

A highly porous three-dimensional aluminum phosphonate with hexagonal channels: synthesis, structure and adsorption properties†

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A 3D porous aluminum(III) trisphosphonate, constructed from 1D inorganic aluminum phosphate chains and tripodal organic linkers, contains large hexagonal channels (1.24 nm in diameter) and a highly accessible void (50.3%) which allow it to have a fast and relatively high uptake of H₂, N₂ and CO₂.

Metal-organic frameworks (MOFs) or porous coordination polymers (CPs) have attracted a great deal of interest in the past two decades for their promising applications in the field of gas storage,¹ separation² and catalysis,³ which are mainly related to their high porosity, high specific surface area and pore size/shape tunable character. Understanding the structure-property relationship and controlling the structures and properties of MOFs are vital to maximize the gas storage capacity and separation efficiency. Effective strategies, including enlargement of surface area and pore size, proper pore shape, high unsaturated coordination site density, and so on, have been developed to improve the design, synthesis and gas storage capacity.^{4–6} However, chemical and physical stability must be considered to reach the requirement of application. Currently most studied MOFs are assembled from rigid or flexible carboxylic acids and N-containing neutral ligands with first-row transition metals. Some of them really have very good performance in terms of gas capacity and selective uptake but suffer from poor stability, for example ZnO₄ tetrahedra tend to hydrolyse in the presence of water vapor.^{7,8}

We have special interest in the design and synthesis of metal phosphonates for their intriguing structures, properties and importantly their close relationship to aluminum silicate or phosphate zeolites which are chemically and mechanically robust.⁹ Shimizu and coworkers reported that the water stability of MOFs can be greatly enhanced *via* phosphonate

monoester linkers.¹⁰ However, metal phosphonates are usually not porous but have layered structures which are not suitable for the application of gas storage/separation. For a long time porous metal phosphonates were very rare and very few were tested for gas storage/separation application.^{11–14} Al(III) has long been the focus of research interest in the field of MOFs in the consideration of enhancing weight gas uptake^{15–20} and at the same time it is also the important component of zeolites. Thus we decided to continue our work to explore new Al-phosphonates with novel structure, high porosity and good stability. But it is a challenge to construct porous Al-phosphonates due to poor crystallinity. Until now very few three-dimensional Al-phosphonates have been reported and most of them were structurally characterized from the powder technique.²¹ There is no report on porous Al-phosphonate with a channel size larger than 1 nm. Luckily, by carefully altering the ligand/metal (L/M) molar ratio, solvent and temperature, one aluminum(III) trisphosphonate, Al(H₃L)(H₂O) (**1**) (H₆L = (2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene)triphosphonic acid), was successfully obtained hydro(solvo)thermally from H₆L and Al₂(SO₄)₃·18H₂O (L/M: 0.8) in a mixed solvent of CH₃CH₂OH–H₂O (v/v: 9:1) at 140 °C (see the Experimental section in ESI†). Here the structure and gas adsorption properties are presented and discussed.

Compound **1** has a three-dimensional framework structure containing regular hexagonal channels along the *c*-direction. It crystallizes in the *R* $\bar{3}$ space group with 18 molecules in each unit cell (see Table S1†). There is one crystallographic independent aluminum ion, one triply deprotonated trisphosphonate ligand, and one coordinated water molecule in each asymmetric unit. The crystallographic independent aluminum(III) ion is six-coordinated by five phosphonate oxygen atoms of four trisphosphonate ligands and one aqua ligand, forming an AlO₆ octahedron (see Fig. 1a). The Al–O, P–O and C–P distances are found in the range of 1.841(3)–1.999(3), 1.487(3)–1.558(3) and 1.797(4)–1.808(4) Å (see Table S2†), respectively, which are all comparable to those of other reported aluminum-phosphonates.²² The three phosphonate groups in the trisphosphonate ligand are all singly protonated and adopt a

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† Electronic supplementary information (ESI) available: H bonds, PXRD, IR and Langmuir and BET graphs for CO₂ adsorption on activated **1**; X-ray crystallographic files for **1** in CIF format. CCDC 969636. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53167h

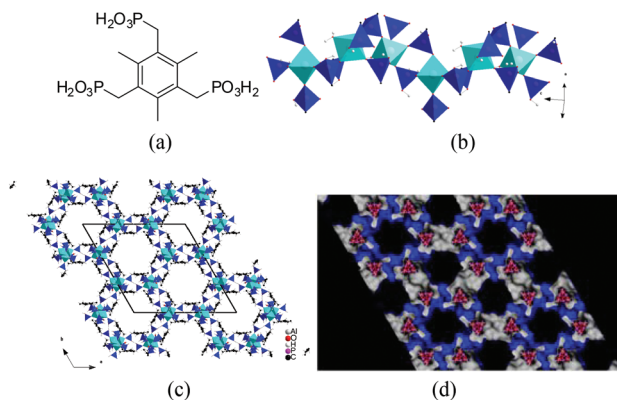


Fig. 1 Ligand H_6L (a), a one-dimensional aluminum phosphate chain along the c -direction (b), a three-dimensional framework structure viewing along the c -direction (c) and a Connolly surface diagram viewing along the c -direction (d) in compound **1**. The AlO_6 octahedra and $-CPO_3$ tetrahedra are shaded in cyan and blue, respectively.

cis-cis-cis conformation which is rarely observed for tripodal ligands in 3D structural compounds.^{9a} Two of the three $-PO_3$ groups are bidentate whereas the third is monodentate; therefore, the coordination mode of the trisphosphonate ligand can be denoted as $\mu^4:\eta^0:\eta^1:\eta^1:\eta^0:\eta^1:\eta^1:\eta^0:\eta^1$, which means each trisphosphonate ligand binds four aluminum ions in total with its five oxygen atoms. Neighboring aluminum ions are chelated by the bidentate phosphonate groups into 1D infinite aluminum phosphate chains along the c -direction (see Fig. 1b) which are further bridged in three directions by the monodentate phosphonate groups into a three-dimensional framework structure leaving large regular hexagonal channels along the c -direction (see Fig. 1c). The diameter of the channel is found to be about 12.4 Å, whereas in the remaining two directions the parallelogram channels are much smaller (3.5×5.8 Å²; see Fig. S1†). It is noticeable that the hexagonal channels connect with the parallelogram channels at the edges of the hexagons and the inner surfaces of the hexagonal channels are mainly lined with benzene rings, suggesting a hydrophobic character (see Fig. 1d). The accessible void is estimated by PLATON to be about 50.3%, in which a large amount of solvent molecules are accommodated, forming a few O–H...O bonds with the uncoordinated phosphonate oxygen atoms (see Table S3†).

Thermal gravimetric analysis (TGA) and powder X-ray diffraction (PXRD) measurements were carried out to examine the thermal and moisture stability of **1**. The TGA curve of as-synthesized **1** shows the release of guest molecules from 21 to 160 °C, leading to a weight loss of 16.43% (Fig. S2, ESI†). To facilitate the removal of guest molecules and protect the structural integrity, as-synthesized crystals were solvent-exchanged by soaking in acetone for three weeks and further treated under vacuum (about 10^{-6} mbar) at 100 °C for 6 hours. The good agreement of the experimental and simulated XRD patterns of activated **1** demonstrates that the framework structure of **1** can be retained after the removal of guest molecules. To test the stability of **1** to water, the as-synthesized crystals were also soaked in cold water for 3 days and boiling water for

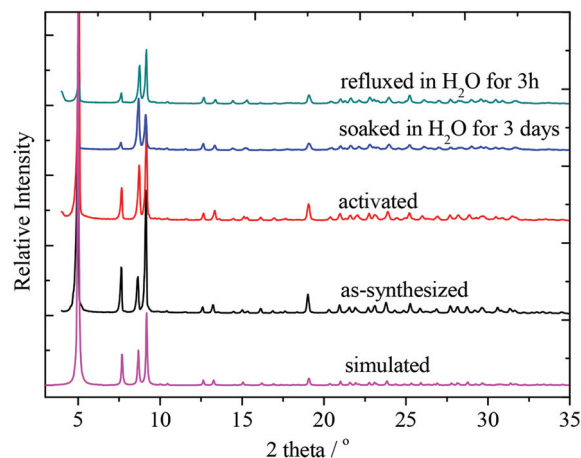


Fig. 2 PXRD patterns of simulated, as-synthesized, activated and treated in water samples of **1**.

3 hours. The PXRD experiments also verified the framework stability (see Fig. 2), suggesting its good resistance to water, and could be ascribed to the chemical stability of metal phosphonates and the hydrophobic channel of **1**.

To investigate the porosity of this Al(III) compound, nitrogen, carbon dioxide and hydrogen adsorptions were performed gravimetrically using an Intelligent Gravimetric Analyzer (IGA). The sample of about 100 milligrams was loaded into the IGA and degassed at 100 °C under vacuum ($\sim 10^{-6}$ mbar) for six hours to a constant weight. The adsorption isotherms are presented in Fig. 3a–3c; obviously activated sample **1** can reversibly and quickly adsorb N_2 , H_2 and CO_2 at different investigated temperatures and their adsorption isotherms can be classified as typical Type I adsorption curves according to the IUPAC standards.²³

The uptake capacity of N_2 at 77 K and 1 bar was determined to be 26% (wt) (208 ml g^{-1} STP), suggesting a Langmuir (BET) surface area of 901.5 (687.2) $\text{m}^2 \text{g}^{-1}$ (see Fig. S3 and S4†), and is comparable to those of CPF-1²⁴ and [Ba(HBTB)].²⁵ The total pore volume obtained from the Langmuir isotherm model was calculated to be $0.32 \text{ cm}^3 \text{g}^{-1}$ or 32.41% (v/v), lower than the estimated solvent accessible porosity of 50.3% (v/v) from PLATON. Probably it was caused by the incomplete removal of guest molecules²⁶ and overestimation by the program.²⁷ The adsorption of H_2 on activated **1** was also investigated. At 77 K and 20 bars, the total H_2 uptake was about 2.0% (wt) (226 ml g^{-1} STP). The ascending isotherm clearly indicates the unsaturated uptake of H_2 under 20 bars and a weaker adsorbate–adsorbent interaction. The adsorption of CO_2 on activated **1** was carried out at 195, 273 and 298 K, respectively. At 195 K the uptake of CO_2 was very fast and amounted to 33.5% (wt) (171 ml g^{-1} STP) at 1 bar, comparable to that of DUT-30(Zn).²⁸ When the temperature was increased to 273 and 298 K, the adsorption of CO_2 obviously reduced. Based on the sorption data of CO_2 at 273 and 298 K, the isosteric adsorption heats (Q_{st}) on activated **1** were calculated from Virial analysis combined with the Clausius–Clapeyron equation. As shown in Fig. S5,† the enthalpies lie in the range of 15.9–18.8 kJ mol^{-1} ,

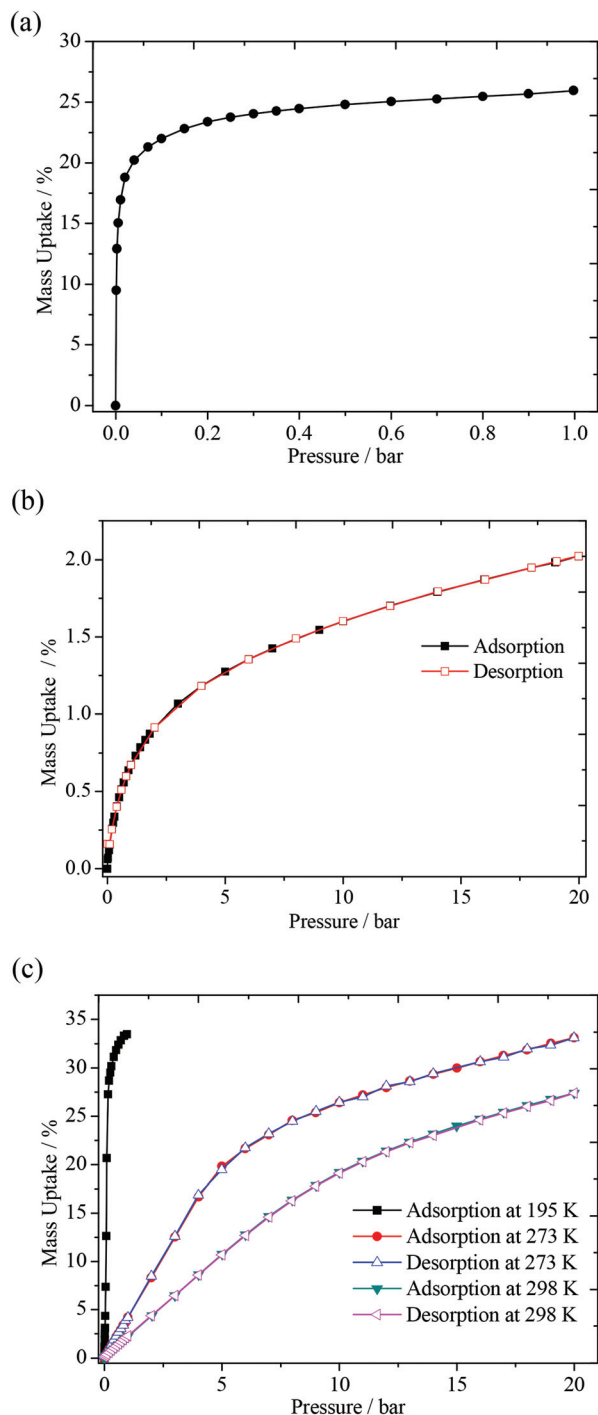


Fig. 3 Adsorption isotherms for N₂ (a) and H₂ (b) at 77 K, CO₂ (c) at 195, 273 and 298 K on activated 1.

which are lower than the common values observed for CO₂ adsorption on porous MOF materials,² suggesting a quite non-polar surface.

In summary, one porous aluminum(III) phosphonate has been successfully synthesized from a trisphosphonate ligand. It has a very interesting 3D framework structure which is constructed from 1D inorganic aluminum phosphate infinite

chains and *cis-cis-cis* conformational tripodal organic linkers and contains hexagonal channels of 1.24 nm in diameter. It has good thermal stability and shows good resistance to water. The adsorption results clearly suggest that it has a fast and relatively high uptake of H₂, N₂ and CO₂. To further improve the stability, rigid phosphonate ligands will be employed for the construction of porous MOFs in future work.

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