# *Electronic Supplementary Information*

## The First Route to Highly Stable Crystalline Microporous Zirconium Phosphonate Metal-Organic Frameworks

*Marco Taddei, Ferdinando Costantino, Fabio Marmottini, Angiolina Comotti, Piero Sozzani, and Riccardo Vivani*

**Table of contents**

**Table 1S.** Structural data and refinement details for UPG-1.

| | |
|---|---|
| empirical formula | $C_{48}H_{64}N_6O_{28}P_6Zr$ |
| formula weight | 1449 |
| crystal system | trigonal |
| space group | *R* -3 |
| *a*/Å | 60.674(2) |
| *c*/Å | 5.1278(3) |
| volume/Å$^3$ | 16348(1) |
| *Z* | 9 |
| calculated density/g·cm$^{-3}$ | 1.25 |
| data range/ $2\theta$deg$^{-1}$ | 3.5 - 70 |
| wavelength | 1.54056 |
| n. of data points | 3912 |
| n. of reflections | 1559 |
| n. of parameters | 158 |
| n. of restraints | 136 |
| $R_p$ [a] | 0.0568 |
| $R_{wp}$ [b] | 0.0750 |
| $R_F2$ [c] | 0.1098 |
| *GOF* [d] | 5.17 |

[a] $R_p = \Sigma\ |I_o\text{-}I_c|\ /\ \Sigma\ I_o$; [b] $R_{wp} = [\Sigma\ w(I_o\text{-}I_c)^2\ /\ \Sigma\ wI_o^2]^{1/2}$; [c] $R_F2 = \Sigma\ |F_o^2 - F_c^2|\ /\ \Sigma\ |F_o^2|$; [d] $GOF = [\Sigma\ w(I_o\text{-}I_c)^2 / (N_o - N_{var})]^{1/2}$

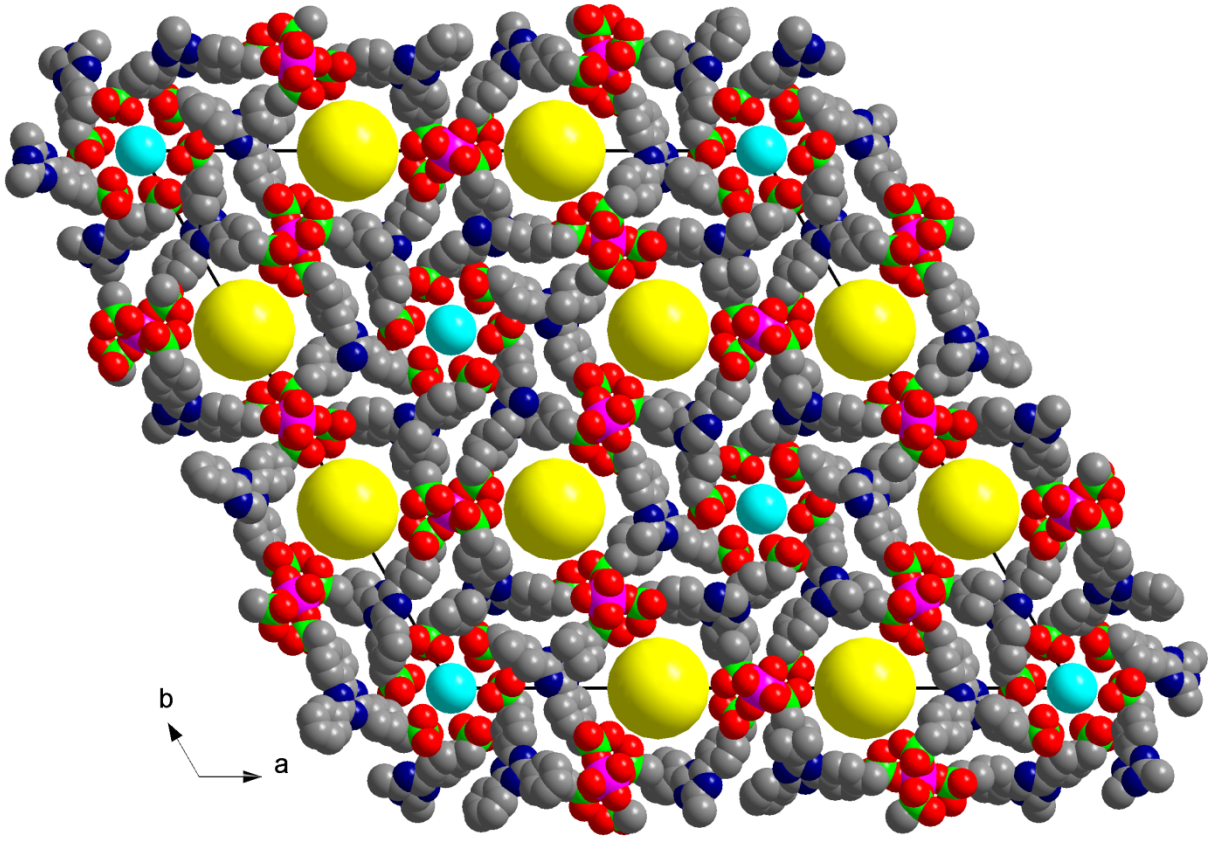


**Figure 1S.** Space filling model of the structure of UPG-1 viewed along the *c*-axis. The 10 Å channels are represented in yellow, the 5 Å channels are in light blue.

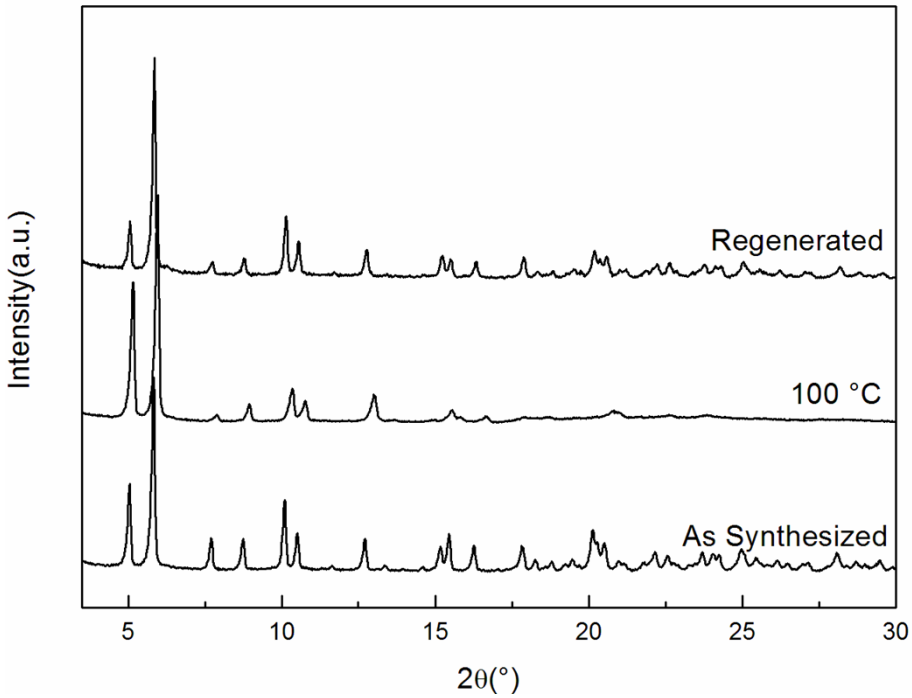


**Figure 2S.** PXRD patterns of UPG-1 as-synthesized, after heating at 100 °C, and after regeneration in hot water.

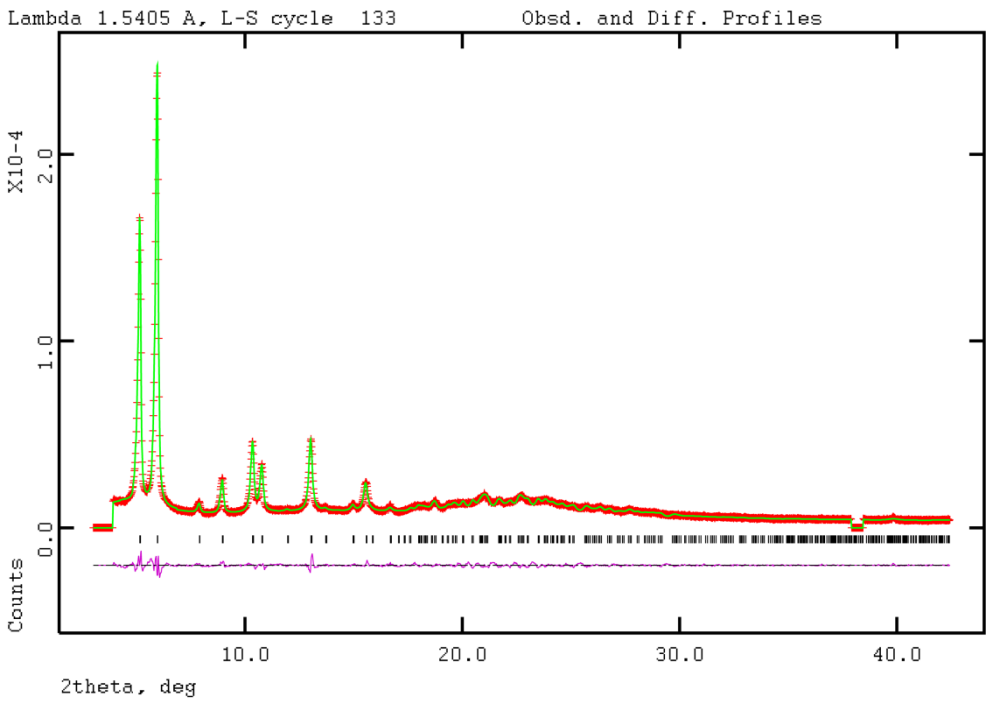


**Figure 3S.** Le Bail plot for the anhydrous form of UPG-1 after outgassing at 160 °C for 24 h. The peak at about 38.5 °2theta, relative to alminium sample holder, was cut out.

$R_p = 0.034$; $R_{wp} = 0.043$.

$R_p = \Sigma\, |I_o\text{-}I_c| \,/\, \Sigma\, I_o$; [b] $R_{wp} = [\Sigma\, w(I_o\text{-}I_c)^2 \,/\, \Sigma\, wI_o^2]^{1/2}$

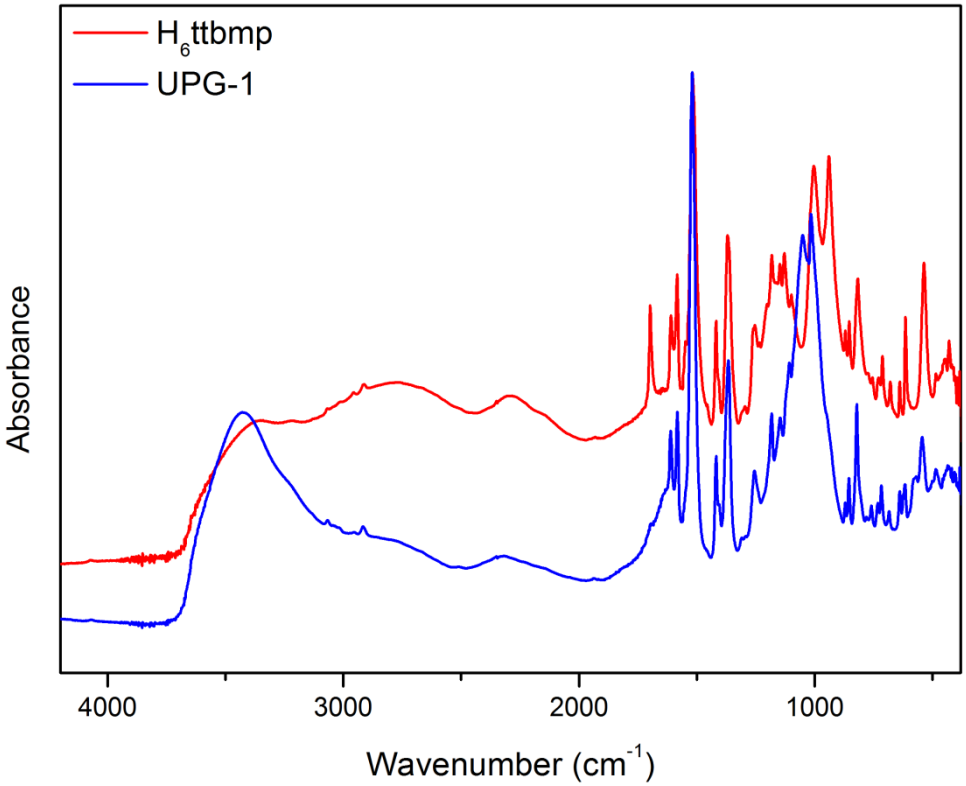


**Figure 4S.** FT-IR spectrum of UPG-1 (blue line) compared with that of the free $H_6$ttbmp ligand (red line). The broad band around 3500 $cm^{-1}$ of UPG-1 spectrum is due to O-H stretching of crystallization water; he C−H stretching vibrations are visible between 2800 and 3150 $cm^{-1}$; the broad bands around 2800 and 2350 $cm^{-1}$ and the sharp band at 1700 $cm^{-1}$, stronger in the free ligand than in the metal derivative, can be assigned to P-OH stretching vibrations; major features between 1600 and 1100 $cm^{-1}$, due to CC stretching and CH, CN, and PC bendings, are very similar in the two spectra, while the P-O stretching region, between 1100 and 900 $cm^{-1}$, is obviously different.

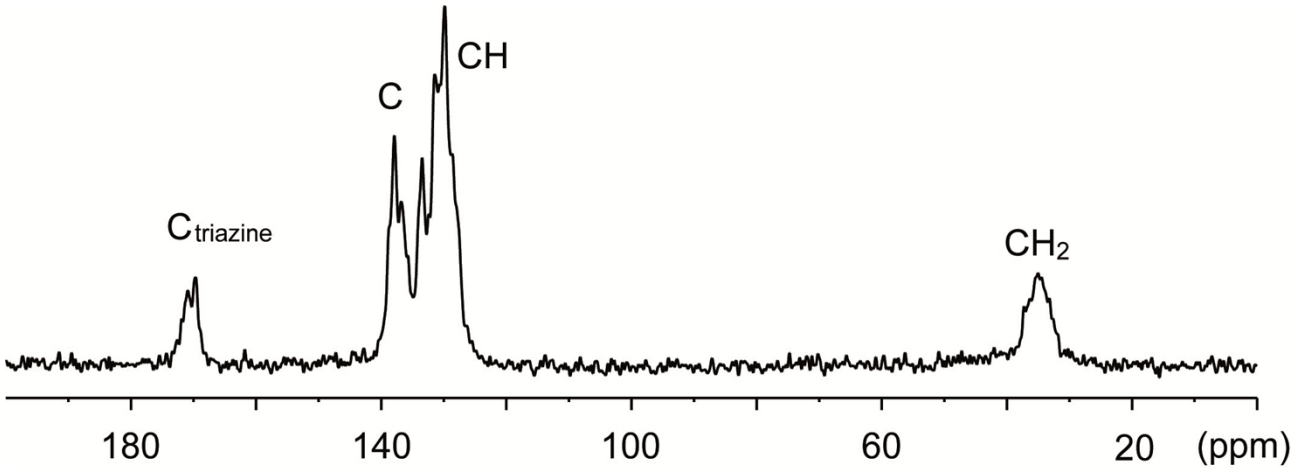


**Figure 5S.** 75MHz $^{13}C$ CP MAS NMR spectrum of UPG-1. A 12.5 kHz spinning speed and a contact time of 2 ms were applied. The multiplicity observed for the triazine signals is mainly due to the coupling with neighboring nitrogen atoms. As concerns the aromatic signals at 140-130 ppm, their number is of at least 5, a number that is larger than 4, the number of 4 being relative to a single phenylene ring. Therefore, the larger multiplicity, indicated also by the unbalanced intensity distribution, is a clear indication of the fact that the phenylene rings are distinguished in the solid state. This is consistent with the unit cell which has not such a high symmetry to degenerate the signal number of only 4: in fact, consistently with the unit cell the number of independent aromatic carbon atoms is very large and MAS NMR cannot resolve them individually. From methylene point of view, a broad resonance composed by three signals can be recognized, which is in agreement with the crystal packing in which the three methylene carbons are distinct.

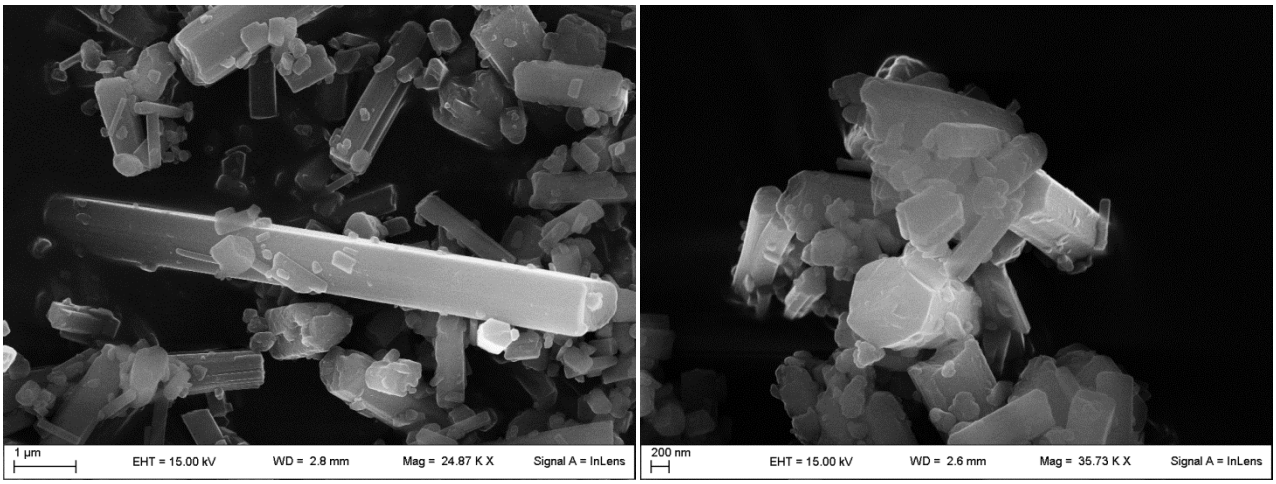


**Figure 6S.** FE-SEM images of UPG-1.

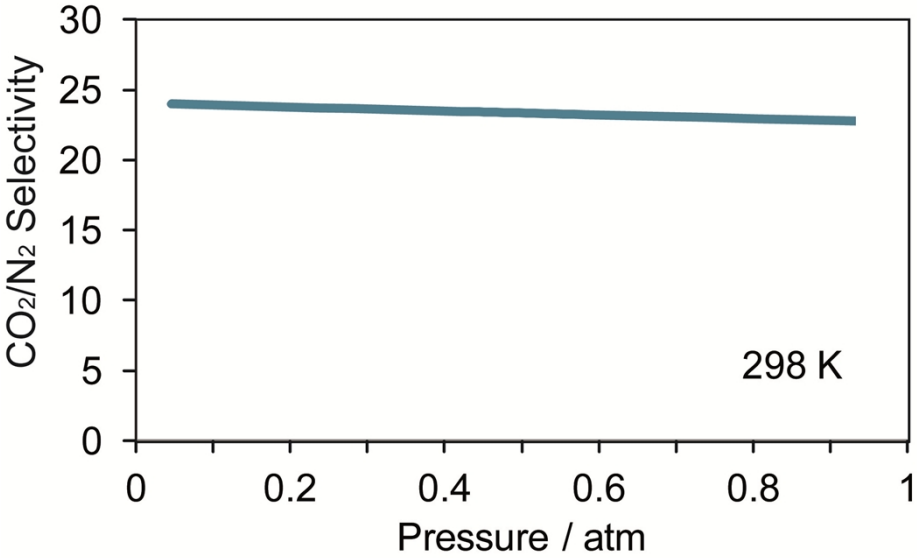


**Figure 7S.** $CO_2/N_2$ selectivity of UPG-1 as function of loading as calculated by IAST method considering a binary mixture of 15:85 $CO_2$:$N_2$.

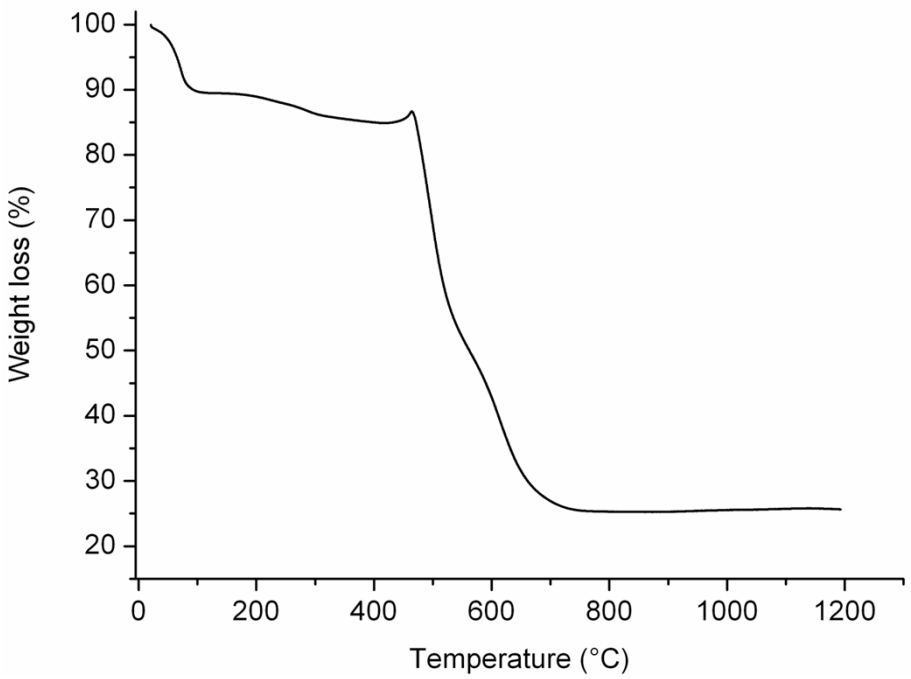


**Figure 8S.** TGA curve for UPG-1. The first weight loss, at about 100 °C, is due to the loss of about 8 water molecules / formula unit (% exp.: 10.5; calcd.: 9.9); the second weight loss, occurring between 200 and 350 °C, can be attributed to the remaining 2 hydration water molecules, and to the condensation of uncoordinated phosphonate groups into pyrophosphonate groups (% exp.: 4.5; calcd.: 3.7). Around 450 °C the organics start to oxidise and the compound decomposes.

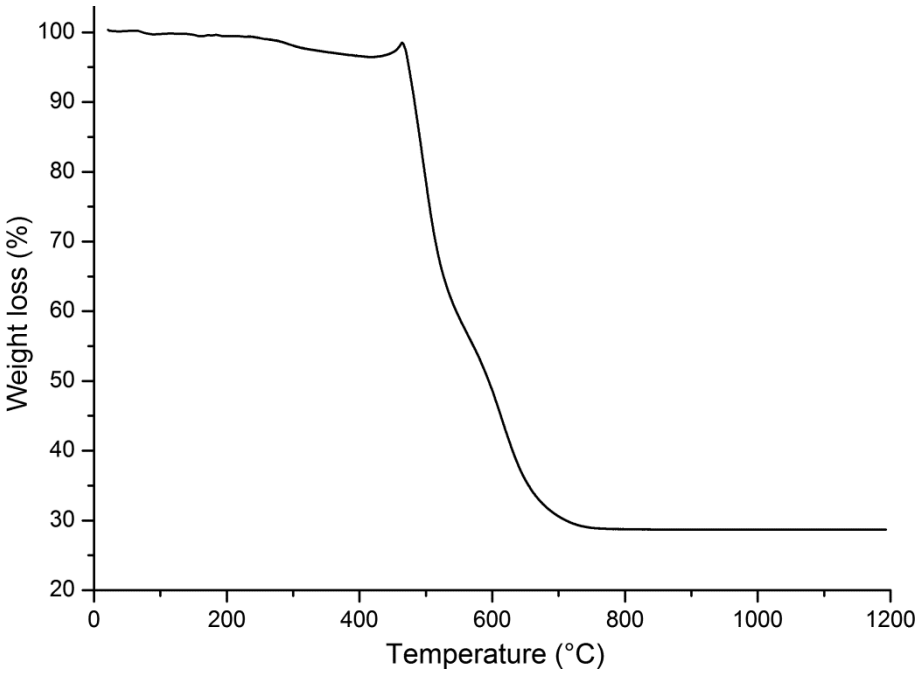


**Figure 9S.** TGA curve for UPG-1 after outgassing at 160°C for 24 h.

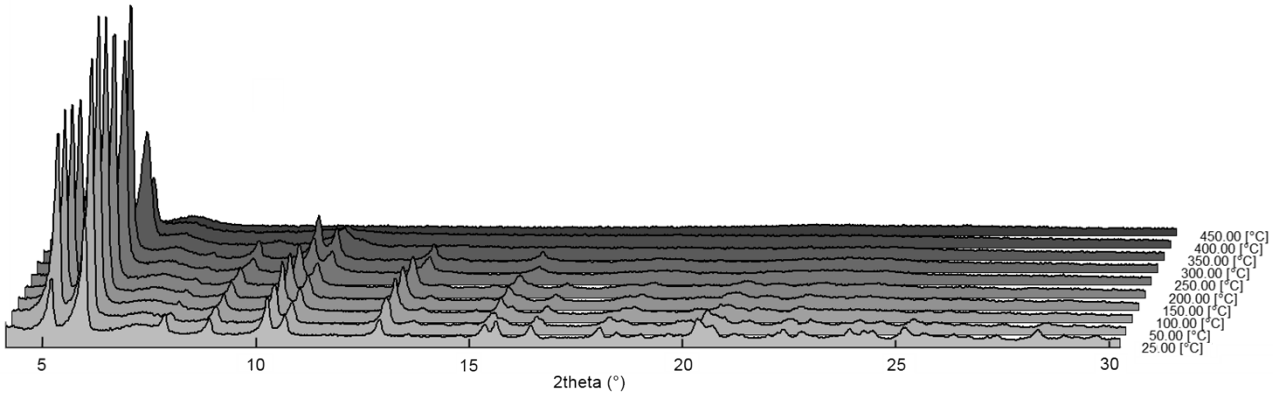


**Figure 10S.** TDXD plot for UPG-1.

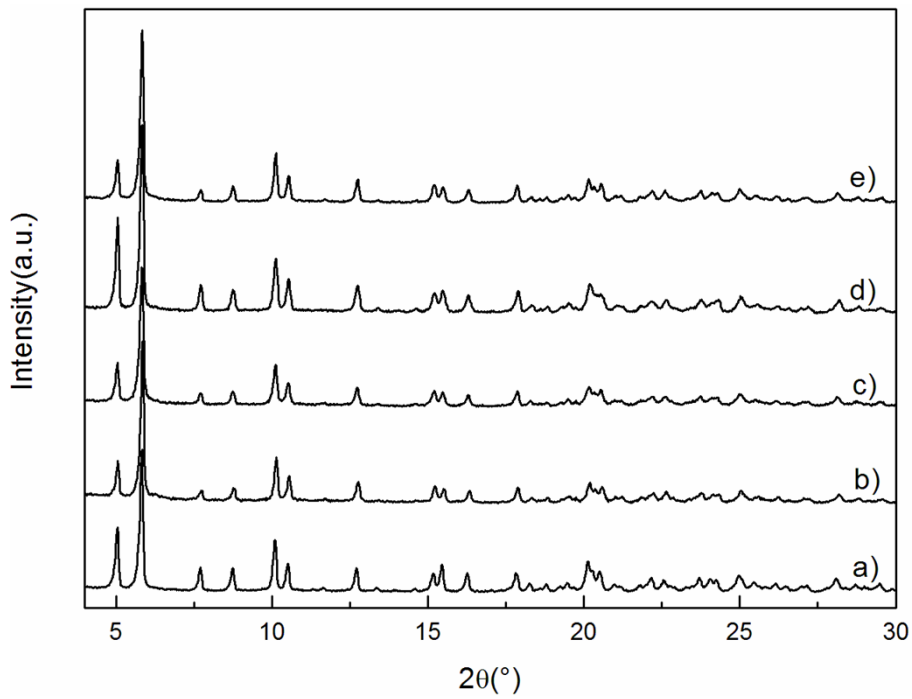


**Figure 11S.** PXRD patterns of UPG-1 as synthesized (a), after a 3-day treatment in $H_2O$ at 120 °C (b), after a 2-day treatment in $H_2O$ at 200 °C (c), after a 3-day treatment in HCl at 80 °C (d), and after a 3-day treatment in HCl at 120 °C (e).

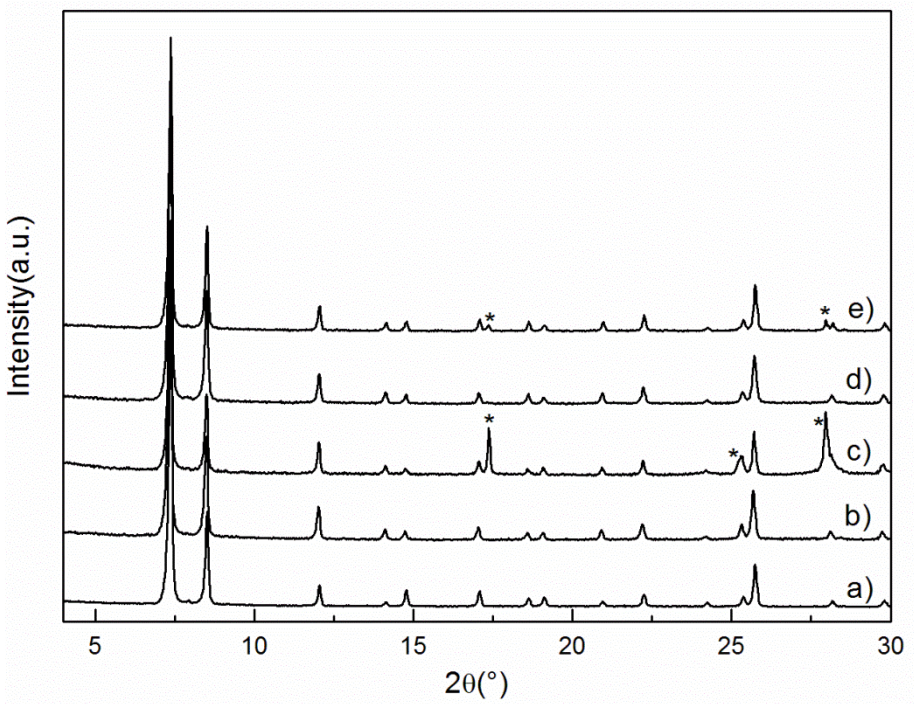


**Figure 12S.** PXRD patterns of UiO-66 as synthesized (a), after a 3-day treatment in $H_2O$ at 120 °C (b), after a 2-day treatment in $H_2O$ at 200 °C (c), after a 3-day treatment in HCl at 80 °C (d), and after a 3-day treatment in HCl at 120 °C (e). The marked peaks in (c) and (e) are due to the terephthalic acid formed by hydrolysis of the MOF.

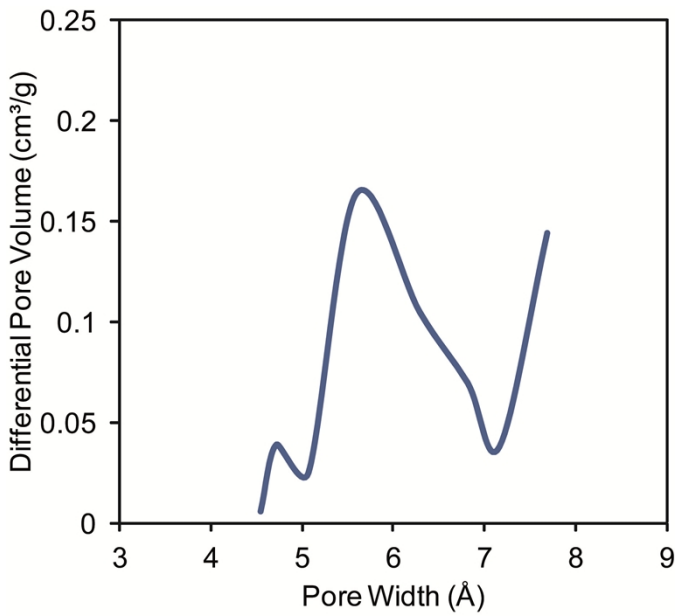


**Figure 13S.** Pore size distribution calculated by DFT analysis of $CO_2$ adsorption isotherm at 273 K in the low relative pressure range ($2\times10^{-4} < P/P° < 0.03$)

**Synthetic procedures**

*Synthesis of 2,4,6-tris[4-(bromomethyl)phenyl]-1,3,5-triazine (ttbmBr).*

4-Bromomethyl-benzonitrile (5 g, 25.5 mmol) was introduced an a dry 100 mL round-bottom flask kept at 0°C, then trifluoromethanesulfonic acid (5 mL) was progressively added under $N_2$. After the addition, the flask was capped and sealed and the mixture was warmed to room temperature and stirred for 20 h. Then, the orange mixture formed was poured into ice and neutralized with concentrated ammonium hydroxide. The solid phase was collected by filtration and washed with water and acetone. The white solid was dried in an oven at 60°C. 4.8 g of product were recovered (Yield: 96%)

$^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ = 8.7 (d, 6H, aromatic), 7.5 (d, 6H, aromatic), 4.6 (s, 6H, *Ph*-$CH_2$-Br) ppm.

*Synthesis of 2,4,6-tris[4-(diethylphosphonomethyl)phenyl]-1,3,5-triazine ($Et_6$ttbmp).*

ttbmBr (2 g, 3.4 mmol) and triethylphosphite (3.5 mL, 20.4 mmol) were introduced in a dry 100 mL round bottom flask and the mixture was heated under reflux for 4 h 30 min under $N_2$. After cooling, a white solid slowly crystallized from the hot liquid. Hexane was added and the mixture was stirred for 1 h, then the solid was filtered under vacuum, washed with hexane, and dried in an oven at 60°C. 2.45 g of product were recovered (Yield: 95%)

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.73 (d, 6H, aromatic), 7.53 (d, 6H, aromatic), 4.07 (m, 12H, *O*-$CH_2$-), 1.68 (s, 6H, *Ph*-$CH_2$-*P*), 1.30 (t, 18H, -$CH_3$) ppm.

$^{31}$P NMR ($CDCl_3$, 400 MHz): $\delta$ = 26.70 ppm.

*Synthesis of 2,4,6-tris[4-(phosphonomethyl)phenyl]-1,3,5-triazine ($H_6$ttbmp).*

In a 250 mL round bottom flask, $Et_6$ttbmp (3.3 g, 4.4 mmol) was dissolved in 50 mL of anhydrous acetonitrile. Then, trimethylchlorosilane (5 mL, 40 mmol) and potassium iodide (6.6 g, 40 mmol) were added. The flask was heated to reflux under $N_2$ for 4 h.

The mixture was then filtered to remove the byproduct potassium chloride, and the liquid phase was evaporated under vacuum. The residue was treated with water to hydrolyze the trimethylsilylester, and sodium hydroxide was added until complete dissolution of the phosphonic acid. This mixture was washed chloroform to remove the trimethylsilanol. The water phase was recovered and a concentrated solution of hydrochloric acid was added until the pH became sufficiently acid to precipitate the phosphonic acid. The solution was vacuum filtered and the solid was washed with isopropanol and dried in an oven at 80 °C. 2.2 g of product were recovered (Yield: 85%)

$^1$H NMR ($D_2O$+$K_2CO_3$, 400 MHz): $\delta$ = 8.42 (d, 6H, aromatic), 7.49 (d, 6H, aromatic), 4.71 (s, 6H), 2.98 (d, 6H, -OH) ppm.

$^{31}$P NMR ($D_2O$+$K_2CO_3$, 400 MHz): $\delta$ = 18.66 ppm.

*Synthesis of $Zr(H_4ttbmp)_2 \cdot 10H_2O$ (UPG-1).*

124 mg of $ZrOCl_2 \cdot 8H_2O$ (0.4 mmol) were dissolved in 7.0 mL of HF 2.9 M (20 mmol) in a plastic bottle. The mixture was diluted with 5 mL of methanol and 10 mL of water, then 236 mg of $H_6$ttbmp (0.4 mmol) were added. The bottle was closed and put in an oven at 80 °C for two days. The white solid was then filtered under vacuum, washed with water, a 3:1 water/methanol mixture, and methanol, and dried at room temperature. 250 mg of product were recovered (Yield: 86%, based on $H_6$ttbmp).

Analysis: Calcd for $C_{48}H_{64}N_6O_{28}P_6Zr$: C = 39.8%, H = 4.4%, N = 5.8%, P = 12.8%, Zr = 6.3%; Found: C = 36.9%, H = 4.6%, N = 5.5%, P = 11.4%, Zr = 6.6%.

**Hydrolysis resistance tests.**

100 mg of UPG-1 and UiO-66 were used for each test, in the following conditions:

- 10 mL of water, 120 °C, 3 days, hydrothermal bomb;
- 10 mL of water, 200 °C, 2 days, hydrothermal bomb;
- 10 mL of HCl 0.1 M, 80 °C, 3 days, plastic bottle;
- 10 mL of HCl 0.1 M, 120 °C, 3 days, hydrothermal bomb;

At the end of each treatment, the solids were filtered, washed with water and methanol, ground and weighed. Assuming that a small fraction of material went lost during filtration and grinding, less than 10% of UPG-1 underwent hydrolysis in each test. UiO-66 lost less than 10wt% at each treatment, except for the treatment at 200 °C in water, after which only 50% of the starting material was recovered, with formation of terephthalic acid, as shown in figure 8S. Traces of terephthalic acid were also observed in the sample after treatment in HCl 0.1 M at 120 °C.

**Analytical methods.**

*Elemental Analysis.* The zirconium and phosphorus contents were obtained by inductively coupled plasma optical emission spectroscopy using a Varian Liberty Series II instrument working in axial geometry, after mineralization of the sample with hydrofluoric acid.

The carbon, hydrogen, and nitrogen contents were obtained with an EA 1108 CHN Fisons instrument.

*Powder X-Ray Diffraction.* The PXRD patterns were collected in the 3-70 °2$\theta$ range and with a 150 s/step counting time with the CuKα radiation on a PANalytical X'PERT PRO diffractometer, PW3050 goniometer, equipped with an X'Celerator detector. The long fine focus (LFF) ceramic tube operated at 40 kV and 40 mA.

*Temperature dependent X-ray diffraction.* TDXD was performed under air with an Anton Paar HTK 1200N hot chamber mounted on a Philips X'PERT PRO diffractometer in the 25 - 450 °C temperature range with a heating rate of 5 °C/min and a 10 minutes isotherm prior to each measurement.

*Thermogravimetric Analysis.* TGA was performed using a Netzsch STA490C thermoanalyser under a 20 mL min−1 air flux with a heating rate of 5 °C min−1.

*Fourier Transform infrared spectroscopy.* FT-IR spectra were recorded in the solid state, with a Jasco IMV4000 spectrophotometer using the KBr pellet method.

*Field Emission Scanning Electron Microscopy.* FE-SEM images were collected with a LEO 1525 ZEISS instrument, working with an acceleration voltage of 15 kV.

*Gas Sorption measurements*. A Micromeritics 2010 apparatus was used to obtain the adsorption and desorption isotherms with nitrogen at 77 K and *n*-butane at 273 K. Before the adsorption analysis the sample was outgassed at 100 °C overnight. Non-porous α-ZP was used as reference material with the aim to calculate the value of the *n*-butane cross-section and used in the $\alpha_s$-plot analysis.
High pressure $CO_2$, $CH_4$, and $N_2$ isotherms were carried out, with a Micromeritics ASAP 2050 apparatus, at 273 K and 298 K and up to 10 bar. $CO_2$ isotherm at 195 K was collected up to 1 bar. The sample was outgassed for 24 h at 160 °C before collecting the isotherms.

**Structure Determination and Refinement.**

The crystal structure of UPG-1 was solved *ab initio* from PXRD data. Indexing was performed using the TREOR program. The analysis of systematic extinctions for space group assignment was performed using the Chekcell program. Two possible cells were found: one with lattice parameters

*a* = 60.674 Å, *c* = 5.128 Å, the other with the same *a* axis length and with *c* = 10.2556 Å. The former was best fit in the *R* -3 space group, whereas the latter in the *R* -3*c* space group. Le Bail fits performed for both cells gave very similar results, hence the smaller cell was chosen for structure solution. Combining information about the stoichiometry (P/Zr ratio = 6) and the need to place an integer number of tritopic ttbmp ligands inside the unit cell, it was concluded that the cell content was necessarily constrained to be multiple of 1 Zr and 2 ttbmp (6 P). Since the Z of the *R* -3 space group is 18, the correct unit cell content was found to contain 9 Zr and 18 ttbmp, with the Zr atom lying in a site with multiplicity of 9 (inversion center). On the basis of this information, the structural model was determined using the real space global optimization methods implemented in the FOX program: one ttbmp fragment and one $ZrO_6$ octahedron, placed in the inversion center, were input. Trial structures were generated using the "Parallel Tempering" algorithm implemented in FOX, using the following antibump distances: P-Zr = 3 Å, P-P = 3 Å, C-Zr = 4 Å, C-O = 2.5 Å, O-O = 2.5 Å, O-N = 4 Å, P-N = 4 Å.

Rietveld refinement of the structural model was performed using the GSAS program.

First, zero-shift, unit cell, background, and profile-shape parameters were refined. A corrected pseudo-Voigt profile function (six terms) with two terms for the correction of asymmetry at the low-angle region was used. Then, atomic coordinates were refined by restraining the bond distances to the following values: Zr-O = 2.00(5) Å, P-O = 1.55(5) Å, P-C = 1.80(5) Å, aromatic C-C = 1.39(5) Å, and C-N = 1.32(5) Å. The statistical weight of these restraints was decreased as the refinement proceeded. At the end of the refinement the shifts in all parameters were less than their standard deviations.