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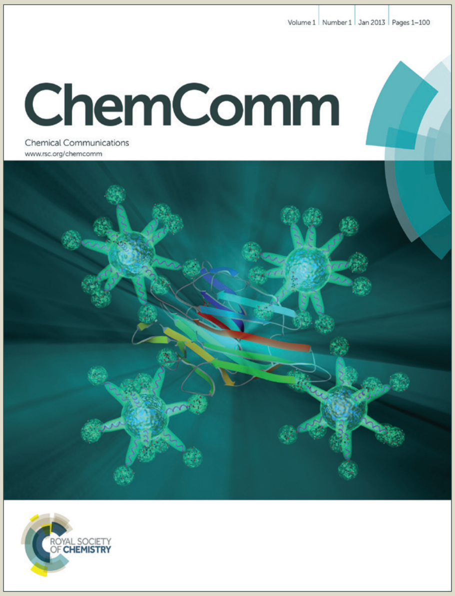

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The use of a rigid tritopic phosphonic ligand for the synthesis of a robust honeycomb-like layered zirconium phosphonate framework

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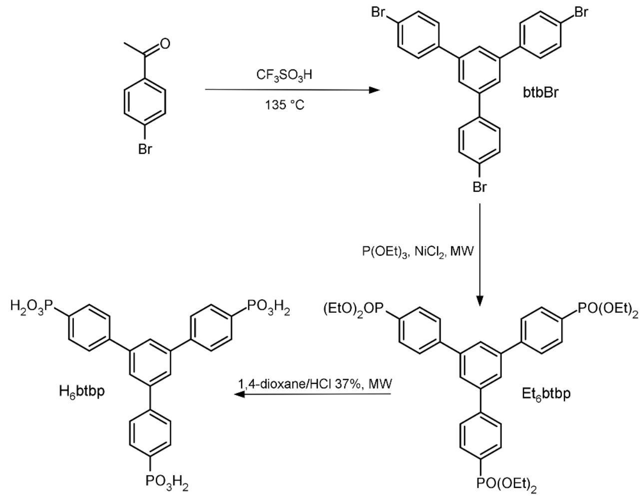
1,3,5-tris(4-phosphonophenyl)benzene was synthesized via a microwave heating assisted route and was subsequently used for the preparation of a new zirconium phosphonate with honeycomb-like structure displaying remarkable thermal stability and hydrolysis resistance.

The search for new porous open framework architectures, built from the connectivity of organic ligands and metal ions, has been a popular topic of interest since metal-organic frameworks (MOFs) have become promising materials for a number of applications.[1] Among MOFs, only a few examples utilize metal phosphonates,[2] which seem to be far less prone to create open frameworks than the more commonly used metal carboxylates. The difference in the use of these systems likely arises from the geometrical arrangement of the PO_3C group, which favours the formation of highly connected inorganic clusters, often leading to dense structures.[3] In contrast, many metal carboxylate based frameworks are limited by their low chemical stability, especially towards hydrolysis, which metal phosphonates are far more resistant to. A particularly notable exception are the zirconium carboxylate MOFs that show remarkable chemical and thermal stability.[4] Therefore, combining phosphonate ligands and zirconium to prepare new MOFs may represent an important step for obtaining very robust materials.

Zirconium phosphonates are a class of compounds known to be highly insoluble and thermally and chemically resistant, and have proven to be versatile materials.[5] However, to date they revealed to be not truly suitable for the rational design of porous materials because of their strong tendency to form dense layered structures, and only a few examples of porous compounds have been reported.[6] In this work, we describe the use of 1,3,5-tris(4-phosphonophenyl)benzene (H_6btbp): such a rigid phosphonate ligand, having trigonal shape, should avoid the formation of undesired densely packed structures. As a matter of fact, this ligand has recently been investigated as a potential candidate for the preparation of phosphonate based MOFs.[7] For example, Shimizu and co-workers reported on a porous Sn(IV) phosphonate framework based on this ligand,[7c] and, even though the crystallinity of the compound was insufficient for structural characterization, it was shown that the trigonal phosphonate ligand could be used to form new stable porous materials.

Herein, we report on the microwave-assisted preparation of the H_6btbp ligand (Scheme 1) and the synthesis and structural characterization (from powder X-ray diffraction data, PXRD) of a zirconium framework with this building block.

The synthesis of aromatic phosphonates is usually performed following a modified Arbuzov procedure that involves the use of a metal salt, typically a Ni(II) or Pd(II) halide, to promote the nucleophilic aromatic substitution of triethylphosphite (TEP) on the haloaromatic substrate.[8]



Scheme 1 The synthesis of 1,3,5-tris(4-phosphonophenyl)benzene (H_6btbp)

The use of microwave irradiation for the synthesis of several aromatic monophosphonic esters was recently described,[9] but in this work we developed an efficient method for the preparation of the hexaethyl ester of btbp (hereafter Et_6btbp); in our case the major challenge was to find the optimal conditions for ensuring the complete conversion of the starting reagent into the triphosphonic ester, with no residual undesired monosubstituted or disubstituted products. The microwave-assisted preparation of Et_6btbp from the tribromide precursor (hereafter btbBr) afforded an 82% yield, considerably reducing both the reaction time and the amount of catalyst, compared to the conventional approach; in addition, no solvent was used to perform the reaction (Table 1).

Table 1 Comparison between the conventional and the microwave-assisted routes for the synthesis of Et_6btbp.

	conventional heating[a]	MW-assisted
time	20 h	45 min
temperature	180 °C	225 °C
solvent	1,3-diisopropylbenzene	no solvent
TEP/Br ratio	6	5
mol% Ni catalyst	17%	5%
isolated yield	60%	82%

[a] See Ref. 7c

Furthermore, we performed the microwave assisted hydrolysis of the ester, which was completed after just 10 min of microwave heating at 120 °C in 1,4-dioxane/HCl (the typical procedure requires overnight heating to reflux in concentrated HCl). The final yield of H_6btbp was 67%, based on the starting amount of btbBr.

The synthesis of the zirconium derivative was attempted in both aqueous media, the usual route for the preparation of zirconium phosphonates, and dimethylformamide (DMF), the most common solvent for the preparation of MOFs. By combining $ZrOCl_2 \cdot 8H_2O$ and H_6btbp at 80°C in a mixture of water and methanol in the presence of HF as a mineralizer, a compound of formula $Zr_3(H_3btbp)_4 \cdot 15H_2O$ (hereafter Zrbtbp) was obtained and characterized. Use of DMF inevitably afforded crystallization of the dimethylammonium salt of the ligand; the formation of this species is evidence that the coordination of btbp to Zr(IV) in this solvent is prevented by the hydrolysis of DMF to yield formic acid and dimethylamine (likely promoted by the strong acidity of the ligand). Hence, DMF does not seem to be suitable for these frameworks under the present conditions. It is notable that varying the synthetic parameters (F/Zr ratio, P/Zr ratio, time, temperature) did not produce other phases. Zrbtbp was always obtained, although with different degrees of crystallinity, indicating that this compound is highly favored and no other structural arrangements are easily accessible with the btbp ligand.

The structure of the dehydrated form of Zrbtbp (Zrbtbp-a) was solved from PXRD data (Table S1 and ESI for details). Zrbtbp-a crystallizes in the space group $P\text{-}31c$ and its lattice parameters are a = 16.3472(8) Å, c = 28.021(2) Å (final Rietveld and difference plots are shown in Figure S1). It is a layered compound, in which every layer is based on the connection of discrete inorganic building units (IBUs), each containing three ZrO_6 octahedra; these IBUs are not a common motif and have only been previously observed in a recently reported 3D Zr phosphonate (Figure 1).[5c]

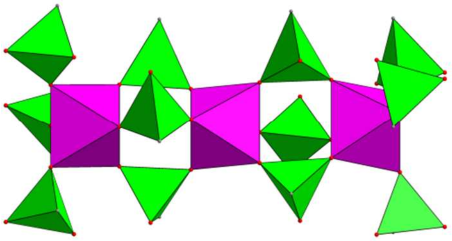


Fig. 1 Structure of the IBU found in Zrbtbp-a. ZrO_6 octahedra are represented in purple, PO_3C tetrahedra are represented in green.

The IBUs are connected in the *ab* plane via the bridging organic ligands, so that an extended inorganic connectivity is missing. The central ZrO_6 octahedron is connected with two crystallographically equivalent terminal ZrO_6 octahedra; six bidentate PO_3C tetrahedra connect the central octahedron to the terminal ones and six monodentate PO_3C tetrahedra (three per terminal Zr atom) fill the remaining vertices of the terminal octahedra. Each IBU is connected to its six nearest neighbors by means of three stacks of four btbp ligands, thus giving rise to layers having considerable thickness (about 14 Å) and showing large open regions, with an available space of about 10 Å diameter, which are likely filled with disordered water molecules in the hydrated phase (Figure 2, Figure S2).

The layers stack on each other along the c-axis direction with an ABA sequence, so that every open region of one layer is capped by IBUs belonging to adjacent layers (Figure 3a, Figure S3); stacking occurs via different types of noncovalent interactions: a number of possible hydrogen bonds between the free P-O groups belonging to adjacent layers is observed, based on the O-O mean distances.

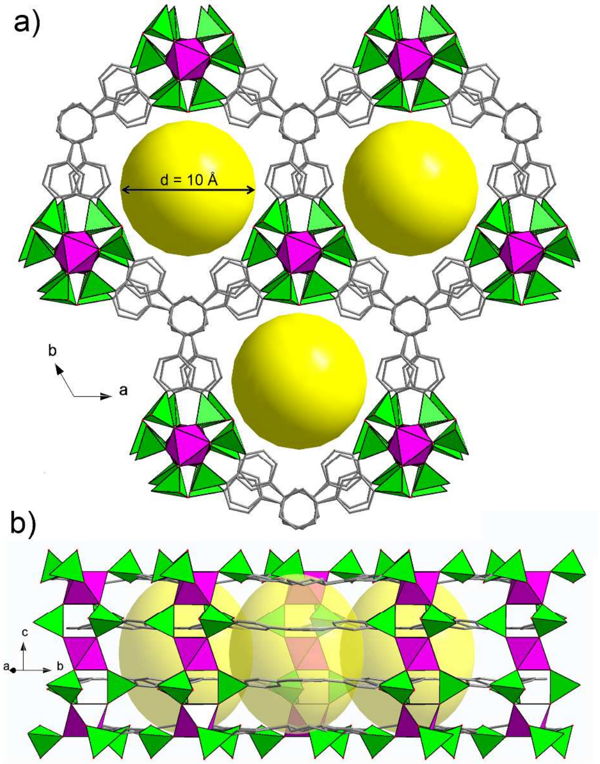


Fig. 2 View of a single layer of Zrbtbp-a along (a) and perpendicular (b) to the c axis.

The central phenyl rings of the btbp molecules are involved in π-π stacking interactions infinitely extended along the c-axis direction (the peripheral rings are not perfectly aligned and are not well stacked even within a single layer) (Figures S3, S4). The combined effect of these interactions results in an efficient stacking of the layers. Indeed, the crystallites show a hexagonal prismatic morphology rather than the common lamellar morphology expected for a layered compound, indicative of the stacking along the c-axis (Figure 3b). The structure of the hydrated form was not solved because the presence of water molecules likely induces a disordering in the layered arrangement, causing a considerable loss of crystallinity (Figure S5). The calculated void volume on the basis of the crystal structure is about 35% of the total volume.

However, despite the open framework structure of each layer and the capability of the compound to reversibly uptake 30 water molecules per unit cell, Zrbtbp was not porous to N_2 (BET surface area <10 m^2/g) and showed a low CO_2 adsorption capacity (33.2 cm^3/g, 6.5 wt%, measured at 196 K and 1 atm, Figure S6).[10] As previously noted, this fact can be mainly ascribed to the mutual capping of the layers cavities due to the alternate stacking along the c-axis. The void volume is comparable to many other similar microporous materials, so that it would be desirable to make these voids accessible through an efficient exfoliation process or by increasing the interlayer distance.

The stability of Zrbtbp was investigated and compared to that of the benchmark Zr based MOF UiO-66, performing thermogravimetric analysis (TGA), temperature-dependent X-ray diffraction, TDXD), and hydrolysis tests (Figures S7-S9). Zrbtbp did show good thermal stability up to almost 400 °C. Hydrolysis resistance was tested under several conditions, with the crystallinity of the material completely unchanged even after 16 h at 150°C in 0.1 M HCl. In light of these results, we can assess that Zrbtbp and UiO-66 have comparable stability.

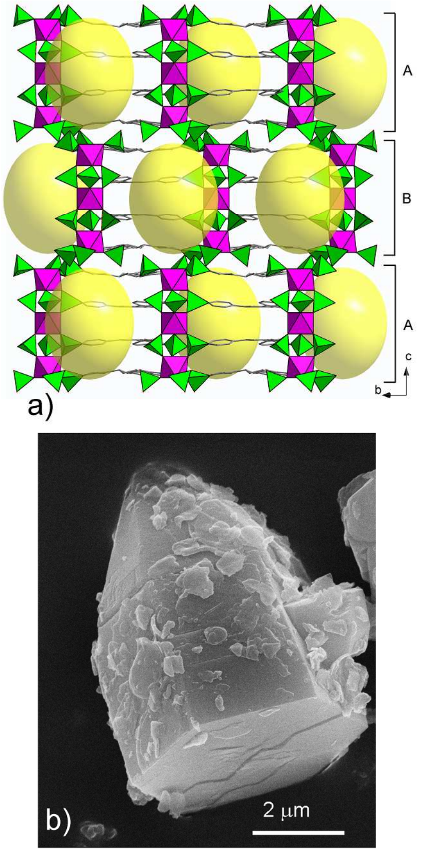


Fig. 3 View of the stacking of layers in Zrbtbp-a (a) and SEM image of a microcrystal (b).

In conclusion, we developed a microwave assisted route for the synthesis and hydrolysis of Et$_6$btbp in solvent-free conditions, reducing both the reaction time and the amount of catalyst, to obtain H$_6$btbp. The trigonal shape of the btbp ligand allowed us to obtain the desired honeycomb-like motif when combined with zirconium, though the presence of zero dimensional IBUs prevented the expansion of the structure in the third dimension. Despite the non porosity, Zrbtbp represents a promising first step towards the attainment of chemically and thermally stable porous open framework zirconium phosphonates based on tritopic ligands, owing to the following features: large void regions are formed, accounting for 35% of the total volume, and the density is unusually low if compared to other zirconium phosphonates (1.25 g/cm^3 for the dehydrated form, whereas typical densities range around 2 g/cm^3), the thermal analysis and the TDXD reveal a good thermal stability, and the compound's resistance to hydrolysis ranks among the highest reported to date. Efforts are currently being devoted to prepare other tritopic ligands and their zirconium derivatives.

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Notes and references

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10 Zrbtbp was activated by evacuating 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 for a minimum of 12 h or until the outgas rate was <5 mmHg/min.