

A Snapshot of a Coordination Polymer Self-Assembly Process: the Crystallization in of a 3D Metastable Network Followed by the Spontaneous Transformation in Water to a 2D Pseudopolymorphic Phase

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Supplementary information

Materials and Methods

All reagents were analytical-grade commercial products and were used without further purification. The P,P'-diphenylethylenediphosphinic acid (H₂pc₂p) was prepared as previously described in reference 1S.

Synthesis of $\{[\text{Cu}(\text{4,4}'\text{-bipy})(\text{pc}_2\text{p})(\text{H}_2\text{O})]\cdot 2.5\text{H}_2\text{O}\}_n$, **1:** H₂pc₂p (40 mg, 0.13 mmol) and 4,4'-bipy (20 mg, 0.13 mmol) were dissolved in 18 ml of H₂O at room temperature and then Cu(CH₃COO)₂·H₂O (26 mg, 0.13 mmol) dissolved in 2 ml of H₂O was added to the resulting solution. At once thin blue needles of the complex precipitated; the mixture was gently stirred for 10 min to complete the precipitation. The compound was filtered, washed with water and dried in air, at room temperature. Yield 72 mg, 90%. The simulated powder X-ray diffraction (XRD) pattern was found to match the experimental one of the as-synthesized compounds **1**.

Crystals suitable for X-ray diffraction were precipitated from the reaction system H₂pc₂p/4,4'-bipy/Cu(NO₃)₂·4H₂O, in a quite diluted aqueous solution, at 80-90°C. Anal. Calcd for C₂₄H₂₉CuN₂O_{7.5}P₂: (591.01): C, 48.77; H, 4.95; N, 4.74. Found: C, 48.40; H, 5.03; N, 4.67.

Synthesis of $\{[\text{Cu}(\text{4,4}'\text{-bipy})(\text{pc}_2\text{p})(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}\}_n$, **2:** Crystals of complex **1** were suspended in water at room temperature. The needle crystals slowly started to dissolve whereas blue block crystals of **2** started to form. After ca. a week all the crystals of **1** were disappeared and only well-shaped rectangular prisms of **2** remained. The solid was filtered and dried as in the case of **1**. The yield was practically quantitative. Operating at 80-90°C the process was completed in ca. 6-8 h (depending on the dimensions of the starting crystals). The simulated powder X-ray diffraction (XRD) pattern was found to match the experimental one of the as-synthesized compounds **2**. Anal. Calcd for C₂₄H₃₀CuN₂O₈P₂: (599.98): C, 48.04; H, 4.96; N, 4.67. Found: C, 48.15; H, 5.10; N, 4.60.

Single crystal Xray diffraction: Data collections on both complexes were carried out on a Oxford Diffraction Xcalibur3 diffractometer equipped with Mo K_α radiation (0.71073 Å). Data were

collected at room temperature. Data collections were performed with the program CrysAlis CCD^{2s} and data reductions were carried out with the program CrysAlis RED^{3s}. Absorption correction was applied through the program ABSPACK^{3s}. The structures were solved with direct method implemented in the program Sir97^{4s} and the refinement was completed by full-matrix least squares against F^2 using all data implemented in SHELXL^{5s}.

The crystal of **1** used for the data collection was selected after a long screening process. Due to the quality of the data collected it was not possible to locate the hydrogen atoms of the water molecules from the Fourier map. Some of the water molecules have partial population factor and for this reason refined isotropically and for consistency all the crystallization water molecules were refined in this way. In compound **1** a merohedral twinning is present and the twin component was found to be 0.52(1). A double position was found for the atoms O(32), P(3) and the aromatic ring bound to it: these residues were refined isotropically and the population factor of part A is 0.474(5). All the other non-hydrogen atoms, but the water molecules, were refined anisotropically and the H atoms were fixed in calculated positions and refined isotropically with thermal factors depending on the ones of the atom to which they are bound. The carbon atoms belonging to the benzene rings were fitted on a regular hexagon. Moreover in the asymmetric unit 18 water molecules were found, eight of which has a population factor of 0.5.

In compound **2**, the low data resolution is due to the poor diffracting power of the crystals. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms, except the ones of the water molecules, which were found in the Fourier map, were set in calculated position and all refined isotropically

Geometrical calculations were performed by PARST97^{6s} and molecular plots were produced by the program ORTEP3^{7s} and SCHAKAL97^{8s}.

The coordination geometries of the metal atoms in **1** and **2** are square pyramidal considering the τ index^{9s}. In fact all the values are close to zero, indicating the preferred square pyramidal coordination instead of the trigonal bipyramid. Moreover in **1** it can be pointed out the presence of a sixth coordination oxygen ligand for Cu(1) and Cu(4) opposite to the axial donor atoms respectively OW10 and OW9 (Cu(1)—OW10 2.946(9) Å and Cu(4)—OW9 3.174(9) Å), pointing straight to the metal centre (OW1—Cu(1)—OW10 176.9(°) and OW4—Cu(4)—OW9 175.9(°)). Figure 1S and Figure 2S report an ORTEP drawing of the asymmetric unit of **1** and **2** respectively.

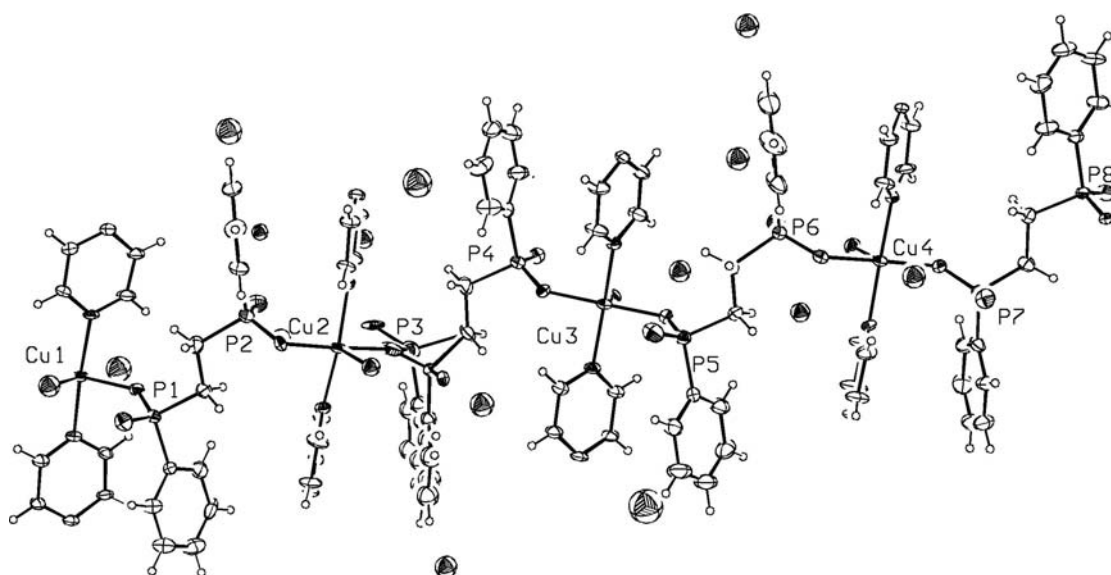


Figure S1: Asymmetric unit of **1**. Ellipsoids are shown at 30% probability.

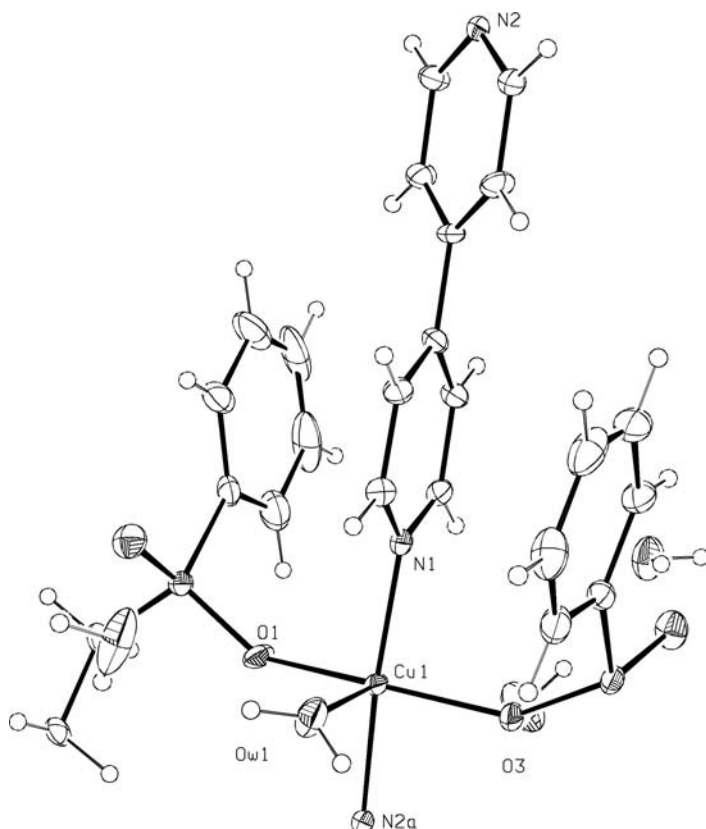


Figure S2: Asymmetric unit of **2**, with the symmetry equivalent N2a nitrogen atom, generated using the transformation $-x+3/2, y+1/2, -z+1/2$. Ellipsoids are shown at 30% probability

Xray Powder diffraction: XRPD measurements were carried out using a Panalytical X'PERT PRO diffractometer equipped with the X'Celerator[®] solid state detector and working in the $3 - 70^\circ$ 2θ region. Qualitative temperature-dependent X-ray diffraction (TDXD) was performed under flowing air with a powder diffractometer equipped with a curved-position-sensitive detector (INEL CPS 120) and a high-temperature attachment from Rigaku. The detector was used in a semi-

focusing arrangement by reflection ($\text{CuK}\alpha_1$ radiation). With this geometry, the stationary sample is deposited on a flat sample holder located at the centre of the goniometer. The counting time was 45 min. for each diffraction pattern. Decompositions were carried out in flowing air with a heating rate of $10\text{ }^\circ\text{C h}^{-1}$ between 17 and $600\text{ }^\circ\text{C}$. (Temperature calibration was carried out with standard materials in the involved temperature range.)

High quality Temperature dependent X-Ray powder diffraction spectra were collected using an Anton Paar HTK 1200N Oven camera, equipped with a PHILIPS X'PERT APD PW3020 diffractometer and working with a Ni filter on the diffracted beam. The heating rate was $5\text{ }^\circ\text{C}/\text{min}$ for all the compounds. The measurements were carried out at ambient pressure under a mild N_2 flow.

Thermogravimetric analysis and adsorption experiments

Coupled thermogravimetric (TG) and differential thermal (DTA) analysis was performed with a Netzsch STA490C thermoanalyser under a 20 mL min^{-1} air flux with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The coupled TG-DTA curve for **1** is shown in figure S3,a.

Four discrete weight losses can be evidenced in the $25 - 800\text{ }^\circ\text{C}$ temperature range.

The first one (about 10 %) has been observed in the $25 - 130\text{ }^\circ\text{C}$ range and it is related to the loss of the all 3.5 water molecules (calculated 10.7 %).

The second weight loss (about 27%) can be observed up to $230\text{ }^\circ\text{C}$ and it is in good agreement with the losses of 4,4'-bipyridine (calculated 26.4%).

The third and the fourth weight losses can be attributed to the combustion of the pcp phenyl rings (obs 24 %, calcd 24.4 %).

The coupled TG-DTA curve for **2** (figure S3, b) shows four discrete weight losses in the $25 - 280\text{ }^\circ\text{C}$ temperature range (total observed mass change = 18 %) at which correspond four well defined endothermic peaks in the DTA curve.

The calculated weight losses corresponding to the dehydration of the compound (4 water molecules) should correspond to 12 %.

However the fourth endothermic peak, observed around $300\text{ }^\circ\text{C}$ can be attributed to the loss of the 4,4'-bipyridine and the remaining weight losses to the combustion of the organic part of the compound (two strong exothermic peak at $350\text{ }^\circ\text{C}$ and $500\text{ }^\circ\text{C}$)

In the $300 - 400\text{ }^\circ\text{C}$ temperature range a well defined plateau should indicate the presence of a stable anhydrous phase for which the mass calculation is compatible with the $\text{Cu}(\text{pcp})_2$ compound.

The cumulative observed weight loss in the $200 - 1200\text{ }^\circ\text{C}$ temperature range is about 52 % and it is in good agreement with the total calculated weight loss (54%) derived from the combustion of the organics (4,4'-bipyridine and phenyl pcp rings).

Methanol adsorption was performed, at 0°C, using a computer controlled Micromeritics ASAP 2010 apparatus. Analytical-grade commercial methanol, supplied by Aldrich Co., after double distillation, was used as vapour source at room temperature.

Prior to adsorption measurements, the sample was outgassed under vacuum overnight at 110°C.

During the analysis the burette containing the sample was maintained in an ice-bath.

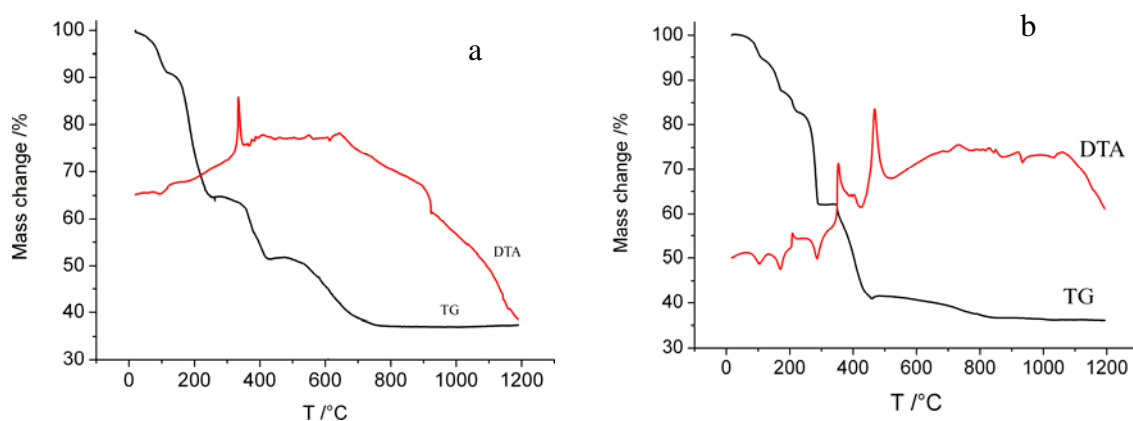


Figure S3 Coupled TG-DTA curves for **1** (a) and **2** (b)

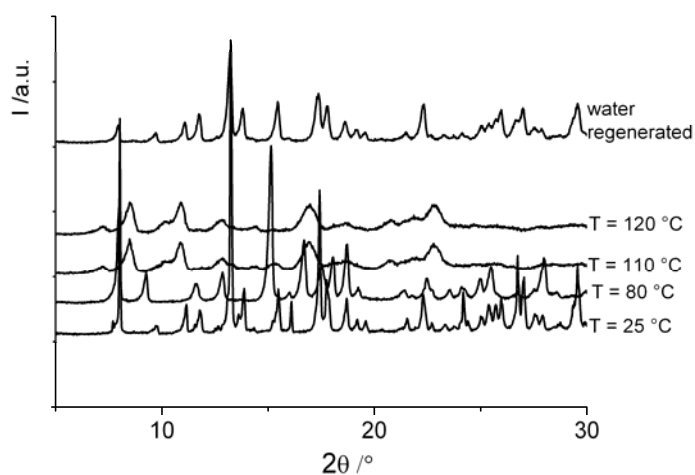


Figure S4 thermal patterns for phase **2** in the 25 - 120 °C temperature range. After regeneration in water the phase **2** is restored.

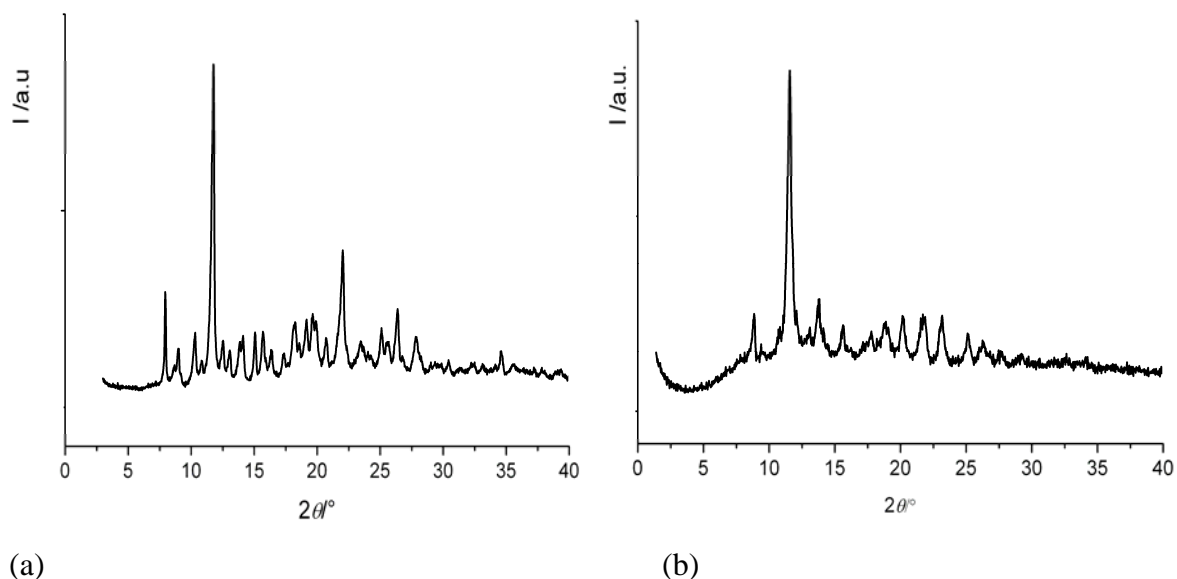


Figure S5: XRD pattern of a sample of **1** used for the methanol absorption and desorption measurement. Pattern recorded before the methanol absorption (a) and after the desorption (b).

References

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