

Supporting Information

Hydrogen Storage in Polymer-Based Processable Microporous Composites

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1. N₂ adsorption at 77 K

All samples were activated overnight at 150 °C under vacuum prior to N₂ adsorption experiments. Owing to the slow mass transfer of N₂ through the pores of the composites at 77 K, a limited number of points were recorded and used to determine their BET surface areas.

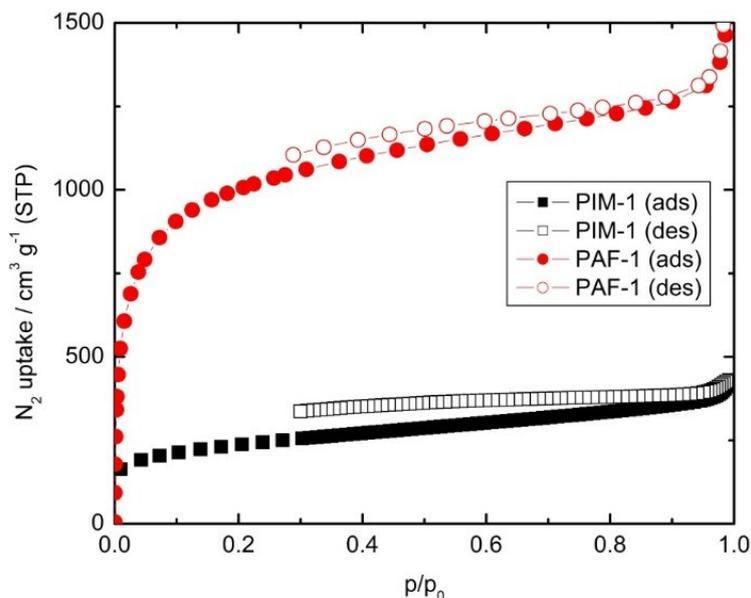


Figure S1. N₂ isotherms (77 K) of PIM-1 (black) and PAF-1 (red) starting materials used to prepare the composites studied in this work. Filled and open symbols represent adsorption (ads) and desorption (des) branches, respectively.

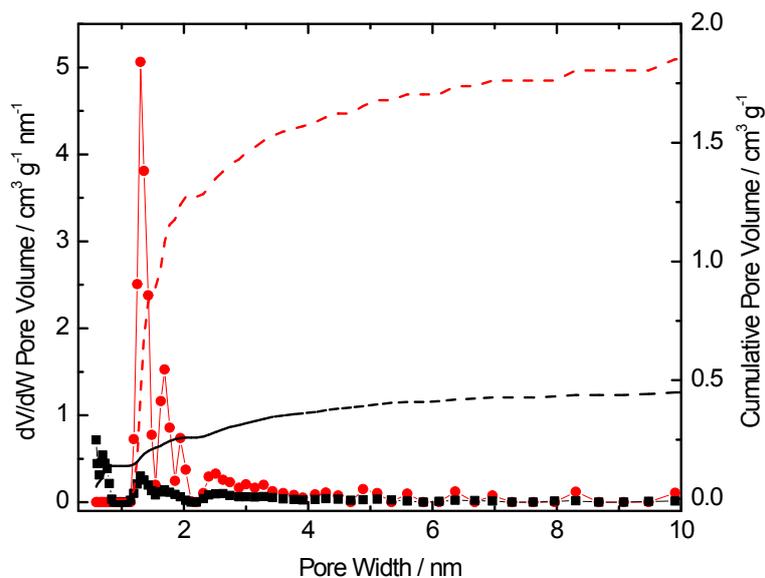


Figure S2. Pore size distributions of PIM-1 (black) and PAF-1 (red) starting materials used to prepare the composites studied in this work. Dashed lines represent the cumulative pore volumes. Data obtained by NLDFT analysis (slit-shaped pore model on carbon at 77 K) of nitrogen adsorption isotherms measured at 77 K.

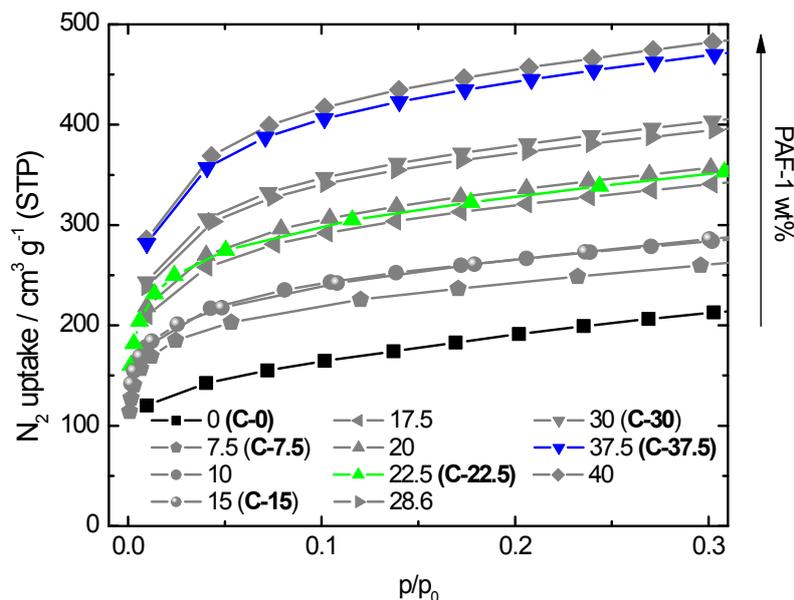


Figure S3. Partial N_2 isotherms at 77 K of the PIM-1/PAF-1 composite films studied in this article. The captions refer to the wt% of PAF-1 in each composite, and are coded as in the main text.

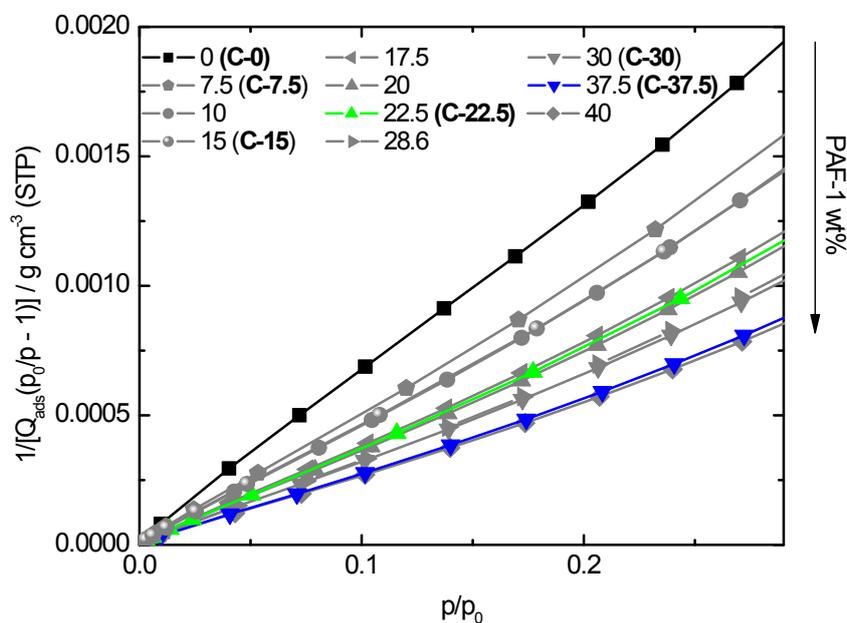


Figure S4. BET transform applied to the isotherms shown in Figure S3. Applying the guidelines of Rouquerol *et al.*,¹ the data points measured in the range $0.04 < p/p_0 < 0.17$ were used for calculation of the BET surface areas that are reported in Table 1 (with the exception of the film made of PIM-1 only (C-0, black), where the determined range was $0.04 < p/p_0 < 0.23$).

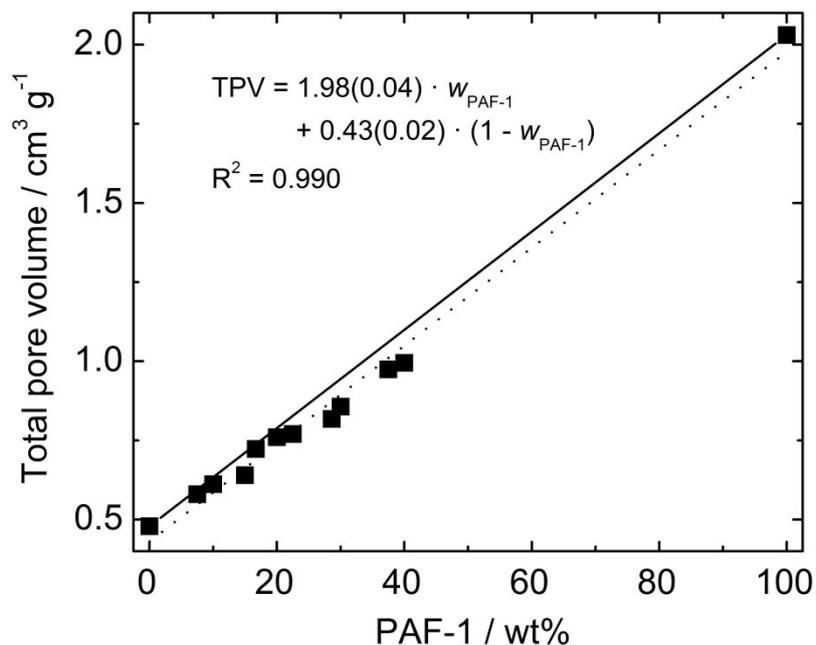


Figure S5. Total pore volume of PIM-1/PAF-1 composite films as a function of the weight percentage of PAF-1. Solid and dotted lines represent theoretical and experimental “rule of mixtures”, respectively, and the fitting equation is given with standard errors.

2. CO₂ adsorption at 273 K

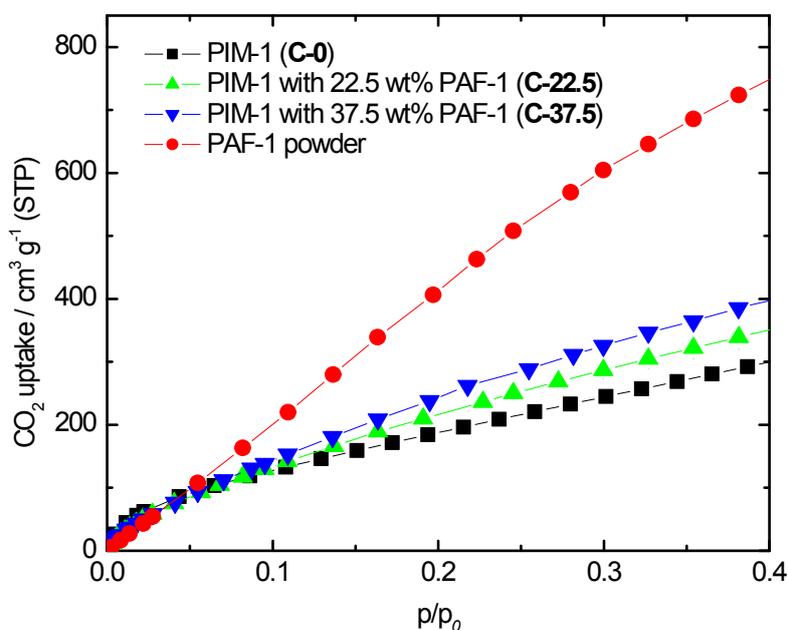


Figure S6. CO₂ isotherms measured at 273 K for a series of PIM-1 based films, and pure PAF-1 powder.

3. Thermogravimetric Analyses

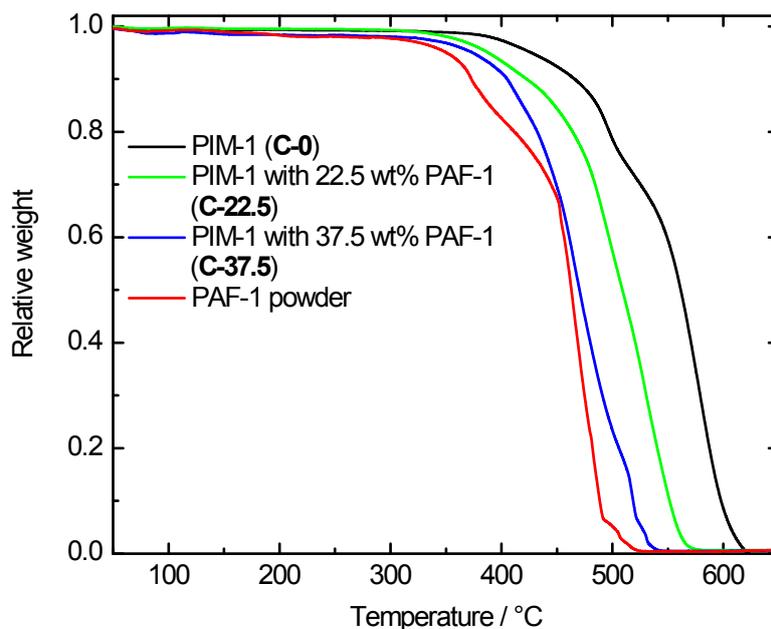


Figure S7. Thermogravimetric analyses of composite films made of PIM-1 and PAF-1, along with that of pure PAF-1 powder, measured in air (10 K min^{-1}).

4. Additional mechanical analysis data

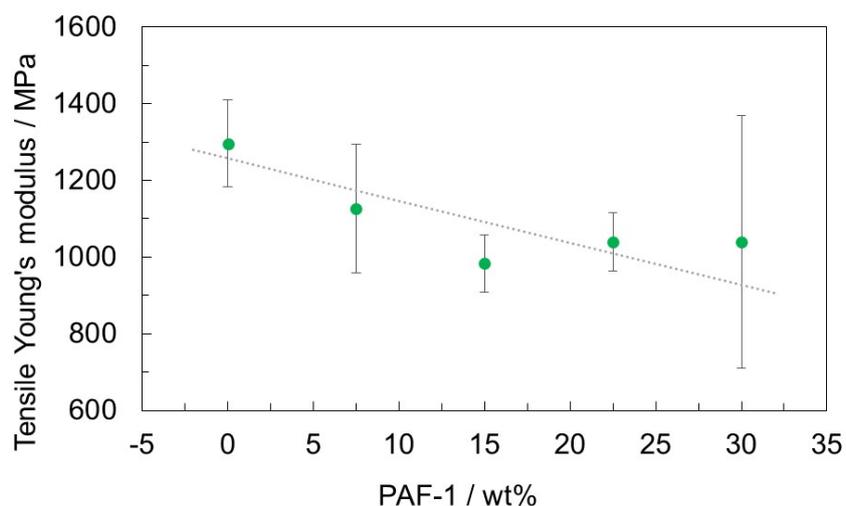


Figure S8. Dependency of tensile Young's modulus on the weight content of PAF-1 filler in PIM-1 matrix obtained with tensile testing experiments. The weighted trendline is adjusted to the number of replicate samples.

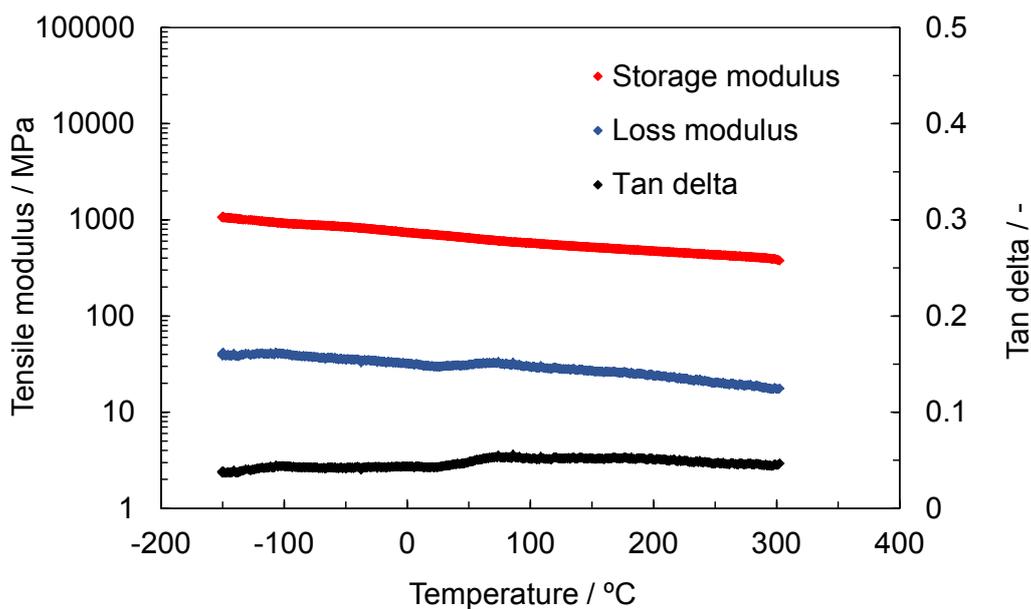


Figure S9. Example plot of the evolution of storage modulus, loss modulus and $\tan(\delta)$ with increasing temperature obtained from dynamic mechanical thermal analysis performed under tension (sample C-15).

5. Low-pressure hydrogen uptake

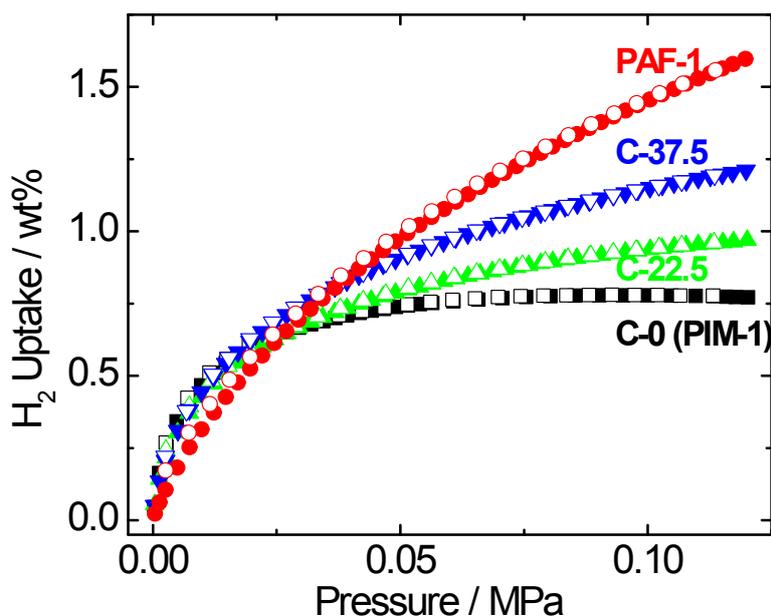


Figure S10: Low-pressure hydrogen isotherms (0 – 0.12 MPa) at 77 K of PIM-1 (C-0, black), composites C-22.5 (green) and C-37.5 (blue), and PAF-1 (red). Filled and empty symbols represent adsorption and desorption branches, respectively

6. Additional characterization data on investigated composites

Table S1. Complete list of materials investigated in this study. Italicized entries correspond to materials that have been selected for detailed surface and high-pressure hydrogen uptake analyses, whereas greyed entries indicate materials subjected to mechanical testing.

Sample	PAF-1 [wt%]	BET SA [m ² g ⁻¹] ^a	BET SA [m ² g ⁻¹] ^b	TPV [cm ³ g ⁻¹] ^c	Void fraction ϕ [%] ^c	Micro-porous vol. [cm ³ g ⁻¹] ^d	Micro-porous SA [m ² g ⁻¹] ^d	Skeletal density [g cm ⁻³] ^e	Bulk density [g cm ⁻³]	H ₂ uptake (0.1 MPa, 77 K) [wt%]	H ₂ uptake (10 MPa, 77 K) ^f [wt%]	H ₂ uptake (10 MPa, 77 K) ^f [g L ⁻¹]
C-0	0	681	1028	0.48	37	0.53	1184	1.24	0.78	0.78	2.60	20.2
C-7.5	7.5	873		0.58						0.80		
C-10	10	969		0.61						0.86		
C-15	15	955		0.64						0.92		
C-16.7	16.7	1171		0.72						0.98		
C-20	20	1229	1239	0.76	49	0.593	1213	1.28	0.65	0.92		
C-22.5	22.5	1197	1338	0.77	48	0.614	1245	1.20	0.62	1.02	4.08 (4.08)	25.5 (22.7)
C-28.6	28.6	1373		0.82						1.00		
C-30	30	1399		0.86						0.96		
C-37.5	37.5	1639	1603	0.97	55	0.711	1339	1.25	0.56	1.15	4.79 (5.07)	27.0 (24.4)
PAF-1	100	3787	4876	2.03	72	1.34	2063	1.25	0.35	1.43	9.18	31.5

^a) Determined from N₂ adsorption isotherms at 77 K; ^b) Determined from CO₂ adsorption isotherms at 273 K; ^c) Total pore volume at $p/p_0 \approx 0.97$ on N₂ isotherms at 77 K; ^d) Calculated from total pore volumes and skeletal densities; ^e) Microporous volume and surface area (SA) determined by NLDFIT analysis of CO₂ isotherms at 273 K; ^f) Determined by helium pycnometry; ^g) Total uptakes; values in brackets are expected results based on rule-of-mixtures calculations.

7. High-pressure hydrogen uptakes at 77 K modelling results.

Table S2. Isotherm model parameters obtained from fitting the excess H₂ uptakes of compounds **C-0** (PIM-1), **C-22.5**, **C-37.5** and **PAF-1** at 77 K, and calculated theoretical maximum uptakes.

Sample	ρ_A [g cm ⁻³]	b [MPa ⁻¹]	c [-]	V_p [cm ³ g ⁻¹] ^b	Max uptake [wt%] ^c
C-0 (PIM-1)	0.068 (0.001) ^a	2546 (1522)	0.22 (0.01)	0.48	3.3 (0.3) ^d
C-22.5	0.0848 (0.0004)	397 (32)	0.197 (0.002)	0.77	6.5 (0.7)
C-37.5	0.069 (0.001)	381 (161)	0.213 (0.009)	0.97	6.7 (0.7)
PAF-1	0.0486 (0.0002)	2.7 (0.1)	0.60 (0.01)	2.03	9.9 (1.0)

^a) Uncertainties are standard errors; ^b) experimental values at $p/p_0 \approx 0.97$ on N₂ isotherms at 77 K; ^c) Maximum theoretical uptake = $100 \cdot \rho_A \cdot V_p$; ^d) Error calculated assuming 10 % uncertainties on V_p values.

8. High-pressure H₂ loading/unloading cycles at 77 K

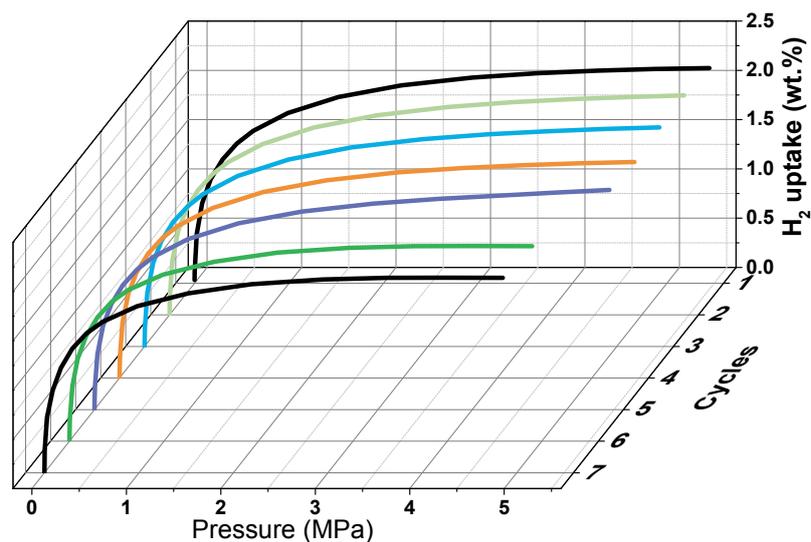


Figure S11. Consecutive excess H₂ uptakes of composite C-37.5 at 77 K. The sample was degassed at 120 °C for 8 h prior to each adsorption experiment. Seven adsorption isotherms were performed consecutively without any detectable loss of capacity or degradation.

9. Detailed H₂ uptake analysis of composites

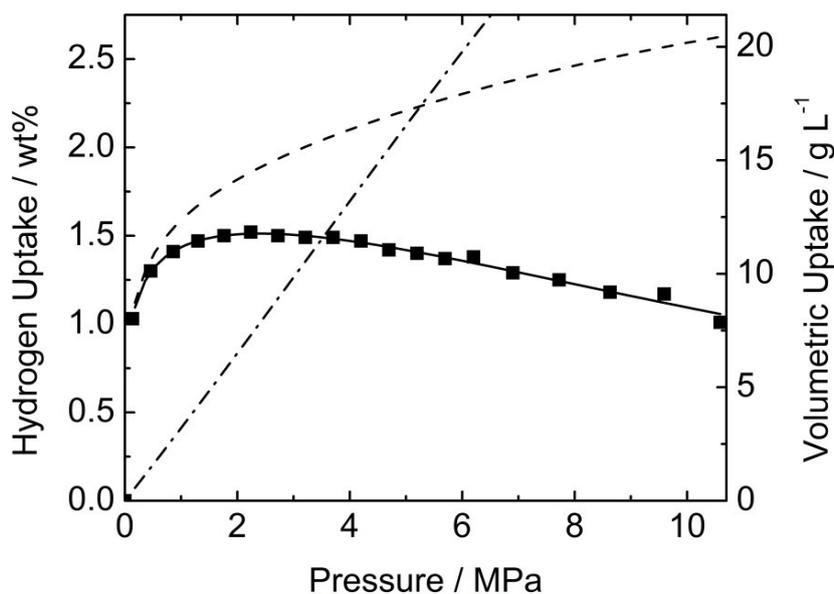


Figure S12: Hydrogen uptake of PIM-1 (C-0) and comparison with volumetric density of H₂ at 77 K. The black squares represent the experimentally measured excess adsorption isotherm, the solid line is the fitting isotherm, the dashed line represents the calculated total uptake, and the dash-dotted line represents the volumetric density of compressed hydrogen at 77 K, referring to the right y-axis.

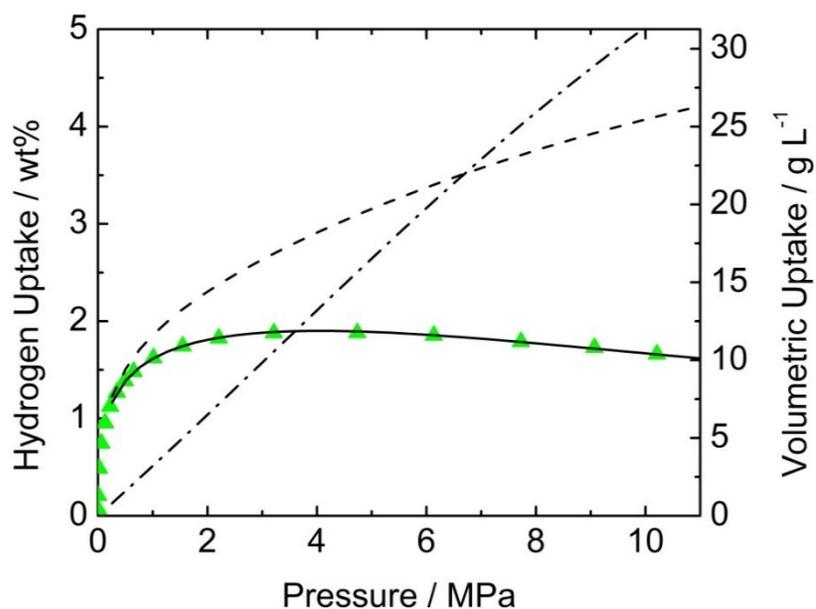


Figure S13: Hydrogen uptake of composite **C-22.5** and comparison with volumetric density of H₂ at 77 K. The green triangles represent the experimentally measured excess adsorption isotherm, the solid line is the fitting isotherm, the dashed line represents the calculated total uptake, and the dash-dotted line represents the volumetric density of compressed hydrogen at 77 K, referring to the right y-axis.

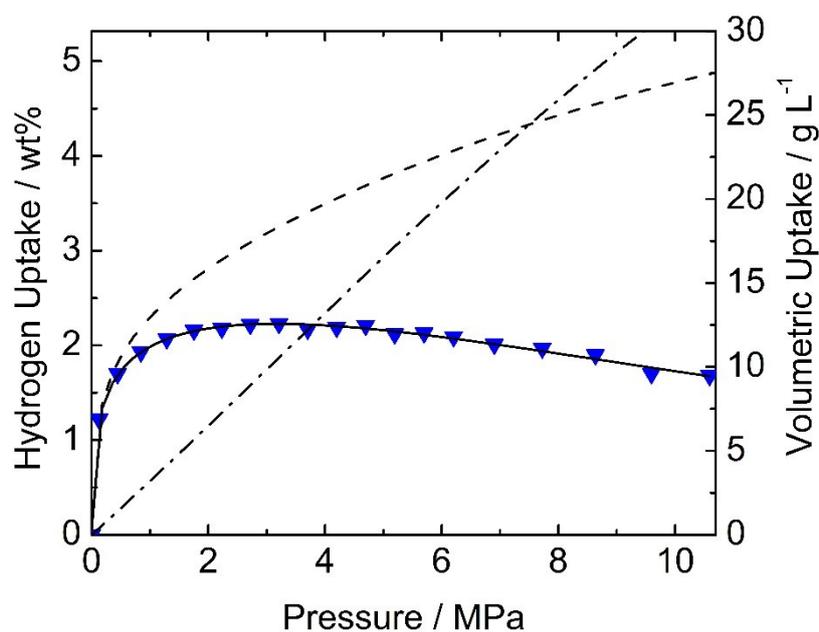


Figure S14: Hydrogen uptake of composite **C-37.5** and comparison with volumetric density of H₂ at 77 K. The blue triangles represent the experimentally measured excess adsorption isotherm, the solid line is the fitting isotherm, the dashed line represents the calculated total uptake, and the dash-dotted line represents the volumetric density of compressed hydrogen at 77 K, referring to the right y-axis.

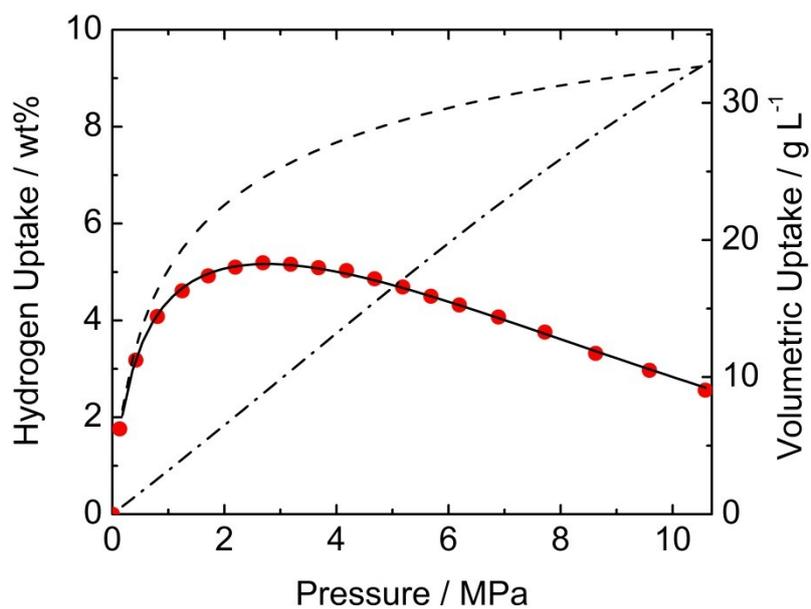


Figure S15: Hydrogen uptake of PAF-1 and comparison with volumetric density of H₂ at 77 K. The red circles represent the experimentally measured excess adsorption isotherm, the solid line is the fitting isotherm, the dashed line represents the calculated total uptake, and the dash-dotted line represents the volumetric density of compressed hydrogen at 77 K, referring to the right y-axis.

10. Usable hydrogen storage capacities

Table S3. Total and usable hydrogen storage capacities of compounds **C-0** (PIM-1), **C-22.5**, **C-37.5** and **PAF-1** at 77 K, calculated from the model based on the Tóth equation.

Sample	Uptake at 0.2 MPa ^a [wt%]	Uptake at 5.0 MPa ^b [wt%]	Usable capacity [wt%] ^c	% of total ^d	Uptake at maximum useful pressure [wt%] ^e	Usable capacity ^f [wt%]	% of total
C-0 (PIM-1)	1.15	2.21	1.06	48	2.23	1.08	48
C-22.5	1.14	3.16	2.02	64	3.47	2.33	67
C-37.5	1.44	3.77	2.33	62	4.33	2.89	67
PAF-1	2.31	8.07	5.76	71	9.24	6.93	75

^a) The minimum required back pressure is assumed to be 0.2 MPa; ^b) Hypothesis of a storage tank working at a 5 MPa maximum pressure; ^c) Difference of uptakes at 5.0 and 0.2 MPa; ^d) Usable capacity as % of the total uptake at 5 MPa; ^e) Maximum useful pressure defined as the pressure at which the total volumetric capacity equals the volumetric capacity of compressed hydrogen (intersects of dashed and dash-dotted lines on Figures S12 – S15): the values are 5.25 MPa (**C-0**), 6.45 MPa (**C-22.5**), 7.5 MPa (**C-37.5**) and 10.5 MPa (**PAF-1**); ^f) Useful capacities between 0.2 MPa and the maximum useful pressures.

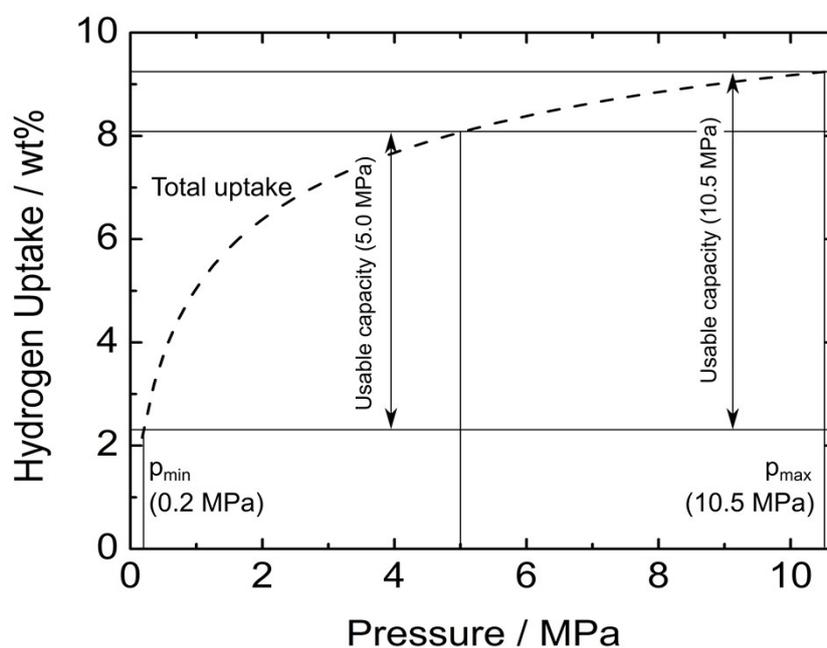


Figure S16: Determination of usable capacities using the case of PAF-1 at 77 K as an example. A minimum back pressure of 0.2 MPa is requested (p_{\min}), and usable capacities at 5.0 MPa and 10.5 MPa (the maximum useful pressure, p_{\max}) are illustrated.

11. Derivation of the rule of mixtures for the surface area of PIM-1/PAF-1 composites

Considering a composite **C** made of the matrix **PIM-1** and the filler **PAF-1**, Equation 6 of the main text can be derived as follows:

$$\begin{aligned}\text{Surface Area(C)} \left[\text{m}^2 \text{g}^{-1} \right] &= \frac{\text{Area(C)}}{\text{Mass(C)}} = \frac{\text{Area(PIM - 1)} + \text{Area(PAF - 1)}}{\text{Mass(C)}} \\ &= \frac{\text{Area(PIM - 1)}}{\text{Mass(C)}} + \frac{\text{Area(PAF - 1)}}{\text{Mass(C)}} \\ &= \frac{\text{Surface Area(PIM - 1)} \cdot \text{Mass(PIM - 1)}}{\text{Mass(C)}} + \frac{\text{Surface Area(PAF - 1)} \cdot \text{Mass(PAF - 1)}}{\text{Mass(C)}} \\ &= \text{Surface Area(PIM - 1)} \cdot w_{\text{PIM-1}} + \text{Surface Area(PAF - 1)} \cdot w_{\text{PAF-1}}\end{aligned}$$

Where $w_{\text{PIM-1}}$ and $w_{\text{PAF-1}}$ are the weight fractions of PIM-1 and PAF-1, respectively (e.g., $w_{\text{PIM-1}} = \text{Mass(PIM-1)}/\text{Mass(C)}$), and $w_{\text{PIM-1}} + w_{\text{PAF-1}} = 1$.