



HAL
open science

Insight into the Mechanism of Water Adsorption/Desorption in Hydrophilic Viologen-Carboxylate Based PCP

Maxime Leroux, Nicolas Mercier, Jean Pierre Bellat, Guy Weber, Igor Bezverkhyy

► **To cite this version:**

Maxime Leroux, Nicolas Mercier, Jean Pierre Bellat, Guy Weber, Igor Bezverkhyy. Insight into the Mechanism of Water Adsorption/Desorption in Hydrophilic Viologen-Carboxylate Based PCP. *Crystal Growth & Design*, 2017, 17 (5), pp.2828-2835. <10.1021/acs.cgd.7b00279>. <hal-05027339>

HAL Id: hal-05027339

<https://univ-angers.hal.science/hal-05027339v1>

Submitted on 9 Apr 2025

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Cover page

Insight into the mechanism of water adsorption/desorption in hydrophilic viologen-carboxylate based PCP

*Maxime Leroux, Nicolas Mercier, * Jean-Pierre Bellat, Guy Weber and Igor Bezverkhyy**

ABSTRACT - A water stable and highly hydrophilic porous coordination polymer based on viologen-carboxylate type ligand, the 4,4'-bipyridinium,1,1-bis-(3-carboxyphenyl) (pc2), is obtained by solvothermal method: $[\text{Cd}_3(\text{pc}2)(\text{BTC})_2(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ ($[\mathbf{1}(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$; $\text{BTC}^{3-} = 1,3,5$ -carboxy-benzene). Its crystal structure and the ones of two partially dehydrated phases have been determined allowing to get insight into the mechanism of water adsorption/desorption of this PCP material. It is shown that the dehydrated compound $[\mathbf{1}]$ first adsorbs two water molecules which fill the pores, leading to $[\mathbf{1}] \cdot 2\text{H}_2\text{O}$. On the other hand, the partial dehydration of the as-synthesized compound leads to the intermediate phase $[\mathbf{1}(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ in which one H_2O molecule is bound to Cd^{2+} ions of trinuclear building units, and three others are localized in the pores. The structural analysis also reveals that the pyridinium N^+ Lewis sites which interact with water molecules in $[\mathbf{1}(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$, interact with carboxylate groups after structural reorganization in $[\mathbf{1}] \cdot 2\text{H}_2\text{O}$. The water adsorption isotherm clearly shows that the dehydrated compound is highly hydrophilic and adsorbs water in steps: first and second at $P/P_s < 0.01$ and third at $P/P_s \sim 0.1$ with the overall water adsorption reaching 0.13 g $\text{H}_2\text{O}/\text{g}$. This material is also able to reversibly adsorb ammonia (up to 0.3 g/g or 17.6 mmol/g).

nicolas.mercier@univ-angers.fr - MOLTECH-Anjou, UMR-CNRS 6200, Université d'Angers - 2 Bd Lavoisier, 49045 Angers, France. Fax: 33.(2).41.73.54.05; Tel: 33.(2).41.73.50.83.

Insight into the mechanism of water adsorption/desorption in hydrophilic viologen- carboxylate based PCP

Maxime Leroux,[§] Nicolas Mercier,^{§} Jean-Pierre Bellat,[†] Guy Weber[†] and Igor Bezverkhyy^{†*}*

[§] MOLTECH-Anjou, UMR-CNRS 6200, Université d'Angers - 2 Bd Lavoisier, 49045 Angers, France. Fax: 33.(2).41.73.54.05; Tel: 33.(2).41.73.50.83

[†] ICB, UMR-CNRS 6303, Université de Bourgogne-Franche Comté, 9 A. Savary, 21078 Dijon, France.

ABSTRACT. A water stable and highly hydrophilic porous coordination polymer based on viologen-carboxylate type ligand, the 4,4'-bipyridinium,1,1-bis-(3-carboxyphenyl) (pc2), is obtained by solvothermal method: $[\text{Cd}_3(\text{pc}2)(\text{BTC})_2(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ ($[\mathbf{1}(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$; BTC^{3-} = 1,3,5-carboxy-benzene). Its crystal structure and the ones of two partially dehydrated phases have been determined allowing to get insight into the mechanism of water adsorption/desorption of this PCP material. It is shown that the dehydrated compound $[\mathbf{1}]$ first adsorbs two water molecules which fill the pores, leading to $[\mathbf{1}] \cdot 2\text{H}_2\text{O}$. On the other hand, the partial dehydration of the as-synthesized compound leads to the intermediate phase $[\mathbf{1}(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ in which one H_2O molecule is bound to Cd^{2+} ions of trinuclear building units, and three others are localized in the pores. The structural analysis also reveals that the pyridinium N^+ Lewis sites which interact with water molecules in $[\mathbf{1}(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$, interact with carboxylate groups after structural reorganization in

[1]2H₂O. The water adsorption isotherm clearly shows that the dehydrated compound is highly hydrophilic and adsorbs water in three steps: first and second at P/P_s < 0.01 and third at P/P_s ~ 0.1 with the overall water adsorption reaching 0.13 g H₂O/g. This material is also able to reversibly adsorb ammonia (up to 0.3 g/g or 17.6 mmol/g).

Introduction.

In the field of porous coordination polymers (PCPs) or metal-organic frameworks (MOFs), the reactivity of such materials towards water is of great importance.^{1,2} For many applications at the industrial level, such as chemical sensors, gas storage, catalysis, ... the stability of materials towards water is crucial. Unfortunately, many PCPs are moisture sensitive, especially those based on carboxylate ligands and divalent metal cations as the well-known MOF-5 or HKUST PCPs.³⁻⁵ Several strategies have been developed to improve the water stability, by using imidazolate ligands instead of carboxylate ones (ZIFs PCPs as ZIF-8),^{6,7} or by using cations with high valence number as Zr⁴⁺ (Zr-PCPs as UiO66).^{8,9} On the other hand, the adsorption of large amount of water or the adsorption at very low pressure in water stable PCPs is a current hot topic because of potential applications in heat pumps, adsorbent-based chillers, proton conductors or production and delivery of drinking water.

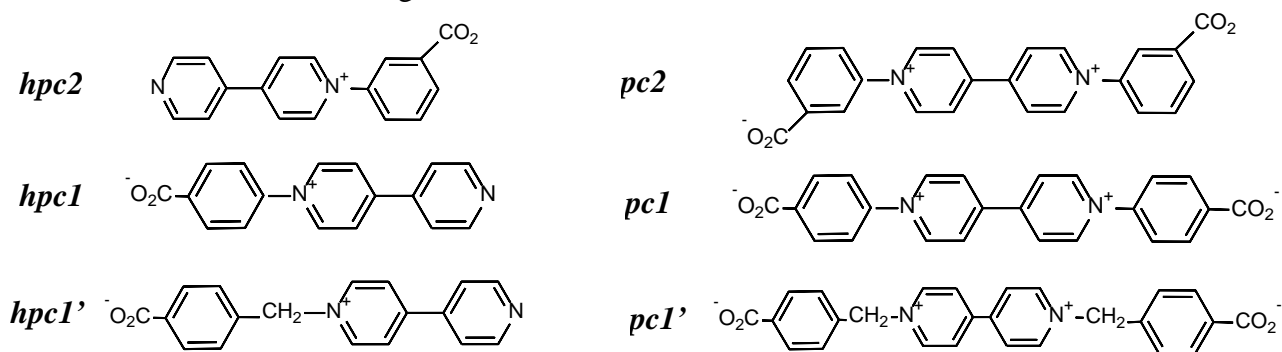
The incorporation of viologen-carboxylate ligands in the framework of PCPs has been quite recently considered. Such a ligand is based on bipyridinium (viologen) units covalently linked to groups bearing carboxylate functions. Viologen is a well-known electron acceptor unit able to interact with electron donor entities.¹⁰ Such donor-acceptor interaction often results in colored solids due to the presence of a charge transfer band in the visible region, or due to a broad band covering all the visible region, typical of the radical cation, in the case of an electron transfer from

a strong electron donor to the viologen.¹¹⁻¹³ Besides its redox property, the bipyridinium unit which is cationic, can also be considered as a Lewis acid. Such sites in PCPs are mainly metal open sites, which are created when solvent molecules bound to metal ions are removed during the activation process. PCPs based on viologen-carboxylate ligands are so expected to be hydrophilic. And in fact, water molecules can strongly interact with nitrogen sites of pyridinium cycles with contact distances as short as 3.00 Å as shown in the structure of the hydrated zwitterionic compounds (pc1)·2H₂O (pc1 = 1,1-bis(4-carboxyphenyl)-4,4'-bipyridinium).¹⁴ On the other hand the cationic nature of viologen-carboxylate ligands is a challenge in the synthesis of PCPs materials. Since bipyridinium units have strong abilities to interact with carboxylate groups of neighboring ligands in the solid state, dense coordination polymers are obtained in most cases, however often exhibiting interesting photochromic properties due to electron transfer from CO₂⁻ groups to viologen units.¹⁵⁻²¹ While some anionic viologen-carboxylate linkers have been used,²²⁻²⁵ most of such linkers are zwitterionic. In scheme 1 are shown the chemical structure of some of them, the asymmetrical ones consisting of one pyridyl unit on one side and one carboxylate function on the other side (hpc1, hpc1', hpc2), and the symmetrical ones (pc1, pc1', pc2). These last based on diquaternized bipyridinium units are expected to have a better electron-acceptor behavior than the former. Finally, we can notice that the number of PCPs based on such viologen-carboxylate ligands has increased these past five years, particularly those based on hpc1,^{26,27} pc1,²⁸⁻³⁰ and pc1'.^{31,33}

Due to the similar characteristics of both NH₃ and H₂O molecules, the network of hydrophilic PCPs are particularly well suited to strongly interact with NH₃. Ammonia is one of the most toxic gases among those produced and used on a large scale. If materials such as zeolites or activated carbons are known to exhibit good adsorption capacities, however, the progressive desorption over time remains a challenging issue.^{34,35} Thus, PCPs materials have appeared as potential candidates

for ammonia storage.³⁶⁻⁴² Recently, we reported on a viologen-carboxylate PCP exhibiting high ammonia uptake.³⁰ However, in this material as in most of the tested PCPs, the networks collapse upon NH₃ adsorption as a result of metal-NH₃ coordination.

Here, we report on the synthesis and adsorption properties of a water stable 3D PCP based on the pc2 viologen-carboxylate ligand (pc2= 4,4'-bipyridinium,1,1-bis-(3-carboxyphenyl), Scheme 1), [Cd₃(pc2)(BTC)₂(H₂O)₂]₂·6H₂O ([1(H₂O)₂]₂·6H₂O) (BTC³⁻= 1,3,5-carboxy-benzene). Its crystal structure as well as that of two partially dehydrated phases [1(H₂O)]·3H₂O and [1]·2H₂O have been determined allowing a detailed description of the structural transitions provoked by water desorption and adsorption processes. We show that a high resolution water adsorption isotherm confirms this three-step adsorption process. It clearly shows the highly hydrophilic nature of the compound: 50 % of water molecules being adsorbed at P/P_S<0.01, which can be related to the presence Lewis acid sites in the structure (metal open sites and pyridinium cycles). In addition the prepared PCP possesses high capacity towards NH₃ attaining the loading of 0.3 g/g (17.6 mmol/g) at 930 hPa. Despite the collapse of the crystalline structure after NH₃ adsorption, the solid capacity for ammonia is restored after regeneration.



Scheme 1. Structural formulas of symmetrical and asymmetrical zwitterionic viologen-carboxylate type ligands

Experimental Section.

Materials and general methods: All starting materials were of analytical grade and obtained from commercial sources without further purifications. 4,4'-bipyridinium,1,1-bis-(3-carboxyphenyl) dichloride dihydrate ((H₂pc2)Cl₂·2H₂O) ligand was synthesized according to literature (SI). Thermogravimetric analyses were performed using a TGA-2050 TA Instruments Systems from room temperature to 1000°C with a heating rate of 10°C/min under nitrogen flow. X-Ray powder diffraction (XRPD) analyses were measured at room temperature on a D8 Bruker diffractometer (Cu K α , λ =1.5418 Å) equipped with a linear Vantec super speed detector.

Preparation of [Cd₃(pc2)(BTC)₂(H₂O)₂]-6H₂O: A mixture of (H₂pc2)Cl₂·2H₂O (25.3mg, 0.05mmol), Cd(ClO₄)₂ hydrate (62.2mg, 0.2mmol), DMF (2mL), and H₂O (2mL) was slowly heated to 105°C at a rate of 10°C/hour for 48h in a 25mL teflon-lined stainless steel autoclave. After the mixture was slowly cooled to room temperature at a rate of 10°C/hour, suitable crystals for X-ray analyses were collected, washed with fresh DMF and air-dried. [Cd₃(pc2)(BTC)₂(H₂O)₂]-6H₂O 60 % yield based on (H₂pc2)Cl₂·2H₂O. Anal. Calc. for Cd₃C₄₂H₃₈O₂₄N₂ (1291.97): C, 39.05 %; H, 2.94 %; N, 2.17%. Found: C, 39.15 %; H, 2.87 %; N, 2.18 %.

Crystallography. X-ray diffraction data were collected on an Agilent Supernova with CuK α radiation (λ =1.5418 Å). Data were collected at 150K from selected single crystals of [1(H₂O)₂]-6H₂O, [1(H₂O)]-3H₂O and [1]-2H₂O under nitrogen atmosphere. Crystals of the two partially hydrated phases were obtained by a slowly heating of as-synthesized crystals. This step has involved a breaking of crystals into many fragments. After several attempts, we could successfully collect data using very small crystals, which further allowed the full determination of

crystals structures. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares method with anisotropic approximation for all non-hydrogen atoms, using the SHELX97 package. For $[\mathbf{1}(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$, three independent water molecules were located in cavities, while another independent molecule is coordinated to the inorganic node, leading to a total of 8 water molecules per formula unit, in good accordance with the TGA experiment and water adsorption isotherm. For $[\mathbf{1}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ whose unit cell is twice greater than the one of $[\mathbf{1}(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$, the asymmetric unit includes three Cd^{2+} (forming the trimeric unit), one H_2O molecule bound to one Cd^{2+} and 3 others in the cavities. For $[\mathbf{1}]\cdot 2\text{H}_2\text{O}$, a centrosymmetrical trimeric unit is found (two independent Cd^{2+}) as in $[\mathbf{1}(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$, the two water molecules per formula unit (one independent molecule) being found in cavities. All non- H_2O hydrogen atoms were treated with a riding model. Absorption was corrected by the program SADABS. Table 1 summarizes the crystallographic data for all the three structures. A complete list of crystallographic data, along with the atomic coordinates, the anisotropic displacement parameters and bond distances and angles for each compound, is given as CIF files. CCDC numbers: 1534001, 1534483, 1534485 for $[\mathbf{1}(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$, $[\mathbf{1}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$, $[\mathbf{1}]\cdot 2\text{H}_2\text{O}$, respectively.

Table 1. Crystallographic data for $[\mathbf{1}(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$, $[\mathbf{1}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ and $[\mathbf{1}]\cdot 2\text{H}_2\text{O}$.

	$[\mathbf{1}(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$	$[\mathbf{1}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$	$[\mathbf{1}]\cdot 2\text{H}_2\text{O}$
Empirical formula	1291.97	1219.93	1183.85
Temperature (K)	150	150	150
crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	11.9733(3)	16.8289(7)	10.7047(4)
b (Å)	13.5156(3)	12.6499(3)	14.6805(5)
c (Å)	13.6585(3)	18.6425(4)	13.2008(6)
β	99.724(2)	93.741(2)	102.416(4)
V (Å ³)	2178.55(9)	3960.2(2)	2025.99(14)
Z	2	4	2
Reflections collected	12945	27916	12014
R _{int}	0.038	0.067	0.038
R1	0.0297	0.0687	0.0519
wR2 (all data)	0.0808	0.2135	0.1362

Adsorption measurements. Adsorption and desorption isotherms of CH₃OH, H₂O and NH₃ on $[\mathbf{1}]$ were recorded at 298 K by gravimetry using a home-built McBain-type thermobalance. Before measurements the samples (ca. 15 mg) were outgassed at 423 K under vacuum (10^{-6} hPa) for 15h. The detailed description of the experimental procedure can be found elsewhere [30]. The estimated experimental error on the adsorbed amount was about 1 mg/g. The accuracy of the pressure measurement was 1%, and the temperature was maintained within 1 K. The in situ XPRD of the sample exposed to NH₃ was recorded using the capillary attached to the balance and sealed off after exposure to the gas (see [30] for details).

Results and discussion.

Thermal behavior and crystal structures.

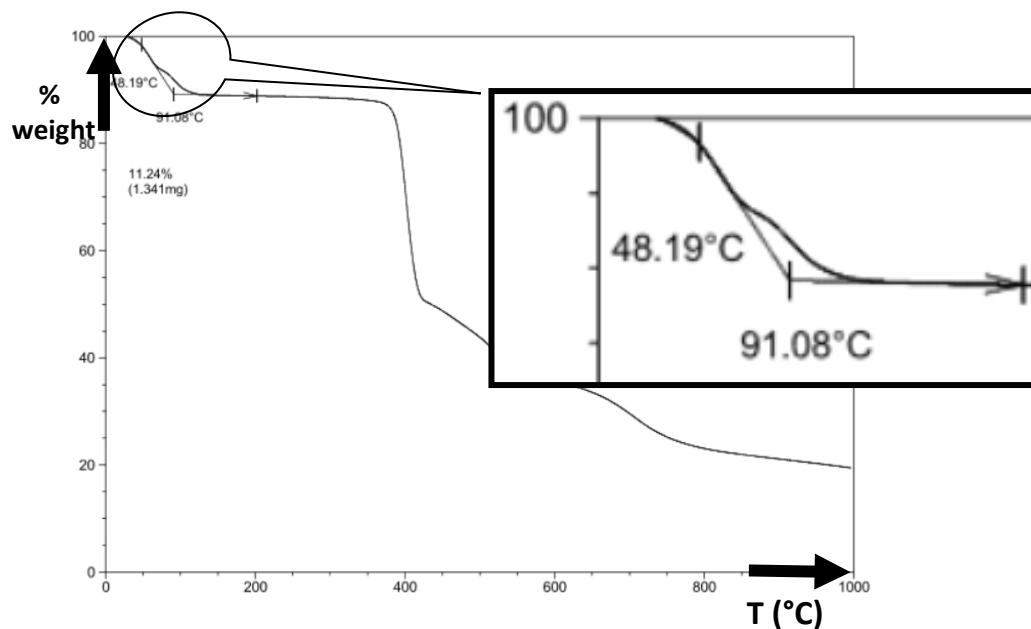


Figure 1. TGA curve of a crystallized sample of $[1(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ showing the dehydration in two consecutive steps and the stability of the dehydrated phase up to 350°C.

The solvothermal reaction of $(\text{H}_2\text{pc}2)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, cadmium perchlorate and H_3BTC led to the pure phase of a new viologen-carboxylate PCP whose formulation, first revealed from the crystal structure determination, is $[\text{Cd}_3(\text{pc}2)(\text{BTC})_2(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ named $[1(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$. The thermogravimetric analysis first confirms the amount of 8 water molecules per formulation unit as the weight loss of 11.24 % well corresponds to the theoretical one of 11.15%. It also shows that the dehydrated compound is stable up to 350°C, and that the water weight loss occurs in two consecutive equivalent steps of 5.65% and 5.59% which can be assigned to the departure of 4 first water molecules following by the departure of the 4 others (Figure 1). The measurement of XRPD patterns at different temperatures (thermodiffractometry) under N_2 atmosphere which have been carried out in the RT-145°C range (RT: room temperature, Figure S2) clearly shows two main

phase transformations: a first change in the peak positions occurs at 35 °C giving a partially dehydrated phase which is stable up to 65 °C, while the second phase transition occurs at 85 °C giving the expected fully dehydrated phase, in accordance with the TGA analysis. We also notice another change of several peak positions at 115 °C revealing a slight change of unit cell parameters of the dehydrated phase.

Taking account these results, we have very slowly heated single crystals of $[\mathbf{1}(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$ up to 65 °C and up to 110°C to see if single-crystal-to-single crystal transitions could occur. The heated crystals were taken off the oven and were immediately put in some drops of oil. While we observed that a breaking of crystals has occurred during the heating process, suitable crystals could be selected for X-ray analysis (N_2 atmosphere at 150 K). From the crystal structure determination, their formulation were found to be $[\mathbf{1}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ for the partially dehydrated compound which is in good accordance with the expected departure of 4 water molecules, and $[\mathbf{1}]\cdot 2\text{H}_2\text{O}$ for the crystal heated at 110 °C. The unexpected presence of two water molecules per formula unit can be explained by the very hydrophilic nature of $[\mathbf{1}]$ (water adsorption for very low water pressure, $P/P_S \approx 0.001$ -see part 2) which has been able to uptake some water molecules from air (during the transfer of crystals from oven to oil) or from oil. Figure 2 shows a comparison between the theoretical XRPD patterns obtained from the crystal structure data collected at 150 K and the experimental XRPD patterns collected under N_2 atmosphere of $[\mathbf{1}(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$ at room temperature, at 65 °C and at room temperature after heating at 145°C. As expected, the experimental and theoretical patterns of $[\mathbf{1}(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$ well fit (Figure 2, down). Interestingly the experimental pattern of the fully dehydrated phase $[\mathbf{1}]$ well fit with the theoretical one of $[\mathbf{1}]\cdot 2\text{H}_2\text{O}$ showing that the adsorption of the two first water molecules doesn't involve a significant structural change. For the sample heated at 65 °C, the pattern doesn't fit perfectly with the

theoretical one of $[\mathbf{1}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$, some lines being slightly shifted one to each other. This may be explained by the different temperature of data collection, $-123\text{ }^\circ\text{C}$ for the single crystal unit cell and $65\text{ }^\circ\text{C}$ for the experimental XRPD pattern.

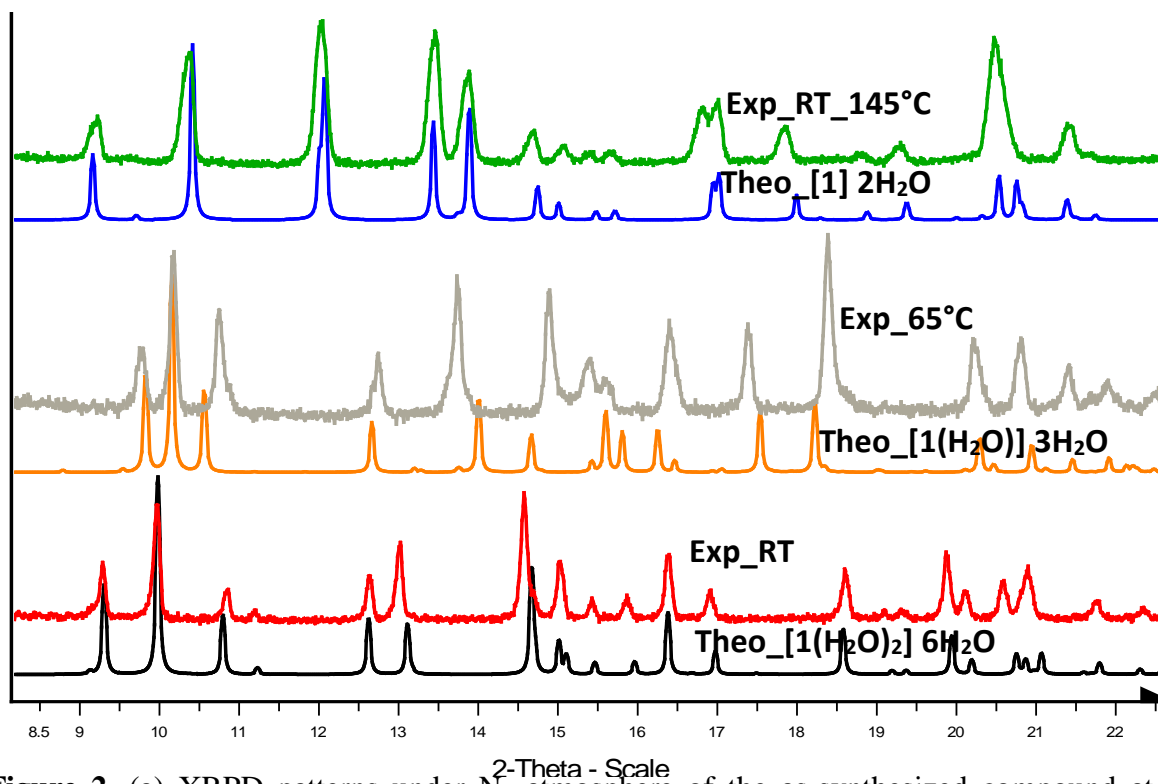


Figure 2. (a) XRPD patterns under N_2 atmosphere of the as-synthesized compound at room temperature (Exp_RT), at $65\text{ }^\circ\text{C}$ (Exp_65°C) and at room temperature after being heated at $145\text{ }^\circ\text{C}$ (Exp_RT_120°C), together with the theoretical ones of the as-synthesized compound (Theo_[$\mathbf{1}(\text{H}_2\text{O})_2$] $\cdot 6\text{H}_2\text{O}$) and the partially dehydrated phases (Theo_[$\mathbf{1}(\text{H}_2\text{O})$] $\cdot 3\text{H}_2\text{O}$) and (Theo_[$\mathbf{1}$] $\cdot 2\text{H}_2\text{O}$) obtained from single crystal studies at 150K.

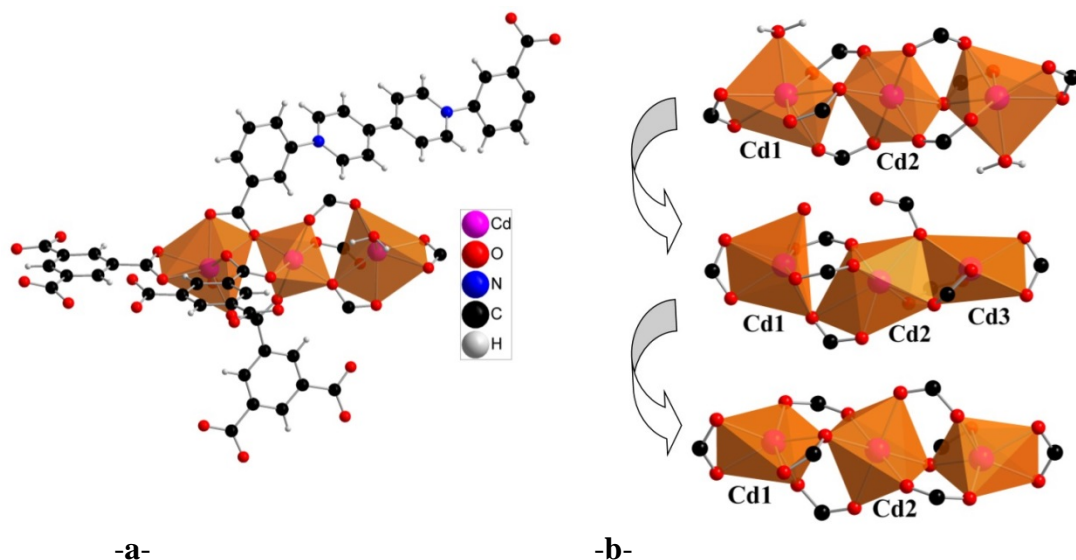


Figure 3. a) the symmetrical trimeric inorganic unit based on 3 Cd^{2+} ions surrounded by 6 BTC^{3-} anions, 2 *pc2* and 2 water molecules (half BTC and *pc2* not shown for clarity) in $[\mathbf{1}(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$; b) Evolution of the inorganic trimeric building block upon dehydration : from the symmetrical unit $[\text{Cd}_3(\text{CO}_2)_8(\text{H}_2\text{O})_2]$ in $[\mathbf{1}(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$ (top) to the symmetrical $[\text{Cd}_3(\text{CO}_2)_8]$ unit in $[\mathbf{1}]\cdot 2\text{H}_2\text{O}$ (down) through the asymmetrical $[\text{Cd}_3(\text{CO}_2)_8(\text{H}_2\text{O})]$ unit in $[\mathbf{1}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ (middle).

The three-dimensional (3D) crystal structure of $[\mathbf{1}(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$ is built up from trimeric inorganic units linked together through the BTC^{3-} and *pc2* ligands. The centrosymmetrical trimeric unit consists of two kinds of polyhedron (Figure 3). The first independent cadmium atom (Cd2) which is located on a symmetry center adopts a common octahedral geometry based on 4 oxygen atoms of bridging carboxylate groups and 2 oxygen atoms of two carboxylate groups shared with neighbouring polyhedra. The second independent cadmium atom (Cd1) which lies on a general position is surrounded by seven oxygen atoms, 4 from bridging carboxylate groups, 2 from another carboxylate group and 1 from a water molecule. The formulation of the resulting centrosymmetrical unit is $[\text{Cd}_3(\text{CO}_2)_8(\text{H}_2\text{O})_2]$, the eight carboxylate groups belonging to 6 BTC^{3-} and 2 *pc2* ligands (Figure 3). The overall structure results from the connection of the inorganic nodes by both *pc2* and BTC^{3-} ligands. Each *pc2* molecule is shared by two trimeric units (roughly

along the *a* direction when the structure is viewed along *c*, Figure 4) while each BTC³⁻ ligand is shared by three inorganic units, leading to a 3D network whose formulation is [Cd₃(pc₂)_{2/2}(BTC)_{6/3}(H₂O)₂] ([Cd₃(pc₂)(BTC)₃(H₂O)₂]). The 3D network which is porous, includes 6 guest water molecules per formula unit in cavities of the structure. The porosity has been estimated to 10 % according to calculations using the Squeeze routine of Platon when guest water molecules are removed (Figure 4b).

Upon dehydration of [1(H₂O)₂]:6H₂O, as already shown by powder diffractometry, two consecutive structural changes occur. As expected from TGA experiment, the crystal structure of the partially dehydrated phase reveals that [1(H₂O)₂]:6H₂O lost half water molecules per formula unit during the first desorption step. However, while it was expected that all the four water molecules were guest molecules containing in pores, it appears that only three such molecules and one water molecule of the trimeric unit were desorbed, leading to the [1(H₂O)]:3H₂O phase. Thus, the trimeric unit whose formulation is [Cd₃(CO₂)₈(H₂O)] becomes asymmetrical in [1(H₂O)]:3H₂O, and consisting of three independent cadmium atoms with the water molecule linked to one external cadmium (Figure 3). We already indicated that the X-ray study had revealed that single crystals heated over 100°C unexpectedly contained two water molecules per formula unit leading to the [1]:2H₂O phase. It must be noted that the two partially dehydrated phases (and certainly the fully dehydrated phase as shown by XRPD), have a similar unit cell volume (V= 3960/2= 1980 Å³ for [1(H₂O)]:3H₂O and V= 2020 Å³ for [1]:2H₂O phase, general view of both structures: Fig. S4-5), which is only 9% less than the volume of [1(H₂O)₂]:6H₂O (2180 Å³). And in fact, the squeeze routine of Platon using the structure of [1]:2H₂O for which water molecules have been removed, show that the crystal structure of the desorbed phase is still porous (porosity of 7%). This may explain the uptake at very low P/P° of the two first water molecules in this

hydrophilic PCP that interact quite strongly with H atoms of the bipyridinium cores (Fig. S6). If the structural breathing effect is not impressive along with these phase transitions, the interesting feature is the structural reorganization upon dehydration in order to satisfy the electron acceptor character of the viologen unit. In $[\mathbf{1}(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$, the pyridinium cycle of the symmetrical pc2 ligand interact at the N^+ site with one water molecule bound to Cd1 (O9) and one guest water molecule (O12, Figure 5). In $[\mathbf{1}] \cdot 2\text{H}_2\text{O}$, a rotation of the planar viologen core has occurred, the dihedral angle between the pyridinium cycle and the phenyl cycle going from 43.1° in $[\mathbf{1}(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ to 82.4° in $[\mathbf{1}] \cdot 2\text{H}_2\text{O}$. As a consequence, the pyridinium unit at the N^+ site is now interacting from each side with two oxygen atoms (O5 and O3) of carboxylate groups (Figure 5).

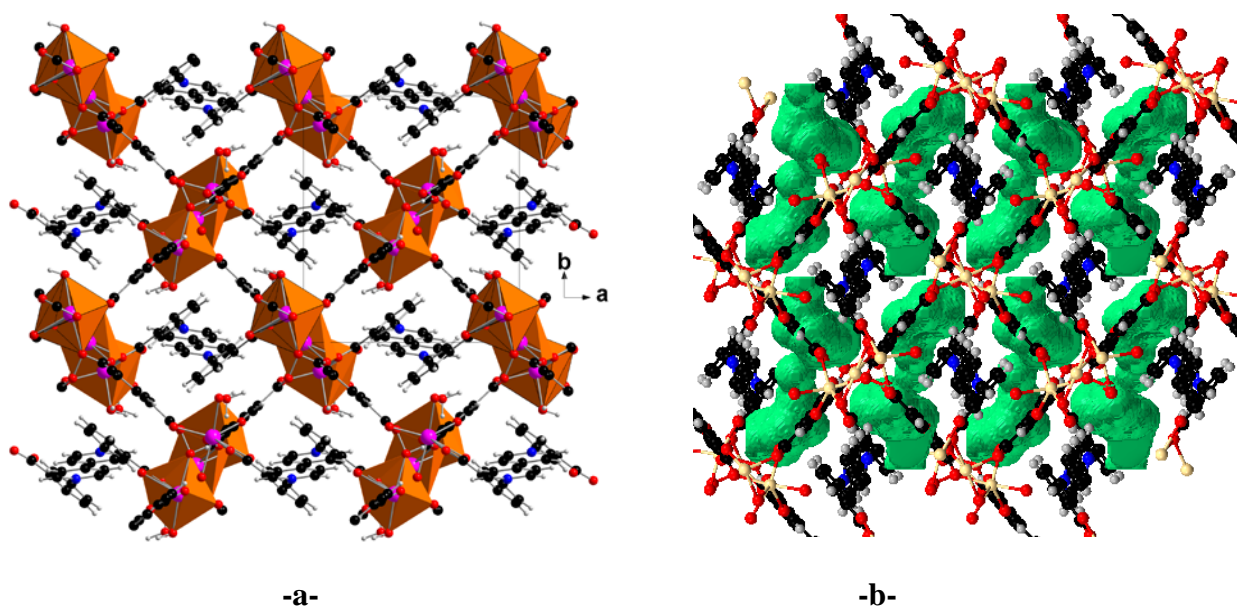


Figure 4. General view of structure of $[\text{Cd}_3(\text{BTC})_2(\text{pc}2)(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ along the c axis (water molecules in pores omitted for clarity): polyhedra representation showing the connectivity between the trimeric units (a), and ball and stick representation showing the cavities present inside the structure representing 13 % of the volume (green volumes) (b).

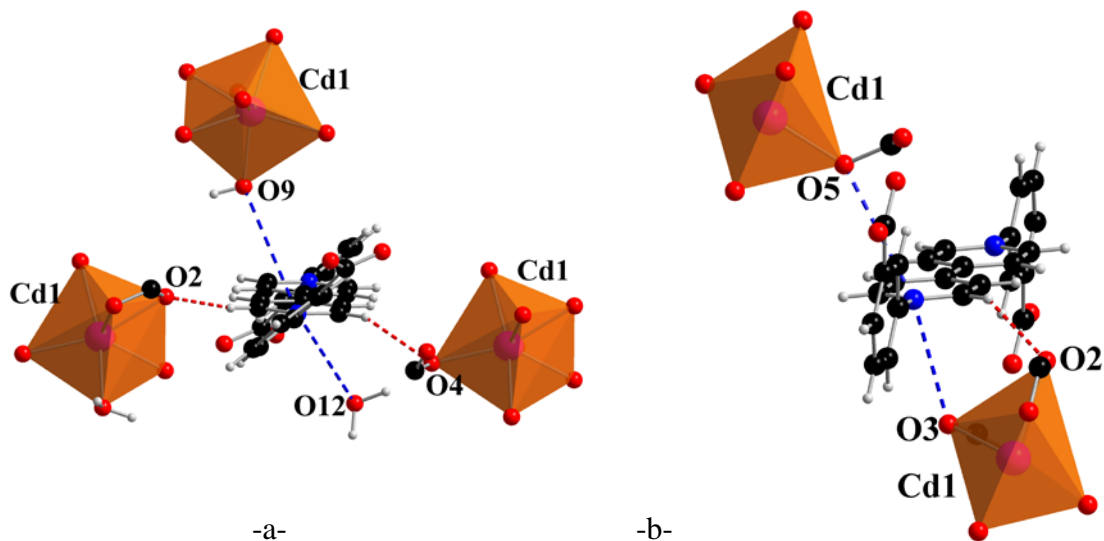


Figure 5. Environment of one pc2 molecule in the as-synthesized compound $[1(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$ (a) and the dehydrated phase $[1]\cdot 2\text{H}_2\text{O}$ (b) showing weak contacts between N^+ or H atoms bearing by C atoms in alpha of N^+ sites and O atoms of water molecules or carboxylate groups: (a) $\text{N}\dots\text{O9}$, 4.329; $\text{N}\dots\text{O12}$, 4.120; $\text{H}\dots\text{O2}$, 2.105, $\text{H}\dots\text{O4}$, 2.531 (b): $\text{N}\dots\text{O5}$, 3.888; $\text{N}\dots\text{O3}$, 3.356; $\text{H}\dots\text{O2}$, 2.225 (only contacts for one pyridinium site of the symmetrical pc2 molecule is shown).

CH_3OH , H_2O and NH_3 adsorption measurements.

The presence of permanent porosity in fully dehydrated **[1]** is confirmed by the adsorption of methanol at 298K (Fig. S7). The shape of the isotherm is characteristic of a microporous solid and the maximum adsorbed amount of methanol (0.09 g/g) corresponds to pore volume of $0.11 \text{ cm}^3/\text{g}$. Isotherm of water adsorption on dehydrated **[1]** compound is presented in Figure 6. The saturation uptake is close to eight molecules of water per formula unit in accordance with TGA and structure determination, corresponding to an adsorption of $0.13 \text{ g}\cdot\text{g}^{-1}$. The step in the isotherm occurring at four H_2O molecules is attributed to the formation of the intermediate phase containing this number of water molecules. This step in the adsorption isotherm and a slight hysteresis are indicative of a structural rearrangement during the transition between the phase containing four H_2O molecules

and the fully hydrated one. Another important feature of the isotherm is a strong adsorption at a very low water pressure: the solid adsorbs a half of water below 0.01 of saturated water pressure, and nearly all the water molecules at $P/P_S = 0.1$. Such a behavior reveals a strong hydrophilic character of [1] in comparison with most of known MOFs as reported in two recent reviews on water adsorption in MOFs.^{1,2} Finally the log scale drawing of the water adsorption isotherm (Figure 6, right) allows to distinguish for the first (4 water molecules) adsorption step, two sub-steps of two water molecules each, the first sub-step corresponding to extremely low water pressure ($P/P_S < 0.001$). And it is worth noting that crystal structure of the phase we expected to be fully dehydrated has revealed the presence of two water molecules per formula unit. In addition to its strong hydrophilic character, [1] shows a remarkable stability towards water. It preserves a constant water capacity in multiply cycles of water adsorption (Fig. S8). Also, its structure is fully preserved after immersion in liquid water as attested by XRPD (Fig.S3).

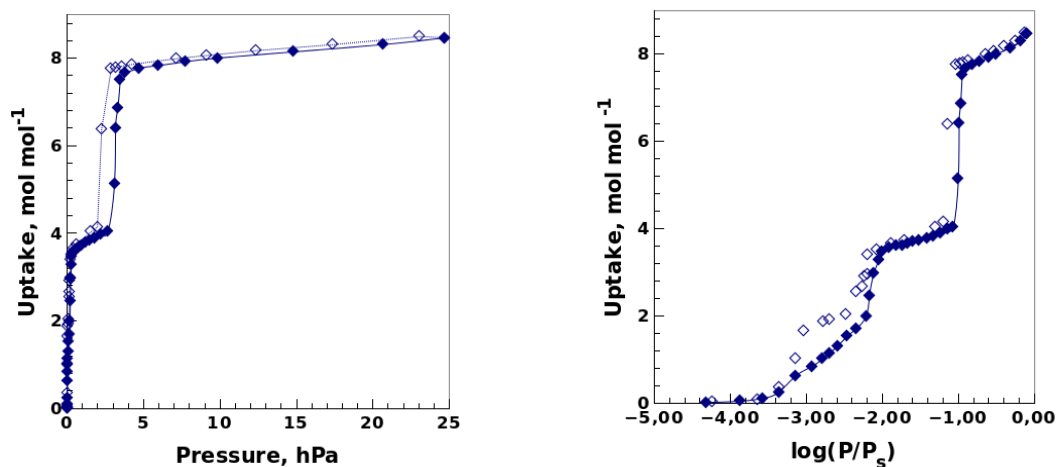


Figure 6. Adsorption isotherms of water on [1] at 298 K on linear (left) and Log (right) scales. Full symbols - adsorption, empty symbols – desorption.

[1] adsorbs significant amount of ammonia attaining 0.3 g/g or 17.6 mmol/g at 930 hPa (Figure 7a). This important uptake is due to chemisorption of NH_3 which interact with Cd^{2+} cations and form $[\text{Cd}(\text{NH}_3)_6]^{2+}$ complex similarly to another Cd-based PCP described in our previous work.³⁰ Giving Cd content in the anhydrous material (2.6 mmol/g), this adsorption mechanism could provide the capacity of 15.6 mmol(NH_3)/g. Such chemisorption should naturally result into degradation of the crystalline structure of the material, which indeed happens in [1] saturated with ammonia as confirmed by in situ XRPD (Figure 7c). It should be noted however that degassing the sample at 298K results in the appearance of a peak at $\sim 9.5^\circ$ in the diffraction pattern indicative of the existence of a partial crystalline order in the degassed sample. Moreover, upon contact with air the peak shifts to $\sim 9.2^\circ$ reflecting the swelling of the partially ordered structure upon insertion of water molecules. Even if the attribution of this peak to any crystalline plane is impossible, this behavior is similar to that of (110) peak located at 10.4° in the dehydrated structure and shifted to 10.0° upon hydration. We suppose thus that the shift of the peak after the contact with air indicates that despite the breakdown of the crystalline structure after NH_3 adsorption the solid preserves (at least partially) its porosity. This is indeed the case as follows from MeOH adsorption isotherm by the sample exposed to NH_3 (Fig. S7). Even if the maximum amount adsorbed is lower than for the pristine solid (0.05 instead of 0.09 g/g) the isotherm confirms the porosity of the amorphous phase obtained after adsorption of NH_3 . Due to this important property [1] shows a fully reversible character of NH_3 adsorption (Figure 7b).

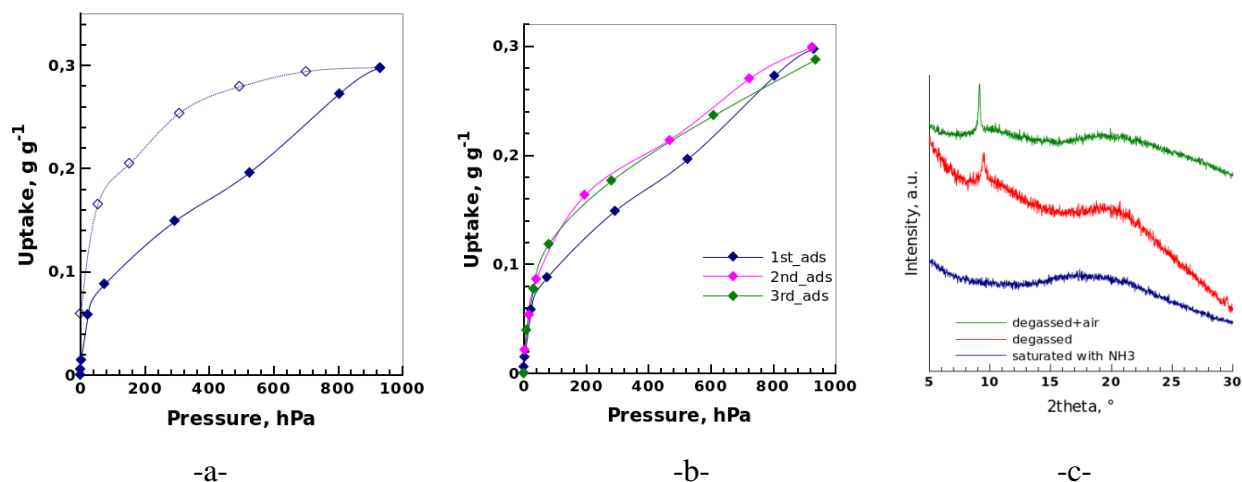


Figure 7. Adsorption isotherms of ammonia on [1] at 298 K: first adsorption-desorption cycle (a), three consecutive adsorption measurements (b) and in situ XRPD of [1] after saturation with NH₃, degassing and degassing followed by exposure to air (c).

Conclusion.

In this work we report on the preparation and adsorption properties of a water stable and highly hydrophilic porous coordination polymer based on viologen-carboxylate type ligand, 4,4'-bipyridinium,1,1'-bis-(2-carboxyphenyl) (pc2), obtained by solvothermal method: [Cd₃(pc2)(BTC)₂(H₂O)₂] \cdot 6H₂O (BTC³⁻= 1,3,5-carboxy-benzene) ([1(H₂O)₂] \cdot 6H₂O). It is found that dehydration of [1(H₂O)₂] \cdot 6H₂O provokes structural transitions in which the crystallinity of the sample is retained. The crystalline structure was determined for the fully hydrated compound as well as for two intermediate phases: [1] \cdot 2H₂O and [1(H₂O)] \cdot 3H₂O. Localization of water molecules and structure of Cd trinuclear building unit are related and shown to be dependent on water content. In [1] \cdot 2H₂O both water molecules are localized in the pores and [Cd₃(CO₂)₈] cluster has a symmetrical structure. In contrast, in [1(H₂O)] \cdot 3H₂O one molecule is coordinated to Cd leading to formation of an asymmetrical unit [Cd₃(CO₂)₈(H₂O)]. The fully hydrated phase ([1(H₂O)₂] \cdot 6H₂O) contains two coordinated molecules and a symmetrical cluster

[Cd₃(CO₂)₈(H₂O)₂]. The existence of the partially hydrated phases with a well-defined water stoichiometry is confirmed by the presence of three well resolved steps in the water adsorption isotherm of **1**. Also, uptake of 50% of water at P/P_S < 0.01 shows a highly hydrophilic nature of dehydrated **1**. The prepared PCP exhibits a high affinity towards another polar molecule, NH₃, achieving at 930 hPa the uptake as high as 0.3 g/g (or 17.6 mmol/g). It is worth noting that this capacity is entirely preserved after regeneration under vacuum at 180°C despite formation of an amorphous phase after NH₃ adsorption.

ASSOCIATED CONTENT

Supporting Information. Details of synthetic procedure, XRPD diffraction at different temperatures, general views of structures of partially dehydrated phases, adsorption isotherm of methanol and repeatability of the water uptake properties of [**1**].

AUTHOR INFORMATION

Corresponding Author

*nicolas.mercier@univ-angers.fr

*igor.bezverkhyy@u-bourgogne.fr

Author Contributions

The manuscript was written through contributions of all authors. All authors have contributed equally and have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

M. Leroux thanks the University of Angers for a Ph.D. grant.

REFERENCES

- (1) Canivet, J.; Fateeva, A.; Guo, Y.; Coasne, B.; Farrusseng, D. *Chem. Soc. Rev.* **2014**, *43*, 5594-5617
- (2) Furukawa, H.; Gandara, F.; Zhang, Y.-B., Jiang, J., Queen, W. L.; Hudson, M. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2014**, *136*, 4369-4381.
- (3) Kaye, S. S.; Dailly, A.; Yaghi, O. M.; Long, J. R., *J. Am. Chem. Soc.* **2007**, *129*, 14176.
- (4) Huang, L. M.; Wang, H. T.; Chen, J. X.; Wang, Z. B.; Sun, J. Y.; Zhao, D. Y.; Yan, Y. S. *Microporous Mesoporous Mater.* **2003**, *58*, 105.
- (5) Schoenecker, P. M.; Carson, C. G.; Jasuja, H.; Flemming, C. J. J.; Walton, K. S. *Ind. Eng. Chem. Res.* **2012**, *51*, 6513.
- (6) Banerjee, R. ; Phan, A. ; Wang, B. ; Knobler, C. ; Furukawa, H. ; O’Keeffe, M. ; Yaghi, O. M. *Science* **2008**, *319*, 939-943.
- (7) Kuesgen, P.; Rose, M.; Senkovska, I.; Froede, H.; Henschel, A.; Siegle, S.; Kaskel, S. *Microporous Mesoporous Mater.* **2009**, *120*, 325.
- (8) Cavka, J.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. *J. Am. Chem. Soc.* **2008**, *130*, 13850–13851.
- (9) Wu, H. ; Chua, Y. ; Krungleviciute, V. ; Tyagi, M. ; Chen, P. ; Yildirim, T. ; Zhou, W. *J. Am. Chem. Soc.* **2013**, *135*, 10525.
- (10) P. M. S. Monk, *The Viologens: Physicochemical Properties, Synthesis, and Application of the Salt of 4, 4'-Bipyridine*, Wiley, New York, **1998**.
- (11) Mercier, N. *Eur. J. Inorg. Chem.* **2013**, 19-31.
- (12) Wang, M-S.; Xu, G.; Zhang, Z-J.; Guo, G-C. *Chem. Commun.* **2010**, *46*, 361-376.

- (13) Leblanc, N.; Allain, M.; Mercier, N.; Sanguinet, L. *Cryst. Growth Des.* **2011**, *11*, 2064-2069.
- (14) Toma, O.; Leroux, M.; Mercier, N.; Allain, M.; Kassiba, A. A.; Swamy, S. K. K.; Dittmer, J. *Eur. J. Inorg. Chem.* **2016**, 1036-1043.
- (15) Li, H.-Y.; Wie, Y.-L.; Dong, X.-Y.; Zang, S.-Q.; Mak, T. C. *Chem. Mater.* **2015**, *27*, 1327-1331.
- (16) Tan, Y.; Chen, H.; Zhang, J.; Liao, S.; Dai, J.; Fu, Z. *CrystEngComm.* **2012**, *14*, 5137-5139.
- (17) Zeng, Y.; Fu, Z.; Chen, H.; Liu, C.; Liao, S.; Dai, J. *Chem. Commun.* **2012**, *48*, 11641-11643
- (18) Zeng, Y.; Liao, S.; Dai, J.; Fu, Z. *Chem. Commun.* **2012**, *48*, 8114-8116.
- (19) Sun, J.-K.; Wang, P.; Yao, Q.-X.; Chen, Y.-J.; Li, Z.-H.; Zhang, Y.-F.; Wu, L.-M.; Zhang, J. *J. Mater. Chem.* **2012**, *22*, 12212-12219.
- (20) Sun, J.-K.; Wang, P.; Chen, C.; Zhou, X.-J.; Wu, L.-M.; Zhang, Y.-F.; Zhang, J. *Dalton Trans.* **2012**, *41*, 13441-13446.
- (21) Sun, J.-K.; Zhang, J. *Dalton Trans.* **2015**, *44*, 19041-19055.
- (22) Aulakh, D.; Varghese, J. R.; Wriedt, M. *Inorg. Chem.*, **2015**, *54*, 1756-1764.
- (23) Li, H.-Y.; Wie, Y.-L.; Dong, X.-Y.; Zang, S.-Q.; Mak, T. C. *Chem. Mater.* **2015**, *27*, 1327-1331.
- (24) Lin, J.-B.; Shimizu, G. K. H. *Inorg. Chem. Front.* **2014**, *1*, 302-305.
- (25) Kanoo, P.; Matsuda, R.; Sato, H.; Li, L.; Joon Jeon, H.; Kitagawa, S. *Inorg. Chem.* **2013**, *52*, 10735-10737.

- (26) Toma, O.; Mercier, N.; Allain, M.; Kassiba, A. A.; Bellat, J.-P.; Weber, G.; Bezverkhyy, I. *Inorg. Chem.* **2015**, *54*, 8923-8930.
- (27) Higuchi, M.; Tanaka, D.; Horike, S.; Sakamoto, H.; Nakamura, K.; Takashima, Y.; Hijikata, Y.; Yanai, N.; Kim, J.; Kato, K.; Kubota, Y.; Takata, M.; Kitagawa, S. *J. Am. Chem. Soc.* **2009**, *131*, 10336–10337.
- (28) Liu, J.-J.; Guan, Y.-F.; Lin, M.-J.; Huang, C.-C.; Dai, W.-X. *Cryst. Growth Des.* **2015**, *15*, 5040-5046.
- (29) Liu, J.-J.; Guan, Y.-F.; Lin, M.-J.; Huang, C.-C.; Dai, W.-X. *Cryst. Growth Des.* **2016**, *16*, 2836-2842.
- (30) Leroux, M.; Mercier, N.; Allain, M.; Dul, M.-C.; Dittmer, J.; Bellat, J.-P.; Weber, G.; Bezverkhyy, I. *Inorg. Chem.* **2016**, *55*, 8587-8594.
- (31) Yao, Q.-X.; Pan, L.; Jin, X.-Hui; Li, J.; Ju, Z.-F.; Zhang, J. *Chem. Eur. J.* **2009**, *15*, 11890-11897.
- (32) Sun, J.-K.; Yao, Q.-X.; Tian, Y.-Y.; Wu, L.; Zhu, G.-S.; Chen, R.-P.; Zhang, J. *Chem. Eur. J.* **2012**, *18*, 1924-1931.
- (33) Higushi, M.; Nakamura, K.; Horike, S.; Hijikata, Y.; Yanai, N.; Fukushima, T.; Kim, J.; Kato, K.; Takata, M.; Watanabe, D.; Oshima, S.; Kitagawa, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 8369-8372.
- (34) Petit, C.; Karwacki, C.; Peterson, G.; Bandosz, T. J. *J. Phys. Chem. C* **2007**, *111*, 12705-12714.
- (35) Petit, C.; Bandosz, T. J. *J. Phys. Chem. C* **2007**, *111*, 16445-16452.
- (36) Rieth, A. R.; Tulchinsky, Y.; Dinca, M. *J. Am. Chem. Soc.* **2016**, *138*, 9401-9404.

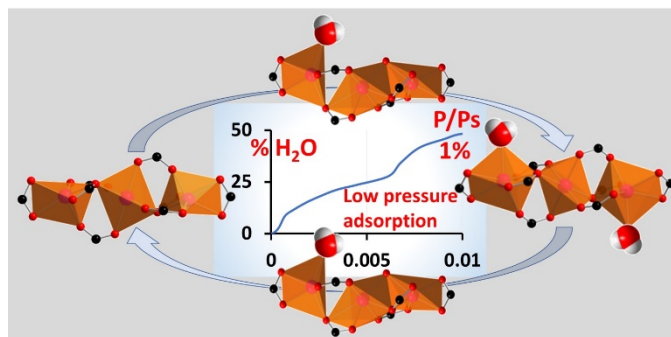
- (37) Tan, B.; Chen, C.; Cai, L-X.; Zhang, Y-J.; Huang, X-Y.; Zhang, J. *Inorg. Chem.* **2015**, *54*, 3456-3461.
- (38) Britt, D.; Tranchemontagne, D.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 11623-11627.
- (39) Peterson, G. W.; Wagner, G. W.; Balboa, A.; Mahle, J.; Sewell, T.; Karwacki, C. J. *J. Phys. Chem. C.* **2009**, *113*, 13906-13917.
- (40) Kajiwara, T.; Higuchi, M.; Yuasa, A.; Higashimura, H.; Kitagawa, S. *ChemComm.* **2013**, *49*, 10459-10461.
- (41) Spanopoulos, I.; Xydias, P.; Malliakas, C. D.; Trikalitis, P. N. *Inorg. Chem.* **2013**, *52*, 855-862.
- (42) Katz, M. J., Howarth, A. J., Moghadam, P. Z.; DeCoste, J. B.; Snurr, R. Q., Hupp, J. T.; Farha, O. K. *Dalton Trans.* **2016**, *45*, 4150-4153.

"For Table of Contents Use Only,"

Insight into the mechanism of water adsorption/desorption in hydrophilic viologen-carboxylate based PCP

Maxime Leroux, Nicolas Mercier, * Jean-Pierre Bellat, Guy Weber and Igor Bezverkhyy*

TOC graphic



SYNOPSIS

A water stable porous coordination polymer based on the viologen-carboxylate ligand pc2, $[\text{Cd}_3(\text{pc}2)(\text{BTC})_2(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ ($[\mathbf{1}(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$) shows under its dehydrated form $[\mathbf{1}]$ a highly hydrophilic behavior with half water molecules adsorbed at $\text{P}/\text{Ps} < 0.01$. The determination of crystal structure of $[\mathbf{1}(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ and of two partially dehydrated phases allows to get insight into the mechanism of water adsorption/desorption.