A snapshot of a coordination polymer self-assembly process: the crystallization of a metastable 3D network followed by the spontaneous transformation in water to a 2D pseudopolymorphic phase†

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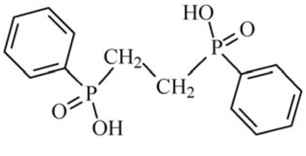
A metastable copper(II) 3D hybrid with 4,4′-bipyridine (4,4′-bipy) and *P*,*P*′-diphenylethylenediphosphinate (pc_2p^{2-}) undergoes a spontaneous, quantitative, transformation to a stable 2D polymorphic species either spontaneously in water, or after thermal dehydration followed by hydration.



Scheme 1

Porous coordination polymers have attracted much interest both from a basic scientific point of view (creation of nanometer-sized spaces) and for their potential applications (*e.g.* gas storage, molecular sieves, catalysis *etc*.).[1] Initially the attention of the scientific community was focused on the synthesis of robust frameworks, able to maintain the crystalline structure also after the release of the guest molecules (zeolitic behaviour). More recently new fascinating compounds having flexible frameworks have been discovered.[2] These latter can change their structure to respond to external stimuli such as temperature, pressure, light, guests *etc*. The flexibility is generally related to the presence of weak bonds such as hydrogen bonds, π–π interactions or kinetically labile coordinative bonds. Such flexible systems could produce different polymorphic or pseudopolymorphic forms during the crystallization that depends on thermodynamic or kinetic balance.

The literature reports a number of coordination polymers capable to show different solid state forms (isomers, pseudopolymorphs) which, quite invariably, occur under different conditions or as mixtures in the same batch.[3]

Here we report the isolation of a 3D metastable coordination polymer in aqueous solution, and its spontaneous transformation to a new 2D pseudopolymorphic phase.

The formation of metastable crystalline phases is a well established process for organic or organometallic molecular solids where inter-molecular non-covalent interactions are present in the crystals,[4] but as far as we know, it is quite unusual in the field of coordination polymers[5] where strong covalent metal–ligand interactions are overriding. Moreover it was generally accepted that networks with higher dimensionality are more stable phases than the ones with lower dimensionality.[6]

The reaction of $Cu(CH_3COO)_2{\cdot}4H_2O$ with equimolar amounts of *P*,*P*′-diphenylethylenediphosphinic acid, H_2pc_2p (Scheme 1), and 4,4′-bipyridine, 4,4′ bipy, in aqueous solution, at room temperature, rapidly affords the hybrid $[[Cu(4,4'\text{-bipy})(pc_2p)(H_2O)]{\cdot}2.5H_2O]_n$, **1**, as thin needle crystals.‡ When these latter are suspended in water at room temperature for several days the new solvate $[[Cu(4,4'\text{-bipy})(pc_2p)(H_2O)]{\cdot}3H_2O]_n$, **2**, is produced in essentially quantitative yield as block crystals.‡ **2** can be obtained in few hours if the suspension is heated at 80–90 °C. The process indicates that water partially dissolves **1** into ionic fragments which then recombine to give the more stable phase **2**.[7]

Noteworthy, some of us recently reported that the related *P*,*P*′ diphenylmethylenediphosphinate, pcp^{2-}, together with 4,4′-bipyridine and copper(II) affords a robust 1D tubelike network $[[Cu(pcp)(4,4'\text{-bipy})_{0.5}]{\cdot}2.5H_2O]_n$, **3**, which is stable up to 250 °C without any modification of the structural framework.[8] Packing of **1** and **2** are shown in Fig. 1 and Fig. 2 respectively. The asymmetric unit of **1** contains four copper ions, four 4,4′ bipy molecules, four pc_2p^{2-} anions and 18 water

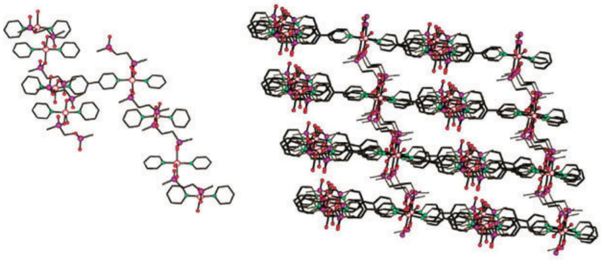


Fig. 1 On the left side, two $Cu(pc_2p)$ lines connected by a 4,4′-bipyridine and on the right side, a packing diagram of the 3D network (cds type) of **1**. Hydrogen atoms, solvent water molecules, phenyl rings are omitted.

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† Electronic supplementary information (ESI) available: Experimental details, TG-TDA diagram for **1** and **2**, temperature dependent XRD diagrams for **2**. CCDC 697650 (**1**) and 697651 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b813222d

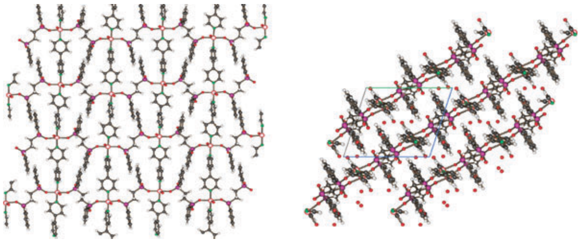


Fig. 2 The 2D slab (left) and the packing of the 2D slabs through the solvent water molecules (right) for **2**.

molecules, eight of which have an occupancy factor of 0.5. All the copper ions have a square pyramidal coordination geometry in which two oxygen atoms belong to two distinct phosphinate moieties, two nitrogen atoms belong to two different bipyridine molecules and the apical position is occupied by a water molecule. The large volume of **1** and the high Z', are consistent with the metastable nature of the crystals.[9]

The asymmetric unit of $[[(4,4'\text{-bipy})\mathrm{Cu(pc_2p)(H_2O)}]\cdot 3\mathrm{H_2O}]_n$ (**2**) consists of one copper ion, one 4,4′-bipy, one $\mathrm{pc_2p^{2-}}$, one water molecule coordinated to the metal atom and three solvent water molecules. The coordination of the copper ion is again square pyramidal and the coordination around the metal centre is with two nitrogen atoms and two oxygen atoms of two $\mathrm{pc_2p^{2-}}$ anions in the basal positions and the water molecule in the apical site. In both cases, each phosphinate moiety is coordinated through only one oxygen atom, the second one being involved in the hydrogen bonds with the non-coordinated water molecules. The network of **1** is a 3D chiral net of cds type,[10] while **2** is characterized by 2D non chiral slabs. The 3D → 2D transformation then also increases the symmetry. The differences and the relationships between the network of **1** and **2** can be better understood with Scheme 2.

The starting point is a series of infinite strips formed by copper metal atoms and 4,4′-bipyridine represented by blue bold lines. As exemplification, Scheme 2 shows two sets of four columns aligned as planes at the forefront and at the background of the sheet. In the framework of **1**, the $\mathrm{pc_2p^{2-}}$ anions (thin red lines) connect metal atoms pairs that belong both to the same plane and to two adjacent planes. The results is the formation of the cds network. In the case of **2**, the $\mathrm{pc_2p^{2-}}$ anions connect the copper atoms only in the same plane forming a series of 2D parallel rectangular grids. The framework of **1** is characterized by the presence of channels hosting the solvent water molecules, while in **2** the solvent molecules connect the 2D slabs through hydrogen bond interactions.

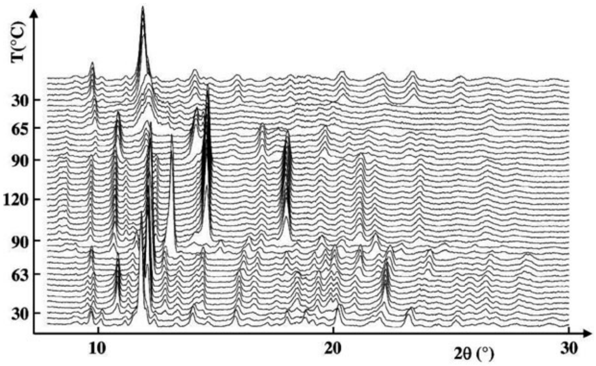
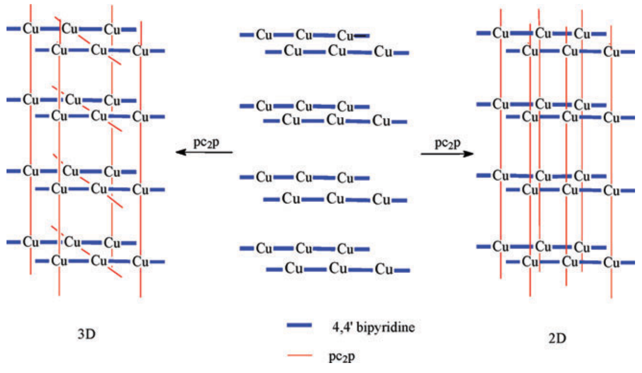


Fig. 3 TDXD plot for the reversible dehydration of **1**.

The stepwise thermogravimetric (TG-TDA) profile of **1** indicates that the all water molecules are released in the 25–140 °C range (found 10%, calculated 10.6%). The 4,4′-bipyridine ligand is released at about 230 °C. The coupled TG-DTA curve for **2** shows four discrete weight losses in the 25–280 °C temperature range (total observed mass change = 18%). The calculated weight losses corresponding to the dehydration of the compound (four water molecules) should correspond to 12%. However the fourth endothermic peak, observed around 300 °C can be attributed to the loss of the 4,4′-bipyridine (more details are given in the ESI†).

The temperature-dependent X-ray powder diffraction analysis of compound **1** (Fig. 3) shows that the framework maintains a good crystallinity up to 120 °C, despite three significant structural changes in intermediate hydrates at 30, 63 and 90 °C, respectively. When cooling down the lowest hydrated sample from 120 °C to room temperature in air, the different hydrates are observed again and the precursor is regenerated. While the dehydration/hydration process is reversible until 120 °C, the total release of the remaining water molecules at 130 °C leads to the poorly crystalline desolvated phase that does not rehydrate any longer at ambient conditions (Fig. 4).

Surprisingly, the amorphous phase, if placed in contact with water for 15 minutes, regenerates in the crystalline form **2**, as shown by comparison between the collected diffraction pattern after rehydration and the calculated one from the crystal structure (see Fig. 4). In addition, the full dehydration of compound **2** at 130 °C, leads to an amorphous phase, which in



Scheme 2

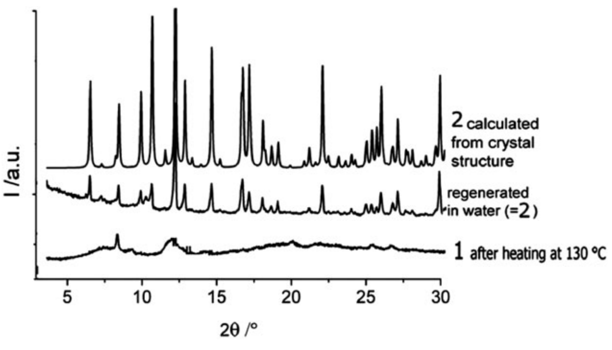


Fig. 4 Water regeneration of **1** into **2** after heating.

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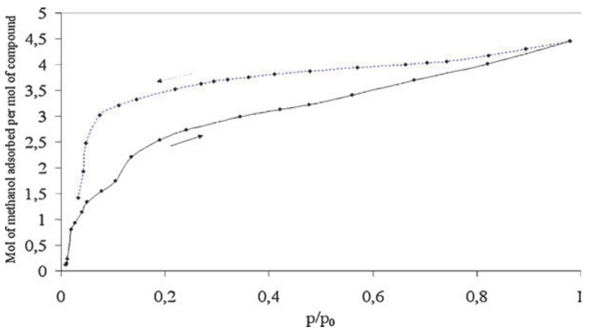

Fig. 5 Methanol adsorption and desorption isotherms on phase **1** measured at 0 °C.

turns back reversibly to crystalline phase **2** after regeneration in water.

Methanol adsorption measurements on the desolvated phase of **1** have been carried out. The adsorption isotherm, performed at 0 °C, is reported in Fig. 5 and shows that the methanol molecules are adsorbed in more unresolved steps at low p/p_0 values which can be related to different energetic interactions between methanol and the P–O or the OH groups of the compound. An adsorption plateau is clearly visible around $p/p_0 \sim 0.10$ which is completed when almost 2.0 mol of methanol per mol of compound were adsorbed. By increasing the relative pressure of methanol until to p/p_0 values near to 1.0, the amount of the adsorbed methanol is slightly higher than 4.0 mol per mol of compound.

An hysteresis between desorption and adsorption isotherms is evident and about 3.5 mol of adsorbed methanol/mol of compound are released at relative pressures p/p_0 lower than 0.10. This amount is similar to that of the hydration water content in the phase **1** and it is reasonable to suppose that these adsorbed methanol molecules corresponds to the saturation of the solvent sites, occupied by water molecules.

The XRPD analysis of the material recovered after the desorption of methanol shows a pattern comparable to that of phase **1** (see ESI†). This findings suggest that the framework of **1** is essentially retained during the methanol absorption.

Then the solids analyses are fully consistent with the metastable nature of **1** and the methanol absorption measurements indicates that the transformation of **1** in **2** observed in the case of water adsorption is not promoted for all solvents.

An interesting question stems from the flexibility of the framework constructed by Cu, pc_2p^{2-} and 4,4′-bipy compared to that involving the pcp^{2-} ligand. From a structural point of view, the Cu–O average bond distances are respectively 1.96, 1.94 and 2.04 in **1**, **2** and **3**. While the bond Cu–O lengths seem to indicate a stronger bonds in **1** and **2** with respect to **3**, it is relevant that the pcp^{2-} ligand coordinates the metal with all four oxygen atoms in a chelating mode. The chelating contribution is missing for pc_2p^{2-}, where only two oxygen atoms are bonded to the copper ion and a potentially labile water molecule completes the metal coordination.

In conclusion we have found an unique example of a 3D metastable coordination polymer that generates a 2D stable pseudopolymorph either spontaneously in water, or after thermal dehydration followed by hydration.

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Notes and references

‡ *Crystal data* for **1**: $C_{96}H_{116}Cu_4N_8O_{30}P_8$; monoclinic, $P2_1$, $M = 2363.89$, $a = 20.845(1)$; $b = 13.503(5)$, $c = 22.010(1)$, $\beta = 116.196(7)°$, $V = 5559(2)$ Å^3, $T = 293(2)$ K; $Z = 2$, $D_c = 1.395$ g cm^{-3}, $\mu = 0.946$ mm^{-1}, $F(000) = 2392$, $\theta_{max} = 28.50°$ ($-26 \leq h \leq 27$, $-17 \leq k \leq 17$, $-29 \leq l \leq 28$); reflections measured 38 395, unique 20 710 ($R_{int} = 0.057$). Final residuals (for 1167 parameters) were $R_1 = 0.0840$, $wR_2 = 0.1781$ for the 13 285 [$I > 2\sigma(I)$] reflections and $R_1 = 0.1306$, $wR_2 = 0.2068$ for all data. GOF = 1.100. Absolute structure parameter was 0.538(17) and residual electron density was 1.043 and –0.676 e Å^3.

Crystal data for **2**: $C_{24}H_{30}CuN_2O_8P_2$; monoclinic, $P2_1/n$, $M = 599.98$, $a = 10.6204(5)$; $b = 22.0127(7)$, $c = 11.9398(5)$, $\beta = 107.253(5)°$, $V = 2665.73(19)$ Å^3, $T = 293(2)$ K; $Z = 4$, $D_c = 1.495$ g cm^{-3}, $\mu = 0.989$ mm^{-1}, $F(000) = 1244$, $\theta_{max} = 22.60°$, ($-11 \leq h \leq 11$, $-23 \leq k \leq 23$, $-12 \leq l \leq 10$); reflections measured 13 643, unique 3505 ($R_{int} = 0.083$). Final residuals (for 334 parameters) were $R_1 = 0.0534$, $wR_2 = 0.09$ for the 2322 [$I > 2\sigma(I)$] reflections and $R_1 = 0.0994$, $wR_2 = 0.1062$ for all data. GOF = 1.061. Residual electron density was 0.41 and –.36 e Å^3.

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7 We may likely suppose that **1** dissolves in water to give ionic species such as pc_2p^{2-} and $[Cu(4,4'\text{-bipy})]_n^{2n+}$. This latter chain species has been well established, see for instance: Masuda and S. Mitra, *Struct. Chem.*, 2007, **18**, 9.

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