

# From Tetrahedral Tetraphosphonic Acids E[ $\rho$ -C<sub>6</sub>H<sub>4</sub>P(O)(OH)<sub>2</sub>]<sub>4</sub> (E = C, Si) to Porous Cu- and Zn-MOFs with Large Surface Areas

Alexandra Schüttrumpf<sup>[a]</sup>, Aysun Bulut<sup>[b,c]</sup>, Nele Hermer<sup>[d]</sup>, Yunus Zorlu<sup>[e]</sup>, Erdoğan Kirpi<sup>[f]</sup>, Norbert Stock<sup>[d]</sup>, A. Özgür Yazaydın<sup>[g]</sup>, Gündoğ Yücesan<sup>[b\*]</sup>, Jens Beckmann<sup>[a\*]</sup>

**Abstract:** This study describes the porous MOFs Cu<sub>2</sub>H<sub>4</sub>STPPA·2 H<sub>2</sub>O (**1**·2 H<sub>2</sub>O), Zn<sub>2</sub>H<sub>4</sub>STPPA (**2**) and Zn<sub>2</sub>H<sub>4</sub>MTPPA (**3**) obtained using the tetrahedral linkers tetraphenylmethane tetrakis-4-phosphonic acid (H<sub>8</sub>MTTPA) and tetraphenylsilane tetrakis-4-phosphonic acid (H<sub>8</sub>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** (48.7%, 794 m<sup>2</sup>/g), **2** (48.1%, 565 m<sup>2</sup>/g) and **3** (51.3%, 927 m<sup>2</sup>/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.<sup>[1]</sup> The well-established inorganic building units (IBUs) in carboxylate based MOFs provided structural control.<sup>[2]</sup> The precise isorecticular expansion of known networks has provided the desired pore sizes for storage, separation, catalysis and drug delivery.<sup>[3]</sup> 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.<sup>[4]</sup> In addition, metal-organophosphonate frameworks provide remarkable structural diversity<sup>[5]</sup> offering a wide range of potential applications including magnetism, porosity, catalysis and bone regeneration.<sup>[6]</sup> 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.<sup>[4]</sup> Only few examples of isorecticular expansions of porous metal-organophosphonates have been reported, which have enabled a nitrogen donor ligand to maintain the position of the metal atoms.<sup>[7]</sup> Another method used the organoimine chelators to engineer the metal coordination to limit the number of phosphonate coordination on the metal atom.<sup>[6b]</sup> The known metal complexes of aromatic organodiphosphonates usually exhibit compact pillared-layered structures and they would exhibit tendency to pack at high densities.<sup>[4,8]</sup> One of the few reported porous metal-organophosphonate framework was synthesized using a tetrahedral tetraphosphonic acid based on a tetrahedral adamantane core.<sup>[9]</sup> 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.<sup>[9,10]</sup>

In this work the recently introduced tetrahedral linkers tetraphenylmethane tetrakis-4-phosphonic acid (H<sub>8</sub>MTTPA) and tetraphenylsilane tetrakis-4-phosphonic acid (H<sub>8</sub>STPPA),<sup>[11]</sup> are exploited for the construction of porous metal organic frameworks with copper and zinc under solvothermal conditions (Scheme 1). Thus, the reactions of H<sub>8</sub>STPPA with Cu(NO<sub>3</sub>)<sub>2</sub>·3 H<sub>2</sub>O and NaOH (approx. molar ratio 1:1:2) in H<sub>2</sub>O/MeOH (approx. volume ratio 1:1) and H<sub>8</sub>STPPA with ZnNO<sub>3</sub> (approx. molar ratio 1:1) in H<sub>2</sub>O/MeOH (approx. volume ratio 4:1) at 150°C provided crops of single crystals of the composition Cu<sub>2</sub>SiC<sub>24</sub>H<sub>16</sub>P<sub>4</sub>O<sub>8</sub>(OH)<sub>4</sub>·2 H<sub>2</sub>O = Cu<sub>2</sub>H<sub>4</sub>STPPA·2 H<sub>2</sub>O (**1**·2 H<sub>2</sub>O) and Zn<sub>2</sub>SiC<sub>24</sub>H<sub>16</sub>P<sub>4</sub>O<sub>8</sub>(OH)<sub>4</sub> = Zn<sub>2</sub>H<sub>4</sub>STPPA (**2**), respectively (the reaction conditions were optimized using high-throughput methods).<sup>[12]</sup> H<sub>8</sub>MTTPA and ZnSO<sub>4</sub>·7 H<sub>2</sub>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<sub>2</sub>C<sub>25</sub>H<sub>16</sub>P<sub>4</sub>O<sub>8</sub>(OH)<sub>4</sub> = Zn<sub>2</sub>H<sub>4</sub>MTPPA (**3**).

The crystal structure of **1**·2 H<sub>2</sub>O shows three distinct phosphonate protonation modes, which consist of a full deprotonated RPO<sub>3</sub><sup>2-</sup>, a half deprotonated RPO<sub>3</sub>H<sup>-</sup> and two fully protonated phosphonate groups RPO<sub>3</sub>H<sub>2</sub> (Figure 1).

- [a] Dr. A. Schüttrumpf, Prof. Dr. J. Beckmann  
Institut für Anorganische Chemie und Kristallographie  
Universität Bremen  
Leobener Straße, 28359 Bremen, Germany  
\*E-mail: j.beckmann@uni-bremen.de
- [b] Prof. Dr. G. Yücesan  
Department of Food Chemistry and Toxicology,  
Technische Universität Berlin  
Gustav-Meyer-Allee 25, 13355 Berlin, Germany  
\*E-mail: yucesan@tu-berlin.de
- [c] Dr. A. Bulut  
Department of Chemistry  
Bogazici University  
34342 Istanbul, Turkey
- [d] Dr. N. Hermer, Prof. Dr. N. Stock  
Institut für Anorganische Chemie  
Christian-Albrechts-Universität zu Kiel  
Max-Eyth-Straße 2, 24118 Kiel, Germany
- [e] Prof. Dr. Y. Zorlu  
Department of Chemistry  
Gebze Technical University  
P.O. Box 141 Gebze, 41400 Kocaeli, Turkey
- [f] Dr. E. Kirpi  
Department of Chemistry  
Yıldız Technical University  
Davutpasa Campus, Esenler, 34010 Istanbul, Turkey
- [g] Dr. A. Ö. Yazaydın  
Department of Chemical Engineering  
University College London  
London WC1E 7JE, United Kingdom  
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**Table 1.** Porosity and specific surface area of **1** - **3** predicted by molecular simulations.

	Void volume <sup>a</sup>	Accessible pore volume <sup>b</sup>	BET surface area <sup>c</sup>
<b>1</b>	48.7 %	40.0 %	794 m <sup>2</sup> g <sup>-1</sup>
<b>2</b>	48.1 %	33.8 %	565 m <sup>2</sup> g <sup>-1</sup>
<b>3</b>	51.3 %	46.0 %	927 m <sup>2</sup> g <sup>-1</sup>

<sup>a</sup>Computed by using a 0 Å probe size. <sup>b</sup>Computed by using a Helium probe.

<sup>c</sup>Calculated by Monte Carlo simulation.

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<sup>[13]</sup> using a helium probe. This mimics the experimental helium porosimetry at room temperature and low pressure.<sup>[14]</sup> 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,<sup>[15]</sup> which is based on the largest sphere that can fit in a pore. BET surface areas were derived from N<sub>2</sub> adsorption isotherms at 77K which were obtained by Monte Carlo simulations in the grand canonical ensemble.<sup>[16]</sup> The percentage void volumes of all three materials are very close to each other. On the other hand, their accessible pore volumes are quite different. This is due to the presence of voids which are not accessible to guest molecules as can be clearly seen in the pore size distributions calculated for **1-3** (Figure S1). Pores with diameters less than about 3 Å are not expected to be accessible to guest molecules. In particular, almost one third of the void volume in **2** is not accessible (48.1% vs 33.8%). Consequently, the accessible pore volume of the unit cells increases in the order **2** (33.8 %) < **1** (40.0 %) < **3** (46.0 %). Similarly, BET surface areas increase in the order **2** (565 m<sup>2</sup>g<sup>-1</sup>) < **1** (794 m<sup>2</sup>g<sup>-1</sup>) < **3** (927 m<sup>2</sup>g<sup>-1</sup>).

In summary, we report 3D porous copper and zinc organophosphonates, which were constructed using aromatic tetraphosphonic acids H<sub>8</sub>STPPA and H<sub>8</sub>MTPPA. 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<sub>2</sub>P<sub>2</sub>O<sub>4</sub> rings. The flexibility of the chains observed in **2** and **3** strengthen the hypothesis that isorecticular 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<sub>2</sub>-adsorption isotherms and BET surface areas. Additional references.

### Acknowledgements

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**Keywords:** Ligand Design • Metal Organic Solids • MOF • Organophosphonates •

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K. Demadis, RSC Publishing, London (2012); N. Stock, *Microporous Mesoporous Mater.* **2009**, *129*, 287-295. b) A micro teflon container (200  $\mu\text{L}$ ) was charged with a 0.07 M solution of  $\text{H}_8\text{-STPPA}$  (100  $\mu\text{L}$ , 5.00 mg, 70  $\mu\text{mol}$ ) in methanol, a 2 M solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (3.8  $\mu\text{L}$ , 1.36 mg, 76  $\mu\text{mol}$ ) in water, a 1 M solution of  $\text{NaOH}$  (15.2  $\mu\text{L}$ , 608  $\mu\text{g}$ , 15.2  $\mu\text{mol}$ ) and water (81  $\mu\text{L}$ ) 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  $\text{Cu}_2\text{H}_4\text{STPPA} \cdot 2\text{H}_2\text{O}$  (1·2  $\text{H}_2\text{O}$ ) suitable for X-ray crystallography were hand-selected. Crystal data for 1·2  $\text{H}_2\text{O}$  ( $\text{C}_{24}\text{H}_{24}\text{Cu}_2\text{O}_{14}\text{P}_4\text{Si}$ ):  $M = 815.48$ , triclinic space group  $P-1$ ,  $a = 26.882(5)$  Å,  $b = 26.885(5)$  Å,  $c = 12.264(2)$  Å,  $\alpha = 102.70(2)^\circ$ ,  $\beta = 101.02(2)^\circ$ ,  $\gamma = 76.26(2)^\circ$ ,  $V = 8308(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calc}} = 1.304$ , crystal dimensions 0.05 x 0.4 x 0.5, 30440 collected and 9971 unique reflections. Final residues  $R_1 = 0.0615$ ,  $wR_2 = 0.1565$  ( $I > 2\sigma(I)$ );  $R_1 = 0.0677$ ,  $wR_2 = 0.1605$  (all data). GooF = 0.91, 1637 parameters. SQUEZZE information: Void 1: 1456 Å<sup>3</sup>, 352 electrons; Void 2: 1341 Å<sup>3</sup>, 326 electrons. c) A micro teflon container (200  $\mu\text{L}$ ) was charged with a 0.07 M solution of  $\text{H}_8\text{STPPA}$  (40  $\mu\text{L}$ , 2.00 mg, 28  $\mu\text{mol}$ ) in methanol, a 2 M solution of  $\text{Zn}(\text{NO}_3)_2$  (3.8  $\mu\text{L}$ , 0.97 mg, 76  $\mu\text{mol}$ ) in water and water (156  $\mu\text{L}$ ) 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  $\text{Zn}_2$

$\text{H}_4\text{STPPA}$  (**2**) suitable for X-ray crystallography were hand-selected. Crystal data for **2** ( $\text{C}_{24}\text{H}_{16}\text{O}_{12}\text{P}_4\text{SiZn}_2$ ):  $M = 779.08$ , orthorhombic group  $I2_12_12_1$ ,  $a = 12.541(3)$ ,  $b = 15.024(3)$ ,  $c = 21.730(4)$ ,  $V = 4094(2)$ ,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.264$ , crystal dimensions 0.3 x 0.4 x 0.8, 6169 collected and 2639 unique reflections. Final residues  $R_1 = 0.0582$ ,  $wR_2 = 0.1563$  ( $I > 2\sigma(I)$ );  $R_1 = 0.0657$ ,  $wR_2 = 0.1622$  (all data). GooF = 1.11, 201 parameters. SQUEZZE information: Void: 1298 Å<sup>3</sup>, 77 electrons. d) A solution of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (200 mg, 0.69 mmol), MTPPA (800 mg, 1.47 mmol) in dimethylformamide (10.0 mL, 129.7 mmol) was stirred briefly and heated to 180 °C for 24 h in a PTFE-lined stainless still acid digestion bomb. Tiny colorless crystals  $\text{Zn}_2\text{H}_4\text{MTPPA}$  (**3**) were recovered in 15% yield. Crystal data for **3** ( $\text{C}_{25}\text{H}_{20}\text{O}_{12}\text{P}_4\text{Zn}_2$ ):  $M = 767.03$ , monoclinic space group  $C2/m$ ,  $a = 23.480(5)$ ,  $b = 15.510(3)$ ,  $c = 12.560(3)$ ,  $\beta = 113.77(3)$ ,  $V = 4186(2)$ ,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.217$ , crystal dimensions 0.05 x 0.08 x 0.1, 21254 collected and 3721 unique reflections. Final residues  $R_1 = 0.0908$ ,  $wR_2 = 0.2575$  ( $I > 2\sigma(I)$ ); 0.1908,  $wR_2 = 0.2948$  (all data). GooF = 1.00, 284 parameters. SQUEZZE information: Void: 1564 Å<sup>3</sup>, 694 electrons.

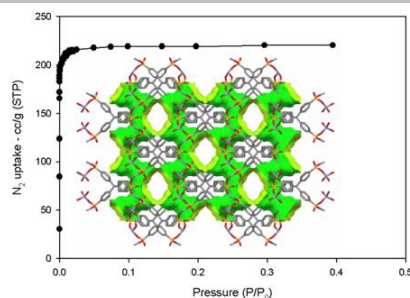
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Layout 1:

## COMMUNICATION

The percentage void volumes and the specific BET surface areas of the MOFs Cu<sub>2</sub>H<sub>4</sub>STPPA (**1**, 48.7%, 794 m<sup>2</sup>/g), Zn<sub>2</sub>H<sub>4</sub>STPPA (**2**, 48.1%, 565 m<sup>2</sup>/g) and Zn<sub>2</sub>H<sub>4</sub>MTPPA (**3**, 51.3%, 927 m<sup>2</sup>/g) obtained from the tetraphenylmethane tetrakis-4-phosphonic acid (H<sub>8</sub>MTTPA) and tetraphenylsilane tetrakis-4-phosphonic acid (H<sub>8</sub>STPPA) under solvothermal conditions are amongst the highest reported for MOFs derived from phosphonic acids



Author(s), Corresponding Author(s)\*

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