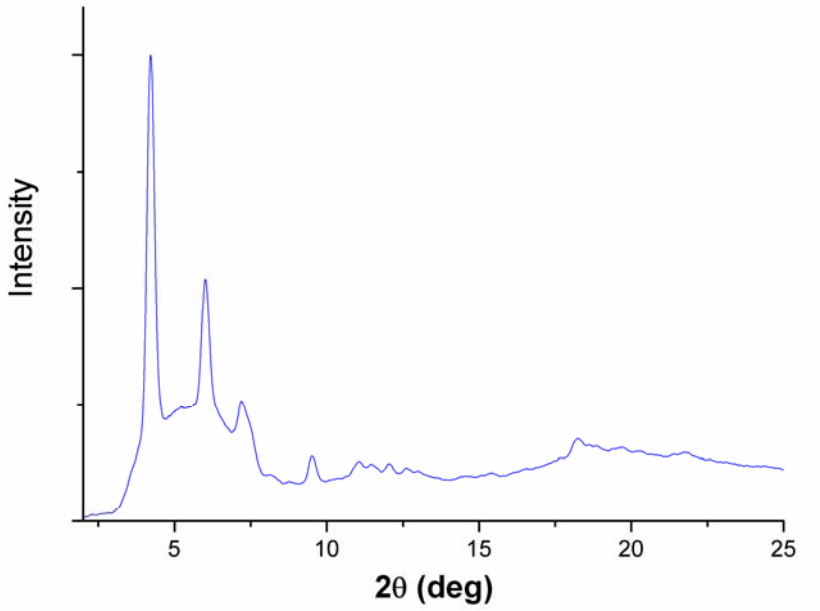


Figure S2. Powder XRD pattern (Cu_{α} radiation) pattern of the alternative phase of **2a**.

References

1. Deshpande, R. K.; Minnaar, J. L.; Telfer, S. G. *Angew. Chem. Int. Ed.* **2010**, *47*, 4598.
2. 1.1.2 ed.; Rigaku Corporation: 2003.
3. Dong, C. *J. Appl. Cryst.* **1999**, *32*, 838.