Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information – The crystallisation of copper(II) phenylphosphonates

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1 Comparison of the powder pattern of γ-$Cu(O_3PC_6H_5)\cdot H_2O$ (3) as synthesized and calculated

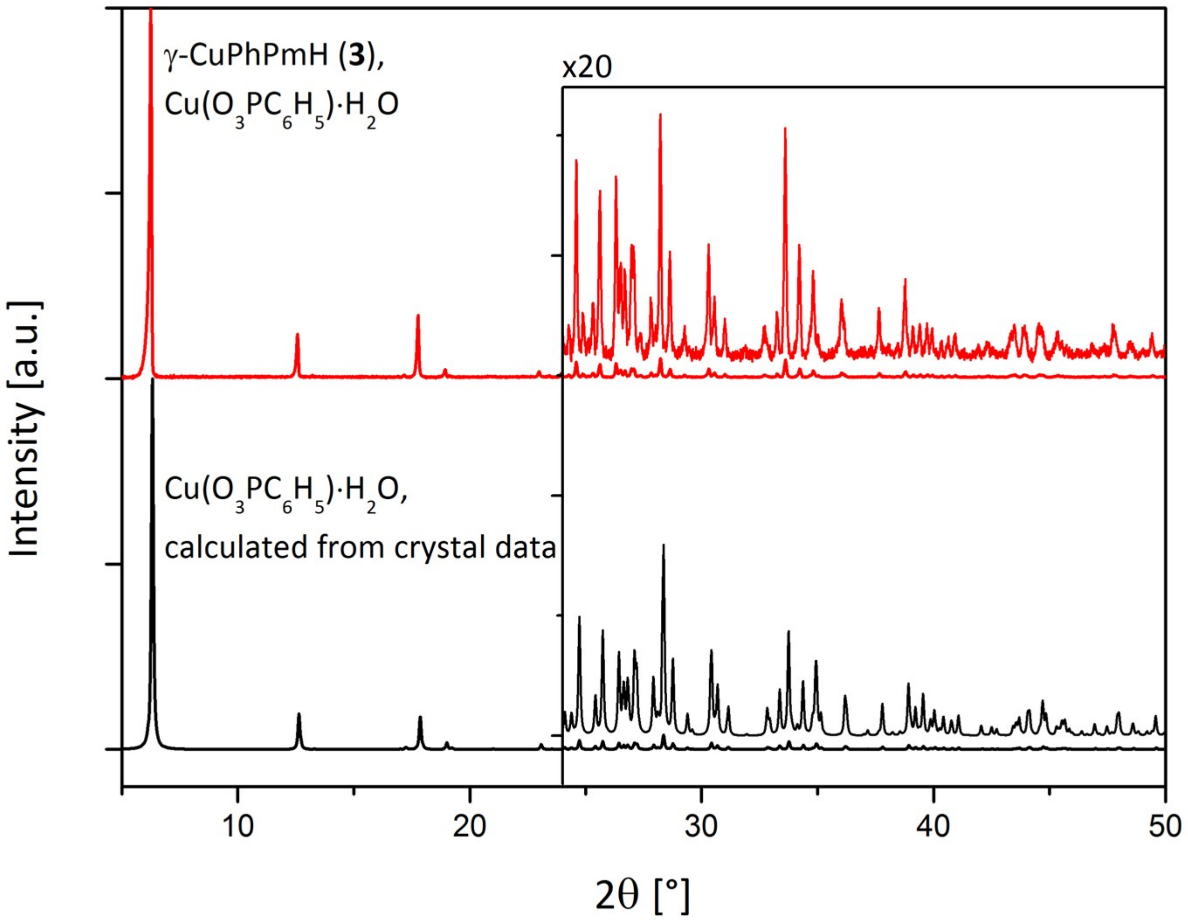

Figure S1: Comparison of the measured PXRD pattern of the synthesized γ-$Cu(O_3PC_6H_5)\cdot H_2O$ (**3**) and the calculated PXRD pattern from the crystal data.[1]

2 Setup of the *in situ* investigations

Setup of the in situ investigation of mechanochemical reactions

A vibration ball mill (Pulverisette 23, Fritsch GmbH, Germany) was used. The compounds were weighed in a 10 mL self-constructed Perspex vessel with two stainless steel balls (4 g, diameter 10 mm). The total load of all solids was 1 g. The reactions were conducted at 30 Hz and 50 Hz. In a typical experiment measurements were carried out every 30 s with a delay time of 3 s to 4 s. The given times are rounded to full 15 s. The *ex situ* investigations of mechanochemical reactions followed the same procedure, except that a stainless steel vessel was used. The reaction was stopped every 30 s and a small amount of powder was retrieved and measured using synchrotron XRD. The time between retaining the sample and measurement was about two hours.

Setup of the in situ investigation of precipitation reactions

In situ investigations of precipitation reactions were conducted with the stopped-flow module SFM3000 (Bio-Logic SAS, France) equipped with a capillary head. The three inner syringes of the SFM were filled with both starting materials and a 1 M HCl washing solution, respectively. The syringes were regulated by the computer program Bio-Kine32 (Version 4.70, Bio-Logic SAS, France). The starting materials were mixed and the reaction solution pushed through the capillary. For the measurements a custom-made extension was used, connecting the end of the capillary head with a second horizontal orientated capillary through exchangeable tubes. To acquire diffraction pattern from early reaction times, measurements were performed on flowing solutions. This allows acquiring longer counting times per measurement for one certain time of the reaction path. The reaction times were calculated from the flow rate and the volume of the whole distance the reaction mixture has passed. Every point was measured two times. The setup is shown in Figure S2. For the measurements of particular times a single measurement with 30 s measuring time was carried out. For scan measurements the reaction solution was pushed in the horizontal capillary and then stored for the investigation. The scan measurements were carried out every 30 s with a delay time of 3-4 s. The given times are rounded to full 15 s.

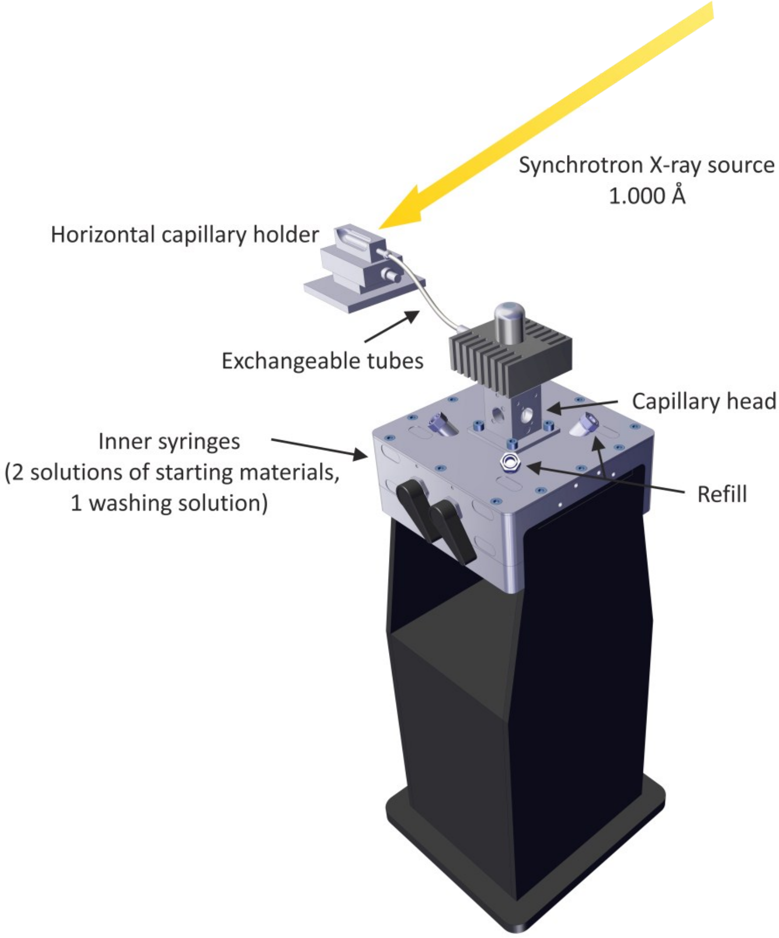

Figure S2: Setup of the stopped flow module SFM-3000 as used for the *in situ* investigations of precipitation reactions. The measurements took place in the horizontal capillary holder. For measurements of reaction times between 1 s and 10 s the times were achieved by varying the tube length and the flow rate.

3 Selected bond length and angles for compound (1), (2), and (4)

Table S1: Selected bond length and angles for α-$Cu(O_3PC_6H_5)\cdot H_2O$ (**1**).

Atoms	Contacts [Å]	Atoms	Angle [°]
Cu1 -O1	1x 2.00(2)	O1-Cu1-O2	76.2(3)
-O2	2x 2.191(9)	O1-Cu1-O2	95.3(3)
-O2	2x 2.224(9)	O2-Cu1-O2	61.2(4)
-O3	1x 2.24(2)	O2-Cu1-O2	98.7(4)
P1 -O1	1x 1.552(9)	O2-Cu1-O2	100.9(3)
-O2	2x 1.59(1)	O2-Cu1-O3	91.4(3)
		O2-Cu1-O3	93.9(3)
		O2-P1-O2	91.8(5)
		O1-P1-O2	121.6(4)

Table S2: Selected bond length and angles for β-$Cu(O_3PC_6H_5)\cdot H_2O$ (**2**).

Atoms	Contacts [Å]	Atoms	Angle [°]
Cu1 -O3	1.925(2)	O1-Cu1-O1	87.74(6)
-O2	1.964(2)	O1-Cu1-O2	89.65(6)
-O1	1.969(2)	O1-Cu1-O3	109.26(6)
-O4	1.992(2)	O1-Cu1-O4	88.10(7)
-O1	2.343(2)	O2-Cu1-O1	90.31(7)
P1 -O3	1.527(2)	O2-Cu1-O3	93.50(7)
-O2	1.532(2)	O4-Cu1-O1	81.41(6)
-O1	1.536(2)	O4-Cu1-O3	90.64(7)
		O1-P1-O2	111.53(9)
		O1-P1-O3	111.50(9)
		O2-P1-O3	111.67(9)

Table S3: Selected bond length and angles for $Cu(HO_3PC_6H_5)_2$ (**4**).

Atoms	Contacts [Å]	Atoms	Angle [°]
Cu1 -O3	2x 1.934(3)	O2-Cu1-O4	89.75(4)
-O4	2x 2.192(2)	O2-Cu1-O4	90.25(4)
-O2	2x 2.312(2)	O2-Cu1-O3	88.0(1)
P1 -O3	1.511(3)	O2-Cu1-O3	92.0(1)
-O1	1.541(2)	O3-Cu1-O4	87.79(7)
-O2	1.542(2)	O3-Cu1-O4	92.21(7)
		O1-P1-O2	106.2(1)
		O1-P1-O3	115.0(1)
		O2-P1-O3	112.9(1)

3 EXAFS data and fit parameter for compound (1)-(4)

The beam was monochromatized using a double-crystal monochromator (DCM). The size of the beam spot was 3 x 1 mm. The measurement was performed at Cu-K edge (8979 eV) in transmission. The excitation energy was varied from 8826 eV to 9831 eV, with varying energy steps. For the pre-edge region, the energy was varied in 10 eV steps; for the region around the edge, energy was tuned in 0.5 eV steps and in the EXAFS region with a constant step in the k-space of 0.02 Å^{-1}. For the measurements the samples were mixed with boron nitride and fixed in plastic sample holders. EXAFS data were processed by ATHENA and ARTEMIS.[2] This GUIs program belongs to the main package IFEFFIT (v. 1.2.11). The CuPhP phases were theoretically modelled and fitted to the measured spectra using ARTEMIS.

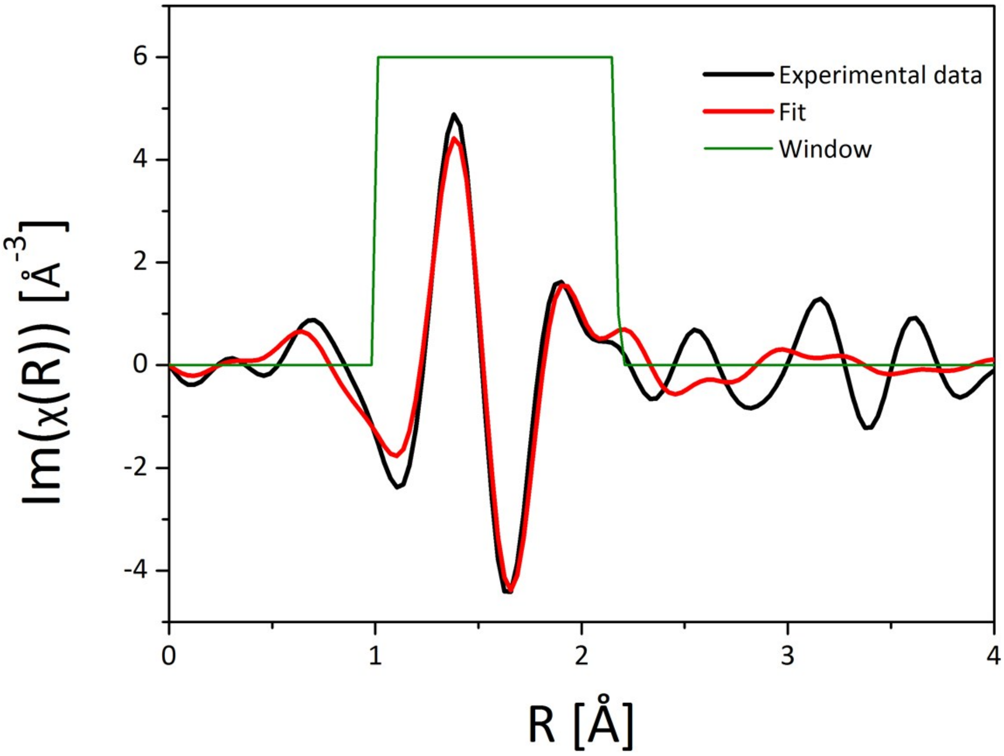

Figure S3: Cu K-edge EXAFS data shown in real space for compound α-CuPhPmH (**1**). R = 0.028; experimental data: black, fit results: red, window: green.

Table S4: EXAFS fit parameters of α -CuPhPmH (**1**). The root mean square error (RMSE) is 0.197 Å.

Scattering path	R_{model} [Å]	R_{fit} [Å]	R_{diff}^2 [Å^2]
Cu1 -O1	2.00	2.25	0.0625
-O2	2.19	1.97	0.0484
-O2	2.22	2.01	0.0441
-O3	2.24	2.25	0.0001

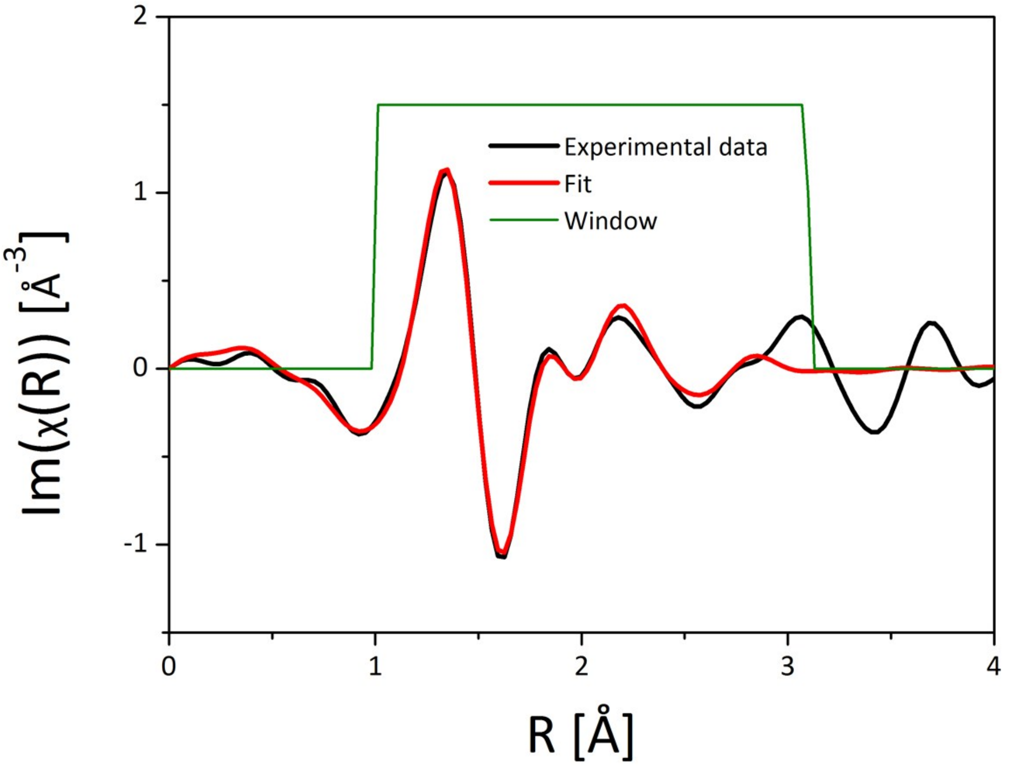

Figure S4: Cu K-edge EXAFS data shown in real space for compound β-CuPhPmH (**2**). R = 0.015; experimental data: black, fit results: red, window: green.

Table S5: EXAFS fit parameters of β-CuPhPmH (**2**). The root mean square error (RMSE) is 0.051 Å.

Scattering path	R_{model} [Å]	R_{fit} [Å]	R_{diff}^2 [Å^2]
Cu1 -O3	1.92	1.84	0.0064
-O2	1.97	1.94	0.0009
-O1	1.97	1.94	0.0009
-O4	1.99	1.97	0.0004
-O1	2.34	2.35	0.0001
-P1	3.06	3.02	0.0016
-P1	3.07	3.02	0.0025
-Cu1	3.12	3.03	0.0081

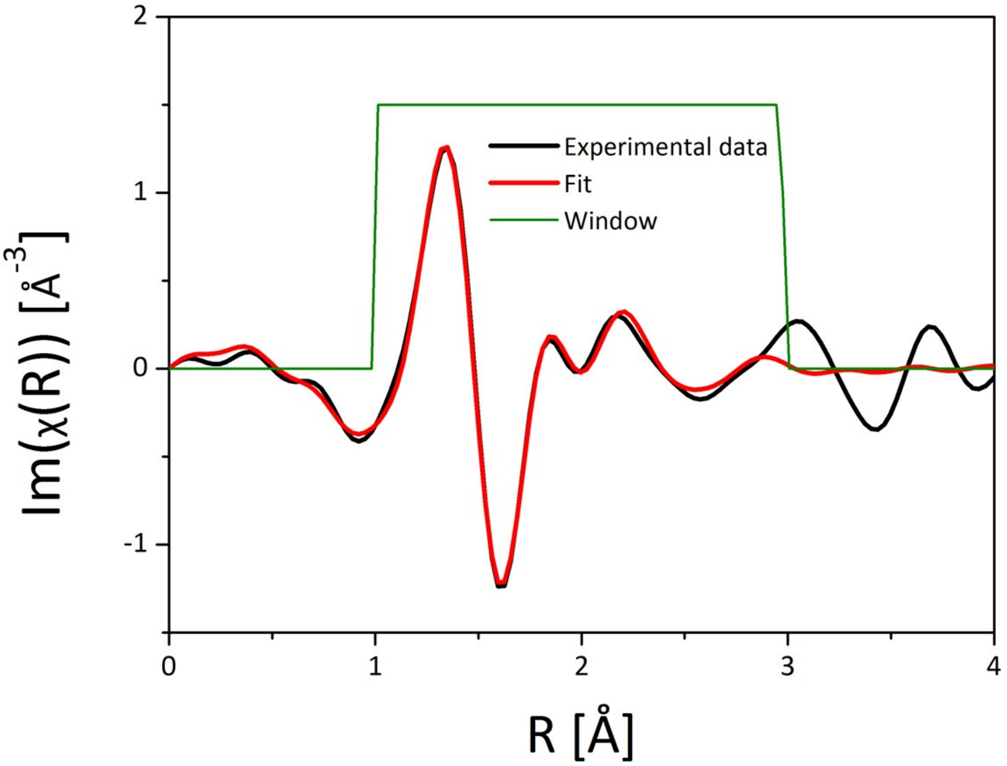

Figure S5: Cu K-edge EXAFS data shown in real space for compound γ-CuPhPmH (**3**). R = 0.01; experimental data: black, fit results: red, window: green.

Table S6: EXAFS fit parameters of γ-CuPhPmH (**3**). The root mean square error (RMSE) is 0.04 Å.

Scattering path	R_{model} [Å]	R_{fit} [Å]	R_{diff}^2 [Å^2]
Cu1 -O3	1.92	1.83	0.0081
-O2	1.95	1.95	0.0000
-O4	1.96	1.95	0.0001
-O1	1.99	1.95	0.0016
-O4	2.34	2.38	0.0016
-P1	3.02	3.03	0.0001
-P1	3.05	3.06	0.0001
-O2	3.10	3.11	0.0001
-Cu1	3.10	3.05	0.0025

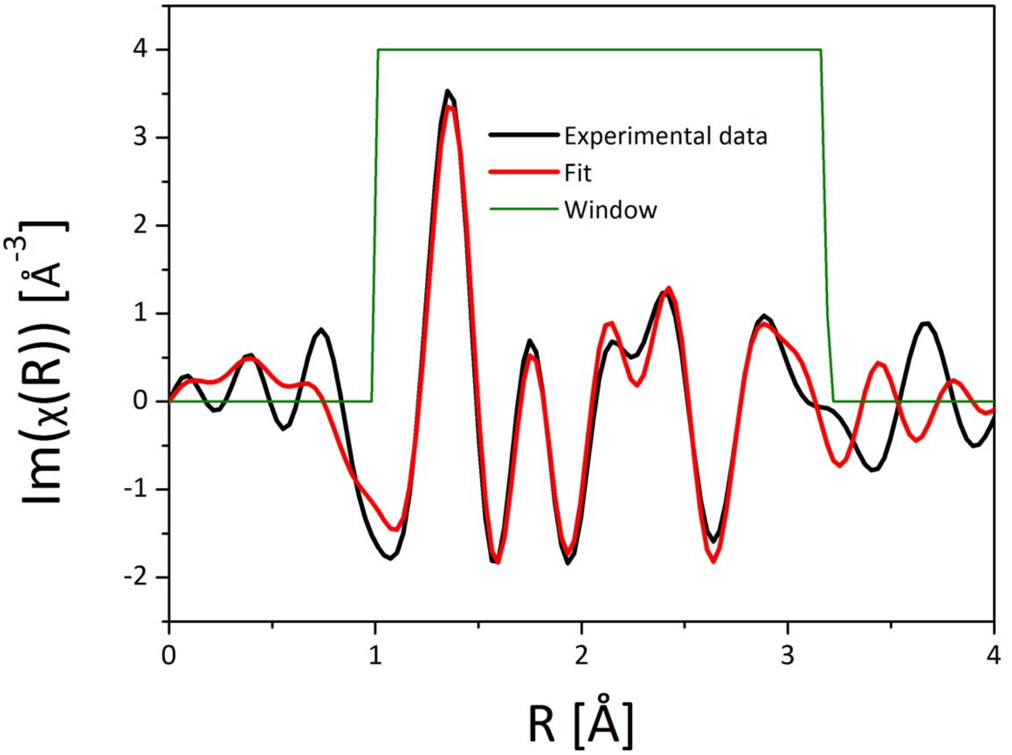

Figure S6: Cu K-edge EXAFS data shown in real space for compound CuPhP2mH (**4**). R = 0.01; experimental data: black, fit results: red, window: green.

Table S7: EXAFS fit parameters of CuPhP2mH (**4**). The root mean square error (RMSE) is 0.089 Å.

Scattering path		R_{model} [Å]	R_{fit} [Å]	R_{diff}^2 [Å²]
Cu1	-O3	1.93	1.89	0.0016
	-O4	2.19	2.04	0.0225
	-O2	2.31	2.24	0.0049
	-P1	3.18	3.19	0.0001
	-O1	3.47	3.23	0.0196
	-O2	3.55	3.58	0.0009
	-P1	3.60	3.68	0.0064

5 Formation of anhydrous copper(II) phenylphosphonates investigated by PXRD and DTA-TG data for compound (1)-(4)

Heating the compounds (**1**)-(**3**) up to 200 °C leads to the formation of the same anhydrous copper(II) phenylphosphonate, as mentioned by Cunningham *et al.*[3] The respective PXRD patterns are shown in Figure S7. At low 2θ three strong reflections can be obtained (5.7°, 11.4°, 17.2°) suggesting that the layered structure is still intact. Because of the low quality of the other reflections a structure solution from the powder data is not possible. Heating CuPhP2mH (**4**) up to 200 °C also leads to a transformation (Figure S7). The PXRD pattern is different than the patterns for compounds (**1**)-(**3**) after the annealing process.

For the DTA and TGA measurements the thermobalance SETARAM TAG24 in 1600 °C configuration was used. The measurements were performed in a N_2/synthetic air flow in an open Pt jar. The used heating rate was 10 K/min. No cycle measurements were taken.

The plots of the DTA-TG measurements for the compounds (**1**)-(**3**) are shown in Figure S8-S10, respectively. The mass loss of one water molecule per formula unit for the three polymorphs is theoretically 7.6%.

The DTA-TG measurements show that α-CuPhPmH (**1**) loses about 7.9% of its mass at 180 °C, β-CuPhPmH (**2**) loses 8% of its mass at 222 °C, and γ-CuPhPmH (**3**) exhibits a weight loss of 7.9% at 186 °C. In all three cases the loss of the one water molecule can be obtained. This supports that the products are anhydrous copper(II) phenylphosphonates after the annealing process.

For CuPhP2 (4) two mass losses can be obtained. The first is at 112 °C with a mass loss of 4.7% and the second one at 220 °C with a mass loss of 4.4%. The theoretically value for the mass loss of the one water molecule in the formula unit is 4.6%. The water molecule is included in the coordination of the Cu^{2+}-ion and bridges two CuO_6-octahedra. Compared with the results of the DTA-TG measurements of the compounds (**1**)-(**3**) the temperature at 220 °C is more suitable for the loss of the water molecule. The first mass loss is probably the results of some adsorbed surface water. The crystal structure does not contain some space for a second water molecule in the network.

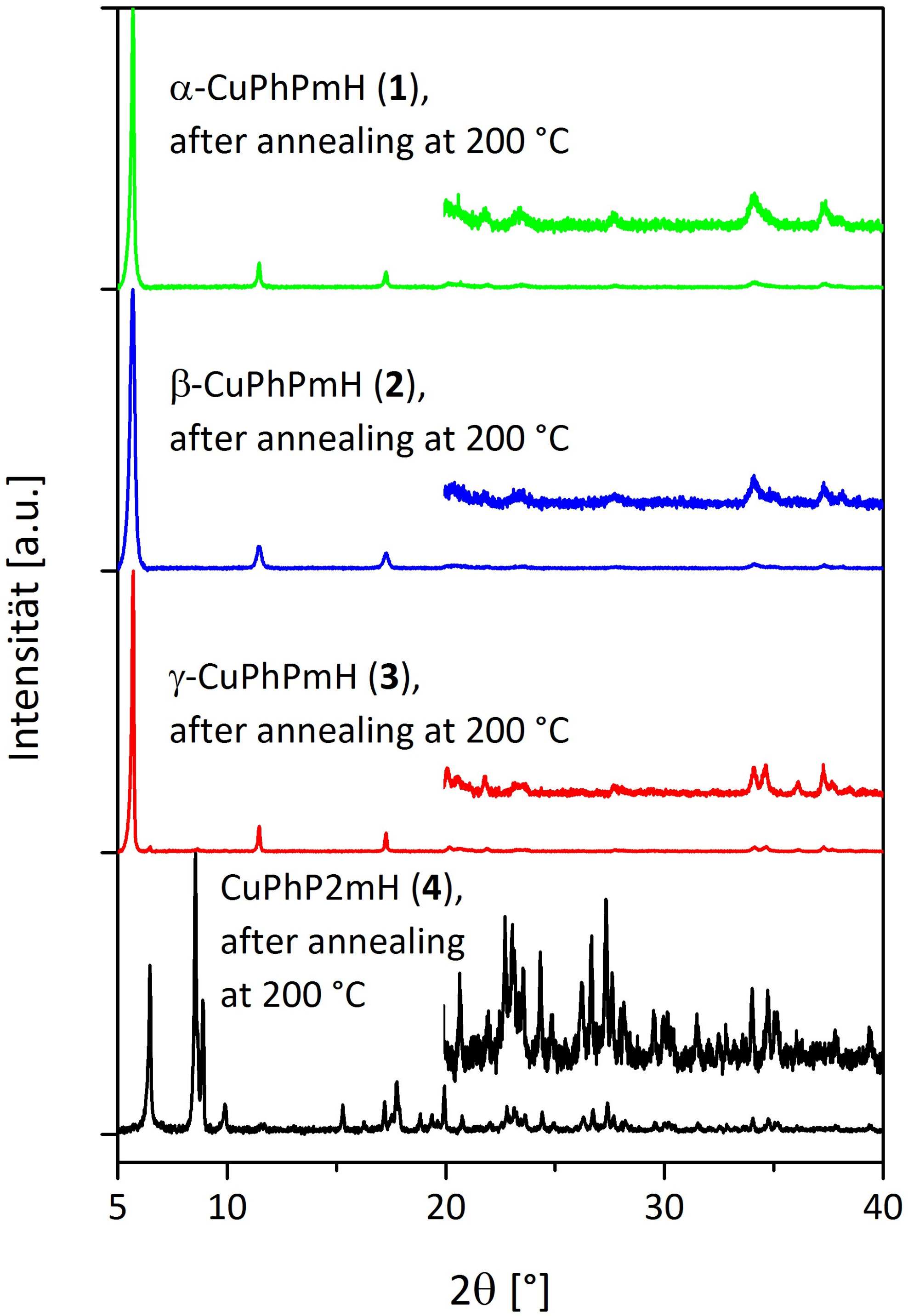

Figure S7: PXRD pattern of α-CuPhPmH (**1**) (green), β-CuPhPmH (**2**) (blue), γ-CuPhPMH (**3**) (red), and CuPhP2MH (**4**) (black) after annealing at 200 °C.

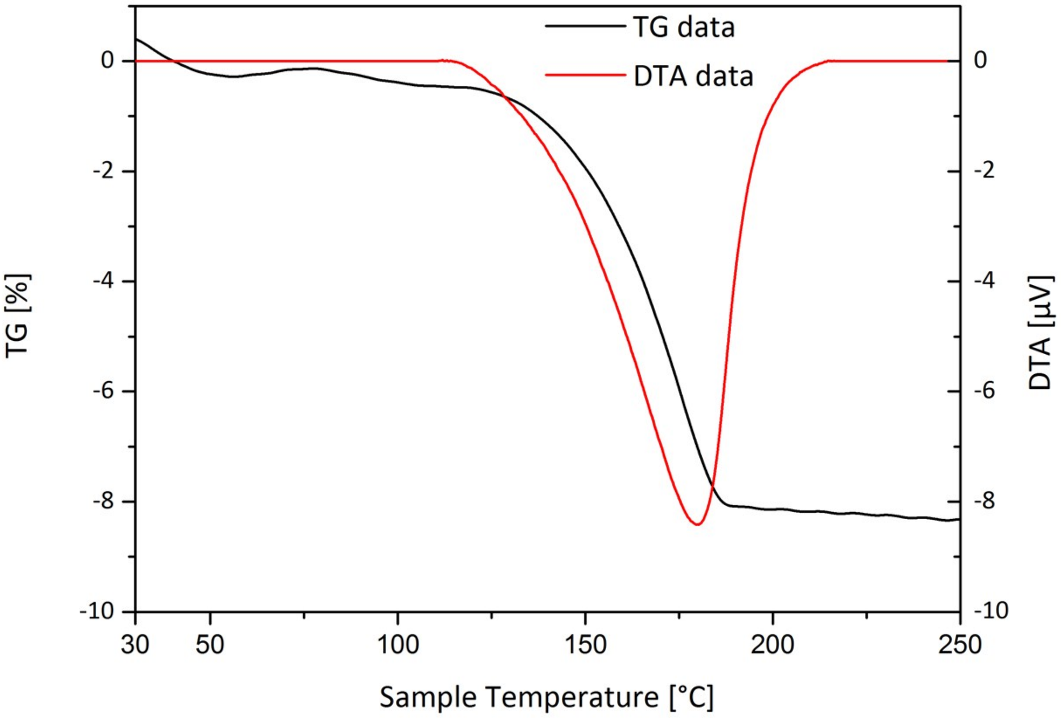

Figure S8: Plots of the thermogravimetric (TG) and difference thermo analysis (DTA) of α-CuPhPmH (**1**).

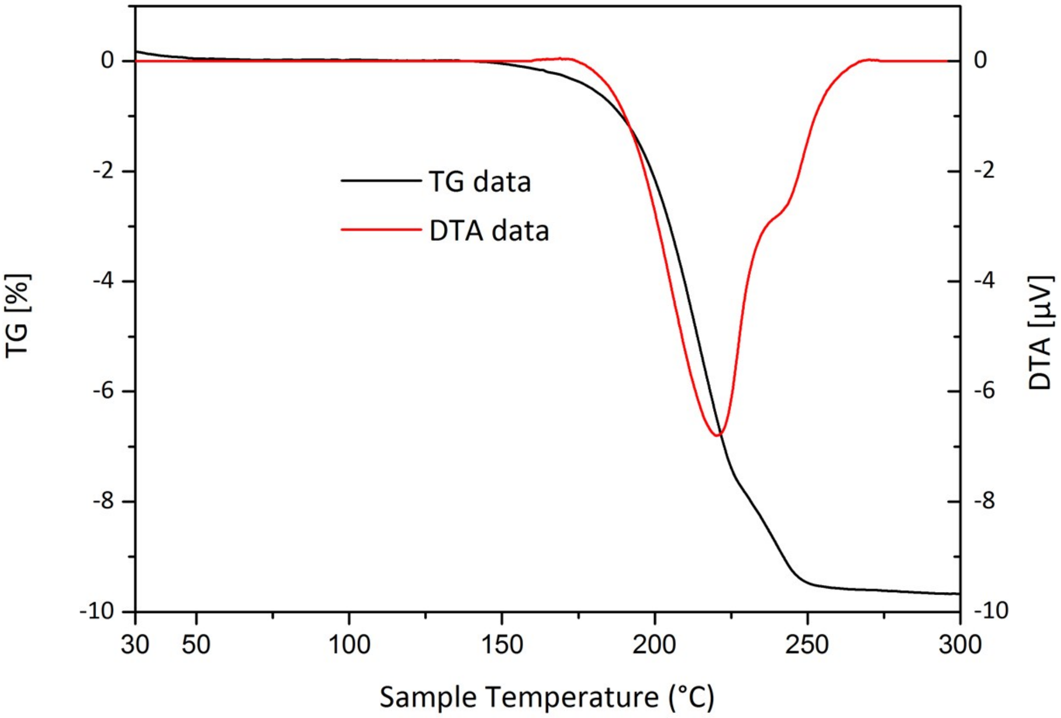

Figure S9 Plots of the thermogravimetric (TG) and difference thermo analysis (DTA) of β-CuPhPmH (**2**).

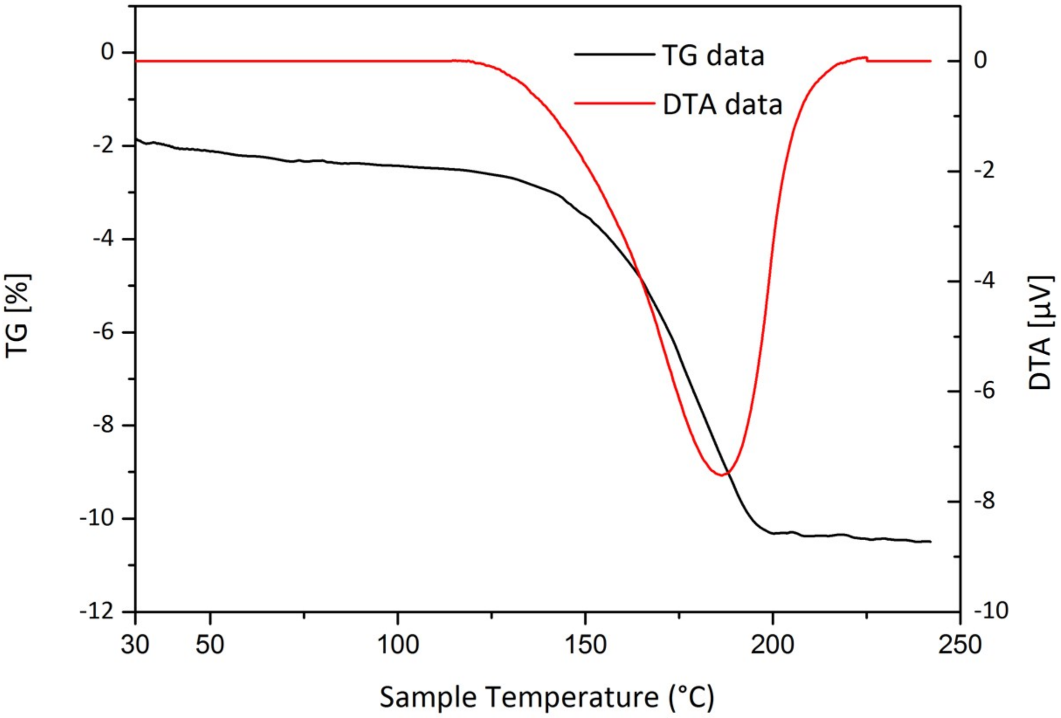

Figure S10: Plots of the thermogravimetric (TG) and difference thermo analysis (DTA) of γ-CuPhPmH (**3**).

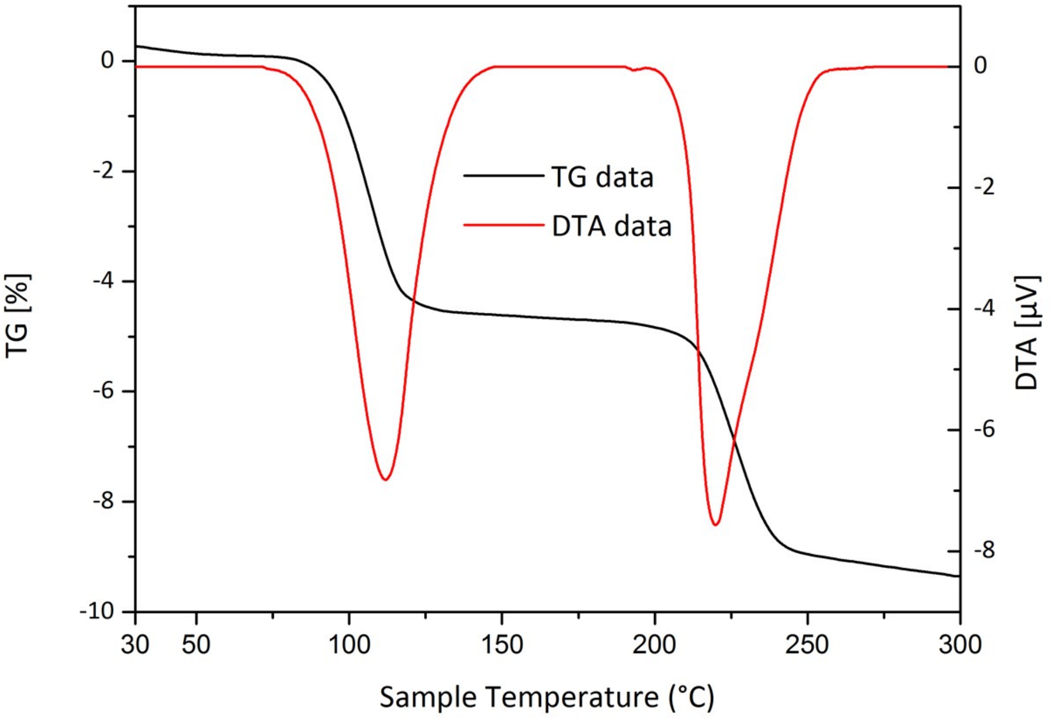

Figure S11: Plots of the thermogravimetric (TG) and difference thermo analysis (DTA) of CuPhP2mH (**4**).

6 PXRD pattern of the product of the synthesis done with copper(II) acetate monohydrate and an excess of phenylphosphonic acid in a 1:1 mixture of water and methanol

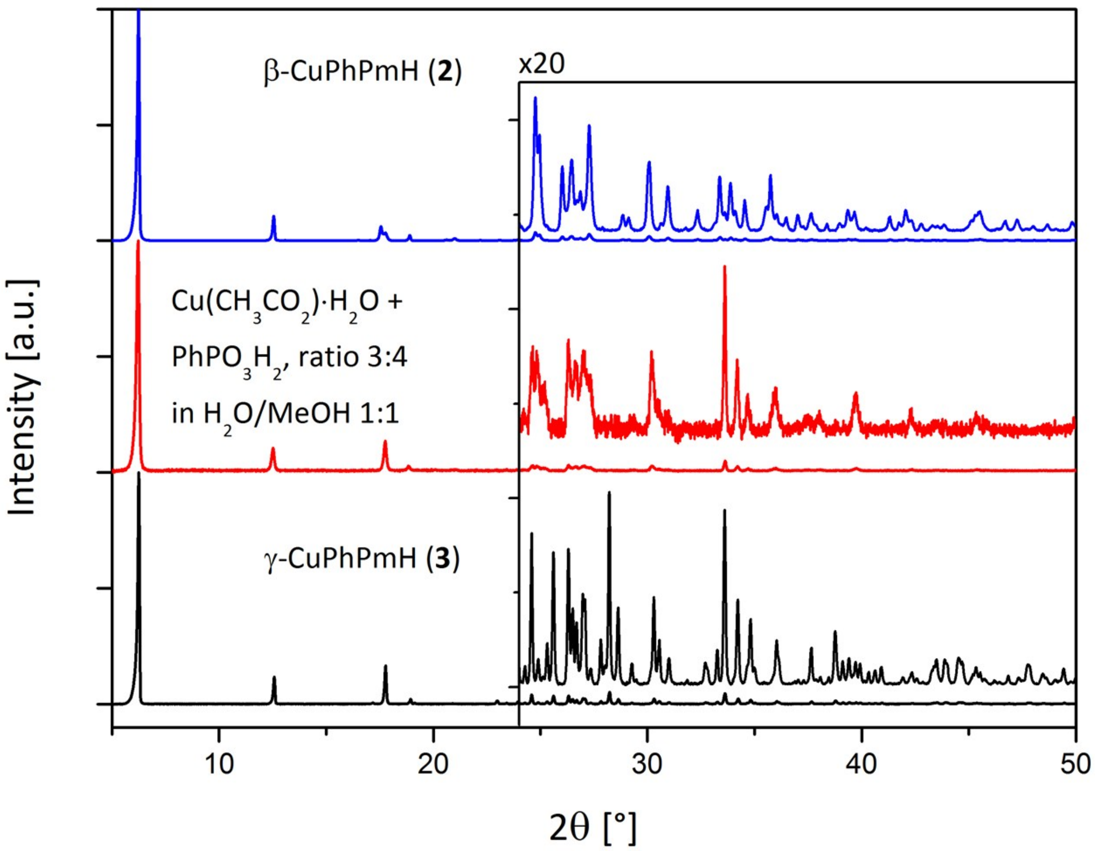

Figure S12: Comparison of the PXRD pattern of the product of the synthesis: 599 mg (3 mmol) copper(II) acetate monohydrate + 632 mg (4 mmol) phenylphosphonic acid in 60 mL of a 1:1 mixture of water and methanol with the PXRD pattern of β-CuPhPmH (**2**) and γ-CuPhPmH (**3**).

7 Investigations on the product of the 1:1 (copper(II) acetate monohydrate : phenylphosphonic acid) mechanochemical reaction

The mechanochemical synthesis in a 1:1 starting ratio of copper(II) acetate monohydrate and phenylphosphonic acid results in a blue compound. The EXAFS spectrum of the product of the mechanochemical 1:1 synthesis is shown in Figure S13. The spectrum was fitted with the structure of β-CuPhP (**2**). The parameters of that fit are given in Table S7. The root mean square error (RMSE) of the atom distances is with 0.062 Å very low. That proofs the tetragonal pyramidal coordination of this compound and agrees with its blue color, which is a result of the Cu^{2+}-coordination. The comparison of the PXRD pattern of the product of the mechanochemical synthesis with a 1:1 ratio of the starting materials with the obtained PXRD patterns of β-CuPhP (**2**) and γ-CuPhP (**3**) is shown in Figure S14. The crystallinity of the product is weak and results in broad reflections. This is a big difference to the also mechanochemical synthesized CuPhP2 (**4**). The comparison shows that the product is with a higher probability β-CuPhP (**2**), but a mixture of both not well formed compounds seems to be possible, too.

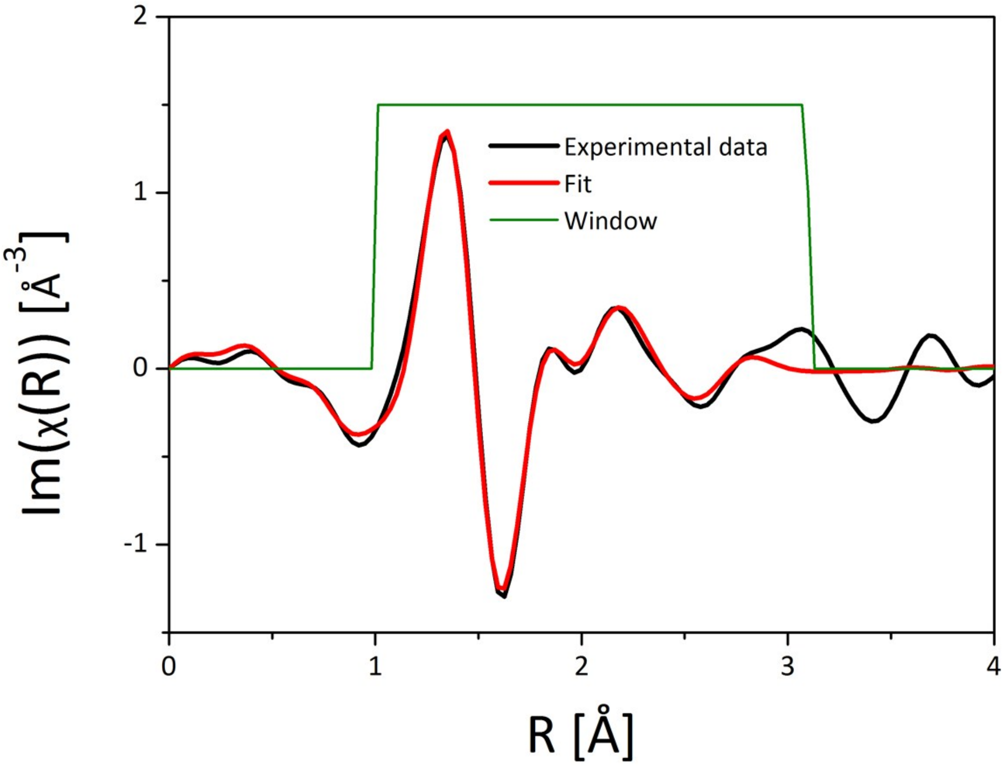

Figure S13: Cu K-edge EXAFS data shown in real space for the product of the 1:1 (copper(II) acetate monohydrate : phenylphosphonic acid) mechanochemical reaction. R = 0.01; experimental data: black, fit results: red, window: green.

Table S7: EXAFS fit parameter of the product of the mechanochemical 1:1 synthesis (copper(II)-acetate monohydrate : phenyl phosphonic acid) with the structure of β-CuPhP (**2**). Root mean square error (RMSE) is 0.062 Å.

Scattering path		R_{model} [Å]	R_{fit} [Å]	R_{diff}^2 [Å^2]
Cu1	-O3	1.92	1.95	0.0009
	-O2	1.97	1.91	0.0036
	-O1	1.97	1.91	0.0036
	-O4	1.99	1.93	0.0036
	-O1	2.34	2.39	0.0025
	-P1	3.06	3.01	0.0025
	-P1	3.07	3.01	0.0036
	-Cu1	3.12	3.02	0.0100

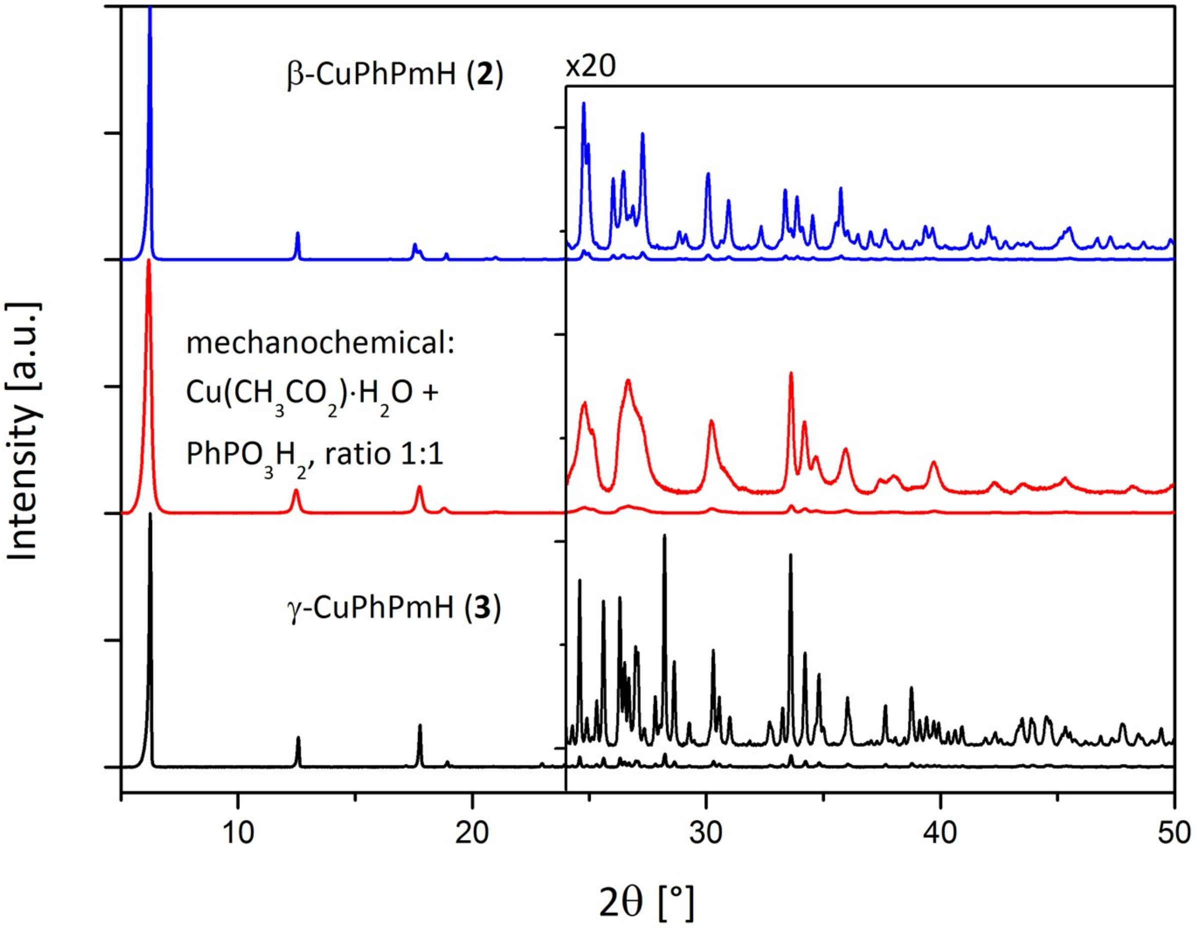

Figure S14: Comparison of the PXRD pattern of the product of the mechanochemical synthesis with a 1:1 ratio of the starting materials with the obtained PXRD patterns of β-CuPhPmH (**2**) and γ-CuPhPmH (**3**).

8 Investigation of the mechanochemical synthesis of β-CuPhP (2) *ex situ* at 30 Hz and *in situ* at 50 Hz

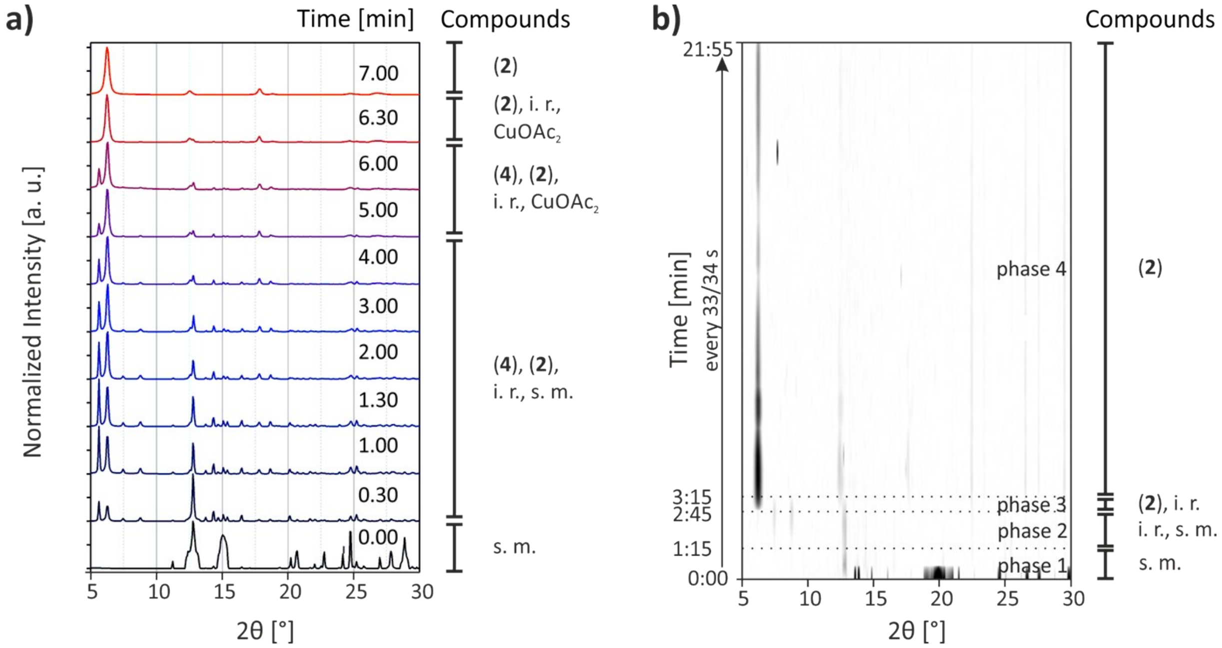

Figure S15: Synchrotron PXRD pattern of the Investigations of mechanochemical reactions **a)** *ex situ* for the synthesis of β-CuPhPmH (**2**) at 50 Hz, **b)** *in situ* for the synthesis of β-CuPhPmH (**2**) at 50 Hz with descriptions of the time and the detected compounds. (**2**) = β-CuPhPmH (**2**), (**4**) = CuPhP2mH (**4**), i. r. = intermediate reflections of unknown compounds, s. m. = starting materials, CuOAc$_2$ = copper(II)-acetate monohydrate.

The milling synthesis of β-CuPhPmH (**2**) with a 1:1 ratio of the starting materials was investigated with synchrotron XRD *ex situ* at 50 Hz and *in situ* at 30 Hz and 50 Hz.

The resulting powder patterns of the *ex situ* monitoring are shown in Figure S15a. After 30 s of milling time the powder pattern shows reflections for CuPhP2mH (**4**) (2θ = 5.6°, 11.2°, 18.2° etc.), the final product (2θ = 6.2°, 12.5°, 17.8° etc.), copper(II)-acetate monohydrate (2θ = 12.8°, 14.3°, 15.1° etc.), only little intense for phenylphosphonic acid (2θ = 13.7°, 14.7°, 20.1° etc.) and two reflections of an unknown phase (2θ = 7.4° and 8.8°). In the next minute the intensity of the reflections of the starting materials decreases compared to the other compounds. The intensities of the reflections of CuPhP2mH (**4**) and the final product are almost equal and increase while the two unknown reflections do not change their intensity. After 2 min of total milling time the intensity of CuPhP2mH (**4**) and of both unknown reflections starts to vanish. After 5 min of milling time the reflections of phenylphosphonic acid are vanished. 1.30 min later, the reflection of CuPhP2mH (**4**) is vanished, too. The reaction is finished after 7 min, when only reflections of the final product can be detected.

The *in situ* monitoring of the milling synthesis at 50 Hz leads to different results (Figure S15b). At the beginning and for the first minute of milling time only reflections for the starting materials can be detected. After this minute the two reflections of the unknown phase appear. The reflections of the phenylphosphonic acid disappear after two minutes, the ones of copper(II) acetate monohydrate after 2.45 min and both of the unknown phase 30 s later. The reflections of the product appear after three minutes and for this one measurement, reflections of the unknown phase and the product can be detected together. There are no reflections of CuPhP2mH (**4**).

References

1. Y. P. Zhang and A. Clearfield, *Inorg. Chem.*, 1992, **31**, 2821-2826.
2. B. Ravel and M. Newville, *J. Synchrotron Radiat.*, 2005, **12**, 537-541.
3. D. Cunningham and P. J. D. Hennelly, *Inorg. Chim. Acta*, 1979, **37**, 95-102.