From Tetrahedral Tetraphosphonic Acids \(E[p-\text{C}_6\text{H}_4\text{P(O)(OH)}_2]_4\) (\(E = \text{C, Si}\)) to Porous Cu- and Zn-MOFs with Large Surface Areas

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Abstract: This study describes the porous MOFs Cu\(_2\)H\(_4\)STPPA-2 H\(_2\)O (1:2 H\(_2\)O), Zn\(_2\)H\(_4\)STPPA (2) and Zn\(_2\)H\(_4\)MTPPA (3) obtained using the tetrahedral linkers tetraphenylmethane tetras-4-phosphonic acid (H\(_4\)MTPPA) and tetraphenylsilane tetras-4-phosphonic acid (H\(_4\)STPPA) under solvothermal conditions. X-ray structures reveal 3D frameworks with large assessable voids. The percentage void volumes and the specific BET surface areas of 1 (45.7%, 794 m\(^2\)/g), 2 (48.1%, 565 m\(^2\)/g) and 3 (51.3%, 927 m\(^2\)/g) predicted by molecular simulations are among the highest reported for MOFs derived from phosphonic acids.

The recent efforts in carboxylate based metal organic frameworks (MOFs) provided valuable insight in the area of designing tailor-made three dimensional porous networks.\[1\] The well-established inorganic building units (IBUs) in carboxylate based MOFs provided structural control.\[2\] The precise isoreticular expansion of known networks has provided the desired pore sizes for storage, separation, catalysis and drug delivery.\[3\] Although most of the known aromatic carboxylic acid ligands have been used in MOF synthesis, vast structural potential for novel carboxylate bridging ligands and their yet unexplored properties make the MOF chemistry a very attractive research area. Organophosphonate linker molecules are the most promising candidates to take the current MOF research into a different level. Metal organophosphonates are less air sensitive and exhibit better heat resistance compared to the present carboxylate based MOFs.\[4\] In addition, metal-organophosphonate frameworks provide remarkable structural diversity\[5\] offering a wide range of potential applications including magnetism, porosity, catalysis and bone regeneration.\[6\] There is not yet a methodology to control the structural diversity in metal-organophosphonate solids to synthesize predictable networks. Unfortunately, the current literature on aromatic organophosphonates and the number of known aromatic organophosphonate linkers are very limited to derive reasonable pathways towards the designed synthesis of metal organophosphonates.\[7\] Only few examples of isoreticular expansions of porous metal-organophosphonates have been reported, which have enabled a nitrogen donor ligand to maintain the position of the metal atoms.\[8\] Another method used the organoamine chelators to engineer the metal coordination to limit the number of phosphonate coordination on the metal atom.\[9\] The known metal complexes of aromatic organophosphonates usually exhibit compact pillared-layered structures and they would exhibit tendency to pack at high densities.\[10,11\] One of the few reported porous metal-organophosphonate framework was synthesized using a tetrahedral tetraphosphonic acid based on a tetrahedral adamantane core.\[9\] Therefore the judicious choice of the bridging ligand is very important in the synthesis of porous metal organophosphonates. In this sense, tetrahedral tetraphosphonic acid ligands exhibit remarkable geometrical orientation with four open trigonal pyramidal cavities.\[12,13\]

In this work the recently introduced tetrahedral linkers tetrathyphenylmethane tetras-4-phosphonic acid (H\(_4\)MTPPA) and tetraphenylsilane tetras-4-phosphonic acid (H\(_4\)STPPA)\[1,3\] are exploited for the construction of porous metal organic frameworks with copper and zinc under solvothermal conditions (Scheme 1). Thus, the reactions of H\(_4\)STPPA with Cu(NO\(_3\))\(_2\)-3 H\(_2\)O and NaOH (approx. molar ratio 1:1:2) in H\(_2\)O/Methanol (approx. volume ratio 1:1) and H\(_4\)STPPA with Zn(NO\(_3\))\(_2\) (approx. molar ratio 1:1) in H\(_2\)O/Methanol (approx. volume ratio 4:1) at 150°C provided crops of single crystals of the composition Cu\(_2\)Si\(_2\)C\(_6\)H\(_4\)P\(_2\)O\(_8\)(OH)\(_2\)·2 H\(_2\)O = Cu\(_2\)H\(_4\)STPPA-2 H\(_2\)O (1:2 H\(_2\)O) and Zn\(_2\)Si\(_2\)C\(_6\)H\(_4\)P\(_2\)O\(_8\)(OH)\(_2\) = Zn\(_2\)H\(_4\)STPPA (2), respectively (the reaction conditions were optimized using high-throughput methods).\[12\] H\(_4\)MTPPA and ZnSO\(_4\)-7 H\(_2\)O (approx. molar ratio 1:2) was stirred briefly in dimethylformamide and heated to 180 °C for 24 h in a PTFE-lined stainless steel acid digestion bomb, which afforded single crystals of the composition Zn\(_2\)O\(_3\)-H\(_2\)P\(_2\)O\(_5\)(OH)\(_2\) = Zn\(_2\)H\(_4\)MTPPA (3).

The crystal structure of 1·2 H\(_2\)O shows three distinct phosphate protonation modes, which consist of a full deprotonated \(\text{PO}_4^{3-}\); a half deprotonated \(\text{PO}_4^{2-}\) and two fully protonated phosphate groups \(\text{PO}_4^{3-}\) (Figure 1).
These phosphonate groups coordinate to the square pyramidal Cu\(^{2+}\), two square pyramidal hydrated (Cu(H\(_2\)O))\(^{2+}\) and one double hydrated (Cu(H\(_2\)O))\(^{2+}\) forming the Cu\(_4\)P\(_7\)O\(_{21}\) cluster (Figure 1b), which is connecting the two STPPA moieties to form the three dimensional porous framework of 1·2 H\(_2\)O (Figure 1c). Within the tetranuclear cluster [Cu4-P2O5] the Cu-O distances. Each of the [Cu4-O] rhombi are connected by two fully deprotonated and one of the half deprotonated phosphonate groups to form the cluster structure. The overall three dimensional porous framework structure of 2 and 3 is formed by connecting the 1D chain of corner-shared Zn\(_2\)P\(_2\)O\(_4\) rings with H\(_3\)STPPA\(^{4-}\) and H\(_4\)MTPPA\(^{4-}\) moieties, respectively (Figures 2 and 3).

The major difference between the structures of 2 and 3 originates as a result of angular difference between the Si and C cores in 2 and 3, which strains the chain structure of corner-shared Zn\(_2\)P\(_2\)O\(_4\) in 2 as seen in Figures 2a and 3a. Although both compounds have the same structural components and tetrahedral Zn coordination pattern, they show different porosities due to this angular difference between the Si and C cores of STPPA and MTPPA units.

Pore volumes, pore size distributions and Brunauer–Emmett–Teller (BET) surface areas of 1 - 3 were predicted with molecular simulations (Table 1 and Figure S1, see Supporting Information).
The void volumes were calculated by trial insertions of a 0 Å probe size (a randomly chosen point in the system) within the entire volume of the unit cell. This allowed us to determine the volume of the simulation cell that is not occupied by framework atoms. The accessible pore volumes were computed with the Widom insertion method\(^1\) using a helium probe. This mimics the experimental helium porosimetry at room temperature and low pressure.\(^2\) It should be noted that calculation of the void space is based solely on the system geometry, i.e. radii of atoms, whereas the accessible pore volume is based on a thermodynamic definition. Pore size distributions were obtained by the method of Gelb and Gubbins,\(^3\) which is based on the largest sphere that can fit in a pore. BET surface areas were derived from N\(_2\) adsorption isotherms at 77K which were determined using a helium probe. This mimics the probe size.

In summary, we report 3D porous copper and zinc organophosphonates, which were constructed using aromatic tetraphosphonic acids H\(_4\)STPPA and H\(_4\)MTTPPA. Surface areas derived from Monte Carlo simulations have shown that tetrahedral aromatic organophosphonates determine the porous three-dimensional metal organic solids having exceptionally large surface areas. The Zn-MOFs 2 and 3 comprise very similar structures consisting of chains of corner-shared Zn\(_2\)PO\(_4\) rings. The flexibility of the chains observed in 2 and 3 strengthen the hypothesis that isoreticular expansions could be possible by increasing the tether length of the tetrahedral ligands. We are currently working on producing larger surface areas following up this hypothesis.

Supporting Information Summary

X-ray crystallography, Molecular simulation, Void volumes, Accessible pore volumes, Pore size distribution, N\(_2\)-adsorption isotherms and BET surface areas. Additional references.
COMMUNICATION

K. Demadis, RSC Publishing, London (2012); N. Stock, Microporous Mesoporous Mater. 2009, 129, 287-295. b) A micro teflon container (200 µL) was charged with a 0.07 M solution of H₃STPPA (100 µL, 5.00 mg, 70 µmol) in methanol, a 2 M solution of Cu(NO₃)₂·3H₂O (3.8 µL, 1.36 mg, 76 µmol) in water, a 1 M solution of NaOH (15.2 µL, 608 µg, 15.2 µmol) and water (81 µL) and sealed. Under autogenous pressure, the reactor was heated within 24 h to 150°C, kept for 24 h at the same temperature before it was cooled down with 16 h to room temperature. The container was opened and single crystals of Cu₆H₃STPPA·2H₂O (1:2 H₂O) suitable for X-ray crystallography were hand-selected. Crystal data for 1:2 H₂O (Cu₆H₃CuO₅P:Si): M = 815.48, triclinic space group P-1, a = 26.882(5) Å, b = 26.885(5) Å, c = 12.264(2) Å, α = 102.70(2)°, β = 101.02(2)°, γ = 76.26(2)°, V = 8308(3) Å³, Z = 2, R_int = 1.304, crystal dimensions 0.05 x 0.4 x 0.8 mm, 694 electrons. Selected reflections were hand-collected and 9971 unique reflections. Final residues R = 0.1622, wR = 0.1563 (I > 2σ(I)); R_p = 0.1565 (I > 2σ(I)); R_p = 0.0677, wRp = 0.1605 (all data), Goof = 0.91, 1637 parameters. SQUEEZE information: Void 1: 1456 Å³, 352 electrons; Void 2: 1341 Å³, 326 electrons. c) A micro teflon container (200 µL) was charged with a 0.07 M solution of H₃STPPA (40 µL, 2.00 mg, 28 µmol) in methanol, a 2 M solution of Zn(NO₃)₂ (3.8 µL, 0.97 mg, 76 µmol) in water and water (156 µL) and sealed. Under autogenous pressure, the reactor was heated within 24 h to 150°C, kept for 24 h at the same temperature before it was cooled down with 16 h to room temperature. The container was opened and single crystals of Zn₆H₃STPPA (2) suitable for X-ray crystallography were hand-selected. Crystal data for 2 (Cu₆H₃O₅P·4ZnSi): M = 779.08, orthorhombic group P2₁2₁2₁, a = 12.541(3), b = 15.024(3), c = 21.730(4), V = 4974(2), Z = 4, \( \mu = 1.264 \), crystal dimensions 0.3 x 0.4 x 0.8 mm, 6169 collected and 2639 unique reflections. Final residues R = 0.0582, wR = 0.1563 (I > 2σ(I)); R_p = 0.0657, wRp = 0.1622 (all data). SQUEEZE information: Void 1: 1298 Å³, 77 electrons. d) A solution of ZnSO₄·7H₂O (300 mg, 0.69 mmol), MTTPA (800 mg, 1.47 mmol) in dimethylformamide (10.0 mL, 129.7 mmol) was stirred briefly and heated to 180 ºC for 24 h in a PTFE-lined stainless steel acid digestion bomb. Tiny colorless crystals Zn₆H₄MTTPA (3) were recovered in 15% yield. Crystal data for 3 (Cu₆H₃O₅P·4ZnSi): M = 767.03, monoclinic space group C2/m, a = 23.480(5), b = 15.510(3), c = 12.560(3), \( \beta = 113.77(3) \), V = 4186(2), Z = 4, \( \mu = 1.217 \), crystal dimensions 0.05 x 0.08 x 0.1 mm, 21254 collected and 3721 unique reflections. Final residues R = 0.0908, wR = 0.2575 (I > 2σ(I)); 0.1908, wR = 0.2948 (all data). Goof = 1.00, 284 parameters. SQUEEZE information: Void 1: 1564 Å³, 694 electrons. [13] B. Widom, J. Chem. Phys. 1963, 39, 2802-2812. [14] O. Talu, A. L. Myers, Colloids Surf. A 2001, 187-188, 83-93 [15] L. Geb, K. Gubbins, Langmuir 1999, 15, 305–308. [16] S. Brunauer, P. H. Emmett, E. Teller, J. Am. Chem. Soc. 1938, 60, 309-319
The percentage void volumes and the specific BET surface areas of the MOFs Cu$_2$H$_4$STPPA (1, 48.7%, 794 m$^2$/g), Zn$_2$H$_4$STPPA (2, 48.1%, 565 m$^2$/g) and Zn$_2$H$_4$MTPPA (3, 51.3%, 927 m$^2$/g) obtained from the tetraphenylmethane tetrakis-4-phosphonic acid (H$_8$MTTPA) and tetraphenylsilane tetrakis-4-phosphonic acid (H$_8$STPPA) under solvothermal conditions are amongst the highest reported for MOFs derived from phosphonic acids.