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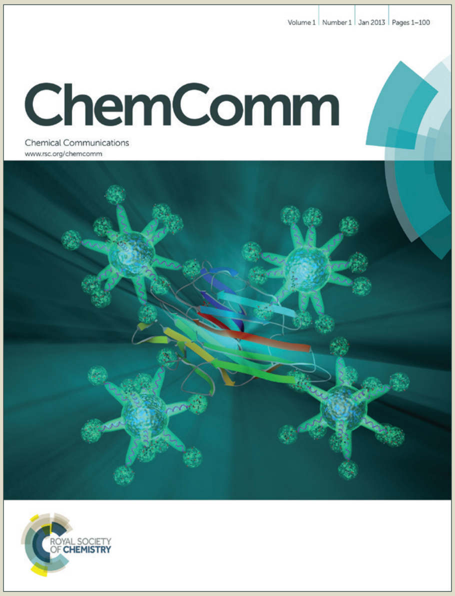

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ARTICLE TYPE

The first route to highly stable crystalline microporous zirconium phosphonate metal-organic frameworks

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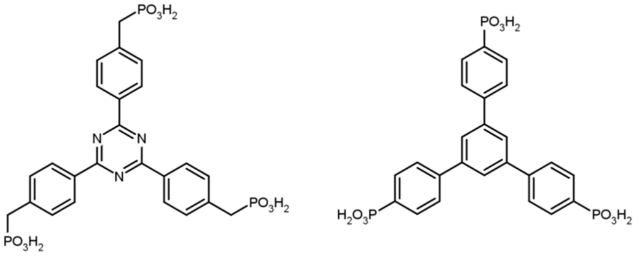
The first crystalline microporous zirconium phosphonate Metal-Organic Framework (UPG-1) was synthesized using the novel tritopic ligand (2,4,6-tris(4-(phosphonomethyl)phenyl)-1,3,5-triazine. Its crystal structure was solved ab initio from laboratory powder X-ray diffraction data. UPG-1 displays remarkable thermal stability and hydrolysis resistance and has a good absorption affinity towards *n*-butane and CO_2.

Metal-Organic Frameworks (MOFs) based on Zirconium (hereafter Zr-MOFs) are attracting a growing interest in the scientific community due to their unique features in term of enhanced robustness and stability towards high temperature and hydrolysis.[1] As a matter of fact, as compared to the vast number of MOFs reported in the literature, MOFs containing Zr oxo clusters as Secondary Building Units (SBUs) are much more resistant to aggressive conditions and then useful for applications in which an enhanced stability is required, such as heterogeneous catalysis in oxidizing reagents,[2] CO_2 storage and separation from industrial flue gases,[3] and so on. The Zr-MOFs reported in the literature are based either on simple aromatic carboxylates, such as terephtalic acid (UiO-66 and MIL-140),[1a,b] or on more bulky ligands like pyrene- (NU-1000)[1c] and porphyrine-tetracarboxylates (PCN-222, 224 and MOF 525, 545).[1d,e,f]

Phosphonate ligands are considered as good candidates for the attainment of highly robust MOFs as well, despite their marked tendency to yield extended dense structures. Indeed, only a few examples of crystalline phosphonate based MOFs with permanent microporosity were reported to date, mostly based on divalent or trivalent metals.[4]

In this context, the preparation of zirconium phosphonate MOFs with permanent porosity is an attractive goal that, in the past, has been mainly pursued by combining small and large ligands, in order to generate interlayer microporosity.[5] However, the obtained compounds suffered from scarce crystallinity and stability. There are also some examples of micro- and meso-porous zirconium phosphonates displaying absorption and separation properties, but none of them was obtained in microcrystalline form, therefore their structure was not determined.[6] On the other hand, a few crystalline open-framework zirconium phosphonates were reported, but they did not display permanent porosity.[7] From the above considerations, it emerges that the synthesis of microporous and crystalline Zr phosphonate MOF has been a challenge to date.



H_6ttbmp H_6btbp

Chart 1 Molecular structure of H_6ttbmp, in comparison with that of H_6btbp.

In a recent paper, we used a tritopic phosphonic ligand with zirconium, namely the 1,3,5-tris(4-phosphonophenyl)benzene (H_6btbp), in order to prevent the formation of dense layered motifs.[8] The obtained compound (Zrbtbp) had an unprecedented honeycomb-like layered structure, featuring large cavities, but no permanent porosity was detected. The lack of porosity was attributed to the formation of zero-dimensional (0D) inorganic building units, which did not allow the expansion of the structure in the third dimension. Moreover, the layers stacked in such a way that the cavities were capped, thus making them non accessible to N_2 and CO_2. The btbp ligand is very rigid and can only adopt a planar arrangement, which might induce the formation of the layered structure of Zrbtbp. A further improvement was then addressed to the synthesis of a similar tritopic ligand possessing a slightly higher conformational freedom: the novel (2,4,6-tris(4-(phosphonomethyl)phenyl)-1,3,5-triazine (hereafter H_6ttbmp), whose structure is shown in Chart 1. To the best of our knowledge, this ligand was never used for the preparation of MOFs.

H_6ttbmp and H_6btbp differ for two main features: the inner core in H_6ttbmp is an s-triazine instead of the benzene in H_6btbp, simply because the precursor 4-(bromomethyl)benzonitrile is a commercially available and cheap product; furthermore, H_6ttbmp contains benzylphosphonic groups in place of phenylphosphonic groups, in order to impart some flexibility to the molecule. Details of the synthesis of H_6ttbmp are reported in the ESI: it was carried out in three steps, each with a very good yield (96%, 95%, and 85%, respectively).

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The synthesis of the Zr-MOF based on ttbmp (hereafter UPG-1, UPG = University of Perugia) was carried out in water/methanol at 80 °C starting from $ZrOCl_2$ and using hydrofluoric acid as a mineralizer (see ESI for details). UPG-1 is a very insoluble compound and it is obtained as a microcrystalline powder. Its formula is $Zr[H_4ttbmp]_2 \cdot 10H_2O$. The crystal structure of UPG-1 was solved and refined by laboratory Powder X-Ray Diffraction (PXRD) data. It crystallizes in the trigonal space group R -3 and its lattice parameters are a = 60.674(2) Å, c = 5.1278(3) Å. Final Rietveld and difference plot is shown in Figure 1 (see ESI for crystallographic data and refinement details).

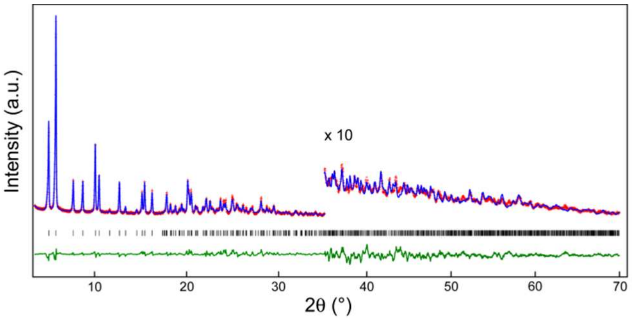

Fig. 1 Final Rietveld and difference plot for UPG-1.

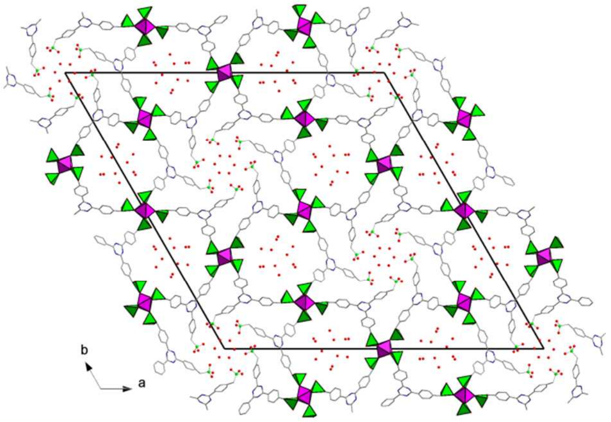

Fig. 2 The crystal structure of UPG-1 viewed along the c-axis. ZrO_6 octahedra are represented in purple, coordinating PO_3C tetrahedra are in green.

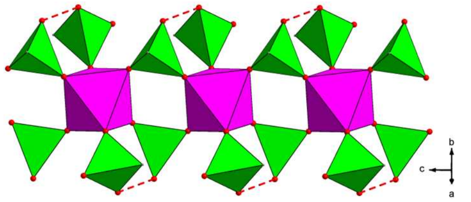

Fig. 3 The structure of the inorganic chains found in UPG-1. ZrO_6 octahedra are represented in purple, PO_3C tetrahedra are in green. Hydrogen bonds are represented as red dashed lines.

The cell volume of 16348 Å^3 is by far the largest ever reported for any zirconium phosphonate, and the calculated density of 1.25 g cm^{-3} matches that of the anhydrous form of Zr-btbp as the lowest ever observed. The calculated solvent accessible volume is about 5367 Å^3, which represents the 32.8% of void volume. H-atoms were omitted in the structural refinement but considered for the void calculation. The structure of UPG-1 is shown in Figure 2.

The open framework structure is based on the connection of 1D chains, composed of ZrO_6 octahedra and PO_3C tetrahedra and extended along the c-axis, via the ttbmp ligands. The zirconium atom lies on an inversion center and it is coordinated by six oxygen atoms belonging to six different phosphonate tetrahedra: two of them are monodentate, whereas the remaining four are bidentate, connecting zirconium atoms along the c-axis, as shown in Figure 3. Inorganic chains based on the same connectivity were previously observed only in another 3D zirconium phosphonate.[9]

Each ttbmp ligand features three different phosphonate groups: two of them are connected to the zirconium atoms as described above, whereas the third is non coordinated and points toward the *-3* symmetry operator; it is worth to note that uncoordinated phosphonate groups are rarely found in similar systems. The ttbmp ligands are efficiently stacked along the c-axis direction, acting as bridges between adjacent inorganic chains. Two kinds of channels with different sizes are formed in the structure: one has a free diameter of about 10 Å, and it is lined by both free P-O groups and aromatic rings; the other has a free diameter of about 5 Å and is lined only by the uncoordinated PO_3C groups (Figure 1S). 10 water molecules per Zr atom are accommodated in these channels and are involved in intricate hydrogen bond networks.

The use of the more flexible ttbmp ligand, if compared with the previously reported btbp, allowed a crucial improvement to the framework assembly process: as a matter of fact, the possibility of the phosphonic tetrahedra to be out-of-plane with respect to the aromatic internal core induced a different connection to zirconium atoms thus overcoming the formation of 0D SBU found in Zr-btbp, which were stacked in an unfavourable way to form infinite channels. In UPG-1 the conformation of the ligand favoured the assembly of infinite 1D CBUs running along the c-axis and the hexagonal channels here formed are accessible to gases.

The comparison of the PXRD patterns for the as-synthesized and the anhydrous compound suggests that the structure undergoes small changes upon removal of water. This process is fully reversible and the solvent can be re-adsorbed if the solid is kept in hot water (Figure 2S). Unfortunately, the diffraction pattern of the anhydrous compound shows a relevant loss of crystallinity, not allowing a complete crystal structure refinement. However, a full profile refinement procedure, performed with the Le Bail method, on UPG-1 outgassed at 160 °C for 24 h, that is after the same treatment used before performing gas adsorption measurements (Figure 3S), revealed that the crystal structure and space group of the as synthesized compound were found to be retained. The refined unit cell parameters [a = 59.071(2) Å, c = 5.202(1) Å] show a very small change, and the volume of this cell, 15720(3) Å^3, is about 4% smaller than that of the hydrated compound, suggesting that the solid retains its crystalline framework upon dehydration.

^{13}C CP MAS NMR spectrum of UPG-1 (Figure 5S) exhibits the presence of the organic phosphonate ligand and a signal multiplicity in agreement with the number of independent carbons in the unit cell. No impurities are shown.

Field Emission-Scanning Electron Microscopy (FE-SEM) images (Figure 6S) show the elongated morphology of the microcrystals as prismatic rods with sizes ranging from 0.5 to 10

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μm, measured along the elongation axis. Some crystals clearly show the hexagonal morphology of the terminal face of the prisms, thus suggesting that the crystal symmetry reflects that of the ligand.

The permanent porosity of UPG-1 was demonstrated by adsorption isotherms of gases. The CO_2 isotherm at 195 K, reported in Figure 4a, shows a Langmuir type-I profile which reaches the value of 112 cm^3/g (22 wt%) at 1 bar. The compound exhibits BET and Langmuir surface areas of 410 m²/g and 514 m²/g, respectively, as calculated by using the relative pressure range $0.02<P/P_0<0.15$. Considering the empty space of 4450 $Å^3$ per unit cell, as explored by a probe sphere of 1.6 Å equal to the kinetic radius of CO_2, and the maximum measured CO_2 capacity of 5 mmol/g, a CO_2 density of 1.07 cm^3/g was calculated. This value is in agreement with the density of CO_2 in the liquid state and enabled the estimation of 0.2 cm^3/g pore volume. This result indicates the complete filling of both large and small channels (10 and 5 Å diameter) which are easily accessible to gas species via diffusion. Considering the uptake values, the effectiveness of this system exceeds that of microporous copper-phosphonate MOFs recently published[4f] and is comparable with microporous phosphonate-based MOFs such as MIL-91(Ti), MIL-91(Al),[4b] phosphonate monoesters with Zn(II),[4e] and the Zr-based MOFs MIL-140 A and MIL-140 B. N_2 adsorption isotherm at 77 K showed a negligible gas uptake probably due to the slow adsorption kinetics at such low temperature.[4e] Contrarily, in the case of CO_2 the higher temperature of adsorption isotherm and the quadrupole moment facilitated the penetration of gas molecules into the cavities.

In order to investigate selective CO_2 capture with respect to other gases, we collected CO_2, CH_4, and N_2 adsorption isotherms of UPG-1 under the mild temperature conditions of 273 and 298 K (Figure 4b). N_2 adsorption isotherms up to 10 bar still show low uptake values and the amount is proportional to the pressure in the range up to 10 bar, indicating an extremely low nitrogen affinity for the absorbent. Concerning CO_2, the maximum uptake values were found to be 76 cm^3/g and 69 cm^3/g at 10 bar, corresponding to 150 mg/g and 136 mg/g for CO_2, respectively. The compound exhibits a good binding affinity for CO_2, as shown by the isosteric heat of adsorption, Q_{st}, of 24 kJ/mol as calculated by Clausius-Clapeyron equation, indicating the formation of favourable interactions of CO_2 with the aromatic rings and the phosphonate groups lining the inner surface of the pores.[9] These results can be exploited favourably for selective absorption of carbon dioxide in a mixture with nitrogen. The selectivity of CO_2/N_2 binary mixtures was determined from the single-component isotherms using ideal adsorbed solution theory (IAST),[10] which has been successfully employed to calculate gas mixture separation by microporous materials. Under the mild conditions of room temperature and low pressure, UPG-1 shows CO_2/N_2 selectivity of 24, in a 15:85 CO_2/N_2 binary mixture, which is representative of industrial operative conditions (Figure 7S). Moreover, the UPG-1 material is selective for CO_2 with respect to CH_4, highlighting the stronger affinity of the system to CO_2 due to its quadrupolar nature.

Interestingly, this system can efficiently adsorb hydrocarbons such as *n*-butane (Figure 4c). The slope at low partial pressure of butane is very steep indicating that butane molecules can favorably interact with aromatic rings of the host structure through $CH\cdots\pi$ interactions. No hysteresis between adsorption and desorption curves was found and, at $P/P_0 = 0.95$, 48 cm^3 STP/g of adsorbed *n*-butane was measured. Considering the density of the liquid *n*-butane at 273 K equal to 0.602 g/cm^3, the limit uptake value of 0.2 cm^3/g can be estimated. Such value is in agreement with that estimated from CO_2 occupancy at saturation at 195K.

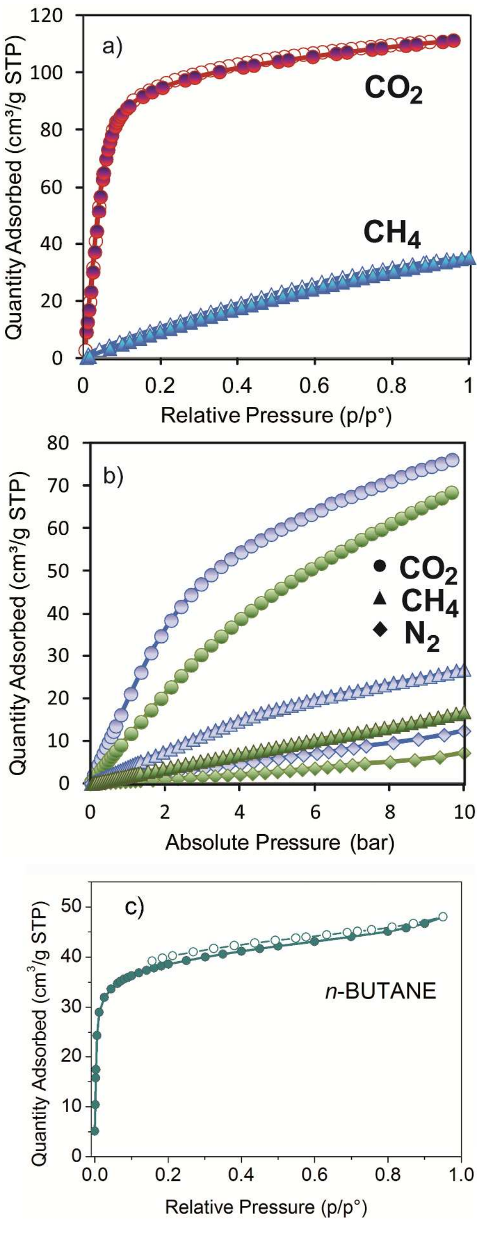

Fig. 4 Adsorption isotherms of porous UPG-1 compound: a) CO_2 (red circles) and CH_4 (blue triangles) isotherms at 195 K and 1 bar, the desorption isotherms are indicated by white circles and triangles, respectively; b) CO_2, CH_4 and N_2 adsorption isotherms collected at 298 K (green labels) and 273 K (blue labels) and up to 10 bar. c) *n*-butane adsorption (filled circles) and desorption (void circles) isotherms at 273 K on UPG-1.

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UPG-1 displays a remarkable thermal stability. Thermogravimetric (TGA) and temperature dependent X-ray diffraction (TDXD) analyses are reported in Figure 8S and 10S, respectively. Based on the TDXD analysis, the compound is stable up to about 430 °C. Between 350 and 400 °C the sample undergoes a phase transformation evidenced by a slight displacement of the first two peaks which are moved towards higher 2θ angles. This new phase is stable up to 430 °C and, after that temperature, the framework collapses and the peaks relative to the formation of zirconium pyrophosphate appear. The thermal stability is then higher than the related Zrbtbp material previously reported and comparable to other carboxylate based Zr-MOFs like UiO-66 and MIL-140.

The stability towards hydrolysis was also investigated by treating UPG-1 in various conditions (see ESI for details). The compound fully retained the crystallinity and the amount of the solid recovered, after each treatment, was nearly the same than the initial weight, indicating that no significant dissolution occurred, whereas in the same conditions UiO-66 underwent partial hydrolysis (Figure 11S and 12S).

Conclusions

A novel Zr-MOF based on a phosphonate ligand is here presented. To the best of our knowledge it represents the first crystalline microporous MOF based on zirconium phosphonate. In this work we found that, by using a tritopic phosphonic ligand with a higher flexibility degree if compared with the previously reported btbp ligand, it was possible to induce the formation of an open framework structure with accessible channels. UPG-1 has permanent microporosity and good selectivity towards CO_2 over N_2, enhanced thermal stability and outstanding resistance to hydrolysis. Future efforts will be addressed to the use of ligands similar to ttbmp, in order to investigate the possibility to obtain other microporous compounds and to perform isoreticular syntheses.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Crystallographic Information File (CIF) for UPG-1 (CCDC: 1013734). Refinement details. Additional figures. Experimental part.]. See DOI: 10.1039/b000000x/

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