A rutile-type porous zinc(II)-phosphonocarboxylate framework: local proton transfer and size-selected catalysis[†]

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The layered-solvothermal synthesis of zinc acetate dihydrate with 5-phosphonobenzene-1,3-dicarboxylic acid yields a three-dimensional rutile-type porous metal-organic framework, which is an anionic open-framework containing local proton transfer with hydrated protons and showing excellent sizeselective properties.

Constructing metal-organic frameworks (MOFs) with accessible porosities has attracted tremendous interest during the past decades due to their potential applications¹ in gas storage and/or separation, molecular recognition, ion exchange, size-selective catalysis and so on. Rational design is crucial for these desired porous MOFs, and some successful strategies have been proposed such as reticular synthesis² and post-synthesis.³ Network topology plays an important role not only in analysis of these MOFs but also in directing further design.⁴ Up to now, more and more MOFs with uninodal networks have been reported such as 3-, 4-, and 6-connected nodes,^{5,6} however uninodal networks are apt to become entangled with each other,^{5a,b} thus possibly leaving no accessible porosity for guest molecules. For example, 4-connected diamond networks, which account for a large portion of the reported uninodal networks,^{5b,d} naturally interpenetrate each other, leaving no or less accessible porosity even in the vertex augmented models.⁷ In contrast, MOFs with mixed nodes such as (3,6)-, (4,6)-, (4,8)-connectivities are currently drawing increasing attention^{8,9} due to the low entanglement.^{10,11} So carefully selecting metal and ligand precursors with connectivity information encoded might finally lead to the formation of mixed-node networks and thus increase the possibility of obtaining accessible porous MOFs. With this consideration in mind, a (3,6)-connected 3-D porous MOF, namely $\{[Zn_3(pbdc)_2] \cdot 2H_3O\}_n$ (1a), was synthesized based on the elaborately selected 3-connected ligand of 5-phosphonobenzene-1,3-dicarboxylic acid (H₄pbdc). Crystal structure studies reveal that 1a is an anionic (3,6)-connected framework with interesting local proton transfer from hydrated protons in the channels to the monodentate carboxylate group on the

Downloaded by Mount Allison University on 18/05/2013 22:14:18. Published on 23 December 2009 on http://pubs.rsc.org | doi:10.1039/B917987A framework under thermal conditions. Catalysis studies of **1a** show excellent size-selected catalysis ability for different substrates.

Rod-like crystals of $\{[Zn_3(pbdc)_2]\cdot 2H_3O\}_n$ (1a)§ were obtained through layered-solvothermal synthesis of H₄pbdc and Zn(OAc)_2·2H_2O with addition of triethylamine (*tea*) as the base. It is worth mentioning that herein a layeredsolvothermal method not the traditional mixed-solvothermal method was used. This method has been proved to be an efficient way to obtain excellent crystalline metal-phosphonocarboxylates.¹² If the ordinary solvothermal method (mixture of the reagents and solvents) was employed, another condensed (3,6)-connected framework, namely $\{[Zn_3(pbdc)_2H_2O]\cdot(Htea)\cdot H_3O\cdot xH_2O\}_n$, was isolated (ESI†).

Single crystal X-ray diffraction study¶ reveals that 1a is a three-dimensional framework consisting of trimeric zinc phosphonocarboxylate clusters (Zn₃(CO₂)₄(PO₃)₂, Zn₃-SBU) and *pbdc* linkers (Fig. 1). Each Zn(II) ion in the Zn₃-SBU is four coordinated (ESI⁺) in severely distorted tetrahedral geometry $(THC_{DA}/100 = 0.67, 0.61 \text{ for } Zn(1) \text{ and } Zn(2),$ respectively). The Zn-O distances fall in the range of 1.91–1.99 Å (ESI[†]), which agrees well with the normally known bond distances for Zn-O in the four coordination geometry. The three Zn(II) ions in the SBU constitute an isosceles triangle with $Zn(1)\cdots Zn(1)^{i}$ and $Zn(1)\cdots Zn(2)$ distances 4.61 Å and 3.56 Å, respectively. The oxygen atoms from phosphonate of *pbdc* are tridentate capturing the isosceles triangle, and the carboxylates of *pbdc* adopt two different coordination modes. One bridges Zn(1) and Zn(2) ions with O(6) and O(7) atoms in syn-syn mode, while the other is monocoordinated to the Zn(1) ion through the O(4) atom. Considering the Zn₃-SBU as a 6-connected node (four C atoms from four carboxylates and two P atoms from two phosphonates as vertex) and the *pbdc* as a 3-connected node (Fig. 1a,b), this infinite 3-D framework of 1a then could be described as a (3.6)-connected network with Schläfli symbol $(4.6^2)_2(4^2.6^{10}.8^3)$ (Fig. 1c), which is characteristic of the rutile $(\mathbf{rtl})^{8,9b}$ and sit net; ^{10b,13} here **1a** belongs to the **rtl** net.

According to the analyses of C–O and P–O bond distances from crystal data (ESI[†]), the H₄pbdc ligand should be totally deprotonated in the decorated **rtl** net. This result also agrees well with the IR and elemental analysis results (ESI[†]). So **1a** is an anionic 3-D porous MOF with **rtl** topology. The counter ions are the hydrated protons located in the channels (close to the O(5) atom of monodentate carboxylate group). There are two kinds of channels in **1a**, the large channels along the *c* axis (Fig. 1d) and the small discrete channels along the *a* or *b* axis. The hydrated protons fill the small channels and serve as walls for the large channels. The calculation results confirmed the accessible porosity of **1a**. The Connolly (Connolly radius set to

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[†] Electronic supplementary information (ESI) available: Detailed measurements, synthesis process for ligand, catalysis process, important bond distances and angles for **1a** and **1b**, detailed figures for **1a**, **1b**, and **1a-100**, PXRD data and TGA data. CCDC 746203 and 746472. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b917987a

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Fig. 1 (a) The simplified $Zn_3(CO_2)_4(PO_3)_2$ SBU in 6-connected node, (b) the simplified 5-phosphonobenzene-1,3-dicarboxylate ligand in 3-connected node, (c) the network of **1a** showing in (3,6)-connected rutile net, (d) the 3-D porous anionic frameworks with regular open channels along the *c* axis.

be 1.0 Å) free volume and surface area per unit cell are calculated to be 4433.09 Å³ and 2586.36 Å², respectively, and the accessible solvent (solvent probe atom radius set to be 1.4 Å) free volume and surface area per unit cell are 1279.57 Å³ and 1609.10 Å², respectively (ESI†).

The bulk purity of **1a** was confirmed by powder X-ray diffraction (PXRD) measurement in which diffraction peaks of experimental data match well with the simulated data from single-crystal X-ray data (ESI[†]). Thermal gravimetric analysis (TGA) was carried out to examine the stability of the framework (ESI[†]). The TGA curve shows a weight loss of 5.37% from 30 to 120 °C corresponding to the loss of two lattice waters (calc. 5.05%) and then an abrupt weight loss from around 300 °C which is attributed to the decomposition of the framework and which ended after 580 °C to give a total weight loss of 41.59%.

The first step weight loss of lattice waters particularly drew our attention. The lattice water in 1a should be in the form of hydrated protons according to the single-crystal structural result, and so they should be restricted in the framework as counter ions. The loss of lattice water indicates some interesting charge transfer processes might happen inside in order to adapt to the total charge balance requirement. We then performed the PXRD measurement of 1a at 200 °C (ESI⁺). The results still match very well with simulated data, indicating no obvious structural change. Fortunately, a detectable crystal (1b) was picked out from the cooling sample. According to the X-ray single-crystal diffraction, the bond distances of carboxylate groups changed in 1b (ESI⁺) compared with those in **1a**. A tentative process was supposed here: (i) the electronic density of the bond C(7)–O(5) (the short one, 1.226 Å) was gradually delocalized to the bond C(7)-O(4) (the long one, 1.242 A), thus shortening the C(7)–O(4) bond while lengthening the C(7)–O(5) bond, which finally could accept the proton immigrated from neighboring hydrated proton $(O(5) \cdots O(8))$



Fig. 2 A view of temperature induced proton transfer in 1a.

distance 3.01 or 3.38 Å, due to the disorder of O(8) atom (ESI[†]) when heating up (Fig. 2)). (ii) This metastable state $(Zn_3(Hpbdc)_2)$ would decompose on continued heating, or give **1b** (C(7)–O(5) bond of 1.248 Å longer than C(7)–O(4) bond of 1.208 Å), in which the hydrated protons were formed again on cooling down. To try to confirm the hypothesis, dehydration experiments on 1a were carried out in a glovebox under N₂ at 100 °C, 150 °C, 200 °C, respectively, and the products were sealed in a glass tube. However, only the crystals heated at 100 °C could be characterized by X-ray single crystal diffraction (ESI⁺, named as 1a-100). Crystal structure study reveals that the small channels in 1a-100 shrink markedly, forcing the waters to go into the large channels. The large rectangular channels in 1a turn to be rhombus in 1a-100. Importantly, as expected the C-O bond was lengthened in 1a-100 (ESI[†]). Combining the crystal structure results and previous related reports,14 the local proton transfer/immigration under high temperature should be reasonable for 1a. This transfer, according to the literature,¹⁵ should belong to the mixed model of Type I (with H_3O^+ , NH_4^+ as carriers in the anionic porous MOFs) and Type II (acid groups on frameworks).

Taking these features described above into consideration, Friedel–Crafts benzylation reactions (Table 1), which are highly desired for heterogeneous catalysis,¹⁶ have been tentatively carried out over **1a**.

The conversion of benzyl bromide in benzylation reaction of toluene with 4-chlorobenzyl bromide (CBB), 3-biphenylmethyl bromide (BPMB) and 3,5-di-*tert*-butylbenzyl bromide (TBBB) was studied at 100 °C over **1a** for 12 h, respectively (ESI†). The results demonstrate that **1a** is an excellent catalyst for CBB conversion (>99%). As for the size enlarged substrate BPMB, the conversion drops to 89.8%. When using bulky TBBB as substrate, no conversion was detected. The size-selective property should originate from the size matching between substrates and channels. The catalysis activity, according to previous literature,^{14a,17} should be related with the presence of H₃O⁺ (or the carboxylic acid under high temperature because of proton transfer phenomena) and the structural property of **1a** that generates new kinds of catalysts with different acidities.¹⁷ Detailed catalysis studies of **1a** are currently underway.

 Table 1
 The Friedel–Crafts benzylation reactions of toluene with various reactant substrates catalyzed by 1a



^{*a*} All reactions were performed under the same reaction conditions (ESI†). ^{*b*} Determined by GC-MS, based on starting materials.

In conclusion, through layered-solvothermal reaction, a 3-D porous rutile-type zinc(II)-phosphonocarboxylate framework **1a** was successfully isolated based on the preselected 3-connected ligand. **1a** shows excellent size-selective properties for Friedel–Crafts benzylation reaction due to the regular porosities. The catalysis activity should be ascribed to the unique structural property of **1a**.

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Notes and references

§ Synthesis of $\{[Zn_3(pbdc)_2]\cdot 2H_3O\}_n$ (1a). A solution of H₄pbdc (0.025 g, 0.1 mmol) and triethylamine (0.04 g, 0.4 mmol) in *i*-PrOH (5 ml) was carefully layered onto a solution of Zn(CH₃COO)₂·2H₂O (0.32 g, 0.15 mmol) in deionized water (5 mL) in a Teflon-lined stainless steel autoclave (15 mL). The mixture was heated at 140 °C for 3 days, followed by cooling to room temperature. Colorless rod-shaped crystals of 1a were collected by filtration (yield: 17% based on H₄pbdc). Elemental analysis calcd for 1a C₁₆H₁₂P₂O₁₆Zn₃ (718.3): C, 26.75; H, 1.68%. Found: C, 26.71; H, 1.73%. IR (cm⁻¹): 3436 m, 3068 w, 2984 w, 1614 s, 1567 m, 1436 m, 1368 m, 1310 w, 1211 m, 1110 m, 1012 m, 990 m, 777 m, 729 m, 574 m, 457 m.

¶ Crystal data for **1a**. $C_{16}H_6O_{14}P_2Zn_3$, $2(H_3O)$, M = 718.31, T = 293(2) K, tetragonal, I-42d, a = 18.310(6), b = 18.310(6), c = 23.222(11) Å, V = 7785(5) Å³, Z = 8, $D_c = 1.226$ g cm⁻³, $\mu = 1.964$ mm⁻¹, F(000) = 2848, GOF = 1.18, Flack = 0.28(3), R_1 and wR_2 are 0.0402 and 0.1471, respectively, for 18 703 total data and 3079 observed data $[I > 2\sigma(I)]$, $R_{int} = 0.0527$. CCDC 746203.

Crystal data for **1b**. $C_{16}H_6O_{14}P_2Zn_3$, 2(H₃O), M = 718.31, T = 293(2) K, tetragonal, *I*-42d, a = 18.218(4), b = 18.218(4), c = 23.552(7) Å, V = 7817(3) Å³, Z = 8, $D_c = 1.221$ g cm⁻³, $\mu = 1.956$ mm⁻¹, F(000) = 2848, GOF = 1.08, Flack = 0.50(5), R_1 and wR_2 are 0.0649 and 0.1935, respectively, for 15733 total data and 2140 observed data $[I > 2\sigma(I)]$, $R_{int} = 0.1222$. CCDC 746472.

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