Supplementary Information

A Hydrogen-Bonded Organic Framework with Ultramicroporous Channels based on Proline and DL-2phenoxypropionic acid

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1. Materials

DL-proline (99 %, Roth) and 2-phenoxypropionic acid (98 %, Alfa Aesar) were used as received. Methanol (HiPerSolv CHROMANORM) and *n*-pentane (AnalaR NORMAPUR) were purchased from VWR and were used without any additional purification.

2. Synthesis of PPA-PRO cocrystal

2.1. Mechanochemical synthesis

The mechanochemical synthesis of PPA·PRO was performed by neat grinding, using a "Retsch Mixer Mill MM 400" equipped with two grinding jars containing five Eppendorf tubes of 2 mL each. Each tube was filled with an equimolar amount (0.1 mmol) of 2-phenoxypropionic acid and proline and two Ø 3 mm stainless-steel beads. Grinding was then performed at 30 Hz for 90 minutes.

2.2. Single crystal for X-ray diffraction

The single crystal suitable for structure determination was obtained by recrystallization of powders obtained by neat grinding in methanol.

2.3. Slurry-mediated transformation

Slurry-mediated samples were prepared according to the following procedure. In a 20 mL vial, 2-phenoxypropionic acid (0.170 g) and DL-proline (0.130 g) were suspended in an equimolar amount (0.1 mol) in 1.58 g of *n*-pentane. The vial was then sealed and the mixture stirred at 500 rpm at RT. After 12 h of stirring, the vial was seeded with traces of all possible solid forms (both parent compounds and cocrystal). After 48 hours, the equilibrium was assumed to be reached, and the powder was filtered, washed and dried.

3. X-ray diffraction from powder for phase identification

Phase identification on the two powder samples used for further analyses were performed both in-house (sample for N_2 and Xe sorption) and at the European Synchrotron Radiation Facility (Sample for variable temperature synchrotron powder diffraction, TGA, DSC and DVS). The experimental setups used for each diffraction measurement are detailed further (sections 7 and 10 for synchrotron and in-house measurements, respectively).

It can be noted that the sample used for variable temperature synchrotron powder diffraction, TGA, DSC and DVS contains a small amount of a crystalline impurity, which impact on the obtained data is detailed in the SI where appropriate. The sample used for nitrogen and xenon sorption is phase pure. The important difference in simulated and experimental relative intensities of the first diffraction peak is due to instrumental limitations (proximity of beamstop).







Fig. SI-2. Comparison of the experimental XRPD patterns measured on the laboratory diffractometer of the HOF obtained by slurry-induced cocrystallization with the calculated pattern (λ = 0.71073 Å).

4. Single crystal X-ray diffraction

Single crystal X-ray diffraction (SCXRD) data were collected on a MAR345 image plate detector using Mo K α radiation (λ = 0.71073 Å), generated by an Incoatec IµS microfocus source (Montel mirrors). Data integration and reduction were performed by CrysAlis^{PRO} and the implemented absorption correction was applied.¹ The structure solution was performed by dual-space direct methods in SHELXT and the structure was further refined against *F*² using SHELXL2018/3.² Non-hydrogen atoms were refined anisotropically; H_{CH} atoms were added in calculated positions; H_{OH} and H_{NH} atoms were either located from a Fourier map or added in calculated positions and refined in riding mode. Symmetry analysis and validation were carried out using PLATON.³ Figures were made using the molecular visualization software Mercury v4.3.⁴ CCDC 2387025 and 2393897 include the supplementary crystallographic data and can be downloaded free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Empirical formula	C14H19NO5	C ₁₄ H ₁₉ NO ₅	
Formula weight	281.30	281.30	
Temperature (K)	297(2)	150(2)	
Wavelength (Å)	0.71073	0.71073	
Crystal system	Trigonal	Trigonal	
Space group	<i>R</i> -3	<i>R</i> -3	
Unit cell dimensions (Å,°)	<i>a</i> = 62.932(2)	<i>a</i> = 62.5573(16)	
	<i>b</i> = 62.932(2)	<i>b</i> = 62.5573(16)	
	c = 5.69893(15)	c = 5.66980(14)	
	<i>α</i> = 90	$\alpha = 90$	
	$\beta = 90$	$\beta = 90$	
	<i>γ</i> = 120	<i>γ</i> = 120	
Volume (Å ³)	19546.7(14) 19215.6(11)		
Z	54	54	
Density (calculated) (g/cm ³)	1.290	1.313	
Absorption coefficient (mm ⁻¹)	0.098	0.100	
F(000)	8100	8100	
Crystal size (mm ³)	0.24 x 0.05 x 0.01	24 x 0.05 x 0.01 0.40 x 0.15 x 0.03	
Theta range for data collection (°)	2.822 to 25.235 2.256 to 26.830		
Reflections collected	26916	21261	
Independent reflections	7814 [R(int) = 0.0738]	9116 [R(int) = 0.0367]	
Completeness to θ = 25.235° (%)	99.5	99.8	
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.81974	1.00000 and 0.94415	
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	
Data / restraints / parameters	7814 / 48 / 543 9116 / 0 / 532		
Goodness-of-fit on F ²	1.097	1.036	
Final R indices [I>2s(I)]	$R_1 = 0.0795, wR_2 = 0.1496$	$R_1 = 0.0500, wR_2 = 0.1109$	
R indices (all data)	$R_1 = 0.1305, wR_2 = 0.1672$	$R_1 = 0.0818$, $wR_2 = 0.1180$	
Δρ (max,min)(e.Å ⁻³)	0.348, -0.260	0.371, -0.250	

Table SI-1. Crystal data and structure refinement for PPA.PRO at 297 K and 150	K.
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5. Thermogravimetric analysis

Thermogravimetric analysis was performed on a Mettler Toledo TGA/DSC³⁺ from 25 to 500 °C using a heating rate of 10 °C/min with a continuous air flow of 100 mL/min in an open alumina crucible.



Fig. SI-3. TGA trace of the HOF under air.

6. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was performed on a DSC2500 from TA Instruments. The sample was heated under nitrogen (50 mL.min⁻¹) at a rate of 10 °C.min⁻¹ from 25 °C to 140 °C in a sealed aluminum crucible.



Fig. SI-4. DSC thermogram of PPA·PRO.

The endothermic signal between 60 °C and 80 °C is correlated with the disappearance of the crystalline impurity and a weight loss of about 1.2 wt% (see TGA in section 5). Melting of the HOF occurs between 110 °C and 120 °C (complete amorphization above 120 °C, see variable temperature diffraction in section 7).

7. Variable temperature synchrotron powder X-ray diffraction

Variable temperature synchrotron X-ray powder diffraction data were collected at the Swiss-Norwegian beamlines (SNBL, BM01) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Samples were heated using a Cryostream, at a heating rate of 10 °C.min⁻¹ (λ = 0.755334 Å).



Fig. SI-5. Variable-temperature synchrotron XRPD patterns of the HOF.

8. Calculation of the theoretical water content in saturated pores

The theoretical water content that can be adsorbed into the channels of the HOF can be deduced from the pore size. There are 3 formula units in the asymmetric unit (Z' = 3) (so 3 times C₉H₁₀O₃, C₅H₉NO₂), and 54 in the unit cell (Z = 54).

There are 3 cavities (all equivalent) in the unit cell, with a total volume of 384-387 Å³.

Given that a water molecule is about 40 Å³, there is a potential of 9.6 water molecules in the unit cell, or otherwise said 9.6 water molecules for 54 formula units or only 0.18 water molecules per formula unit.

This corresponds to a molar weight of 284.5 g.mol⁻¹ for the water saturated HOF $(C_9H_{10}O_3 \cdot C_5H_9NO_2 \cdot 0.18H_2O)$, which is 101.15 % of the unsolvated HOF $(C_9H_{10}O_3 \cdot C_5H_9NO_2 M = 281.3 \text{ g.mol}^{-1})$. The theoretical weight of water adsorbed into the channels thus corresponds to 1.15 wt.%.

9. Nitrogen and carbon dioxide sorption isotherms

The nitrogen (77 K) and CO₂ (0 °C) sorption measurements were performed on an ASAP2020 system from Micromeritics. Prior to analysis, the sample was pre-treated under vacuum at 70 °C for 10 hours to evacuate the solvent from the pores.



Fig. SI-6A. Nitrogen adsorption isotherm of the PPA·PRO HOF at 77 K (S_{BET} = 9.3 m².g⁻¹).



Fig. SI-6B. Barrett-Joyner-Halenda (BJH) pore size distribution derived from N₂ sorption at 77 K.



Fig. SI-6C. Carbon dioxide sorption isotherm of the PPA-PRO HOF at 0 °C.

The calculated adsorbed quantity for full occupancy by CO_2 of the special 6*c* Wyckoff site (as for Xe) is 4.41 cm³/g STP. Although this amount is reached below atmospheric pressure, the isotherm remains linear without asymptotic behavior, unlike typical ultramicroporous materials where adsorption saturates as micropores fill. The crystallographic data reveals a dense structure with small, well-separated channels and low pore volume, suggesting the possibility of significant adsorption on the external surface relative to the internal pores. The contribution of the latter might therefore be difficult to observe.

10. In situ powder X-ray diffraction with xenon

The X-ray diffraction data for gas sorption experiments were collected on a MAR345 image plate detector using Mo K α radiation ($\lambda = 0.71073$ Å), generated by an Incoatec IµS source (parallel beam). The powder sample was loaded in a glass capillary (diameter 0.5 mm, Hilgenberg GmbH) which was connected to a gas control system. Vacuum was first applied and the sample was heated to 80 °C in the capillary for 1 hour to evacuate any solvents from the pores. Subsequently, xenon adsorption and desorption isotherms were measured up to 14 bar at room temperature. For each pressure step, several diffraction powder patterns were measured until equilibrium was reached (i.e. no more observable changes in intensities). The diffraction data were integrated using the Fit2D software, using data from a NIST LaB₆ sample for calibration. The position and occupancies of xenon atoms were determined using the FOX software, using data of the highest Xe loadings (highest pressure point). Sequential refinement was then applied using the Fullprof Suite, and the determined occupancies were plotted against pressure. Data corrections for refinement aberrations were done by setting the occupancy under vacuum at 0 (the value of the refined occupancy at 0 bar was subtracted from all datapoints). The plotted data were fitted using the Langmuir equation using Origin. The dataset represented in the main manuscript (Figure 4) is a total fit (adsorption + desorption points). The individual fittings for sorption and desorption datasets are given below, with the Langmuir fitting parameters and error, for comparison. Both individual and total fittings are in good agreement.



Fig. SI-7. Data points for Xe adsorption and desorption with adsorption, desorption and total Langmuir fittings.

Table SI-2. Fitting parameters for the xenon sorption isotherms.

Equation for fitting	Adsorption fit	Desorption fit	Total fit
$y = \frac{abx}{1 + bx}$	$a = 0.38508 \pm 0.00472$	$a = 0.37562 \pm 0.0047$	$a = 0.38098 \pm 0.00449$
	$b = 0.85604 \pm 0.06214$	$b = 1.19194 \pm 0.07805$	$b = 0.97711 \pm 0.0672$
	$R^2 = 0.99506$	$R^2 = 0.99639$	$R^2 = 0.99005$



Fig. SI-8. XRPD patterns of the HOF under vacuum at 70 °C and under 1.8 bar of xenon at room temperature. Differences in relative intensities, especially for the 3 first peaks, evidences filling of the pores with Xe.



Fig. SI-9. Rietveld refinement of the XRPD pattern of the HOF under vacuum at 70 °C.



Fig. SI-10. Rietveld refinement of the XRPD pattern of the HOF under 1.8 bar of Xe at room temperature.

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