Supporting Information for

Capture of Nerve Agents and Mustard Gas Analogues by Hydrophobic Robust MOF-5 Type Metal-Organic Frameworks

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General methods

All the general reagents and solvents were commercially available and used as received. Carboxen™ 569, diethylsulphide and diisopropylfluorophosphate (**CAUTION: highly toxic**) were purchased from Sigma Aldrich. $[Cu_3(1,3,5\text{-benzenetricarboxylato})_2]$ (HKUST-1)[1] and $[Cr_3F(H_2O)_2O(1,4\text{-benzenedicarboxylato})_3]$ (MIL-101 (Cr))[2] were prepared according to published procedures. Thermogravimetric analyses were performed, using a reactive air atmosphere, on a Shimadzu-TGA-50H equipment, at a heating rate of 20 K min^{-1}. XRPD data were obtained on a D2 PHASER Bruker diffractometer using CuKα radiation (λ = 1.5418 Å). The compounds were manually grounded in an agate mortar, then deposited in the hollow of a zero-background silicon sample holder. N_2 and CO_2 adsorption isotherms were measured, at 77 K and at 195 K, respectively, on a Micromeritics Tristar 3000 volumetric instrument. Water adsorption isotherms were measured at 298 K using a Quantachrome Hydrosorb 1000 apparatus with an equilibration time of 60 s. Prior to measurement, powder samples were heated 7 h (at 453 K for $[Cu_3(btc)_2]$ and at 393 K for **1** and Carboxen™) and outgassed to 10^{-1} Pa.

Synthesis of 3,5-Dimethyl-4-carboxypyrazole (H₂dmcapz): To a solution of 5 mL of ethyl diacetoacetate (26 mmol) in methanol (50 mL) under stirring at room temperature, 2 mL of hydrazine (50-60% hydrated) and 3 mL of HCl (37%) were added. The solution was refluxed for 30 minutes and then concentrated in vacuum. Subsequently, 50 mL of water were added to the solution together with solid NaOH, until the pH reached the range 7-9. The white microcrystalline solid was filtered and refluxed in 50 mL aqueous NaOH (0.2 M) overnight. After addition of HCl (37%) 3,5-dimethyl-4-carboxypyrazole was obtained as a white solid (global yield: 2.1 g, 58%). Anal. calc. for $C_6N_2O_2H_8$: C, 51.42 H, 5.75 N, 19.99; Anal. found C, 50.02 H, 6.35 N, 19.31.

Synthesis of [Zn₄O(dmcapz)₃] (1): A 200 mL ethanol:water (1:24) solution containing 4.2 g of H₂dmcapz (30 mmol) and 8.3 mL of triethylamine (60 mmol) was mixed with another ethanol:water solution (200 mL) containing $Zn(NO_3)_2 \cdot 4H_2O$ (7.83 g, 30 mmol). The resulting white suspension was refluxed for 4 h. Upon cooling, a white microcrystaline material was filtrated and was washed with ethanol and diethylether (yield: 6.0 g, 91.8%). Anal. calc. for **[Zn₄O(C₆H₆N₂O₂)₃]·(CH₃CH₂OH)₃** C, 34.72 H, 4.37 N, 10.12; Anal. found C, 34.91. H, 6.26 N, 11.63.

Synthesis of [Zn₃(OH)₂(dmcapz)₂] (2): 200 mg of **1** were suspended in 20 mL of water and heated under stirring. The evolution of the reaction was monitored by XRPD. After 8 h no further evolution of the reaction was observed and a white microcrystalline powder was recovered, washed with water, ethanol and diethylether. Anal. calc. for **[Zn₃(OH)₂(C₆H₆N₂O₂)₂]** C, 29.19 H, 3.19 N, 10.88; Anal. found C, 28.46. H, 2.79 N, 11.06.

Powder X-Ray Diffraction Structure Analysis

For the sake of simplicity, the structure solution and refinement processes were carried out on the desolvated form of species **1**, obtained by evacuation of the as synthesized material at 373 K under dynamic vacuum 10^{-1} Pa for 7 h. A microcrystalline batch of desolvated **1** was gently ground using an agate mortar and pestle and was deposited in the hollow of an aluminum sample holder equipped with a zero-background plate. Diffraction data were collected by means of an overnight scan in the 2θ range of 5-105° with 0.02°, steps using a Bruker AXS D8 Advance diffractometer equipped with Ni-filtered Cu-Kα radiation (λ = 1.5418 Å), a Lynxeye linear position-sensitive detector, and mounting the following optics: primary beam Soller slits (2.3°), fixed divergence slit (0.3°), receiving slit (8 mm). The nominal resolution for the present set-up is 0.08° of 2θ (FWHM of the α_1 component) for the LaB_6 peak at about 2θ = 21.3°. The generator was set at 40 kV and 40 mA. A standard peak search, followed by indexing through the Single Value Decomposition approach,[3] as implemented in TOPAS-R,[4] allowed the determination of approximate unit cell parameters. A visual inspection of the acquired diffractogram to the calculated one for MOF-5[5] revealed that the two compounds are isostructural. Thus, we resorted to MOF-5 structural details to position the Zn_4O nodes, while we determined the orientation of the (crystallographic independent portion) of the dmcapz spacer by the simulated annealing technique, as implemented in TOPAS-R, employing a rigid, idealized model.[6] The final refinement was carried out by the Rietveld method, maintaining the rigid body introduced at the structure solution stage. The background was modeled by a Chebychev polynomial function. Peak shapes were described by the Fundamental Parameters Approach.[7] A single, refined isotropic thermal parameter was assigned to each metal atom, and this was augmented by 2.0 $Å^2$ for the atoms of the $dmcapz^{2-}$ ligand. The final Rietveld refinement plot is shown in Figure S1. X-ray crystallographic data for desolvated **1** in CIF format have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC-817665. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-335033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Relevant crystal data for **1**, $Zn_4O(dmcapz)_3$, fw = 691.9 g mol^{-1}: cubic, space group *Fm-3m*, a = 20.1581(3), V = 8191.2(3) $Å^3$, Z = 8, $F(000)$ = 2752, ρ = 0.98 g cm^{-3}, μ(Cu-Kα) = 27.5 mm^{-1}; R_p = 0.073, wR_p = 0.101, R_{Bragg} = 0.047.
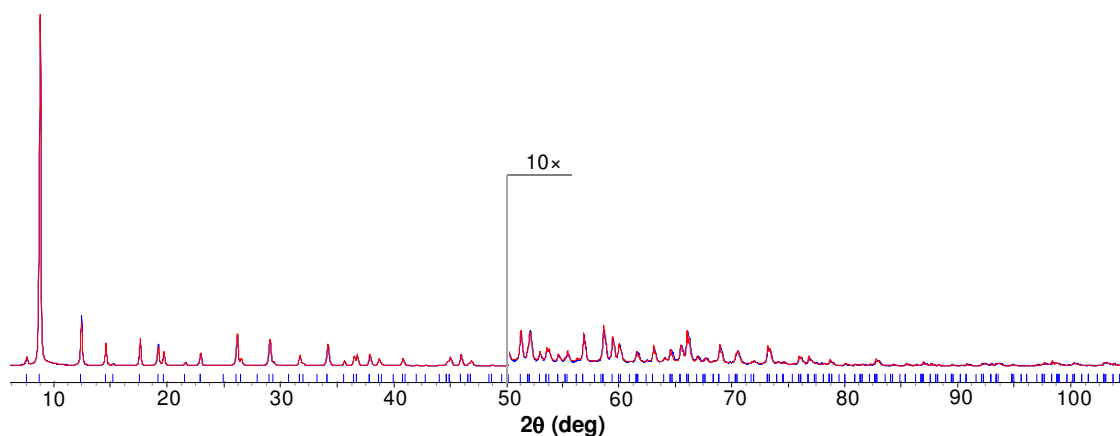
Figure S1. Rietveld refinement results for compound **1** in terms of experimental (blue) and calculated (red) diffraction traces. The peaks markers are shown at the bottom. The portion above 50 deg has been magnified (10×).

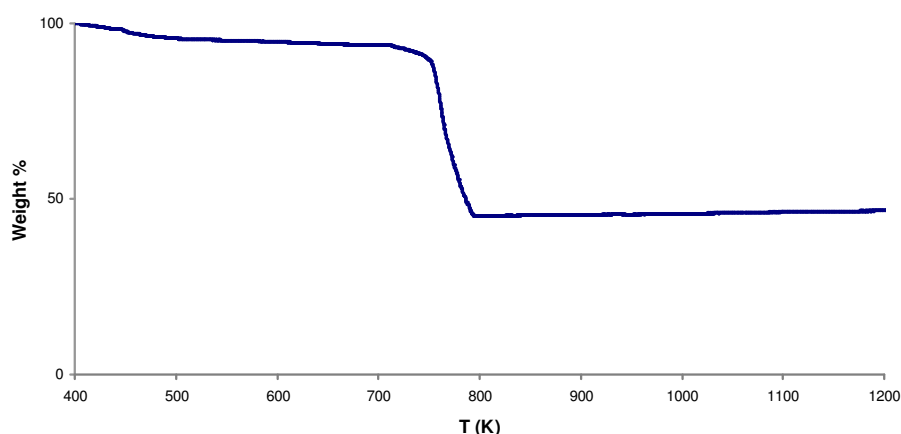## Thermal Analysis

Thermogravimetry

Figure S2. TGA trace for species **1**.

Thermodiffractometry

On the basis of the thermogravimetric analysis, variable-temperature X-ray powder diffraction data were acquired on solvated **1** to probe its structural response to temperature increase. The diffractograms were recorded in a reactive air-atmosphere mounting a custom-made sample heater, assembled by Officina Elettrotecnica di Tenno (Ponte Arche, Italy), on the Bruker AXS D8 automated diffractometer. Prior to measurement, a powdered microcrystalline batch of **1** was pulverized using an agate mortar and pestle and was deposited in the hollow of an aluminium sample holder. The diffractograms were recorded in a significant low-angle 2θ range, heating *in situ* by increments of 20 K, starting from 303 K, until complete loss of crystallinity was observed (Figure S3). By using the whole-profile Le Bail refinement method, a

parametric treatment of those data acquired before the beginning of crystallinity loss was carried out (Figure S4).

When comparing the thermogravimetric and thermodiffractometric results, the reader should be aware that the thermocouple of the latter set up was *not* in direct contact with the sample, potentially leading to slight difference in the temperature at which the same event is detected by the two techniques. The temperatures obtained by thermogravimetric analyses should be considered more reliable.
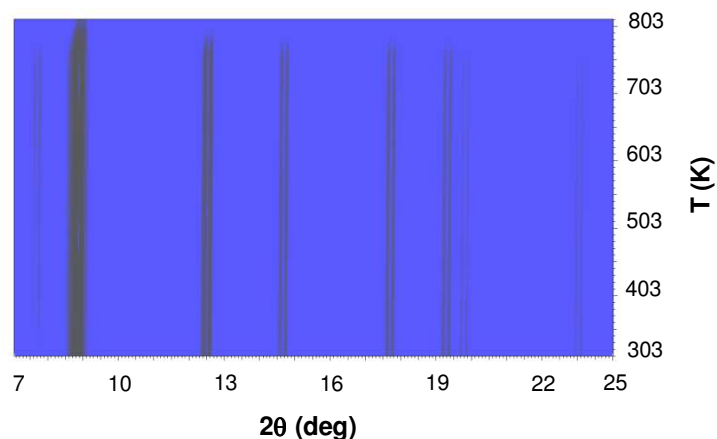

Figure S3. Two-dimensional contour plot of the XRPD data acquired on **1** in the 2θ range 7-25 deg, raising the temperature form 303 K up to 823 K.
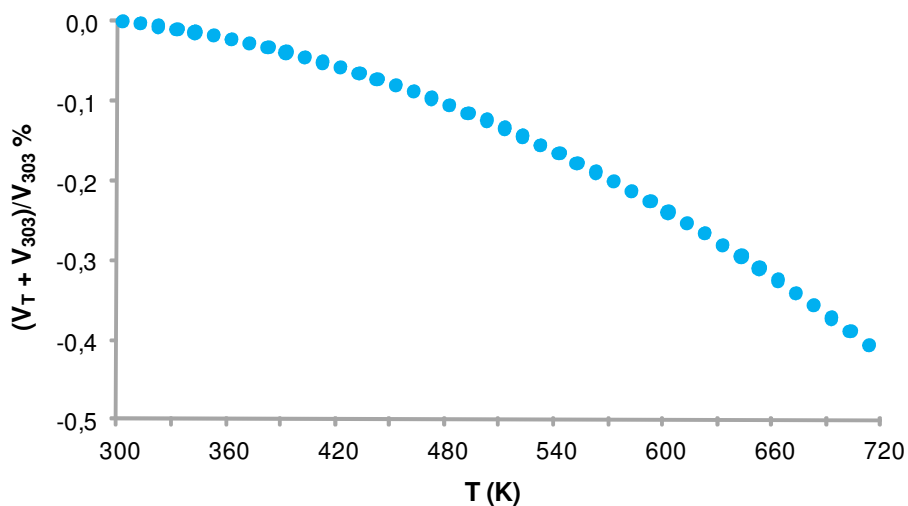

Figure S4. Variation of the unit cell volume of **1** (V_T) normalized to the corresponding 303 K value (V_{303}) as a function of the temperature.

Hydrolysis stability test for 1 at 353 K

100 mg of **1** were suspended in 25 mL of H_2O at 80 ºC. The evolution of the reaction was followed by XRPD. After 8 h of reaction pure $Zn_3(OH)_2(dmcapz)_2$ (**2**) was recovered.
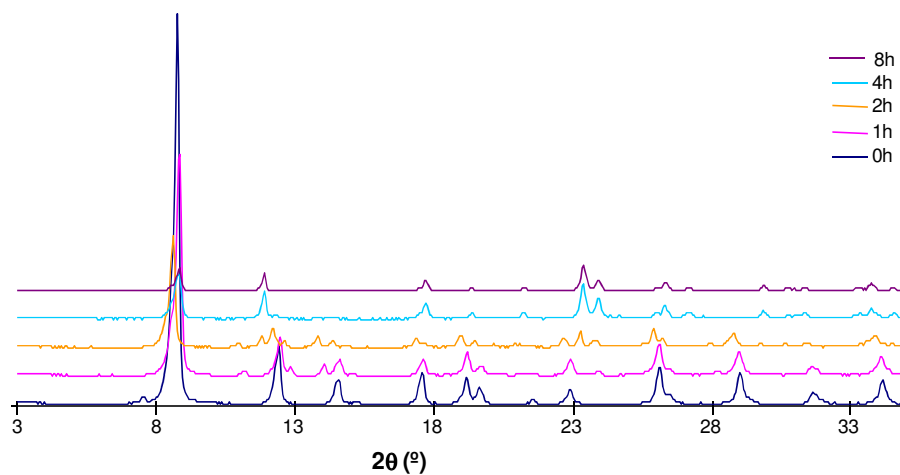

Figure S5. Evolution of hydrolysis reaction of a suspension of **1** in water at 353 K.

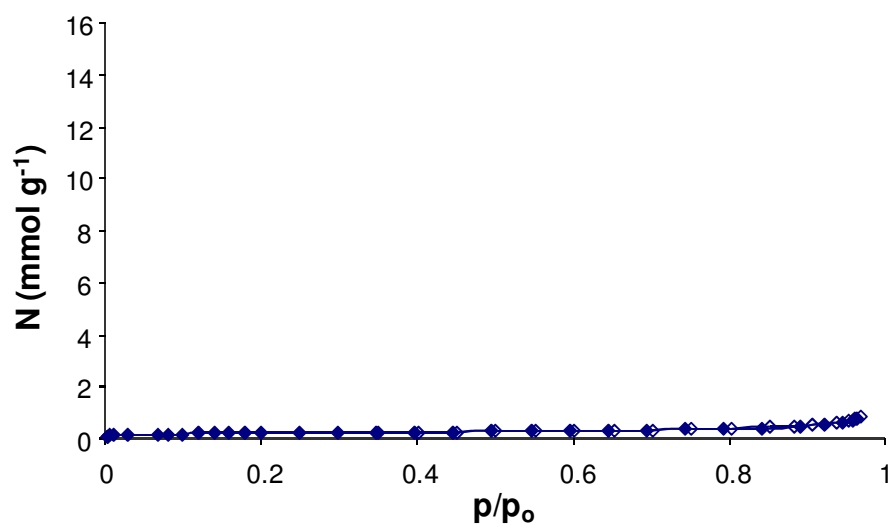**Figure S6.** N_2 adsorption isotherm for **2** at 77 K.

Mechanical Stress Tests

Mechanical stress tests were performed on species **1** and, for the sake of comparison, on $[Cu_3(btc)_2]$ HKUST-1 and $[Cr_3F(H_2O)_2O(bdc)_3]$ MIL-101(Cr). A typical test consisted in the characterization, by XRPD and N_2 adsorption isotherm at 77 K, of pellets fabricated, with 100 mg of the original sample and after grounding trough a 0.5 mm sieve, by the application of specific values of pressure, up to 0.2 GPa (2 tonns cm^{-2}).
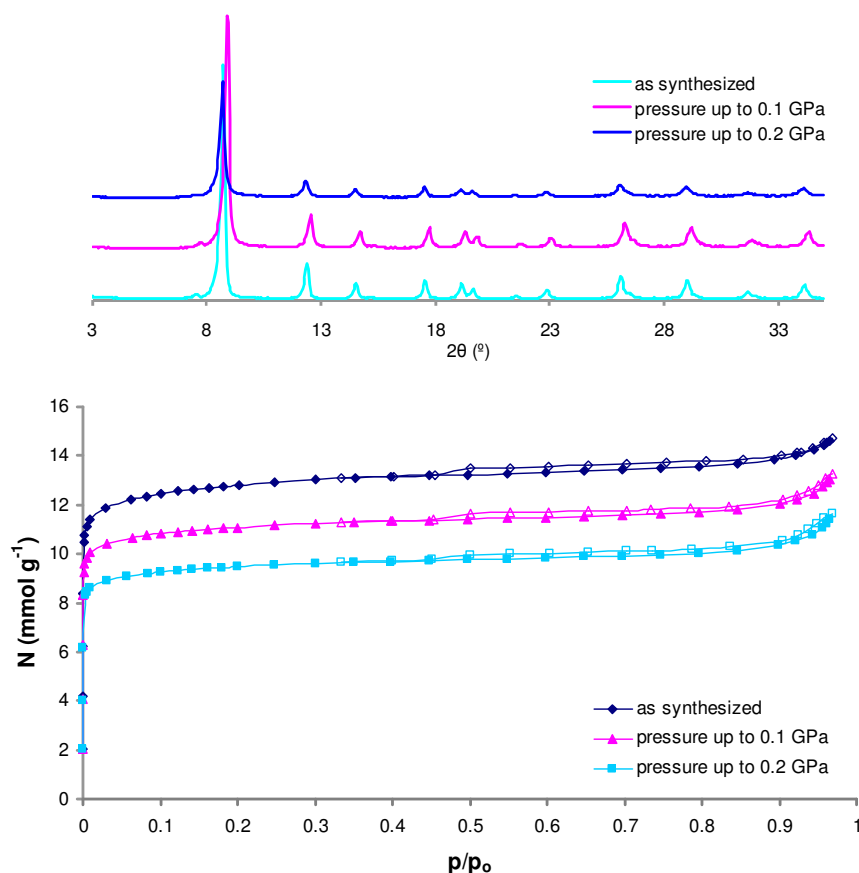

Figure S7. XRPD data (top) and N_2 adsorption isotherms (bottom) for **1** before and after the mechanical stress tests. Desorption branches of the isotherms are depicted with empty symbols.
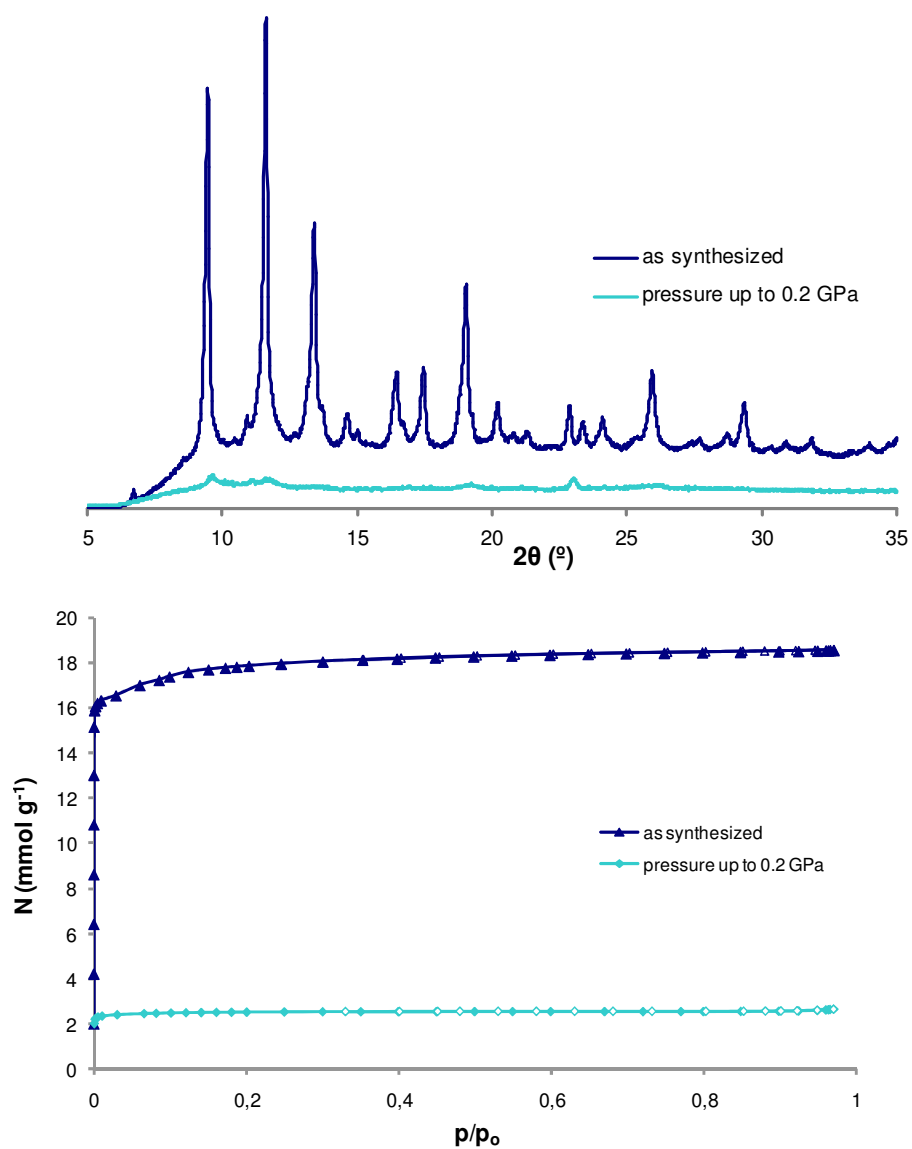
Figure S8. XRPD data (top) and N_2 adsorption isotherms (bottom) for $[Cu_3(btc)_2]$ HKUST-1 before and after the mechanical stress test. Desorption branches of the isotherms are depicted with empty symbols.
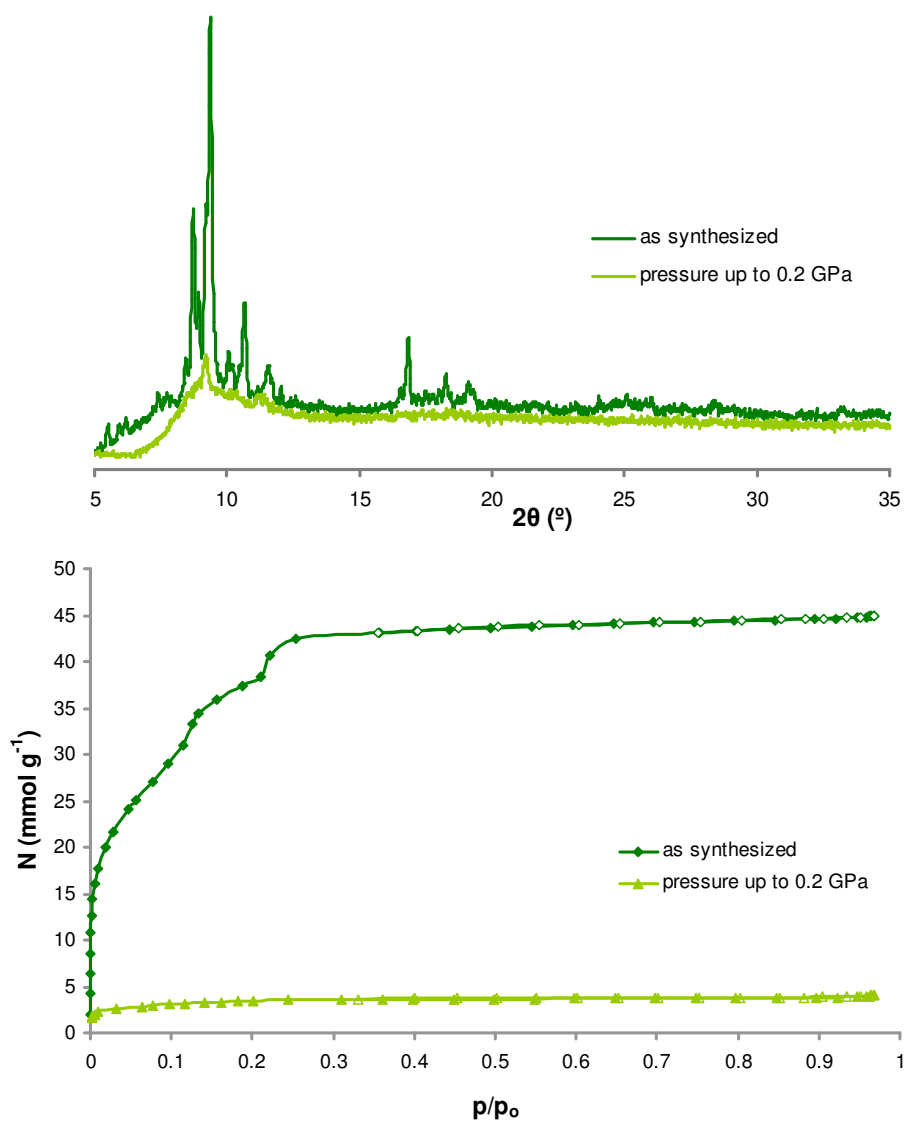
Figure S9. XRPD data (top) and N_2 adsorption isotherms (bottom) for MIL-101(Cr) before and after the mechanical stress test. Desorption branches of the isotherms are depicted with empty symbols.

Dynamic Gas Adsorption Experiments

Variable temperature pulse chromatography

Gas-phase adsorption at zero coverage surface was studied using the pulse chromatographic technique employing a Gas Chromatograph and a 15 cm-column (0.4 cm internal diameter) packed with *ca.* 1 g of 0.5 mm-pellets of the studied materials. As the particles of **1** were too small, and in order to avoid column pressure drops, the particles were aggregated by emulsifying them in a water suspension (1 mL) of starch (0.1 g) at 343 K for 2 minutes. The solvent was removed under reduced pressure. The resulting solid was grounded trough a 0.5 mm sieve and characterized by XRPD and N_2 adsorption, showing that there is no loss of crystallinity and porosity. HKUST-1 was treated in a similar way to **1**. Carboxen^{TM} was used as received. Prior to measurement, samples were outgassed to 10^{-1} Pa and heated 7 h at 453 K for HKUST-1 and at 393 K for **1** and Carboxen^{TM}. The columns were conditioned in He flow (25 mL min^{-1}). Later on, 2 µL of each gas was injected at 1 bar and the separation performance of the chromatographic column was examined at different temperatures (313 K-513 K).

Breakthrough curves

The gas-separation properties of **1** were also examined by breakthrough experiments using 10 mL min^{-1} He flux containing 130 ppm of benzene flowed through the activated samples packed into a 15-cm length, 0.4-cm inner diameter glass column. Helium gas was initially purged into the packed column. A similar experiment was followed containing 50% humidity. The relative amounts of the gases passing through the column were monitored on a mass spectrometer gas analysis system (Pfeiffer Vacoon) detecting ion peak at m/z 78 (benzene).
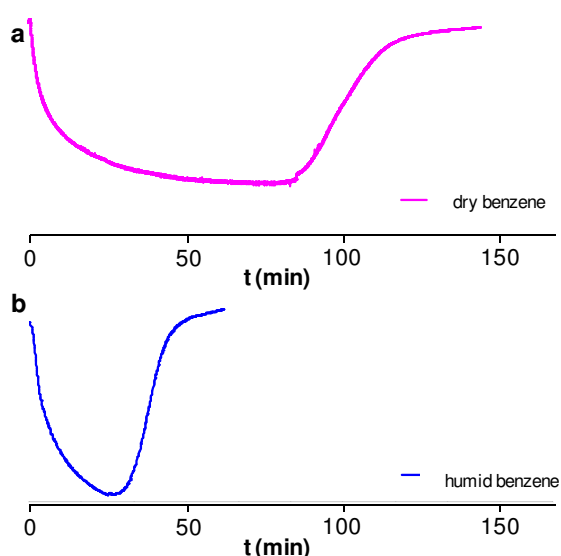

Figure S10. Breakthrough curves of the separation, performed by 1, of 130 ppm of benzene in a 10 mL min-1 He flow in dry (a) and humid (b) conditions.

Notes and References

[1] K. Schlichte, T. Kratzke, S. Kaskel, *Microporous and mesoporous material*, **2004**, *73*, 81–88.

[2] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science*. **2005**, *309*, 2040-2042.

[3] A. Coelho, *J. Appl. Cryst.* **2003**, *36*, 86-95.

[4] TOPAS-R Version 3.0, Bruker AXS **2005**, Karlsruhe, Germany.

[5] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi *Nature* **1999**, *402*, 276-279.

[6] To build the rigid model describing the ligand, bond distances and angles have been adopted according to the results of a query throughout the Cambridge Structural Database on similar moieties. In detail, for the pyrazole ring: C-C, C-N, N-N = 1.36 Å; C-H = 0.95 Å; internal ring angles = 108°; C-C-H = 126°; $C_{pyrazxole}$-$C_{carbovylate}$ = 1.49 Å; $C_{carbovylate}$ - $O_{carbovylate}$ = 1.25 Å.

[7] R. W. Cheary, A. Coelho, *J. Appl. Cryst.* **1998**, *31*, 85-89; *ibid.* 862-868.