

Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard [Terms & Conditions](#) and the [ethical guidelines](#) that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

COMMUNICATION

A Highly Porous Three-dimensional Aluminum Phosphonate with Hexagonal Channels: Synthesis, Structure and Adsorption Properties

Si-Fu Tang, Jin-Jun Cai, Liang-Jun Li, Xiao-Xia Lv, Chao Wang and Xue-Bo Zhao

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

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 high accessible void (50.3%) which allow it to have a fast and relative 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 characters. 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 on gas capacity and selective uptake but suffer from poor stability, for example ZnO₄ tetrahedrons 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 chemical and mechanical 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 uptake¹⁵⁻²⁰ and at the same time it is also the important component of zeolites. Thus we decide 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 for the sake of poor crystallinity. Until now very few of three-dimensional Al-phosphonates have been

reported and most of them were structurally characterized from powder technique.²¹ There is no report on porous Al-phosphonate with channel size large 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 mixed solvent of CH₃CH₂OH/H₂O (v/v: 9:1) at 140 °C (see experimental section in supporting information). Here the structure and gas adsorption properties are presented and discussed.

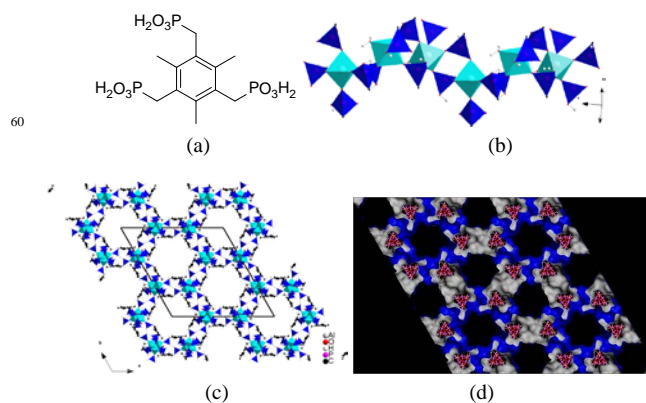


Fig. 1 Ligand H₆L (a), one-dimensional aluminum phosphate chain along *c*-direction (b), three-dimensional framework structure viewing along *c*-direction (c) and connolly surface diagram viewing along *c*-direction (d) in compound **1**. The AlO₆ octahedra and -CPO₃ tetrahedra are shaded in cyan and blue, respectively.

Compound **1** has a three-dimensional framework structure containing regular hexagonal channels along *c*-direction. It crystallizes in *R*-3 space group with 18 molecules in each unit cell (see Table S1). There are 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 Figure 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 *cis-cis-cis* conformation which is rarely observed for tripodal ligands in 3D structural compounds.^{9a} Two of the three $-\text{PO}_3$ groups are bidentate whereas another one is monodentate, therefore the coordination mode of the trisphosphonate ligand can be denoted as: $\mu^4:\eta^0:\eta^1:\eta^1:\eta^0:\eta^1:\eta^1:\eta^0:\eta^0:\eta^1$, 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 *c*-direction (see Figure 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 *c*-direction (see Figure 1c). The diameter of the channel is found to be about 12.4 Å, whereas at the rest two directions the parallelogram channels are much smaller (3.5×5.8 Å²; see Figure S1). It is noticeable the hexagonal channels connect with the parallelogram channels at the edges of the hexagons and the inner surface of the hexagonal channels are mainly lined with benzene rings, suggesting a hydrophobic character (see Figure 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 of O-H...O bonds with the uncoordinated phosphonate oxygen atoms (see Table S3).

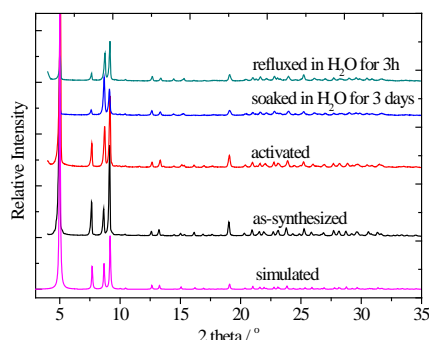
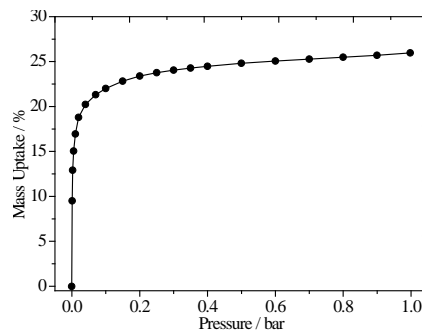
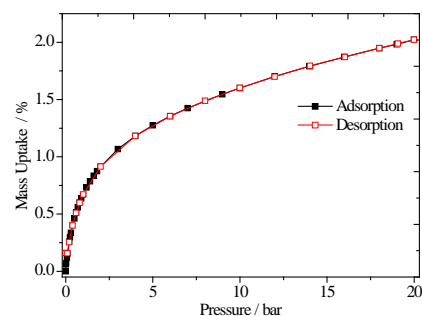


Fig. 2 PXRD patterns of simulated, as-synthesized, activated and treated in water samples of **1**.

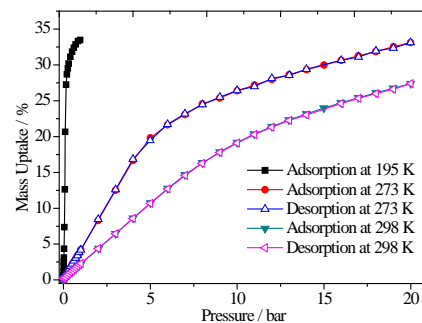
Thermal gravimetric analysis (TGA) and powder X-ray diffraction (PXRD) measurements were carried out to examine the thermal and moisture stability of **1**. The TGA curve of as-synthesized **1** shows the release of guest molecules from 21 to 160 °C, leading to a weight loss of 16.43% (Figure S2, Supporting Information). 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 3 hours. The PXRD experiments also verified the framework stability (see Figure 2), suggesting its good resistance to water and could be ascribed to the chemical stability of metal phosphonates and the hydrophobic channel of **1**.



(a)



(b)



(c)

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

To investigate the porosity of this Al (III) compound, nitrogen, carbon dioxide and hydrogen adsorptions were performed gravimetrically using an IGA system. The sample 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 Figures 3a-3c, obviously activated sample **1** can reversibly and quickly adsorb N₂, H₂ and CO₂ 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 N₂ at 77 K and 1bar was determined to be 26 % (wt) (208 ml g⁻¹ STP), suggesting a Langmuir (BET) surface area of 901.5 (687.2) m²/g (see Figures 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 cm³ 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 H₂ on activated **1** was also investigated. At 77 K

and 20 bars, the total H₂ uptake was about 2.0 % (wt) (226 ml g⁻¹ STP). The ascending isotherm clearly indicates the unsaturated uptake of H₂ under 20 bars and weaker adsorbate-adsorbent interaction. The adsorption of CO₂ on activated **1** was carried out at 195, 273 and 298 K, respectively. At 195 K the uptake of CO₂ 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 CO₂ obviously reduced. Based on the sorption data of CO₂ 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 Figure S5, the enthalpies lie in the range of 15.9–18.8 kJ mol⁻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* 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 relative 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 the future work.

This work was supported by the National Natural Science Foundation of China (No. 21171173 and 21173246).

Notes and references

^a Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China. Fax: 86 0532 80662729; Tel: 86 0532 80662728; E-mail: zhaoxb@qibebt.ac.cn

† 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]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

1 Y. H. Hu, L. Zhang, *Adv. Mater.*, 2010, **22**, E117–E130.

2 K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.*, 2012, **112**, 724–781.

3 C. Zou, Z. Zhang, X. Xu, Q. Gong, J. Li, C.-D. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 87–90.

4 Z. R. Herm, B. M. Wiers, J. A. Mason, J. M. van Baten, M. R. Hudson, P. Zajdel, C. M. Brown, N. Masciocchi, R. Krishna, J. R. Long, *Science*, 2013, **360**, 960–964.

5 D.-X. Xue, A. J. Cairns, Y. Belmabkhout, L. Wojtas, Y. Liu, M. H. Alkordi, and M. Eddaoudi, *J. Am. Chem. Soc.*, 2013, **135**, 7660–7667.

6 H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O’Keeffe, O. Terasaki, J. F. Stoddart, O. M. Yaghi, *science*, 2012, **336**, 1018–1023.

7 K. J. Gagnon, H. P. Perry, A. Clearfield, *Chem. Rev.*, 2012, **112**, 1034–1054.

8 S. S. Kaye, A. Dailly, O. M. Yaghi, J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 14176–14177.

9 (a) S. F. Tang, X. B. Pan, X. X. Lv, S. H. Yan, X. R. Xu, L. J. Li, X. B. Zhao, *CrystEngComm*, 2013, **15**, 1860–1873; (b) S. F. Tang, X. B. Pan, X. X. Lv, X. B. Zhao, *J. Solid State Chem.*, 2013, **197**, 139–146; (c) S. F. Tang, J. L. Song, X. L. Li, J. G. Mao, *Cryst. Growth*

Des., 2007, **7**, 360–366; (d) S. F. Tang, J. L. Song, J. G. Mao, *Eur. J. Inorg. Chem.*, 2006, 2011–2019; (e) S. F. Tang, J. L. Song, X. L. Li, J. G. Mao, *Cryst. Growth Des.*, 2006, **6**, 2322–2326.

10 J. M. Taylor, R. Vaidhyanathan, S. S. Iremonger, and G. K. H. Shimizu, *J. Am. Chem. Soc.*, 2012, **134**, 14338–14340.

11 S. S. Iremonger, J. Liang, R. Vaidhyanathan, I. Martens, G. K. H. Shimizu, T. D. Daff, M. Z. Aghaji, S. Yeganegi, and T. K. Woo, *J. Am. Chem. Soc.*, 2011, **133**, 20048–20051.

12 M. T. Wharmby, J. P. S. Mowat, S. P. Thompson, P. A. Wright, *J. Am. Chem. Soc.*, 2011, **133**, 1266–1269.

13 J. Liang, G. K. H. Shimizu, *Inorg. Chem.*, 2007, **46**, 10449–10451.

14 M. Taddei, F. Costantino, A. Ienco, A. Comotti, P. V. Dau, S. M. Cohen, *Chem. Comm.*, 2013, **49**, 1315–1317.

15 Y. X. Tan, F. Wang, Y. Kang, J. Zhang, *Chem. Commun.* 2011, **47**, 770–772.

16 (a) C. Volkringer, T. Loiseau, M. Haouas, F. Taulelle, D. Popov, M. Burghammer, C. Riekel, C. Zlotea, F. Cuevas, M. Latroche, D. Phanon, C. Knöfel, P. L. Llewellyn and G. Férey, *Chem. Mater.*, 2009, **21**, 5783; (b) C. Volkringer, T. Loiseau, N. Guillou, G. Férey, M. Haouas, F. Taulelle, N. Audebrand, I. Margiolaki, D. Popov, M. Burghammer and C. Riekel, *Cryst. Growth Des.*, 2009, **9**, 2927; (c) C. Volkringer, D. Popov, T. Loiseau, G. Férey, M. Burghammer, C. Riekel, M. Haouas and F. Taulelle, *Chem. Mater.*, 2009, **21**, 5695.

17 P. Serra-Crespo, E. V. Ramos-Fernandez, J. Gascon and F. Kapteijn, *Chem. Mater.*, 2011, **23**, 2565.

18 T. Ahnfeldt, N. Guillou, D. Gunzelmann, I. Margiolaki, T. Loiseau, G. Férey, J. Senker and N. Stock, *Angew. Chem., Int. Ed.*, 2009, **48**, 5163.

19 T. Ahnfeldt, D. Gunzelmann, T. Loiseau, D. Hirsemann, J. Senker, G. Férey and N. Stock, *Inorg. Chem.*, 2009, **48**, 3057.

20 D. Himsl, D. Wallacher and M. Hartmann, *Angew. Chem., Int. Ed.*, 2009, **48**, 4639.

21 (a) K. Maeda, J. Akimoto, Y. Kiyozumi, F. Mizukami, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 1199–1201; (b) K. Maeda, J. Akimoto, Y. Kiyozumi, F. Mizukami, *J. Chem. Soc., Chem. Commun.*, 1995, 1033–1034; (c) H. G. Harvey, B. Slater, M. P. Attfield, *Chem. Euro. J.*, 2004, **10**, 3270–3278; (d) H. G. Harvey, S. J. Teat, M. P. Attfield, *J. Mater. Chem.*, 2000, **10**, 2632–2633; (e) M. Mar Gómez-Alcantara, M. A. G. Aranda, P. Olivera-Pastor, P. Beran, J. García-Muñoz, A. Cabeza, *Dalton Trans.*, 2006, 577–585;

(f) C. Serre, J. A. Groves, P. Lightfoot, A. M. Z. Slawin, P. A. Wright, N. Stock, T. Bein, M. Haouas, F. Taulelle, G. Férey, *Chem. Mater.* 2006, **18**, 1451–1457; (g) H. G. Harvey, J. Hu, M. P. Attfield, *Chem. Mater.* 2003, **15**, 179–188; (h) C. A. Merrill, A. K. Cheetham, *Inorg. Chem.*, 2005, **44**, 5273–5277; (i) H. G. Harvey, B. Slater, M. P. Attfield, *Chem. Eur. J.* 2004, **10**, 3270–3278.

22 (a) A. A. Ayi, T. L. Kinnibrugh, A. Clearfield, *Dalton Trans.* 2011, **40**, 12648–12650; (b) A. F. Richards, C. M. Beavers, *Dalton Trans.*, 2012, **41**, 11305–11310.

23 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemienewska, *Pure Appl. Chem.*, 1985, **57**, 603–619.

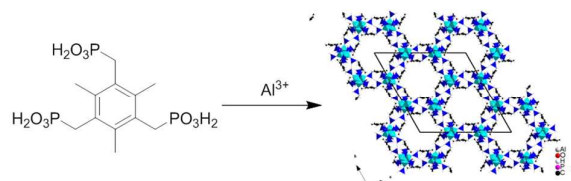
24 Q. Lin, T. Wu, S.-T. Zheng, X. Bu, P. Feng, *Chem. Commun.*, 2011, **47**, 11852–11854.

25 M. L. Foo, S. Horike, S. Kitagawa, *Inorg. Chem.*, 2011, **50**, 11853–11855.

26 (a) J. E. Mondloch, O. Karagiari, O. K. Farha, J. T. Hupp, *CrystEngComm*, 2013, **15**, 9258–9264; (b) L. J. Li, S. F. Tang, X. X. Lv, M. Jiang, C. Wang, X. B. Zhao, *New J. Chem.*, 2013, **37**, 3662–3670.

27 S. S. Iremonger, J. Liang, R. Vaidhyanathan, G. K. H. Shimizu, *Chem. Commun.*, 2011, **47**, 4430–4432.

28 I. M. Hauptvogel, R. Biedermann, N. Klein, I. Senkovska, A. Cadiou, D. Wallacher, R. Feyerherm, S. Kaskel, *Inorg. Chem.*, 2011, **50**, 8367–8374.



A 3D porous aluminum trisphosphonate containing large hexagonal channels displays fast and relative high uptake of H₂, N₂ and CO₂.