Experimental

Synthesis and chemical analysis

Synthesis of 3,3',5,5'-azobenzene tetracarboxylic acid ($TazbH_4$)

$TazbH_4$ was prepared according to the procedure developed by Ameerunisha and Zacharias for other azobenzene derivatives.[1] A mixture of 5-nitroisophthalic acid (19 g, 90 mmol) and NaOH (50 g, 1250 mmol) in 250 mL of distilled water was placed into a 1 L 3-neck round bottom flask and stirred vigorously at 333 K. To this slurry, 100 g of D-glucose dissolved in 150 mL of distilled water was slowly added. The resulting brown mixture was cooled down to room temperature, and air was bubbled for 4 hours always under stirring. The reaction mixture was cooled in an ice-bath and the sodium salt of Tazb recovered by filtration and washed with small amount of cold water. The resulting yellow solid was then dissolved in 200mL of distilled water and this solution was acidified down to pH = 1 by the addition of HCl 37 %. The resulting orange solid was recovered by filtration, washed with distilled water and dried at 373 K under vacuum. Yield 70%.

Synthesis of Ca_2Tazb (BioMIL-3)

BioMIL-3 or Ca_2Tazb was prepared from a reaction mixture of composition Ca(II) nitrate ($Ca^{II}(NO_3)_2(HO_2)_4$) : $TazbH_4$: dimethylformamide (DMF) = 1 : 1 : 129 heated at 473 K in a Teflon-lined autoclave for 24 hours with both heating and cooling ramps equal to 0.14 K/min^{-1}. The solid was recovered by filtration and washed with DMF.

Structure determination

A Single crystal of BioMIL-3 was mounted with paratone oil on a nylon cryoloop, and measured at 100K at the European Synchrotron Research Facilities (ESRF, Grenoble, France) on BM01A (λ = 0.709622 Å), using a MAR345 image plate detector. The data reduction was performed with the Crysalis software; the absorption correction was performed with the SADABS software. All structures were solved and refined by full-matrix least-squares techniques, based on F^2, using the SHELX software package.[2] Regarding the azobenzenetetracarboxylate (azbz-TC) ligands, all non hydrogen atoms were refined anisotropically, whereas hydrogen atoms were introduced geometrically and not refined. Each independent Ca atoms (Ca1 and Ca2) was found to bind to one solvent molecule, which can be either water or N,N'-dimethylformamide (DMF). The occupancy on both sites was found to be correlated, as deduced from intermolecular distances: when one Ca site is occupied by a DMF molecule, the other one is occupied by water. The DMF/water ratio on sites Ca1 and Ca2 were thus simultaneously refined, and finally fixed to 60/40 and 40/60 respectively. All atoms from the bound solvent molecules were refined isotropically, 9 constraints on C-C, C-N and C-O distances where applied for the DMF molecules in order to maintain a suitable geometry during the refinement. More

precisely, C=O, C_{sp2}-N, C_{sp3}-N, C_{sp3}•••C_{sp3} were restrained to 1.2, 1.4, 1.45 and 2.5 Å respectively. Hydrogen atoms bound to sp^2 carbons were introduced geometrically and not refined, whereas the ones from the methyl groups and water molecules were not introduced. Finally, the pores content (free DMF and water molecules) was not refined and discarded using the SQUEEZE routine.[3]

Crystallographic data are summarized in Table S1; Ca-O distances and bond valence calculations are given in Table S2, and an illustration of the disorder of the bound solvent molecules is shown in Figure S1.

Table S1. Crystallographic data and refinement parameters for BioMIL-3 or Ca_2(azbz-TC)(H_2O)(DMF)•$x H_2O$•yDMF (x ~ 0.4, y ~ 0.2) at 100 K.

Empirical formula	$C_{19.6}H_{17.2}Ca_2N_{3.2}O_{10.6}$
Formula weight ($g.mol^{-1}$)	547.33
Temperature (K)	100
Wavelength (Å)	0.709622
Crystal system	triclinic
Space group	P-1
Unit cell dimension (Å)	a = 10.1119(5) b = 11.0499(8) c = 12.7808(8)
	α = 101.472(6)° β = 102.024(4)° β = 108.351(5)°
Volume ($Å^3$)	1270.77(14)
F(000)	540
Crystal size (mm)	0.08x0.04x0.02
Theta range for data collection(°)	1.79-29.58
Limiting indices	-11 < h < 11 -13 < k < 13 -15 < l < 15
Reflections collected	4101
R_{int}	0.0184
Refinement method	Full-matrix least square on F^2
Data/restraints/parameters	4101/9/301
Goodness-of-fit on F^2	1.068
Final R indices [I>2σ(I)]	R_1 = 0.0698; wR_2 = 0.1949
R indices (all data)	R_1 = 0.0733; wR_2 = 0.1976
Largest diff. peak and hole	1.115 and -0.828 $e^-.Å^{-3}$

Table S2. Bond valence calculations for the Ca cations, using the bond parameters proposed by Brese et al. [4] The calculation is in agreement with a +II oxidation state.

Ca	O	Ca-O distance (Å)	υ(Ca-O)	total Ca
Ca1	O11	2.272	0.44	
	O12	2.279	0.43	
	O3	2.334	0.37	
	O1	2.414	0.30	
	O13	2.418	0.30	
	O31B (DMF)	2.37	0.34	**2.17**
	O31A (H_2O)	2.322	0.38	**2.22**
Ca2	O14	2.285	0.42	
	O2	2.31	0.40	
	O4	2.419	0.29	
	O1	2.44	0.28	
	O3	2.488	0.24	
	O2	2.586	0.19	
	O21B (H_2O)	2.595	0.18	**2.01**
	O21A (DMF)	2.179	0.56	**2.39**

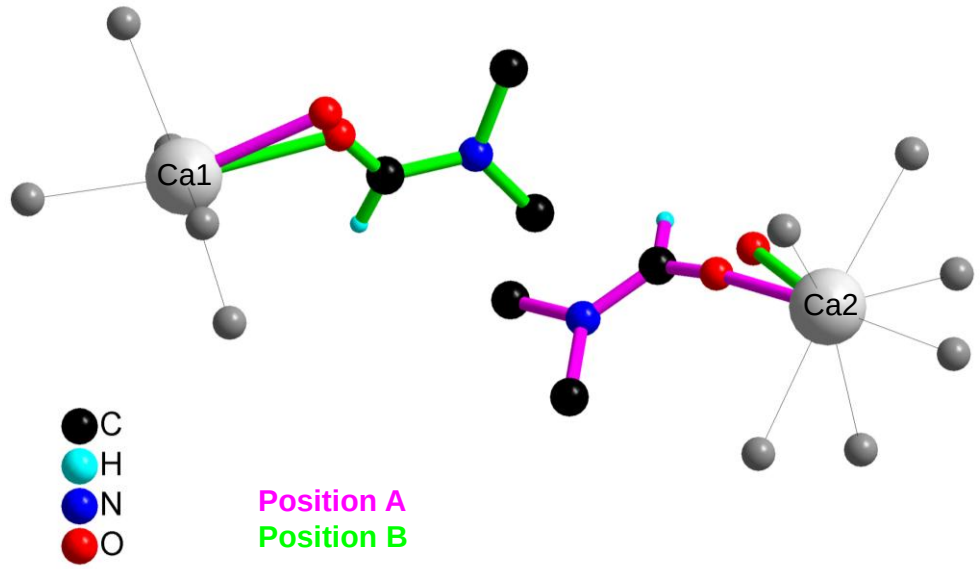

Figure S1 View of the two partially occupied positions of the bound solvent molecules: when one Ca site is occupied by a DMF molecule, the other one is occupied by water (occupancy: pos. A: 40%, pos. B 60%).

X-Ray powder diffraction (XRPD) pattern was collected in a SIEMENS D5000 diffractometer (θ-2θ) using Cu Kα1 radiation (lambda = 1.54056 angstroms) from 3 to 80º (2θ) using a step size of 0.015º and 8s per step in continuous mode (Figure S1).

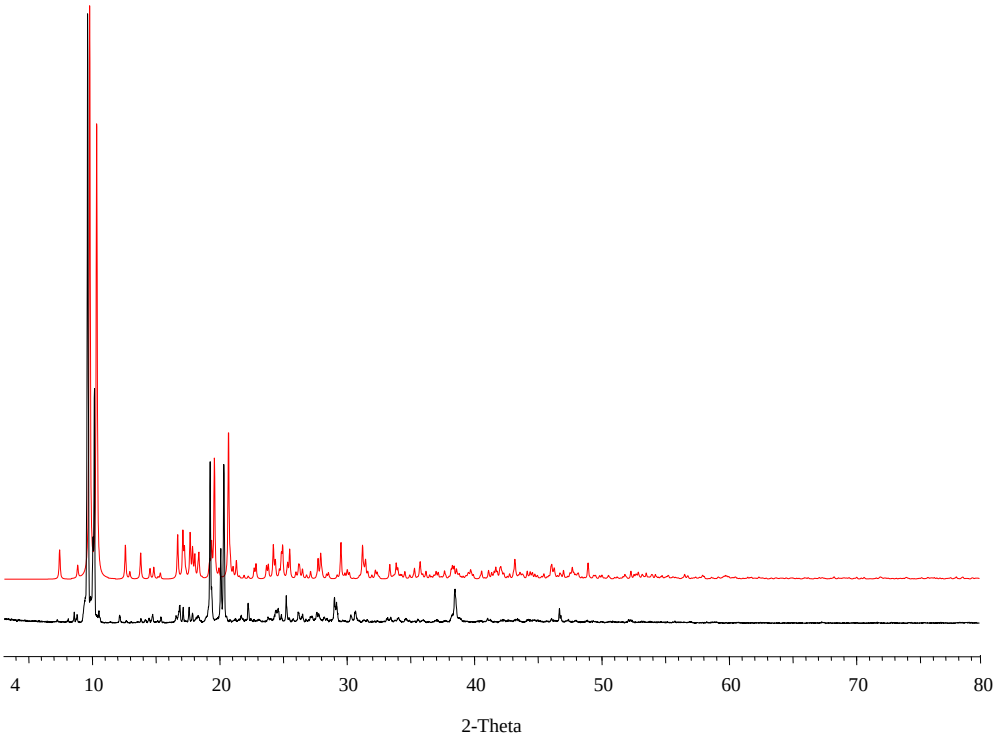

Figure S2. Experimental (bottom) and calculated (top) XRPD patterns of BioMIL-3

Elemental analysis

Table S2. Contents of Ca, C, N and H in BioMIL-3

	Theoretical values	**Experimental values**
% Ca	14.58	13.09
% C	43.06	44.47
% N	8.24	9.40
% H	3.16	3.36

Thermogravimetric analysis

Thermal gravimetric analysis of BioMIL-3 was carried out on a TGA Perkin Elmer apparatus under oxygen gas flow with a heating rate of 2 $K.min^{-1}$ (fig. S2).

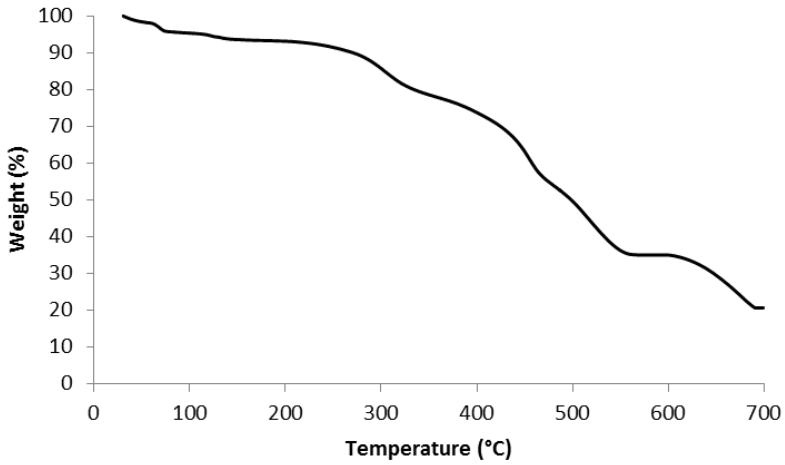

Figure S3. TGA of BioMIL-3

N_2 and CO_2 sorption studies

N_2 isotherms were obtained at 77K using a Belsorp Mini (Bel, Japan). Prior to the analysis, approximately 40-60 mg of BioMIL-3 was evacuated for 16 h at 473 K under vacuum.

CO_2 adsorption was obtained at 298K using an IGA (Hiden, UK). Prior to the analysis, approximately 40-60 mg of BioMIL-3 was evacuated for 16 h at 473 K under vacuum.

NMR

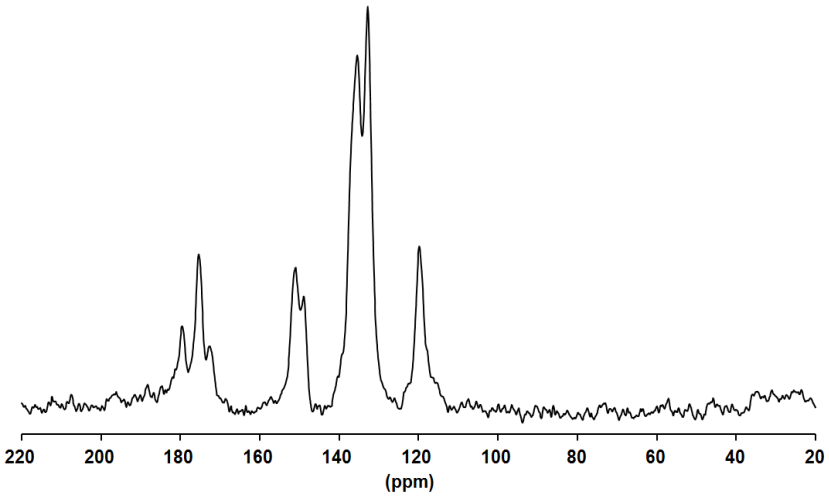

Figure S4. ^{13}C CP MAS NMR spectrum of BioMIL-3 (ν_0 = 75.51 MHz, ν_{rot} = 14 kHz)

The ^{13}C CP MAS NMR spectrum of BioMIL-3 displays multicomponent signals at chemical shifts close to 120, 130, 150 and 180 ppm that can be assigned to the different carbons of the az-bz-TC ligands. The signals at 150 ppm can be assigned to the C=C-N carbons of the aromatic groups while the broad signals at 120 and 130 ppm correspond to the other aromatic carbons (i. e; N-C=C, C=C). The signal around 180 ppm composed of overlapped resonances of different intensity is in good agreement with the presence of four non-equivalent carboxylate groups.

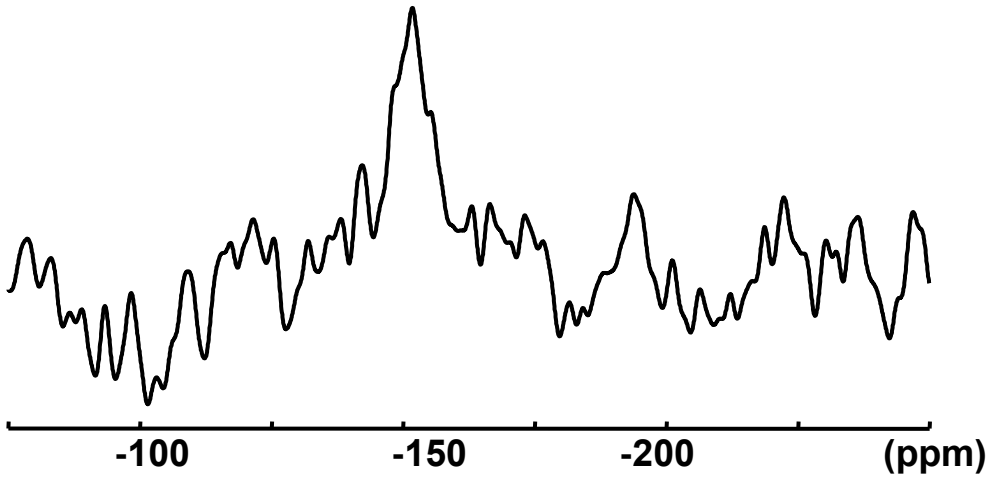

Figure S5. ^{43}Ca MAS NMR spectrum of BioMIL-3 (ν_0 = 57.2 MHz, ν_{rot} = 5 kHz)

The natural abundance ^{43}Ca MAS NMR spectrum was obtained at ultra-high field (19.8 T) using a single tuned 7 mm BRUKER MAS probe. The rotation frequency was set to 5 kHz. The experimental parameters were the following: RAPT enhancement, pulse length: 1.6 μs, relaxation delay: 0.4 s, number of scans: 93000 (~ 10h30).

FTIR spectroscopy with probe molecules

Sample was pressed (10^7 Pa) into self-supported discs (2 cm^2 area, 10–20 $mgcm^{-2}$). The sample was then degassed *in situ* before measurement at 473 K. The infrared cell was made of quartz and was equipped with CaF_2 windows. A movable quartz sample holder allowed the pellet to be moved into the infrared beam for spectral acquisition or into a furnace at the top of the cell for thermal treatment. Transmission IR spectra were recorded in the range 650–4000 cm^{-1} on a Nicolet Nexus spectrometer equipped with an extended KBr beam-splitting device and a mercury cadmium telluride (MCT) cryodetector. The cell was connected to a vacuum line for evacuation, calcination steps ($P_{residual}$=10^{-3}–10^{-4} Pa), and for the introduction of the different gases into the infrared cell. Spectra were recorded at room temperature.

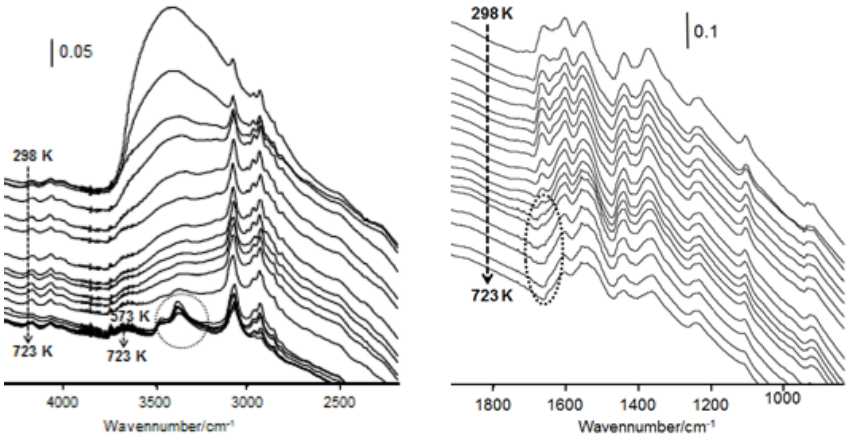

Figure S6. IR spectra of the BioMIL-3 under room atmosphere and then outgassed under secondary vacuum (10^{-5} Torr) at increasing temperatures (25 K steps per 30 min).

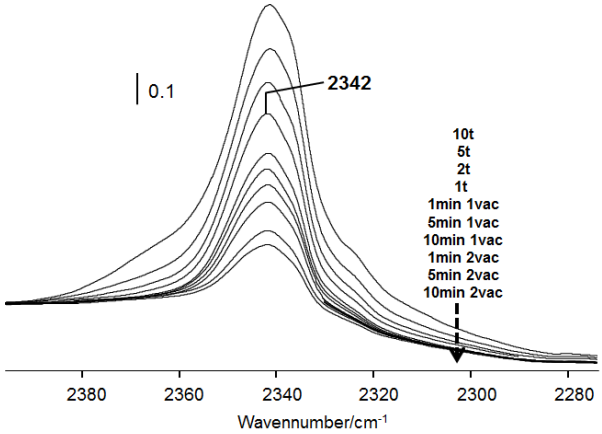

Figure S7. IR spectra of BioMIL-3 outgassed at 473 K after adding 10 Torr of CO_2 at equilibrium pressure, followed by decreasing the pressure and outgassing pressures

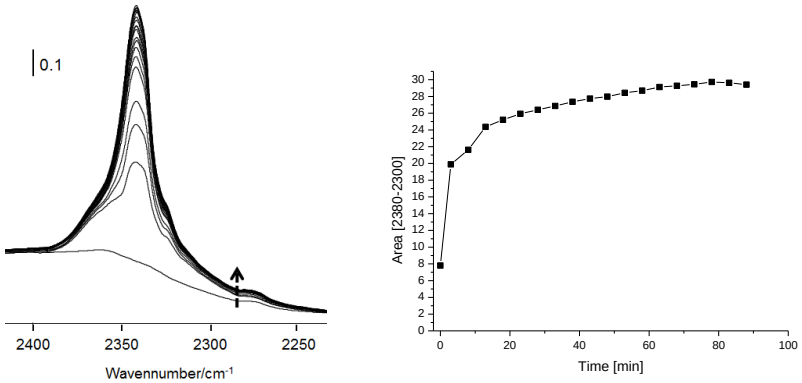

Figure S8. CO_2 stretching region of the IR spectra of BioMIL-3 outgassed at 473 K after adsorption of CO_2. Spectra are recorded every 5 min after introduction of 10 Torr equilibrium pressure. Development of the CO_2 band area over time.

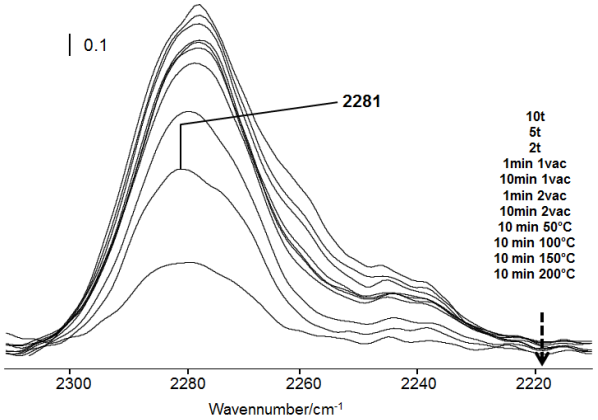

Figure S9. IR spectra of BioMIL-3 outgassed at 473 K after adding 10 Torr of CD_3CN at equilibrium pressure, followed by decreasing the pressure and outgassing pressures at different temperatures.

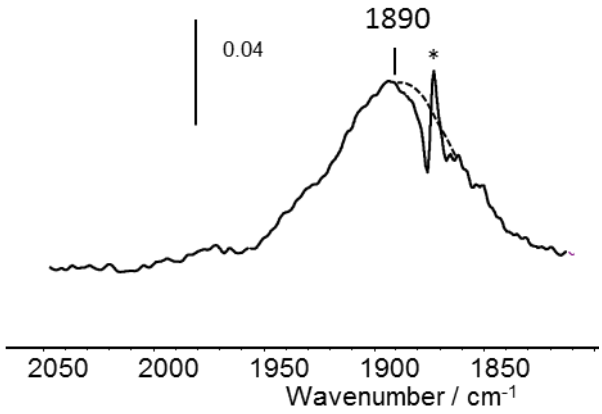

Figure S10. IR spectra of NO adsorbed at room temperature on Ca-MOF (PNO= 300 torrs). (The sample has been previously activated at 200°C under secondary vacuum) The asterisk indicates an artifact due to an unsoustrayable contribution of gaseous NO to the spectrum of adsorbed species.

X-ray thermodiffraction

X-Ray thermodiffractometry was performed under air in a furnace of a Siemens D5000 diffractometer working at the CoKα radiation in the (θ-θ) mode in the 293-373 K temperature range with a 20 K step.

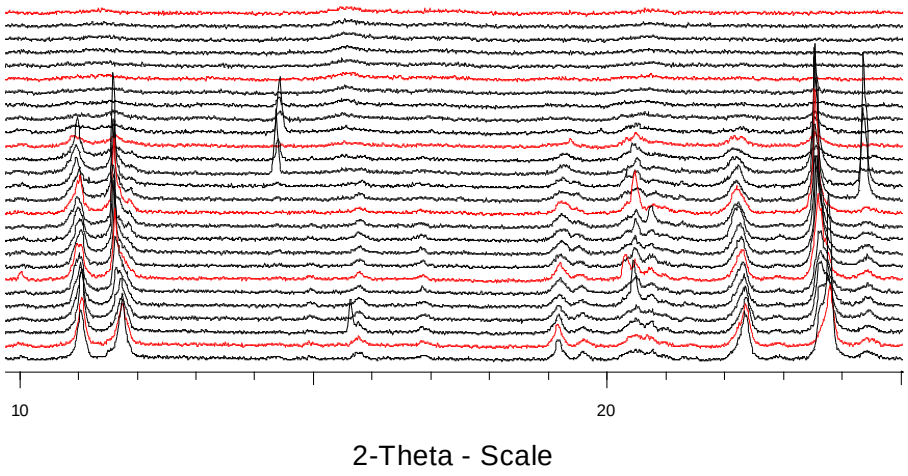

Figure S11. X-ray powder thermodiffractometry (λCo = 1.7906 Å) under air atmosphere of the as-synthesized BioMIL-3; each red pattern corresponds to a multiple of 323 K.

Nitric oxide adsorption/desorption isotherms

Nitric oxide adsorption/desorption isotherms were determined using a gravimetric adsorption system (CI Instruments microbalance) integrated with a thermal stabilizer. BioMIL-3 (~25 mg) was outgassed at 423 K under $1x10^{-4}$ mbar for 18 hours until no further mass loss was observed. Both the sample temperature and the counterbalance were constant at 298 K throughout the experiment. The adsorption isotherm was recorded by introducing dried NO gas (BOC, 99.5 %) with gradual system pressure increments with the uptake of NO noted at the equilibrium mass of the material at each increment point. The desorption isotherm was conducted in a similar manner by gradually decreasing the system pressure and noting the equilibrium mass of the material.

Sample activation and NO loading

BioMIL-3 was dehydrated for 18 hours at 423 K in vacuo (1×10^{-4} bar), cooled to room temperature and exposed to an atmosphere of NO (BOC, 2 atm) for 30 min. The samples were then evacuated and exposed to dry argon (BOC, passed over Drierite). This evacuation and argon exposure was repeated 3 times to ensure total removal of excess NO. The samples were stored under an inert argon atmosphere until required.

Nitric oxide release

Quantification of NO release was performed using a Sievers NOA 280i chemiluminescence Nitric Oxide Analyzer. The instrument was calibrated by passing air through a zero filter (<1 ppb NO) and 91.0 ppm NO gas (Air Products, balance nitrogen). The flow rate was set to 200 mL/min with a cell pressure of approximately 6.5 Torr and an oxygen pressure of 6.1 psig. To measure NO release from the materials, nitrogen gas of known humidity (11% R.H.) was passed over the powders at room

temperature, the resultant gas was directed into the analyzer and the concentration of NO recorded as a function of time.

[1] S. Ameerunisha and P. S. Zacharias, *J. Chem. Soc., Perkin Trans*. **1995,** *2*, 1679
[2] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.
[3] A. L. Spek, *Acta Cryst.* **2009**, *A64*, 112-122
[4] Brese, N. E.; O'Keeffe, M., *Acta. Cryst.* **1991**, *B47*, 192-197.