Supporting Information

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

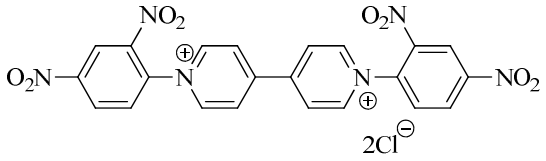
*Maxime Leroux, Nicolas Mercier, * Jean-Pierre Bellat, Guy Weber*

and Igor Bezverkhyy[*]

A- Synthesis

A1- Procedure for the preparation of the pc2 ligand:

First step : synthesis of 1,1'-bis-(2,4-Dinitrophenyl)-4,4'-bipyridinium dichloride ($(DNP)_2Cl$)

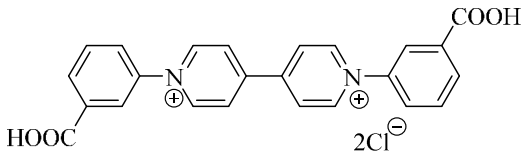


M = 561 g/mol

The mixture of 4,4'-bipyridine (6.20 g, 36mmol) and 2,4-dinitrochlorobenzene (17.0 g, 84 mmol) in 70 mL of ethanol (aq. EtOH, 96 %) is refluxed for 24 h. After cooling to the room temperature, precipitation is filtered and dried under vacuum. 13.3 g (60 %) of pale-green powder is obtained.

RMN ^{1}H (300 MHz, D_2O, ppm): δ=9.52 (d, 4H, J = 9.0 Hz, ArH), 9.45 (d, 2H, J = 3.0 Hz, ArH), 9.00 (d, 2H, J = 3.0 Hz, ArH), 8.97 (d, 4H, J = 9.0 Hz, ArH), 8.34 (d, 2H, J = 9.0 Hz, ArH).

Second step: synthesis of 4,4'-bis(3-carboxyphenyl)-bipyridinium dichloride (H_2PC2Cl_2)



M = 469.4 g/mol

To 4 g (8.5 mmol) of 1,1'-bis-(2,4-Dinitrophenyl)-4,4'-bipyridinium dichloride ($(DNP)_2Cl$) in 150 mL of ethanol (aq. EtOH, 96%), 2.34 g (17.1 mmol) of 3-aminobenzoic acid is added. The mixture is stirred together at 80°C during 24 h, then cooled to room temperature. The brown mixture obtained is filtered, washed with ethanol, diethyl ether and dried under vacuum. Finally, 3.1 g (72%) of the final product as a light brown powder, is obtained.

RMN ^{1}H (300 MHz, D_2O, ppm): δ=9.77 (d, 4H, vio), 9.13 (d, 4H, vio), 8.50 (s, 1 arom H), 8.32 (d, 2 arom H), 8.22 (d, 2 arom H), 7.94 (t, 2 arom H).

A2- Synthesis of the material:

In a 25mL Teflon-lined stainless-steel autoclave; 24.3mg (0.05mmol) of $(H_2pc2)Cl_2$, 21mg (0.1mmol) of H_3BTC and 62.2mg (0.2mmol) of cadmium perchlorate $Cd(ClO_4)_2$ were totally dissolved in a 1:1 mixture of DMF/H_2O (2mL/2mL). The autoclave is then placed in a programmable oven, slowly heat to 105°c in 7h, maintained at this temperature for 48h and slowly cooled to room temperature in 8h. The yellow scale-shaped crystals (see photo) were filtered off and washed with DMF, then air dried.

B-X-Ray Powder Diffraction

B-1-[1(H_2O)$_2$] 6H_2O

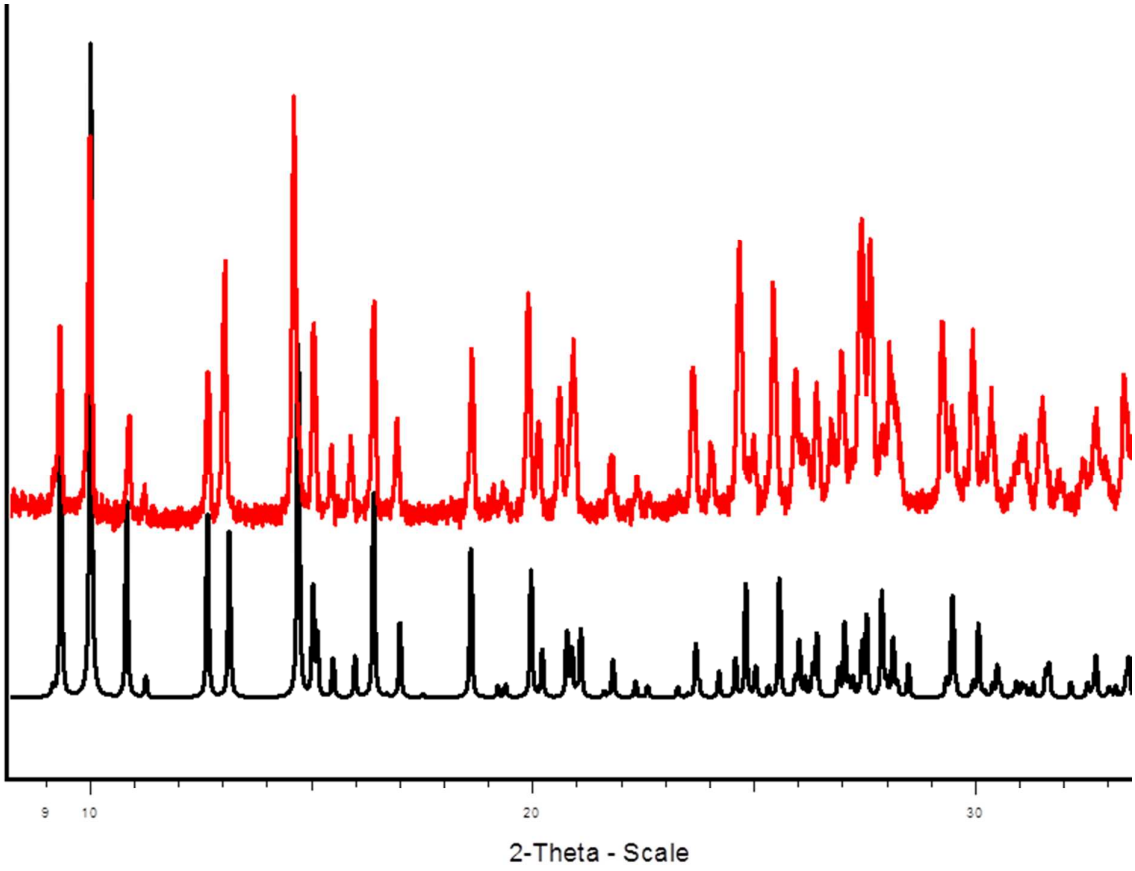


Fig. S1. Theoretical (black) and experimental (red) XRPD of [1(H_2O)$_2$] 6H_2O

B-2-Thermodiffractometry ([**1**$(H_2O)_2$] $6H_2O$; RT-145°C range)

* 1rst transition at 35°C. Partially dehydrated phase stable in the 35°C-65°C range
* 2nd transition at 75°C. Dehydrated phase stable over 75°C
* 3rd transition at 115°C of the dehydrated phase

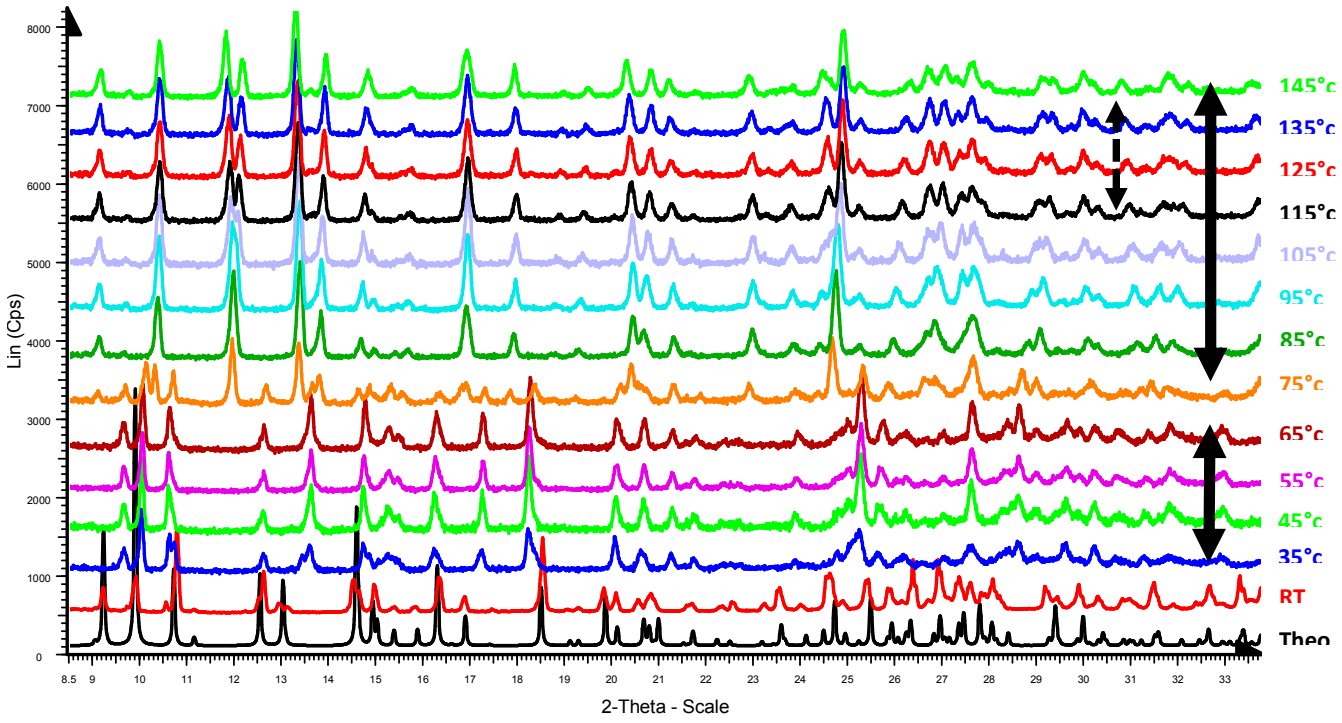


Fig. S2. Thermodiffractometry of [1$(H_2O)_2$] $6H_2O$ in the RT-145°C range.

B-3-Stability of [1(H_2O)$_2$] 6H_2O in water

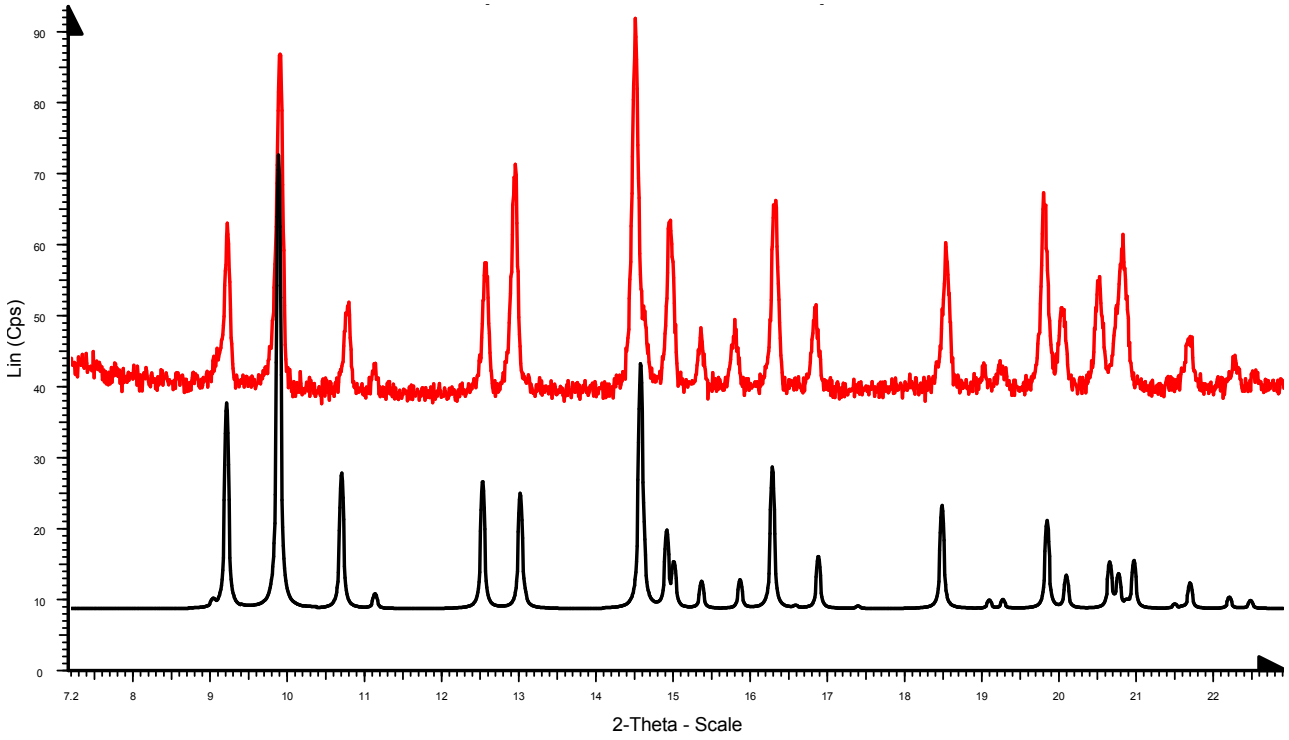


Fig. S3. Theoretical XRPD (black), and experimental XRPD of [1(H_2O)$_2$] 6H_2O after 24h in water solution (red).

C- Crystal structures

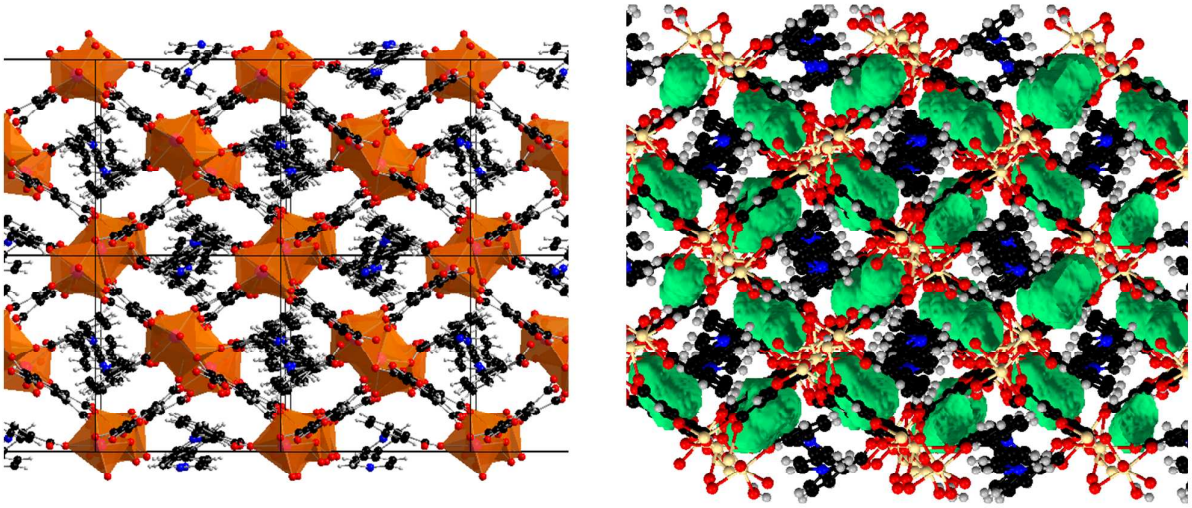


Fig. S4. General view of structure of $[1(H_2O)]\cdot 3H_2O$ along the c axis (water molecules in pores omitted for clarity): polyhedra representation showing the connectivity between the trimeric units (a), and ball and stick representation showing the cavities present inside the structure representing 7 % of the volume (green volumes)

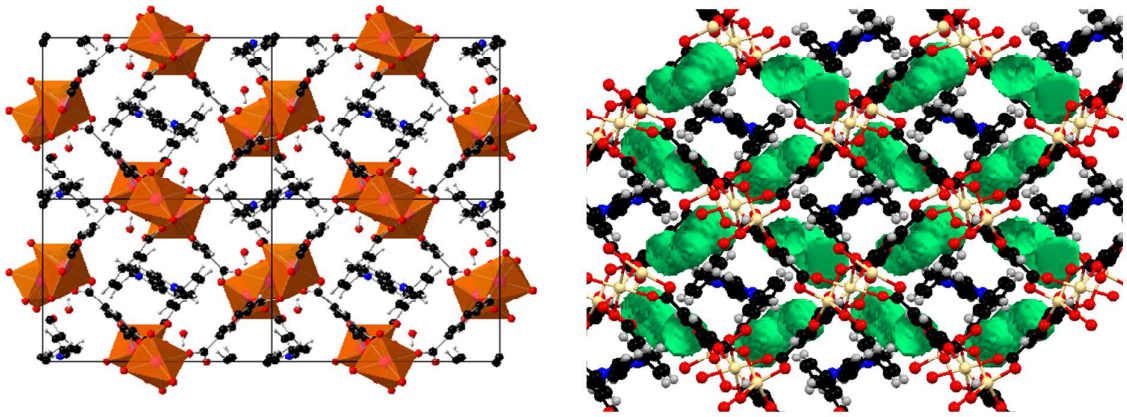


Fig. S5. General view of structure of $[1]^{-2}H_2O$ along the c axis (water molecules in pores omitted for clarity): polyhedra representation showing the connectivity between the trimeric units (a), and ball and stick representation showing the cavities present inside the structure representing 7 % of the volume (green volumes)

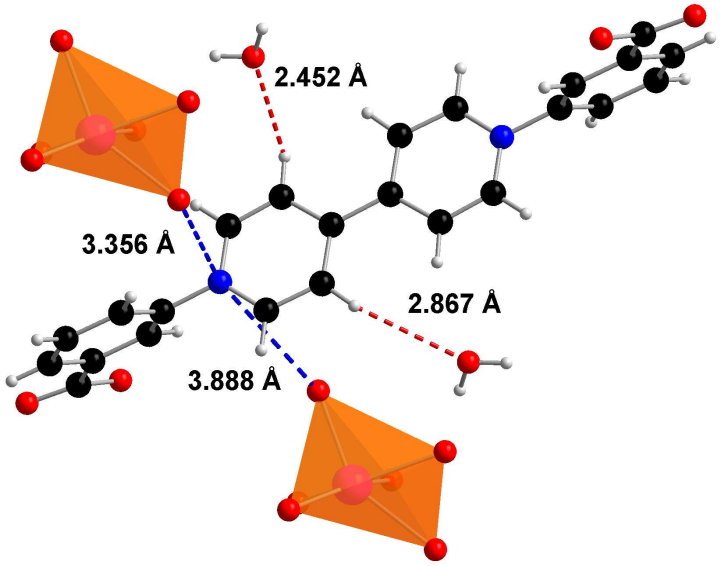


Fig. S6. Detail of the structure of [1]·2H_2O showing the interactions of the guest water molecules with the H atoms of the bipyridinium core.

D- Adsorption measurements

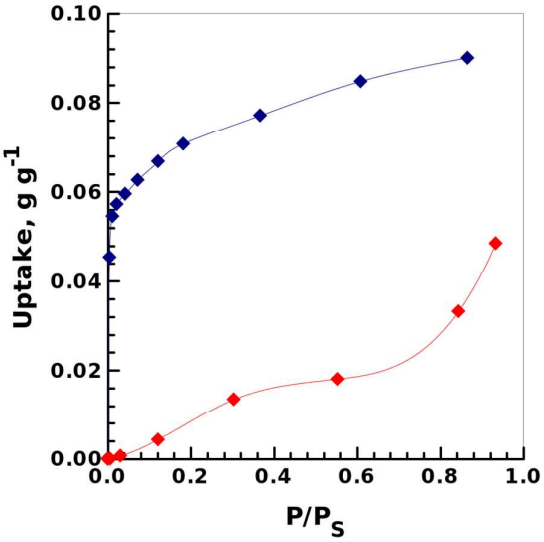


Fig. S7. Adsorption isotherms of methanol on [**1**] at 298 K (blue curve) and on [**1**] after one NH_3 adsorption-desorption cycle (red curve).

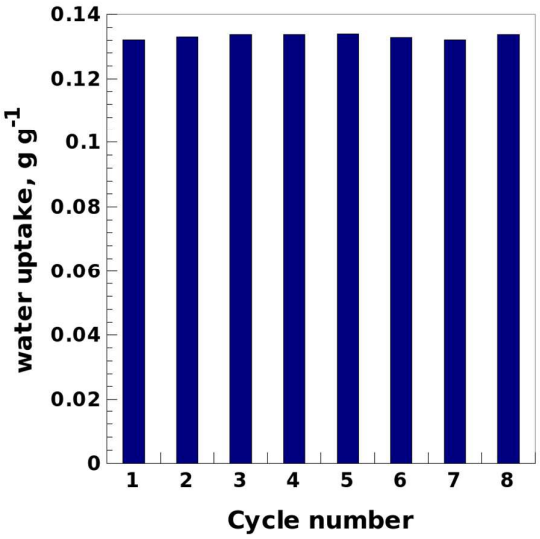


Fig. S8. Water uptake of the material at P/P_s= 0.8 in successive adsorption-desorption cycles.