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COMMUNICATION

Formation of a Non-Porous Cobalt-Phosphonate Framework by small pH Change in the Preparation of the Microporous STA-16(Co)

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The initial pH in the preparation of STA-16(Co) was found to have a great impact on the assembly of the MOF and the resulting porosity. The formation of a non-porous Co(II)-phosphonate pillared layer-structure was observed after 10 changing the initial pH from 6.2 to 7.2 with distinct differences in the coordination environment of the cobalt centres.

Metal-organic frameworks (MOFs) have recently emerged as a class of very promising organic-inorganic hybrid materials for 15 diverse applications like gas storage, gas/vapour separation, catalysis, luminescence, fluorescence and drug storage and delivery.[1, 2]

The vast majority of MOFs contain carboxylate or nitrogen donors (pyridines, polyazolates). There are fewer examples of 20 phosphonate and sulfonate based systems, even though metal phosphonates were among the first microporous inorganic hybrid adsorbents to be investigated.[3-7] Reasons for this include:

- the predisposition of simple metal phosphonates to form dense layered motifs due to the strong affinity and chelation 25 of phosphonate groups to metal ions, which makes forming high surface area materials a challenge;
- the growth of single crystals is generally more difficult as they often precipitate rapidly as less ordered, insoluble phases;
30 - the coordination chemistry of phosphonates is less predictable owing to more possible ligation modes and three possible states of protonation.[8, 9]

However, many research groups, notably those of Clearfield[10-17] and Zubieta[18-22], have pioneered the use of phosphonate ligands 35 in transition-metal chemistry involving solvothermal synthetic procedures. Metal phosphonates find wide range of applications in cation exchange, sorption, catalysis, catalyst supports, sensors

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50 as well as non-linear optics.[23]

The solubility of divalent metal phosphonates is high enough to obtain single crystals by hydrothermal/solvothermal techniques. In contrast to this, trivalent and tetravalent metal phosphonates are highly insoluble and tend to precipitate as poorly ordered 55 layered materials, which are rarely crystalline.[16]

Most metal phosphonates don't possess pores larger than 0.6 nm resulting in a low uptake of adsorbates. However, porous structures can be obtained by incorporation of co-ligands/templates or a direct reaction of metal salts with 60 phosphonic acids.[24, 25] For example the formation of porous structures using *N,N'-4,4'*-bipiperidinebis(methylenephosphonic acid) tetra-hydrate (H_4LL) was successfully accomplished.[26] The organic linker contains two phosphonic acids, both capable of three total states of protonation, as well as two amino nitrogen 65 atoms capable of two protonation states. Wharmby et al. were the first to report the preparation and characterization of a phosphonate MOF containing a hexagonal array of channels parallel to the *c*-axis with a free diameter of 1.8 nm, which is known as STA-16(Co). The framework structure, determined by 70 Rietveld analysis of powder diffraction data, contains one crystallographic distinct cobalt center, which is coordinated in a distorted octahedral fashion to four phosphonate oxygens, one piperazinyl nitrogen and one oxygen atom of a water molecule. Hydrogen bonding of the lattice and coordinated water molecules 75 with the P=O bond projecting into the channels is present. The framework crystallizes in the trigonal space group $R\overline{3}$ and can be described with the empirical formula $Co_2(H_2O)_2[LL]\cdot11H_2O$ ($LL=C_{12}H_{22}N_2P_2O_6$).[27]

In this communication we describe the synthesis and 80 characterisation of a related non-porous cobalt-phosphonate framework (CoMOF), which can be obtained by changing the initial pH during the synthesis of the microporous STA-16 framework from 6.2 to 7.2. The effect of different pH values between 6.2 and 7.9 on the formation of the porous vs. non-85 porous framework was studied.
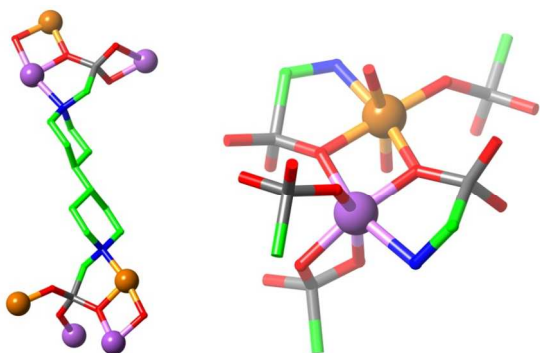
The synthesis was performed under hydrothermal conditions giving purple needle like crystals (‡). The procedure for the synthesis of STA-16(Co) was repeated and in contrast to the pH of 8 stated by Wright et al.,[28] we measured the pH to be 6.2. 90 Increases in the pH to 6.8 resulted in the formation of both STA-16(Co) and CoMOF, while alkaline conditions (pH 7.2, 7.6 and 7.9) were found to form only the non-porous CoMOF.

Fig. 1: The local coordination geometries of the ligand LL and the cobalt atoms. Carbon atoms are shown as green, nitrogen blue, oxygen red, phosphorous grey, Co(1) orange, and Co(2) purple.

5 Structural characterization by single crystal X-ray crystallography showed the empirical formula of the product to be $Co_2(H_2O)_2[LL]$ (LL=$C_{12}H_{22}N_2P_2O_6$). While both CoMOF and STA-16(Co) contain two coordinated water molecules, no lattice water is present in the non-porous framework structure.

10 The Co-MOF crystallizes in the monoclinic space group $P2_1/c$ and features a 3D framework structure. The asymmetric unit contains one LL ligand, two cobalt atoms (Co(1) and Co(2)) and two water molecules coordinated to Co(1). Each ligand LL coordinates to seven metal atoms, three at one end (one Co(1) and 15 two Co(2)) and four at the other end (two Co(1) and two Co(2)). All oxygen and nitrogen atoms of the ligand coordinate (Fig. 1, left).

The two crystallographically distinct cobalt atoms display different coordination environments (Fig. 1, right). The Co(1) 20 center is coordinated in a distorted octahedral geometry by three oxygen atoms of the phosphonate group, one piperazinyl nitrogen atom (N(1)) and two oxygen atoms of water molecules. The Co(1)-N(1) distance is 2.228(2) Å, the Co(1)-O(water) distances are 2.147(2) and 2.162(2) Å and the Co(1)-25 O(phosphonate)distances range from 1.978(2) to 2.099(2) Å. The coordination environment of Co(2) also shows a distorted octahedral geometry, it is built up by the coordination of five oxygen atoms and one piperazinyl nitrogen atom (N(2)) (Co(2)-O(phosphonate): 2.040(2) to 2.542(2) Å, Co(2)-N(2): 2.332(2) 30 Å). At the N(2) end of the ligand two of the oxygens chelate to a Co(2), while the third bridges a Co(1) and a Co(2) in μ_2-fashion. One P=O bond from each phosphonate group forms hydrogen bonds to a water molecule coordinating to the Co(1) centre. The H-bonding distances between the oxygen atoms are 2.758(3) and 35 3.064(4) Å.

The two μ_2-oxygen atoms of the ligands bridge one of each metal type into dinuclear pairs, as shown in Fig. 1(right). These pairs are then bridged by the remaining phosphonate oxygen atoms to adjacent pairs, forming a 2D sheet (Fig. 2, top). While 40 the sheet appears superficially to have (6,3) topology, closer inspection reveals a more complicated connectivity, with one phosphonate bridging two dinuclear clusters, while the other connects three. The sheets are then connected by the organic backbones of the LL ligands, to give an overall 3D pillared-layer 45 type network (Fig. 2, bottom).

The comparison of the measured powder X-ray diffractogram with the theoretical diffractogram of the CoMOF and STA-16 (Fig. 3) confirms the purity of the bulk sample with no STA-16
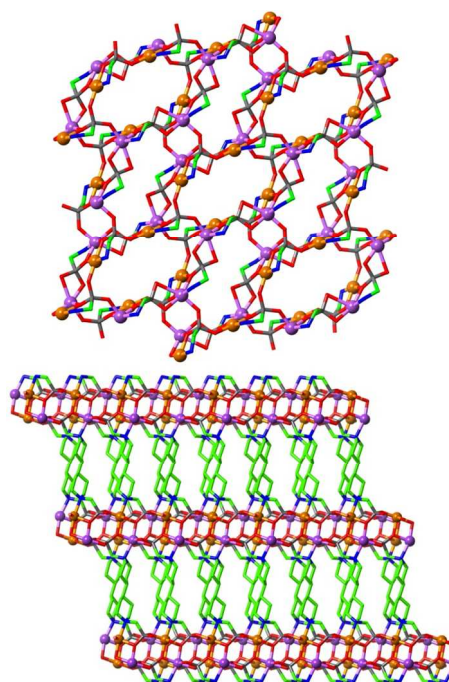
Fig. 2: A 2D layer formed by the bridging of Co$_2$ dinuclear species by the phosphonate groups of the ligand LL (top). The overall 3D pillared layer structure (bottom).
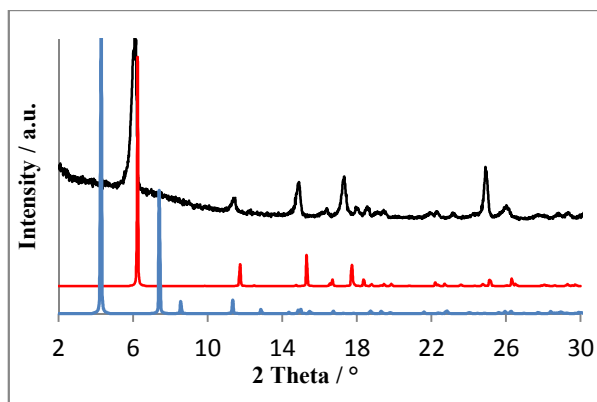
Fig. 3: Comparison of experimental (black, 25 °C) and the predicted diffractograms of CoMOF (red, -150 °C) and STA-16(Co) (blue, -173 °C).

detected. The theoretical diffractograms were calculated from the 60 crystal structures using the module "Reflex Tools" in Materials Studio 6.0.[29] Figure S1 shows the diffractograms obtained from the samples synthesized at different pH values. The results indicate, that STA-16(Co) is formed under slightly acidic conditions, while the formation of a phase pure CoMOF requires 65 slightly basic conditions. Increasing the pH towards 7, results in the formation of a mixed phase material, containing STA-16 and CoMOF.

The SEM image (Fig. 4) shows the formation of elongated crystals of various sizes between 1 to 350 µm. Energy dispersive 70 X-ray analysis indicated a Co:P ratio of 1.8, which is in good agreement with the theoretical value of 1.9 calculated from the empirical formula $Co_2C_{12}H_{26}N_2O_8P_2$ based on a wt% basis.

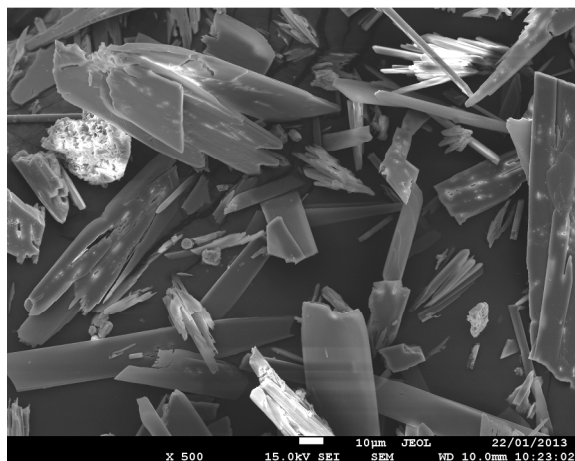Thermogravimetric analysis of the CoMOF shows a plateau

Fig. 4: SEM image of the CoMOF taken at 15 kV.

until 230 °C, after which thermal decomposition of the framework occurs. The decomposition temperature of 230 °C was also reported for STA-16(Co).[27]

Argon sorption data measured at -186 °C using a ASAP 2020 porosimeter indicate a total pore volume of 0.004 cm^3 g^{-1} and a BET surface area of about 3 m^2 g^{-1}, confirming the lack of porosity. In contrast to this, the pore volume of STA-16(Co) was reported to be 0.68 cm^3 g^{-1} (at p/p_0=0.4), which is 170 times higher.[27]

The IR spectrum (Fig. S4) of the CoMOF shows strong bands at 3427 cm^{-1} (O-H stretch) and 1652/1612 cm^{-1} (O-H bend), which are due to the water molecule coordinating to the Co(1) center. The bands at 2907 to 3003 cm^{-1} and 2838/2874 cm^{-1} are characteristic for methylene C-H stretch and P-O(H) stretch vibrations. The second P-O(H) stretch can be found at 869 cm^{-1}. C-C stretches were observed between 1444 and 1389 cm^{-1}. Three characteristic bands of the phosphonate groups are observed at 1346 to 1292 cm^{-1} (P=O stretch), 1271/1256 cm^{-1} (P-O-H bend) and 1005/988 cm^{-1} (P-O stretch). The alkyl C-N stretch can be found at 1271 and 1256 cm^{-1}.

In summary, we have shown that the pH has a big effect on the chelation of the phosphonate groups to the cobalt cations during the synthesis of STA-16(Co). Adjusting the pH to 7.2, results in the formation of a non-porous cobalt-phosphonate framework with a 3D pillared-layer structure, instead of a porous MOF. In both MOFs, the cobalt atoms are coordinated in a distorted octahedral geometry, however the metal phosphonate interactions form a 2D substructure in CoMOF and 1D chains in STA-16(Co). This is the crucial difference between forming porous and non-porous motifs, and suggests that careful control of pH in the synthesis of other non-porous pillared-layer phosphonate systems may lead to new porous phases.

Acknowledgements

Notes and references

‡ All reagents were commercially available and used without further purification except for *N,N'-4,4'*-bipiperidinebis (methylene-phosphonic acid) tetrahydrate (H₄LL) whose synthesis has been described in the literature.[27] The hydrothermal synthesis of the CoMOF was performed by suspending 499 mg of cobalt(II) acetate tetrahydrate and 428 mg H₄LL in 16.2 mL water and adjusting the pH to 7.2 by adding potassium hydroxide. After aging the suspension for 30 minutes at room temperature, the mixture was heated to 220 °C for 72 h. The resulting purple needle like crystals were washed with water and dried at room temperature.

§ Selected crystal data for CoMOF: $Co_2C_{12}H_{26}N_2O_8P_2$, FW = 506.15, monoclinic, *P 21/c*, a = 15.0954(6), b = 11.5689(4), c = 10.6232(4), β = 110.192(4), V = 1741.19(11), Z = 4, 3699 observed reflections [R_{int} = 0.0333], $R_1(I > 2\sigma)$ = 0.0356, wR_2(all data) = 0.0892.

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29 *"Reflex Tools" is a module in the Materials Studio Modeling software package from Accelrys Inc.*

The initial pH of the suspension was found to determine whether the porous STA-16(Co) phase or a non-porous Co(II)-phosphonate pillared layer structure was formed.