Electronic Supplementary Material (ESI) for *CrystEngComm*

Supplementary Information

Meta-phosphonobenzoic acid and copper(II) as precursors of helical chain and lamellar hybrid materials

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Hydrothermal synthesis

Preparation of compound $Cu_6(H_2O)_7(m\text{-}PO_3C_6H_4CO_2)_4$ ***(1)***

In a 50 mL PTFE insert, 1 equivalent of 3-phosphono-benzoic acid (0.1 g, 0.49 mmol) was dissolved in distilled water (15 mL). To this solution was respectively added 1.5 equivalent of $Cu(CH_3COO)_2$ (0.134 g, 0.74 mmol) and 1.5 equivalent of urea (0.044 g, 0.74 mmol) (For pH see Table 1). The insert was then transferred in a Berghof pressure digestion vessel and heated from room temperature to 160°C in 18 hours, further heated at 160°C for 40 hours and cooled to room temperature in 18 hours. After filtration, the resulting compound is obtained as dark green needles crystallites, washed with water, rinsed with absolute ethanol and dried in air (yield: 0.096 g ; 60 %).
$Cu_6H_{30}O_{27}P_4C_{28}$ (1303.69): Calc. C 25.80, H 2.32; Found C 25.21, H 2.79. IR (KBr): 3605, 3350, 3080, 1609, 1566, 1473, 1436, 1400, 1274, 1181, 1128, 1111, 1084, 1050, 998, 973, 949, 773, 763, 750, 692, 670, 579, 486, 418.

Preparation of compound $Cu(H_2O)(m\text{-}PO_3C_6H_4CO_2H)$ ***(2)***

In a 50 mL PTFE insert, 1 equivalent of 3-phosphono-benzoic acid (0.1 g, 0.49 mmol) was dissolved in distilled water (15 mL). To this solution was respectively added 1.5 equivalent of $Cu(CH_3COO)_2$ (0.134 g, 0.74 mmol) (For pH see Table 1). The insert was then transferred in a Berghof pressure digestion vessel and heated from room temperature to 160°C in 18 hours, further heated at 160°C for 40 hours and cooled to room temperature in 18 hours. After filtration, the resulting compound is obtained as light green plate crystallites, washed with water, rinsed with absolute ethanol and dried in air (yield: 0.094 g ; 68 %).
$CuC_7H_7O_6P$ (281.65): Calc. C 29.85, H 2.51 ; Found C 29.75, H 2.81. IR (KBr): 3315, 3175, 2896, 2688, 2609, 2571, 1697, 1598, 1581, 1484, 1431, 1403, 1315, 1270, 1158, 1107, 1074, 1030, 998, 966, 953, 920, 827, 750, 681, 657, 599, 578, 568, 492.

Table S1. Summary of the hydrothermal syntheses of materials **1** and **2**. The syntheses were carried out with 0.1 g of 3-phosphonobenzoic acid (0.49 mmol) in water (15 mL). The hydrothermal conditions are: 160°C for 40 h.

Inorganic Precursor (1.5 eq.)	Urea (eq.)	Initial pH[a]	Final pH[b]	Materials	Compound Number
$Cu(CH_3COO)_2$	1.5	3.9	5.5	$Cu_6(H_2O)_7(m\text{-}PO_3\text{-}C_6H_4\text{-}CO_2)_4$	**1**
$Cu(CH_3COO)_2$	none	3.9	3.4	$Cu(H_2O)(m\text{-}PO_3\text{-}C_6H_4\text{-}CO_2H)$	**2**

[a] measured 15 minutes after stirring the substrates in water [b] measured at the opening of the pressured vessel

Infra Red Spectroscopy

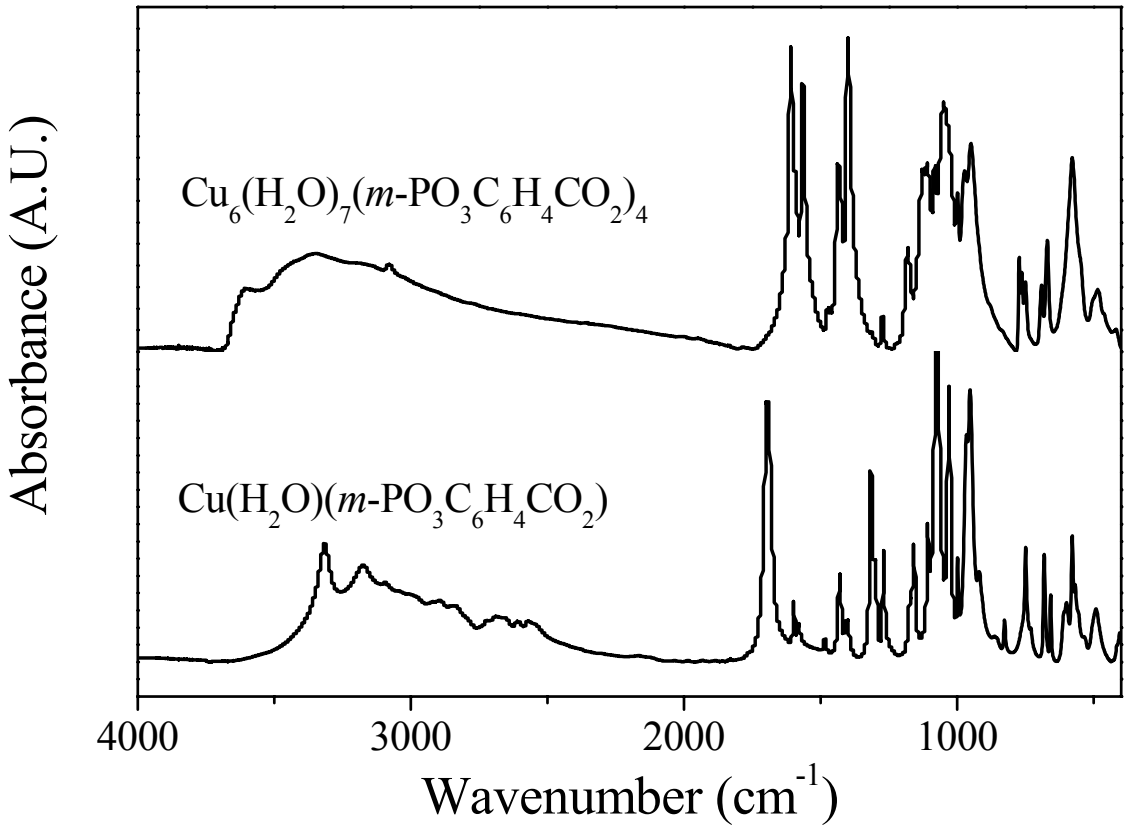

Figure S1. Infra Red spectra of $Cu_6(H_2O)_7(m\text{-}PO_3C_6H_4CO_2)_4$ (**1**) and $Cu(H_2O)(m\text{-}PO_3C_6H_4CO_2H)$ (**2**)

Crystal structure

Table S2 Summary of crystal data, intensity measurement and structure refinement

Chemical formula	$Cu_6(H_2O)_7(m\text{-}PO_3C_6H_4CO_2)_4$ (**1**)	$Cu(H_2O)(m\text{-}PO_3C_6H_4CO_2H)$ (**2**)
Molecular weight	1303.69	281.65
Crystal system	Hexagonal	Monoclinic
Space group	$P6_522$ (179)	$P2_1/n$ (14)
Cell dimensions a	14.656(3)Å	4.8414(3)Å
b	14.656(3)Å	32.557(3)Å
c	16.905(2)Å	5.7845(9)Å
α	90.°	90.°
β	90.°	96.016(7)°
γ	120.°	90.°
Cell volume	3144.8(5)Å^3	906.75(11)Å^3
Z	3	4
density	2.0645	2.0625
μmm^{-1}	3.238	2.589
T min	0.5518	0.7778
T max	0.8430	0.9352
Measured reflections	18435	12609
Independent data	3051	4066
Independent data with I<3σ	1881	3097
Temp. of the data collect.	21°C	21°C
Secondary extinction	0.43(9)	0.0013(4)
Number of variables	171	165
R(Fo)	0.0484	0.0289
Rw	0.0493	0.0295

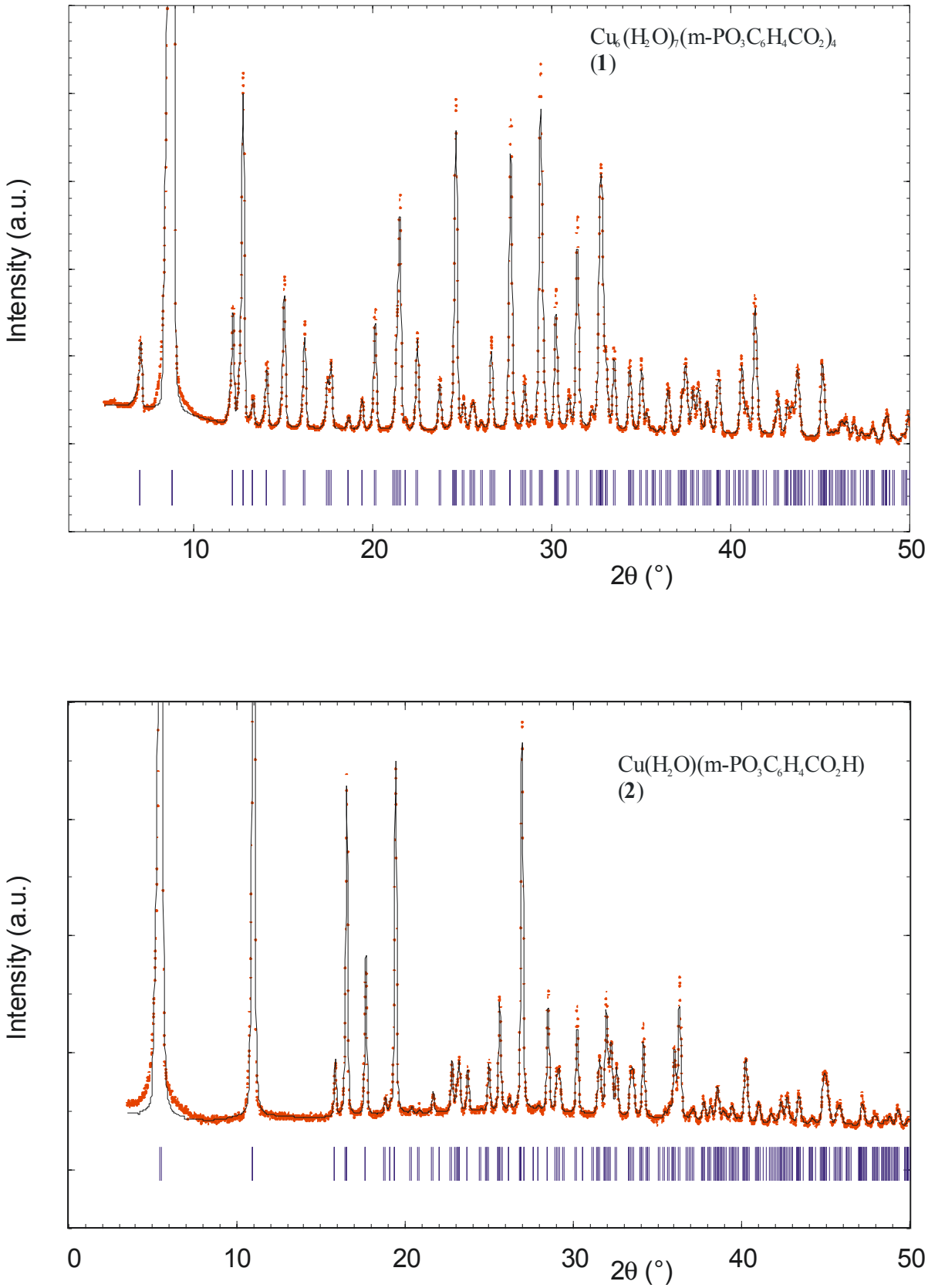

Figure S2 X-ray diffraction data recorded on powder from compound **1** and **2** (The vertical dashes correspond to the calculated position of the peaks, the black line to the calculated pattern).