

**- Supporting Information -**

**Single-crystal and humidity-controlled powder diffraction study of the breathing effect in a metal-organic framework upon water adsorption/desorption**

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## S1. Experimental section

### S1.1. General considerations

All chemical reagents and solvents were purchased from commercial sources and used as received without further purification. Purity of all bulk material batches was confirmed by X-ray powder diffraction (PXRD) patterns collected on an X'Pert PRO MPD analytical diffractometer (Panalytical) at 45 kV, 40 mA using Cu K $\alpha$  radiation ( $\lambda = 1.5419 \text{ \AA}$ ), and compared with single crystal simulated patterns. Thermogravimetric analyses were performed under nitrogen flow using an STA 449 F1 Jupiter–Simultaneous TGA–DSC (NETZSCH) at a heating rate of 5 °C/min. Elemental Analysis measurements were performed on a Flash EA 2000 CHNS (Thermo Fisher Scientific) analyser. Water vapor adsorption–desorption isotherms were measured using a gravimetric instrument DVS Advantage-1 (Surface Measurement Systems Ltd). The weight of the dry powder was constantly monitored and recorded at 25 °C and different relative humidity values. The relative humidity inside the chamber was adjusted by bubbling a carrier gas (N<sub>2</sub>) in pure water until stream saturated in water (95% Relative Humidity). The adsorbed moisture was expressed as  $\frac{g_{\text{water}}}{g_{\text{dry sample}}}$ . Prior to the water adsorption measurements, samples were outgassed each cycle at 110 °C during 3 hours using a heating rate of 0.5 °C/min.

### S1.2. Synthesis of Gd-H<sub>8</sub>-DOTA-4AmP

A solution of DOTA-4AmP (354 mg, 396  $\mu\text{mol}$ ) in water (8 mL) was basified to pH = 10 with 1M sodium hydroxide. Then, a solution of gadolinium chloride hexahydrate (147 mg, 396  $\mu\text{mol}$ ) in water (2 mL) was added dropwise into the DOTA-4AmP solution warmed at 70 °C under continuous stirring. The pH of the stirring mixture was kept at 10 by addition of concentrated NaOH during the addition process. Note that, after each addition of gadolinium chloride into the DOTA-4AmP solution, a white precipitate initially appeared, but dissolved into solution after a few minutes, indicating that Gd-DOTA-4AmP was successfully formed. In this reaction, the absence of free Gd(III) in the reaction mixture was monitored by the xylenol orange test.<sup>1</sup> Thus, the addition of gadolinium chloride was stopped after the xylenol test showed the persistent presence of free gadolinium. Then, the mixture was left at 70 °C under stirring for 18 hours. Finally, the pH was adjusted to pH = 8 by the addition of concentrated HCl (1M). The exact concentration of Gd(III) ions was determined by ICP-MS, and the final concentration of the Gd-H<sub>8</sub>-DOTA-4AmP solution was adjusted to 20 mM by the addition of water to yield an approximate volume of 20 mL.

### S1.3. Synthesis of 1

Twenty mL of an aqueous solution of manganese acetate tetrahydrate (196.07 mg, 0.8 mmol) were mixed with 20 mL of the synthesized Gd-H<sub>8</sub>-DOTA-4AmP (0.4 mmol) solution, which had previously been adjusted to pH = 6. Immediately after mixing, a white precipitate appeared. Then, the pH of the mixture was adjusted to pH = 5.36 by cautious addition of concentrated HCl (1M), at which point the precipitate disappeared. Then, the aqueous mixture was placed in a conical flask and left undisturbed for 10 days, after which time, a white crystalline precipitate appeared at the bottom of the flask. The resulting crystals were washed several times with deionized water and finally, filtered and dried at room temperature.

### S1.4. X-Ray Crystallography

Crystallographic data for **1-op** and **1-cp** were collected at 100 K in the XALOC beamline at the ALBA synchrotron ( $\lambda = 0.88557 \text{ \AA}$ ).<sup>2</sup> Due to crystal degradation during the dehydration process, different crystals of the **1-cp** phase were collected. The best data set enabled us to resolve the structure, but the crystal degradation led to poor crystal data and consequently, to high  $R_{\text{int}}$ . These data were indexed, integrated and scaled using the XDS program.<sup>3</sup> Absorption correction was not applied. The structures were solved by direct methods and subsequently, refined by correction of F<sub>2</sub> against all reflections using SHELXS2013 and SHELXL2013 within the WinGX package.<sup>4</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F<sup>2</sup> using SHELXL2013. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. The hydrogen of the crystal-lattice water molecules present in the structure were not located on the Fourier map, but were added into the empirical formula to enable accurate determination of the density. CCDC 1471149 (**1-op**) and CCDC 1471150 (**1-cp**).

### S1.5. Humidity-controlled PXRD measurements

Thermodiffractometric studies at different relative humidity values were collected on a D8 ADVANCE (Bruker AXS) diffractometer equipped with a Johansson Ge(111) primary monochromator, which gives a monochromatic Mo radiation ( $\lambda = 0.7093 \text{ \AA}$ ), and an Anton Paar MHC-trans chamber. The X-ray tube was operating at 50 kV and 50 mA. The energy-dispersive linear detector LYNXEYE XE 500  $\mu\text{m}$ , optimized for high-energy radiation, was used with the maximum opening angle. Data were collected at 25 °C and relative humidity (RH) values ranged between 5% and 95%. Samples were held at each relative humidity at least for 30 min, before recording any pattern, giving sufficient time for any transformation to occur. For the experiment carried out at 25 °C and at a constant relative humidity of 95%, powder X-ray diffraction patterns

were collected every 15 min. All patterns were measured between  $2^\circ$  and  $27^\circ$  ( $2\theta$ ) with a step size of  $0.017^\circ$  and counting time of 96 s/step. All PXRD patterns were converted from Mo-K alpha to Cu-K alpha.

**Table S1. Crystallographic Table**

<b>Compound reference</b>	<b>1-<i>op</i></b>	<b>1-<i>cp</i></b>
Chemical Formula	C <sub>20</sub> H <sub>51</sub> GdMn <sub>2</sub> N <sub>8</sub> O <sub>23</sub> P <sub>4</sub> ·21(H <sub>2</sub> O)	C <sub>20</sub> H <sub>51</sub> GdMn <sub>2</sub> N <sub>8</sub> O <sub>23</sub> P <sub>4</sub> ·5(H <sub>2</sub> O)
Formula Mass	1541.00	1252.76
Crystal System	Monoclinic	Monoclinic
Space group	P 21/c	C 2/c
a/ Å	12.300(4)	26.090(5)
b/ Å	19.750(4)	14.510(5)
c/ Å	24.630(4)	12.200(5)
α/ °	90	90
β/ °	95.30(4)	110.19(4)
γ/ °	90	90
Unit Cell Volume / Å <sup>3</sup>	5957.7(17)	4335(2)
Temperature/ K	100	100
Z	4	4
Reflections Measured	31272	24777
Independent Reflections	8782	4318
Reflections ( <i>I</i> > 2σ( <i>I</i> ))	8049	1874
R <sub>int</sub>	0.0876	0.4237
R <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.2453	0.1361
wR( <i>F</i> <sup>2</sup> ) ( <i>I</i> > 2σ( <i>I</i> ))	0.2481	0.2856
R <sub>1</sub> (all data)	0.0909	0.1812
wR( <i>F</i> <sup>2</sup> ) (all data)	0.2481	0.3219

**Table S2. Elemental analysis of 1-*op***

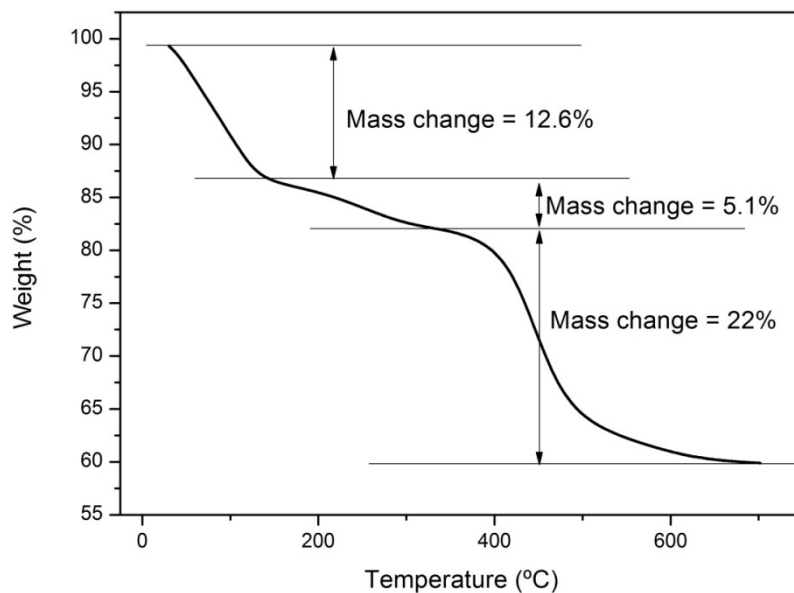
	<b>1-<i>op</i></b> (calc. wt.%) $C_{20}H_{51}GdMn_2N_8O_{23}P_4$ $\cdot 21(H_2O)$	<b>1-<i>op</i></b> (exp. wt.%)
<b>C</b>	15.6	16.0 ± 1.2
<b>N</b>	7.3	8.1 ± 1.1
<b>H</b>	6.1	5.4 ± 1.4

**Table S3. Elemental analysis of 1-*cp***

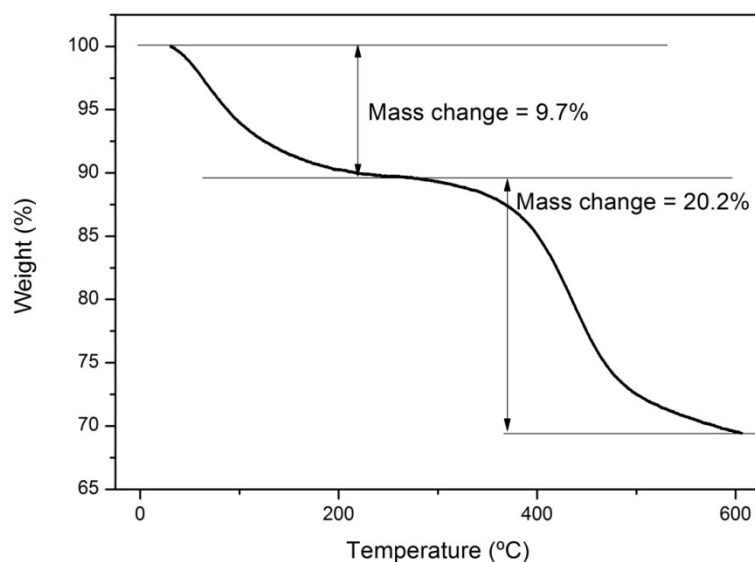
	<b>1-<i>cp</i></b> (calc. wt.%) $C_{20}H_{51}GdMn_2N_8O_{23}P_4$ $\cdot 5(H_2O)$	<b>1-<i>op</i></b> (exp. wt.%)
<b>C</b>	19.2	18.1 ± 1.2
<b>N</b>	8.9	8.3 ± 1.1
<b>H</b>	4.9	5.2 ± 1.4

### Figure S1. Thermogravimetric (TGA) analysis

(a) TGA analysis of **1-op** shows three weight-loss steps. The first step shows a weight loss of 12.6%, corresponding to the loss of 21 guest water molecules (calculated = 13.2%). The second step shows a weight loss of 5.1%, which is attributed to the loss of seven coordinated water molecules (calculated = 4.4%). Finally, the third step corresponds to the decomposition of the framework itself.

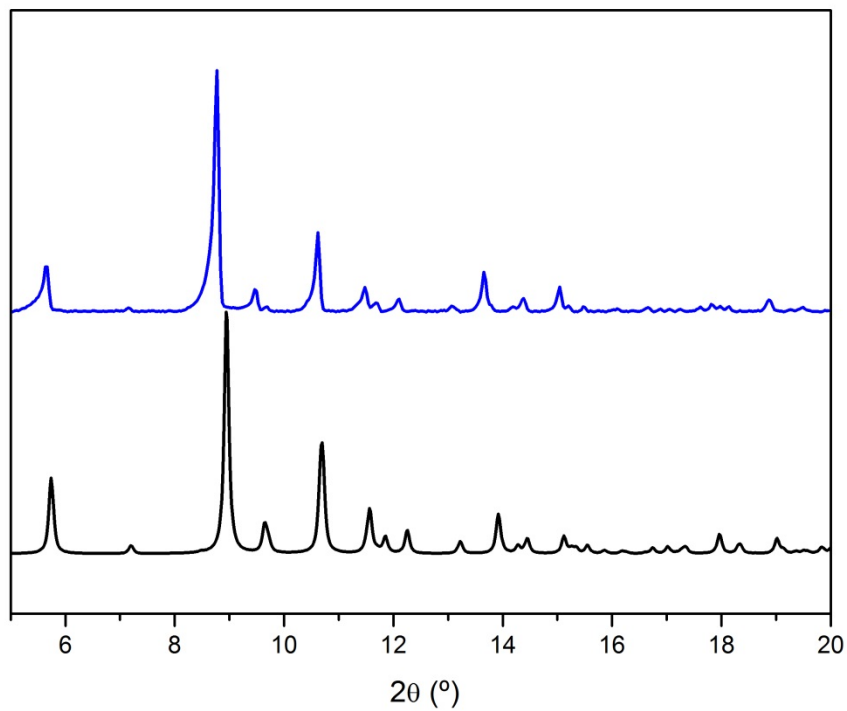


(b) TGA analysis of **1-cp** shows two weight loss steps. The first step shows a weight loss of 9.7%, corresponding to the loss of all 12 water molecules (calculated = 8.5%). The second step corresponds to the decomposition of the framework itself.

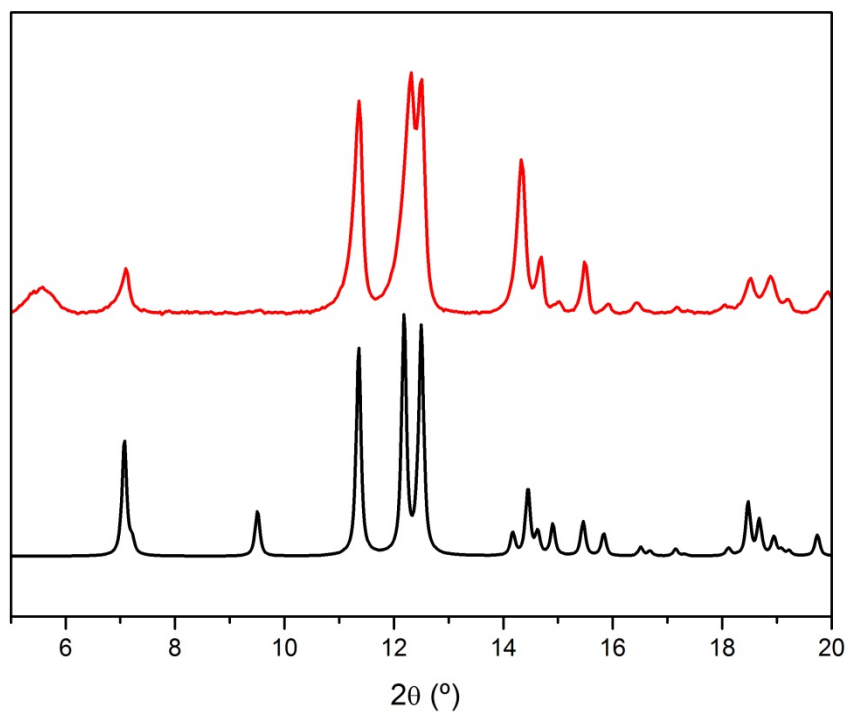


**Figure S2. Powder X-ray diffraction patterns**

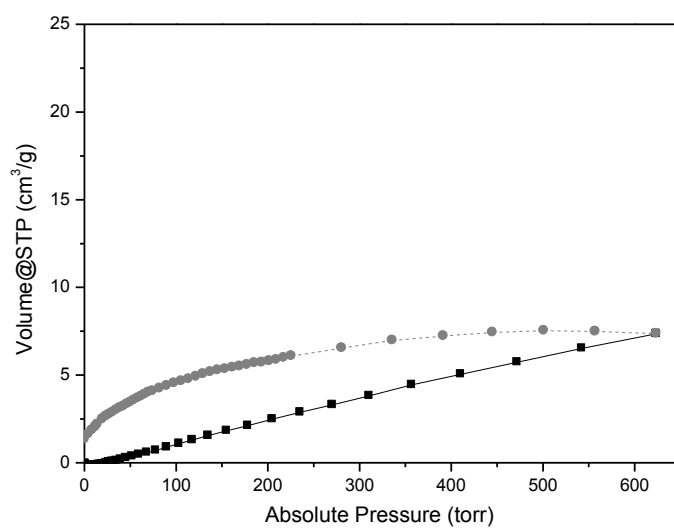
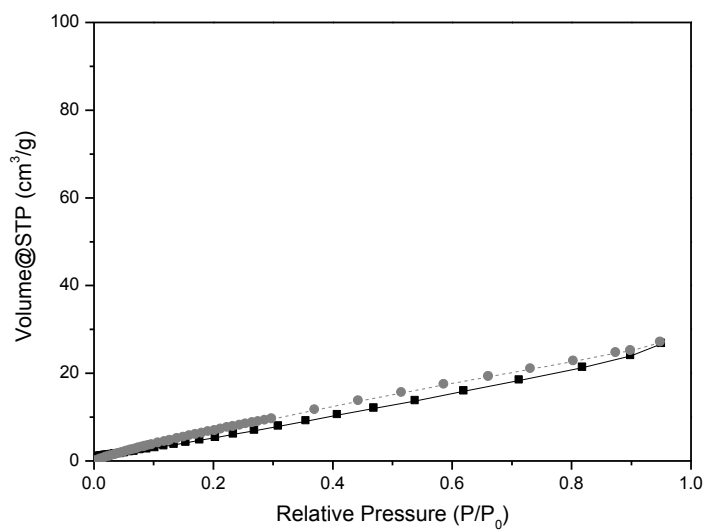
(a) Experimental pattern (blue) for **1-*op*** as compared to the simulated pattern (black)



(b) Experimental pattern (red) for **1-*cp*** as compared to the simulated pattern (black)



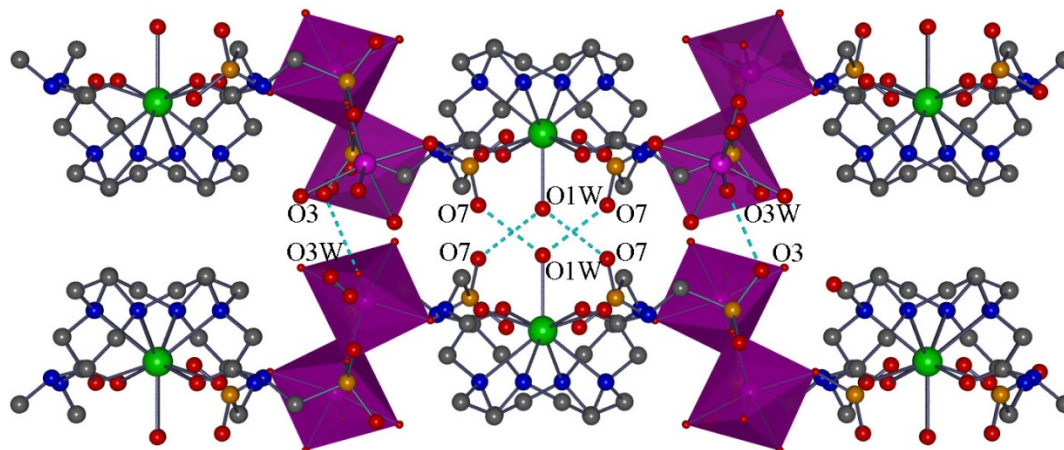
**Figure S3. N<sub>2</sub> (77 K, top) and CO<sub>2</sub> (194 K, bottom) adsorption-desorption isotherms for 1-*cp*.** The data were collected using an AutosorbIQ (Quantachrome Instruments). Prior to the measurement, samples were activated at 30°C under vacuum.



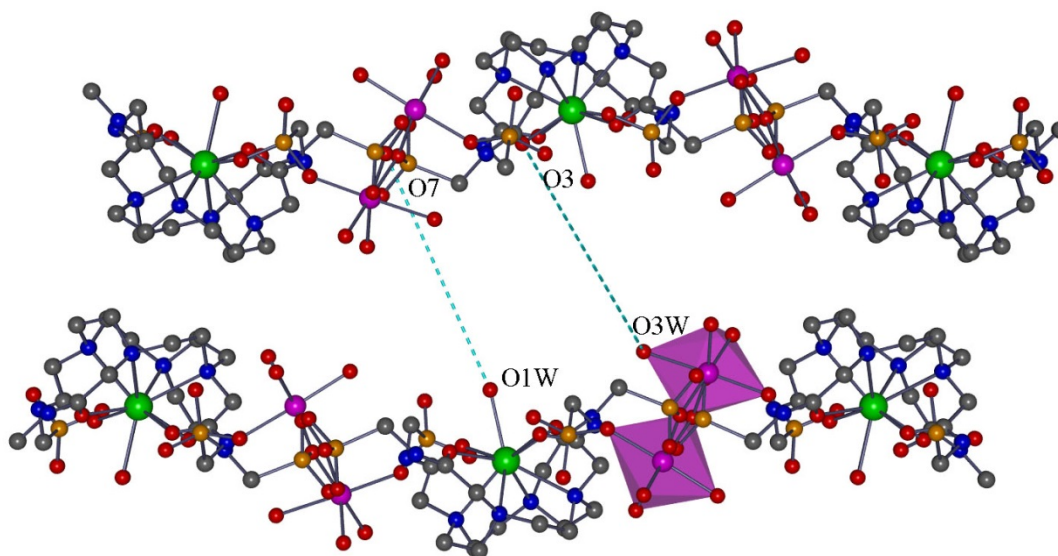


#### Figure S4. Hydrogen-bonding contacts

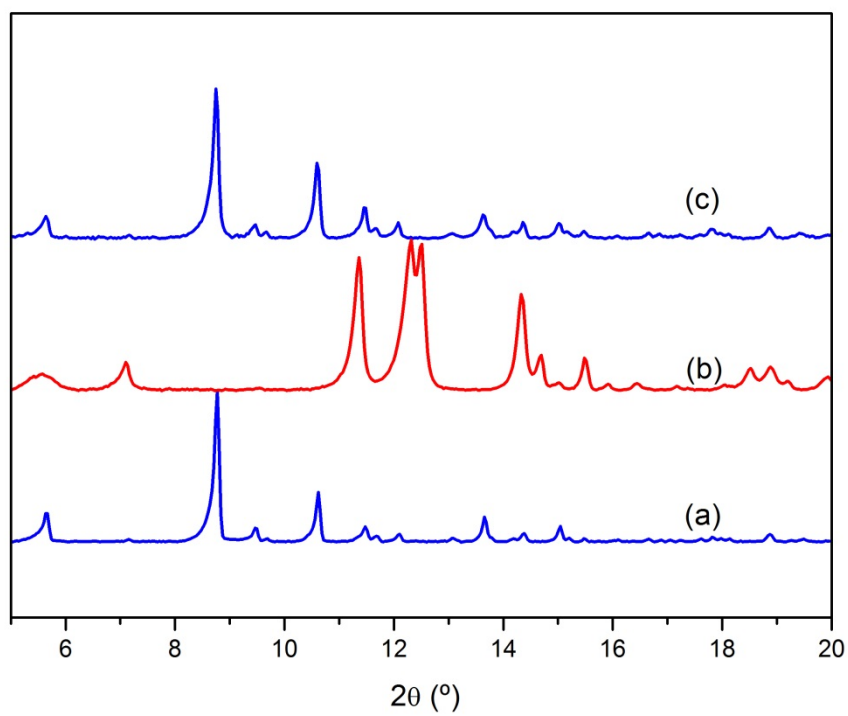
- a) In **1-*cp***, direct hydrogen bonds are established between the coordination layers: (O3W $\cdots$ O3, 2.83 Å) and (O1W $\cdots$ O7, 2.65 Å).



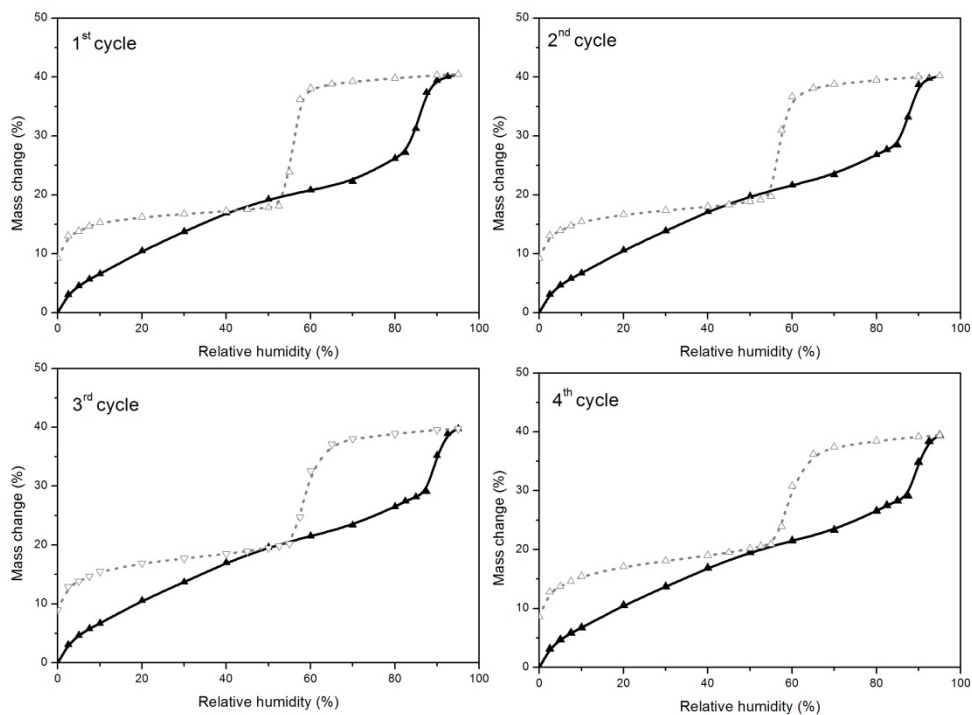
- b) In **1-*op***, direct hydrogen bonds are not established between layers. O3W-O3 and O1W-O7 are separated by distances of 15 Å and 8.6 Å, respectively.



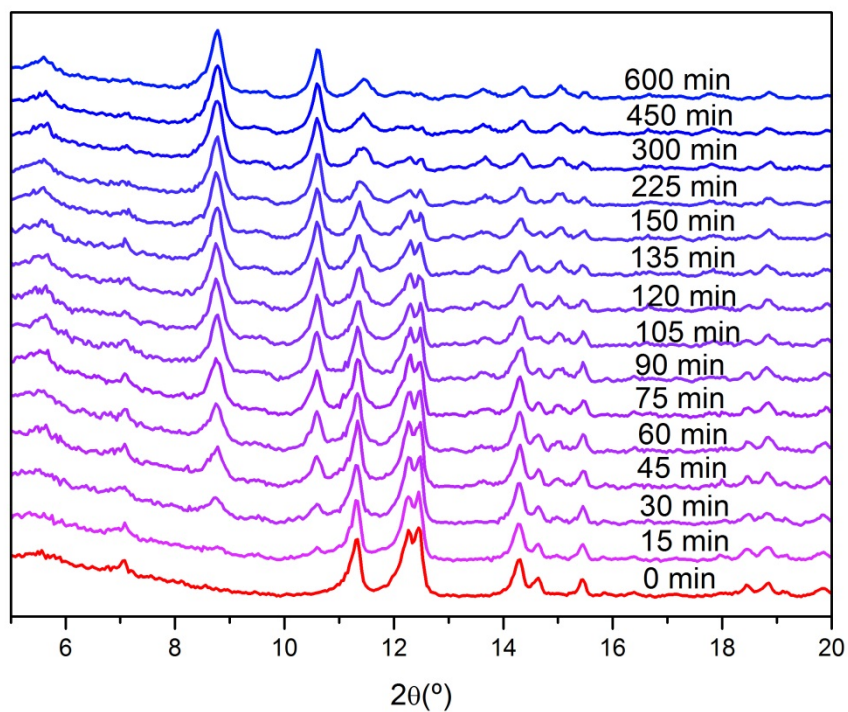
**Figure S5. PXRD measurements confirming the reversibility of the SC-SC  $1-op \leftrightarrow 1-cp$  transformation.** PXRD patterns for (a) synthesized  $1-op$ , (b)  $1-cp$  obtained by drying  $1-op$  at room temperature, and (c)  $1-op$  obtained by incubating  $1-cp$  in water overnight.



**Figure S6. Study on water-sorption recyclability.** Four consecutive cycles of water adsorption/desorption were performed to analyse the reversibility of the water sorption process. Before each cycle, the samples were activated by exposing the crystals to an environment at 110 °C for 2 hours.



**Figure S7. Kinetics study on the transition 1-*cp*→1-*op*.** In this study, 1-*cp* crystals were exposed to an environment at 25 °C and a constant RH of 95%. PXRD patterns were collected every 15 minutes.



## References

- 1 A. Barge, G. Cravotto, E. Gianolio and F. Fedeli, *Contrast Media Mol. Imaging*, **1**, 184–8.
- 2 J. Juanhuix, F. Gil-Ortiz, G. Cuní, C. Colldelram, J. Nicolás, J. Lidón, E. Boter, C. Ruget, S. Ferrer and J. Benach. *J. Synchr. Rad.*, 2014, **21**, 679–689
- 3 W. Kabsch, *J. Appl. Crystallogr.*, 1993, **26**, 795–800.
- 4 G. M. Sheldrick, *Acta Crystallogr. A.*, 2008, **64**, 112–22.