

The use of a rigid tritopicphosphonic ligand for the synthesis of a robust honeycomb-like layered zirconium phosphonate framework

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ELECTRONIC SUPPLEMENTARY INFORMATION

Table S1. Structural data and refinement details for Zrbtbp-a.

empirical formula	C ₃₂ H ₂₄ O ₁₂ P ₄ Zr
formula weight	815
crystal system	trigonal
space group	<i>P</i> -31 <i>c</i>
<i>a</i> /Å	16.3472(8)
<i>c</i> /Å	28.021(2)
volume/Å ³	6485.0(7)
<i>Z</i>	6
calculated density/g·cm ⁻³	1.25
data range/ 2θ deg ⁻¹	5 - 90
wavelength	1.54056
n. of data points	5087
n. of reflections	1678
n. of parameters	99
n. of restraints	83
<i>R</i> _p	0.0709
<i>R</i> _{wp}	0.0952
<i>R</i> _F ²	0.1094
<i>GOF</i>	1.54

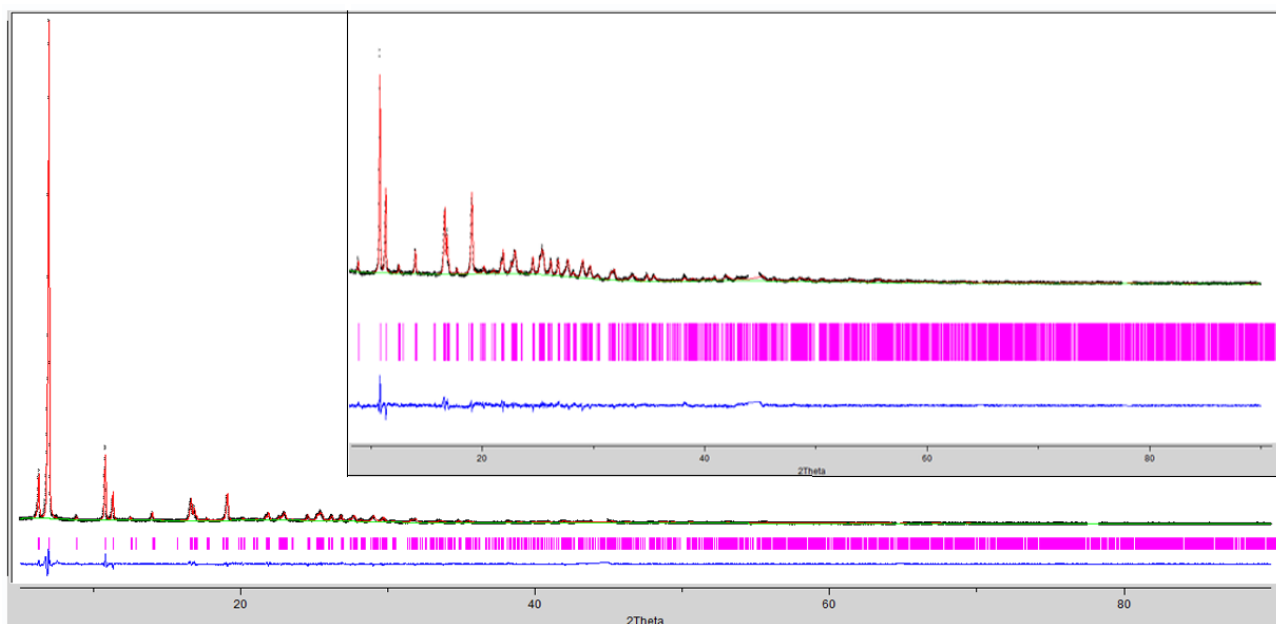


Fig. S1.Final Rietveld and difference plots for Zrbtbp-a.

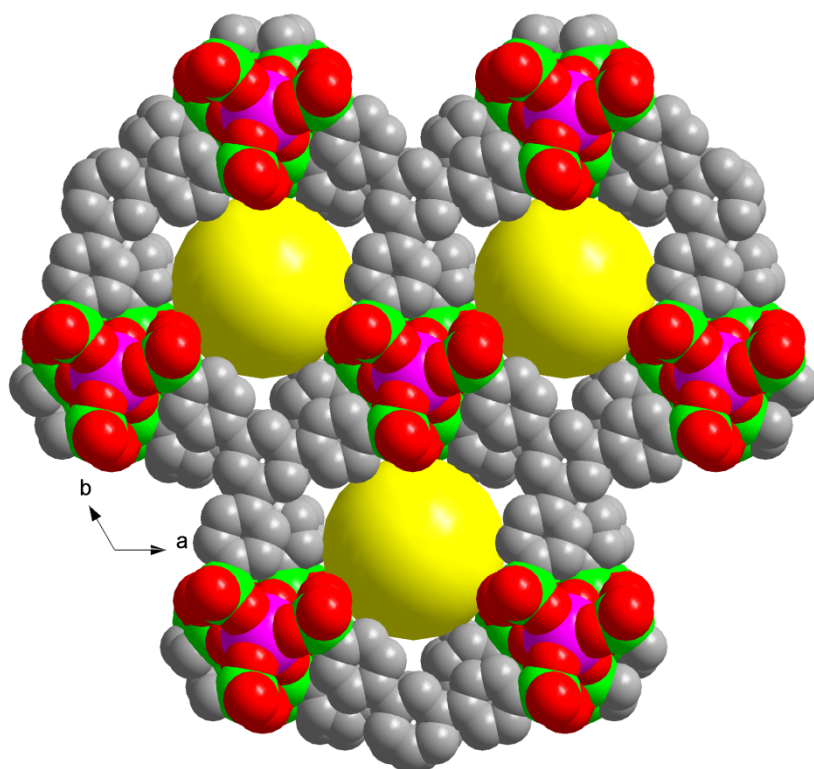


Fig. S2.Space-filling model of the structure of one layer of Zrbtbp-a viewed along the *c* axis, showing the fitting of a 10 Å diameter sphere in the cavity.

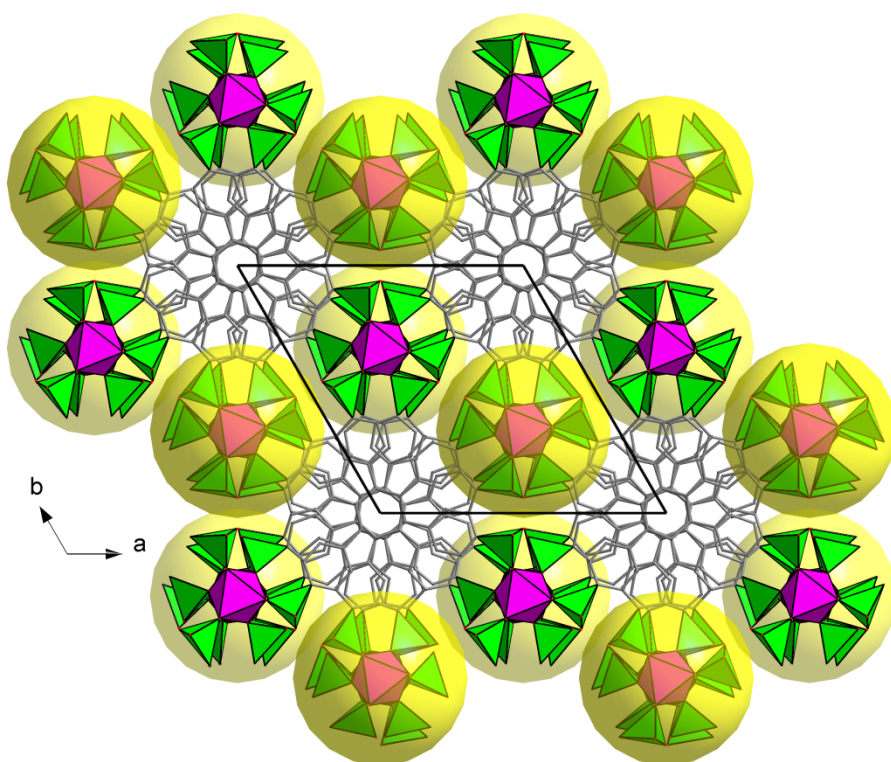


Fig. S3. View of the structure of Zrbitp-a along the *c* axis. ZrO₆ octahedra are represented in purple, PO₃C tetrahedra are represented in green.

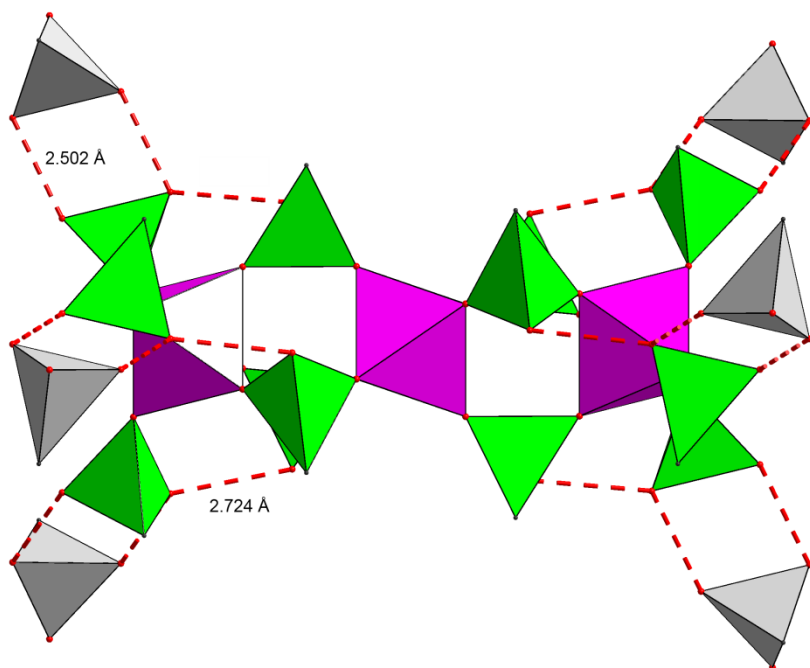


Fig. S4. The H-bonds network observed in Zrbtbp-a, with respect to a single secondary building unit. The green tetrahedra are PO_3C groups belonging to the secondary building unit, the grey ones are those belonging to adjacent layers. Hydrogen bonds are represented as red dashed lines. Bond valence calculations for the oxygen atoms involved in the hydrogen bonds gave the following values: $\text{BV}(\text{O}2) = 1.350$; $\text{BV}(\text{O}4) = 1.376$; $\text{BV}(\text{O}5) = 1.296$. These values show that the charge defect for each oxygen atom is about 0.7, suggesting that tautomeric equilibria might be the best way to describe the system.

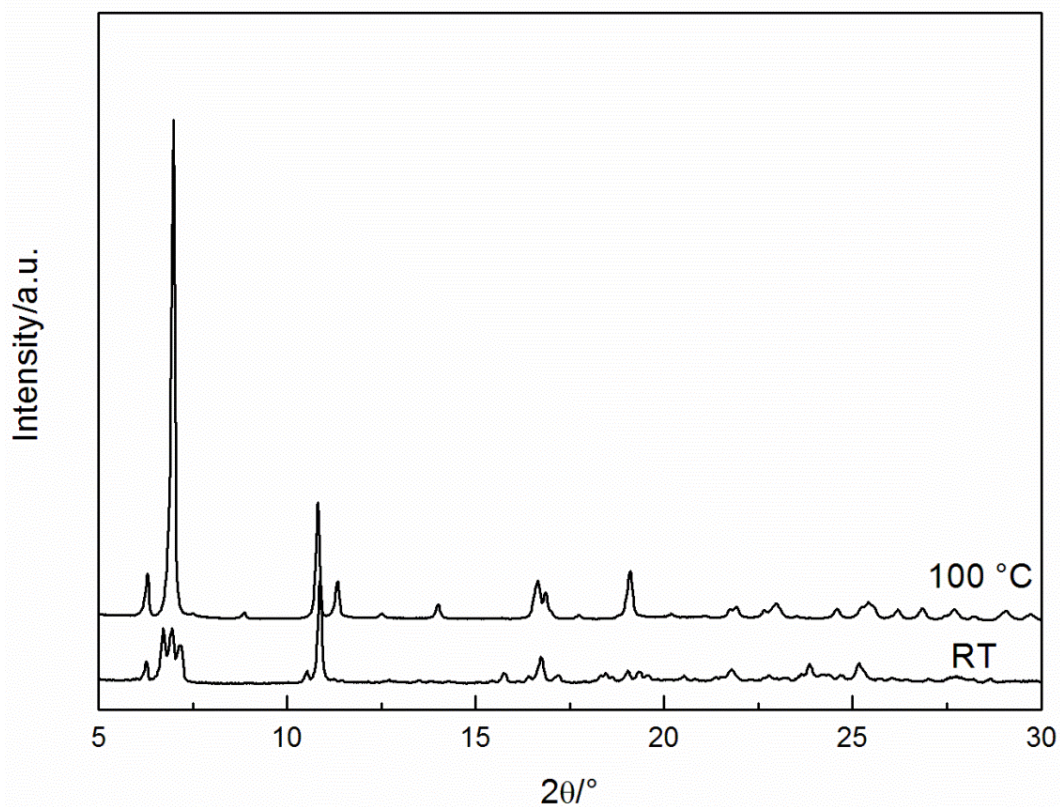


Fig. S5. Comparison between the PXR D pattern of Zrbtbp at RT and at 100 °C.

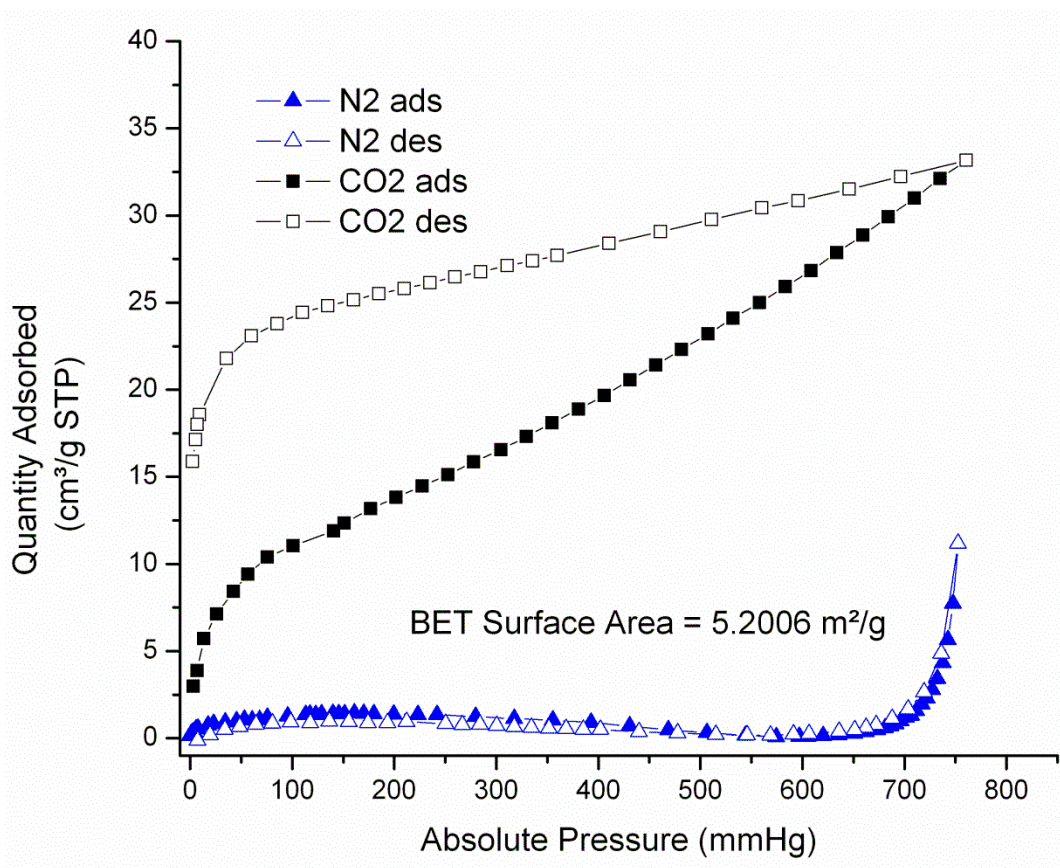


Fig. S6. N₂ (77 K) and CO₂ (196 K) adsorption isotherms for Zrbtbp.

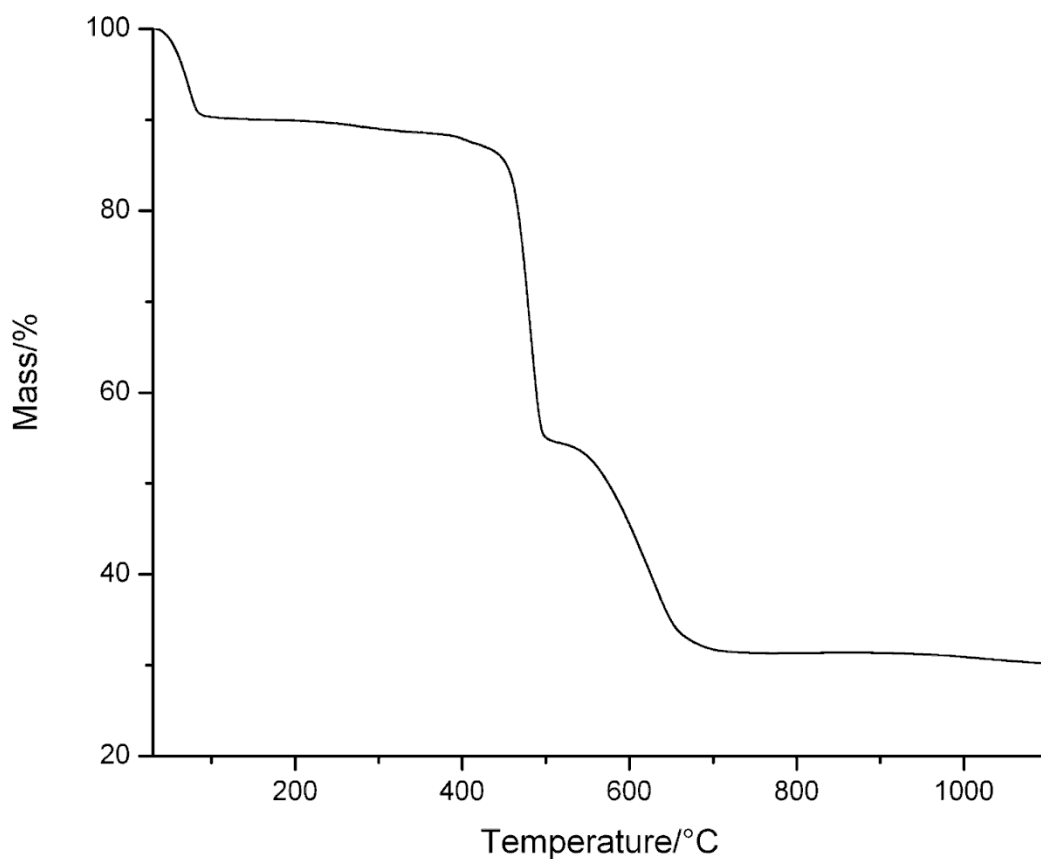


Fig. S7. TG curve for Zrbtbp. After an initial 9.9% weight loss occurring before 100 °C, due to the loss of 5 water molecules per formula unit (calculated: 9.9%), the compound is stable up to about 400 °C, when decomposition of the organic part of the framework begins, followed by the loss of the excess phosphorus; at 1200 °C only ZrP_2O_7 is left and the final weight loss is 70.2%, in good agreement with the calculated value (70.7%).

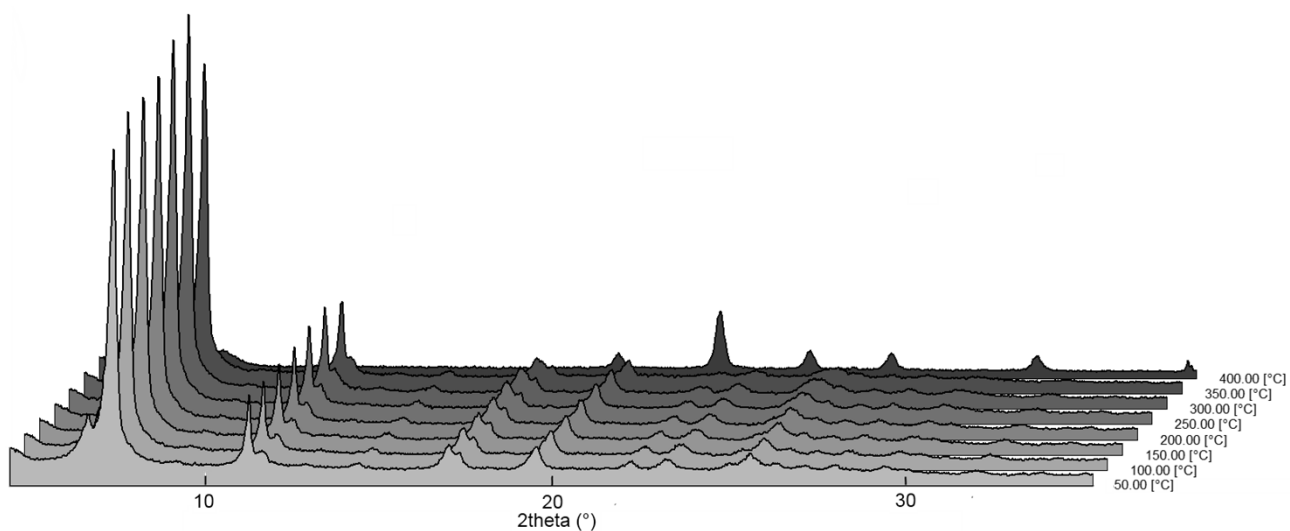


Figure S8. Temperature dependent X-ray diffraction (TDXD) patterns for Zrbbtp.

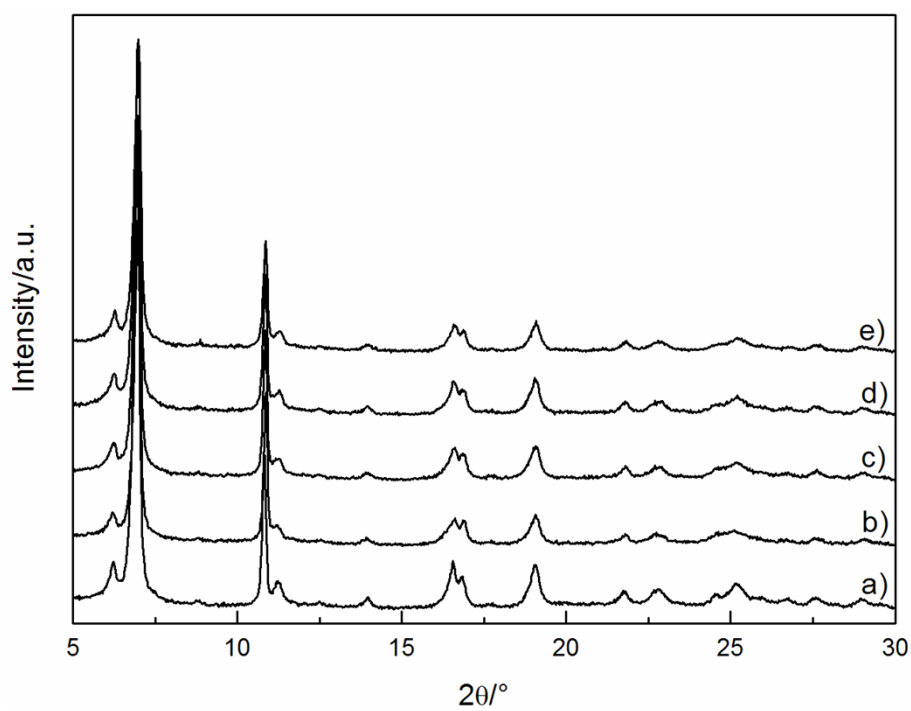


Fig. S8. The PXRD patterns collected at 100 °C of Zrbbtp as synthesized (a), after 2 hours in refluxing H₂O (b), after 16 hours at 150 °C in H₂O (c), after 2 hours in refluxing HCl 0.1 M (d), and after 16 hours at 150 °C in HCl 0.1 M (e).

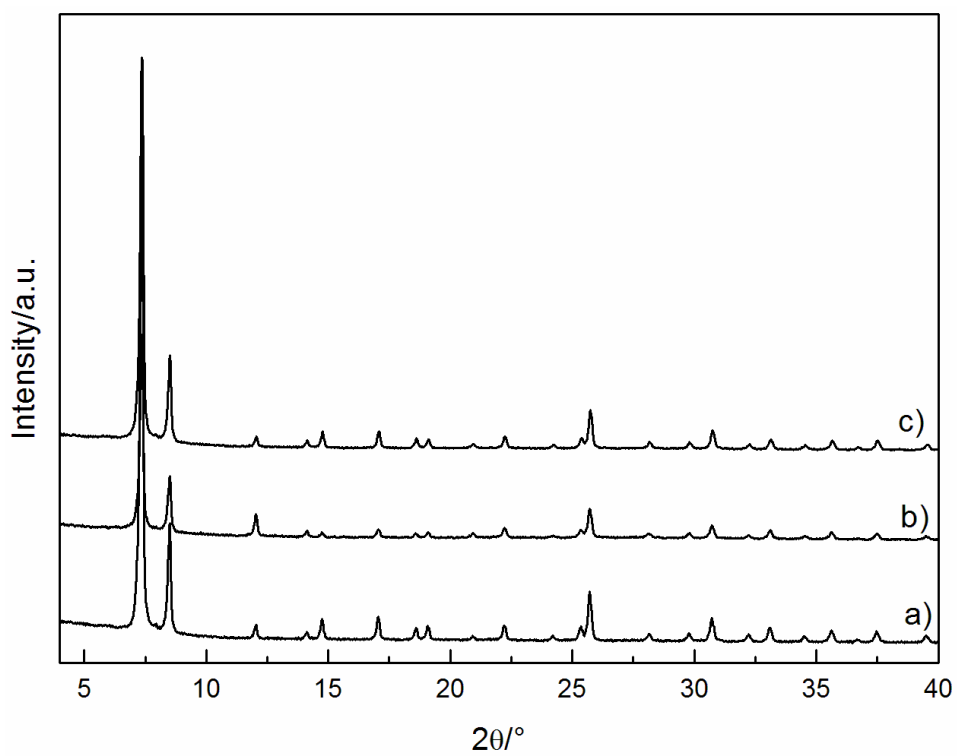


Fig. S9. The PXRD patterns of UiO-66 as synthesized (a), after 16 hours at 150 °C in H₂O (b), and after 16 hours at 150 °C in HCl 0.1 M (c).

EXPERIMENTAL

Chemicals.

All of the chemicals were purchased from Alfa-Aesar and were used as received.

Synthesis.

All reactions were routinely checked by thin-layer chromatography (TLC) on silica gel 60F₂₅₄ (Merck) and visualized using UV illumination.

¹H-NMR and ³¹P-NMR spectra were recorded at 400 MHz with a Bruker Advance-DRX 400 instrument. The chemical shift (δ) values are reported in ppm, and the coupling constants (J) are given in Hz. The abbreviations used are as follows: s, singlet; bs, broad singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet. The spectral data are consistent with the assigned structures.

Synthesis of 1,3,5-tris(4-bromophenyl)benzene (btbBr).

25 g of 4-bromoacetophenone (125.6 mmol) were introduced in a dry 100 mL round bottom flask and trifluoromethanesulfonic acid (1 mL) was slowly added. After the addition, the flask was heated at 135 °C under stirring for 16 h. The mixture was then cooled to room temperature and washed with ethanol. The pale orange solid formed was filtered under vacuum, washed with diethyl ether and dried at room temperature. This solid was recrystallized from a 60:40 Cyclohexane/CHCl₃ mixture. 13.8 g of a pale yellow solid were recovered and ground with a ball mill. (Yield = 63%).

¹H-NMR (CDCl₃, 400 MHz): δ = 7.72 (s, 3H), 7.63 (d, J = 8.4 Hz, 6H), 7.56 (d, J = 8.4 Hz, 6H) ppm.

LC-MS: m/z : 544.8570 (M+H)⁺; t_R : 17.766 min.

Microwave assisted synthesis of 1,3,5-tris(4-diethylphosphonophenyl)benzene (Et₆btbp).

543 mg of btbBr (1 mmol), 19 mg of NiCl₂ (0.15 mmol), 2.5 mL of triethylphosphite (2.57 g, 15 mmol), and an appropriate magnetic stirring bar were introduced in a 2-5 mL glass vial. The vial was sealed with a cap and inserted in the heating lid of a Biotage Initiator instrument. The

instrument was set to operate with the following parameters: Power: Off, Temperature: 225 °C, Pressure: 15 bar, Absorption: High, Cooling: Off.

The mixture was allowed to react for 45 minutes once the set temperature was reached. A sudden pressure increase from 5 bar to 10 bar was observed after 40 minutes. The vial was then cooled and degassed by inserting a needle. The vial was opened, the mixture was diluted with chloroform and filtered over silica to remove the nickel containing residue. The pale yellow solution was then vacuum distilled to remove chloroform, triethylphosphite and diethyl ethylphosphonate. The raw mixture was treated with petroleum ether, yielding 585 mg of Et₆btbp as a white waxy solid that was vacuum filtered and characterized. (Yield = 82%)

¹H-NMR (CDCl₃, 400 MHz): δ = 7.97 (dd, J_1 = 13.2 Hz, J_2 = 8.0 Hz, 6H), 7.86 (s, 3H), 7.81 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 6H), 4.13-4.26 (m, 12 H), 1.39 (t, 18H) ppm.

³¹P-NMR (CDCl₃, 400 MHz): δ = 19.76 ppm.

LC-MS: m/z : 715.2354 (M+H)⁺; t_R : 12.986 min.

Microwave assisted synthesis of 1,3,5-tris(4-phosphonophenyl)benzene (H₆btbp).

500 mg of Et₆btbp were dissolved in 3 mL of a 1:1 1,4-dioxane/ HCl12 M mixture inside a 2-5 mL vial equipped with an appropriate stirring bar. The vial was sealed with a cap and inserted in the heating lid of a Biotage Initiator instrument. The instrument was set to operate with the following parameters: Power: Off, Temperature: 120 °C, Pressure: 10 bar, Absorption: Very High, Cooling: On.

The mixture was allowed to react for 10 minutes once the set temperature was reached. At the end of the reaction the vial was cooled and opened. The solvent was evaporated and the raw mixture was treated with tetrahydrofuran, yielding 410 mg of H₆btbp as a white solid. (Yield = 82%)

¹H-NMR (CD₃OD, 400 MHz): δ = 7.89-7.94 (m, 9H), 7.82 (dd, J_1 = 8.0 Hz, J_2 = 3.2 Hz, 6H) ppm.

³¹P-NMR (CDCl₃, 400 MHz): δ = 15.39 ppm.

LC-MS: m/z : 547.0478 (M+H)⁺; t_R : 0.414 min.

Synthesis of $Zr_3(H_3btbp)_4 \cdot 15H_2O$ (Zrbtbp).

233 mg of $ZrCl_4$ (0.2 mmol) were dissolved in 2.1 mL of HF 2.9 M (6 mmol) in a plastic bottle; 6 mL of water and 2 mL of methanol were added to this solution. 110 mg of H_6BTBP (0.2 mmol) were finally added, the bottle was closed and put in a oven at 80 °C for 3 days. The white solid formed was filtered under vacuum, washed repeatedly with water and methanol and dried at 80 °C. 72 mg of product were recovered. (Yield: 53%, based on H_6BTBP)

Analysis: Calcd for $C_{32}H_{34}O_{17}P_4Zr$: C = 42.4%, H = 3.8%, P = 13.7%, Zr = 10.0%; Found: C = 42.1%, H = 4.5%, P = 13.5%, Zr = 10.1%.

Hydrolysis resistance tests.

About 70 mg of Zrbtbp underwent repeated treatments to check the stability towards hydrolysis. The test conditions were the following: 2 hours in refluxing water, 16 hours at 150 °C in water, 2 hours in refluxing HCl 0.1 M, 16 hours at 150 °C in HCl 0.1 M. The same solid was used for all of the treatments. For the reflux treatments, the solid was put in a 100 mL round bottom flask with 10 mL of solvent and the mixture was refluxed for 2 hours; for the 150 °C treatments, the solid was put in a hydrothermal bomb with 10 mL of solvent and heated under autogenous pressure for 16 h. After each treatment, the solid was filtered under vacuum, washed with water and methanol, and dried at 80 °C. At the end of each treatment, the weight of the solid was checked, showing a less than 10% loss, imputable to incomplete recovery of the material.

UiO-66 was also prepared and tested for comparison.

For both compounds a larger weight loss of the order of 25-30% was observed after the harsher treatment, indicating that part of the samples was dissolved or reduced to very small size and finely dispersed in the solution.

Water uptake tests.

30.7 mg of Zrbtbp were put in an uncapped weighing bottle and heated at 80 °C for 2 hours to evacuate the water held inside the structure. The weighing bottle was capped and left at room temperature until it cooled down: the weight loss of the sample was calculated to be about 11%, in agreement with the value observed from TGA. After 1 hour of exposure at moist air at room temperature, the initial weight was completely recovered. PXRD patterns of the material were also collected, showing that no substantial differences existed before and after the treatment.

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. Carbon and hydrogen contents were determined by elemental analysis by NuMega laboratories (La Jolla, CA, USA).

Liquid Chromatography-Mass Spectroscopy. LC-MS analyses were performed with an Agilent 6540 UHD Accurate Mass Q-TOF instrument, using an Agilent Jetstream source and an Agilent Zorbax Eclipse Plus C18 RRHD 2.1 × 100 mm × 1.8 μm reverse phase column with CH₃CN/H₂O + 0.1% formic acid as eluent for btbBr and Et₆btbp. For H₆btbp, an Agilent Zorbax Eclipse Plus C18 RRHD 2.1 × 50 mm × 1.8 μm reverse phase column was used with CH₃CN/ammonium acetate 10 mM in H₂O as eluent.

Powder X-Ray Diffraction. The PXRD pattern used for structure solution and Rietveld refinement was collected in the 5-90 2θ 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 40kV and 40mA. To minimize preferential orientations of the microcrystals, the sample was carefully side-loaded onto an

aluminum sample holder. The sample was kept at 100 °C by means of a custom made peltier equipped sample holder during the data collection.

Temperature dependent X-ray diffraction. Thermodiffractometric analysis (TDXD) was performed under air with an Anton Paar HTK 1200N hot chamber mounted on a Philips XPERT' PRO diffractometer in the 50 - 400 °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 under a stream of N₂ using a TA Instrument Q600 SDT running from room temperature to 1200 °C with a heating rate of 5 °C/min.

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

N₂ and CO₂ Adsorption. ~30-100 mg of Zrbtbp were evacuated under vacuum for a minimum of ~3 h at 120 °C. The sample was then transferred to a pre-weighed sample tube and degassed at 105 °C on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mmHg/min. The sample tube was re-weighed to obtain a consistent mass for the degassed material. Brunauer-Emmett-Teller (BET) surface area (m²/g) measurements were collected at 77 K with N₂ on a Micromeritics ASAP 2020 Adsorption Analyzer using a volumetric technique. The sample was then manually degassed for at least 2 h prior to N₂ and CO₂ isotherm.

CO₂ measurements were performed up to 1 bar at 196 K with a Micromeritics ASAP 2020. A known weight of the compounds, typically 50 mg, was placed into a sample tube, then the change of the pressure was monitored and the degree of adsorption was measured by the decrease of the pressure at the equilibrium state.

Structure Determination and Refinement. The crystal structure of Zr₆(btbp)₈ 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 *ChekcCell* program, which suggested five possible space groups: *P6₃mc*, *P-62c*, *P6₃/mmc*, *P3c1*, and *P-31c*. Combining information about the stoichiometry (P/Zr ratio = 4) and the need to place an integer number of tritopic btbp ligands inside the unit cell, it was concluded that the cell content was necessarily constrained to be multiple of 3 Zr and 4 btbp (12 P). Since none of the possible space groups allows to place an odd number of atoms in the unit cell, the correct unit cell content was found to be 6 Zr and 8 btbp. Then, attempts to localize at least the Zr atoms were carried out with the program *EXPO*, trying every possible space group. The most reliable positions for the Zr atoms were found in the space group *P-31c*: these positions (one special position with multiplicity of 2 and one special position with multiplicity of 4, giving rise to 0D inorganic building units with internal Zr-Zr distance of about 5.2 Å) resembled those of the inorganic building unit observed in a previously reported compound (see ref. 5c in manuscript). On the basis of this information, the structural model was determined using the real space global optimization methods implemented in the *FOX* program: two independent fragments were input, each consisting of one third of a btbp molecule with one of its oxygen atoms bound to a zirconium atom placed in one of the positions provided by *EXPO*. 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 = 3.5 Å, C-O = 2.5 Å, O-O = 2.5 Å. The ZrO₆ octahedra and the complete btbp molecules were generated by symmetry. Rietveld refinement of the structural model was performed using the *GSAS* program.

Analogous trials were carried out in the remaining possible space groups, generating unrealistic stereochemical models.