

SUPPLEMENTARY INFORMATION

Enhanced porosity in a new 3D Hofmann-like network exhibiting humidity sensitive cooperative spin transitions at room temperature

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Fig. S1. Additional structure information for **1·[bpac,H₂O]**

Fig. S2 $\chi_M T$ versus T plots for the precipitated sample of **1·[bpac,H₂O]**

Fig. S3. Thermogravimetric analysis of **1·[bpac,H₂O]** and **2·[bpac,H₂O]**

Fig. S4. Thermogravimetric analysis revealing dehydration and re-hydration kinetics for **1·[bpac,H₂O]**

Fig. S5. Two perspectives of a fragment of the structure of **1·[tol,H₂O]**

Figure S1. View of a fragment of $1 \cdot [\text{bpac}, \text{H}_2\text{O}]$ along z -direction (a). Due to substitutional disorder the invited bpac molecule appears like an infinite system of chains running along x and y directions (pink ball and stick structure) (a, b). Given that only one of the two orthogonal distributions is possible a more simplified picture of the structure is shown in (c). Taking into account that the occupation factor of the invited molecule of bpac is 0.5 a picture of the framework consistent with the stoichiometry is shown in Fig. 2 of the manuscript. Colour code: Iron (orange), platinum (blue-pink), nitrogen (blue) and carbon (grey).

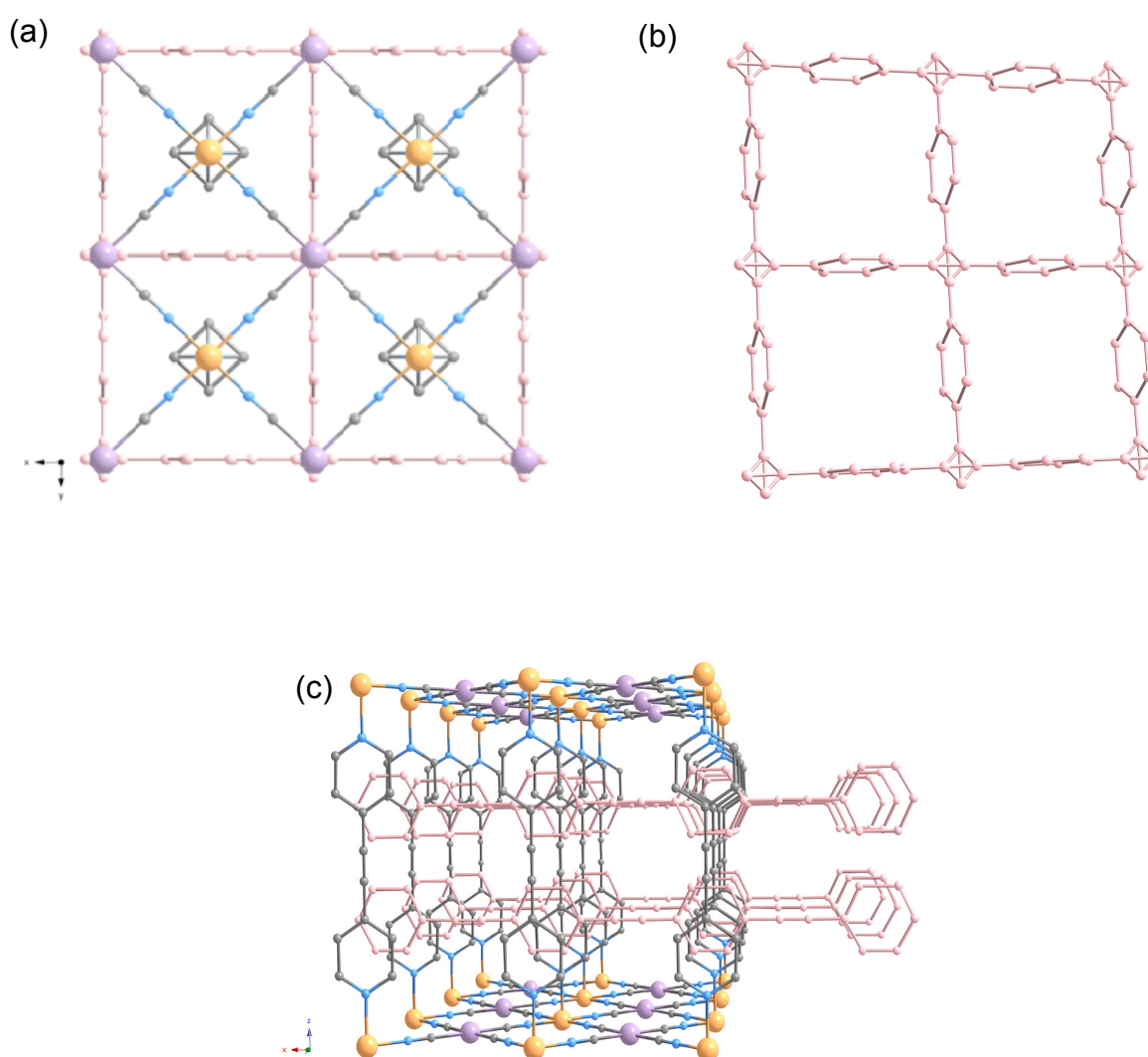


Figure S2. Thermal variation of the $\chi_M T$ product (χ_M is the molar magnetic susceptibility and T temperature) of powder sample. Black and red dots correspond to the hydrated and dehydrated forms, respectively.

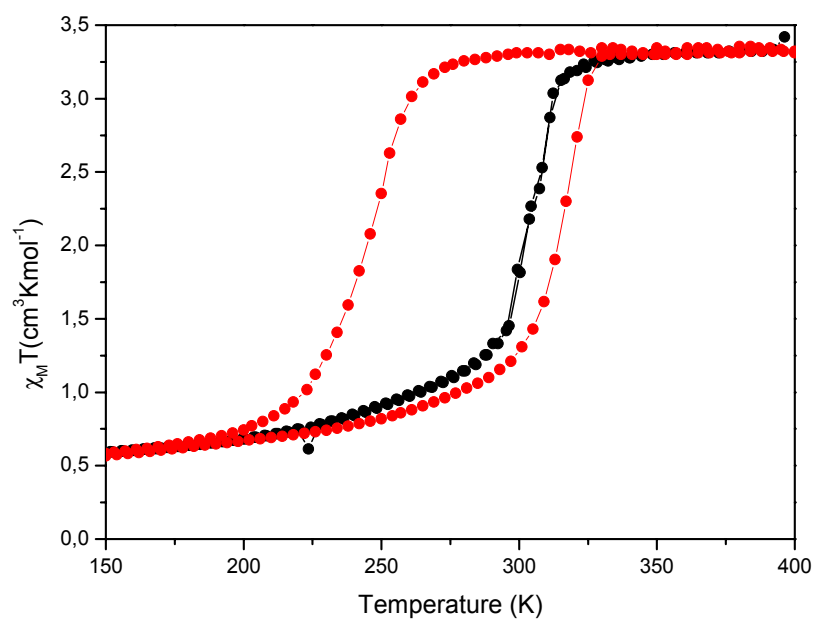
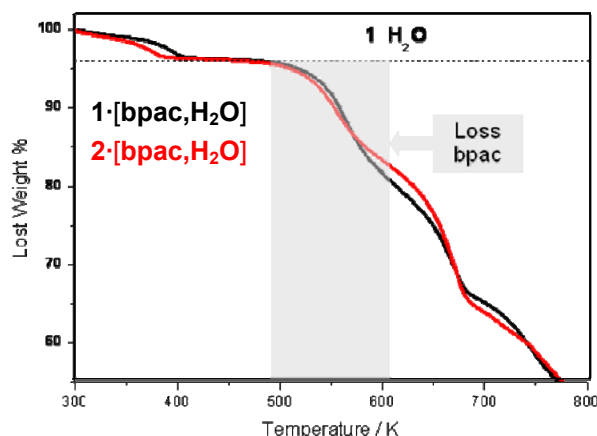
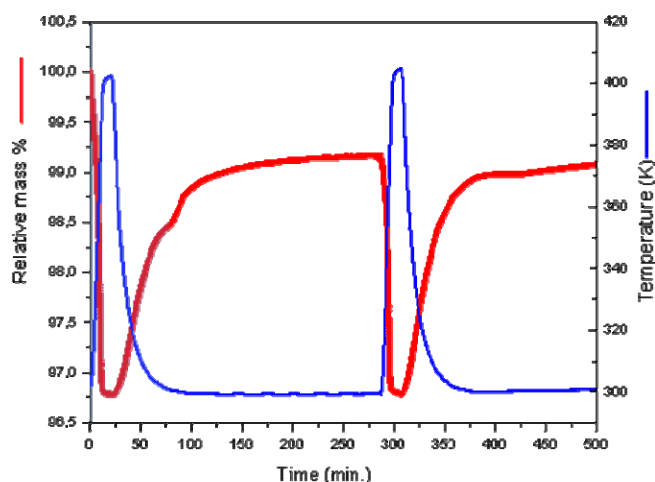


Figure S3. Thermogravimetric analysis of $1 \cdot [\text{bpac}, \text{H}_2\text{O}]$ and $2 \cdot [\text{bpac}, \text{H}_2\text{O}]$.**Figure S4.** Representative thermogravimetric analysis revealing dehydration and re-hydration kinetics for $1 \cdot [\text{bpac}, \text{H}_2\text{O}]$.

Thermogravimetric analysis has been performed using a Mettler–Toledo SDTA851 in order to prove the reversible adsorption of water in $1 \cdot \text{bpac}$. The sample has been heated at 10 K/min from room temperature until 130°C showing the loss of about 1.3 molecules of water. Then, the system is cooled under a stream of dry air (containing traces of water), displaying the partial recovery of water molecules (blue area in the diagram). Following the small plateau, the sample was exposed to atmospheric air (white area) showing additional adsorption of water. A second cycle 25 → 130 → 25°C has been realized fully under atmospheric air.

Figure S5. Two perspectives of a fragment of the structure of **1**·[tol,H₂O] ($\{\text{Fe}(\text{bpac})[\text{Pt}(\text{CN})_4]\}$ ·1tol). Light green spheres represent the highly disordered toluene molecules. Colour code: Fe (orange), N (blue), C (grey) and Pt (blue-pink).

