

## Support Information

# MOF-Derived Hierarchical Nanoporous Carbons for Hydrogen Isotope Adsorption and Separation

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## Calculations of $Q_{st}$ and IAST

The isosteric enthalpy of adsorption is calculated from single-component gas equilibrium adsorption isotherms at different temperatures according to the Virial Method:

$$\ln(P) = \ln(N) + \left(\frac{1}{T}\right) \sum_{i=0}^m a_i \times N^i + \sum_{j=0}^n b_j \times N^j$$

where,  $P$  is the pressure in mmHg,  $N$  is the amount adsorbed in  $\text{mg}\cdot\text{g}^{-1}$ ,  $T$  is the temperature in K,  $a_i$  and  $b_j$  represents virial coefficients, and  $m$  and  $n$  specify the number of coefficients needed for a precise description of the isotherms. The values of the virial coefficients  $a_0$  to  $a_m$  were further used to determine the isosteric enthalpy of adsorption according to the following equation:

$$Q_{st} = -R \times \sum_{i=0}^m a_i \times N^i$$

where  $Q_{st}$  is the coverage-dependent isosteric enthalpy of adsorption in  $\text{kJ}\cdot\text{mol}^{-1}$  and  $R$  is universal gas constant with the value of  $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

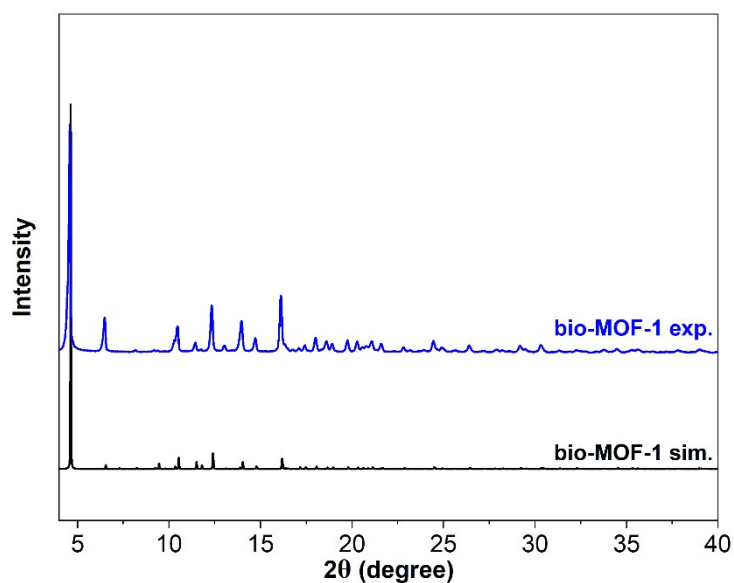
The complete breakthrough of  $\text{D}_2$  was determined using downstream gas composition reaching that of feed gas. Based on the mass balance, the gas adsorption capacities can be attained from the following equation:

$$q_i = \frac{C_i V}{22.4} \times \int_0^t \left(1 - \frac{F}{F_0}\right) dt$$

Where  $q_i$  refers to the equilibrium adsorption capacity of gas  $i$  ( $\text{mmol}\cdot\text{g}^{-1}$ ),  $C_i$  represents the feed gas concentration,  $V$  refers to the volumetric feed flow rate ( $\text{cm}^3\cdot\text{min}^{-1}$ ),  $t$  represents the adsorption time (min),  $F_0$  and  $F$ , respectively, refer to the inlet and outlet gas molar flow rates, and  $m$  represents adsorbent mass of (g). The separation factor ( $\alpha$ ) of breakthrough experiment can be calculated as follows:

$$\alpha = \frac{q_A y_B}{q_B y_A}$$

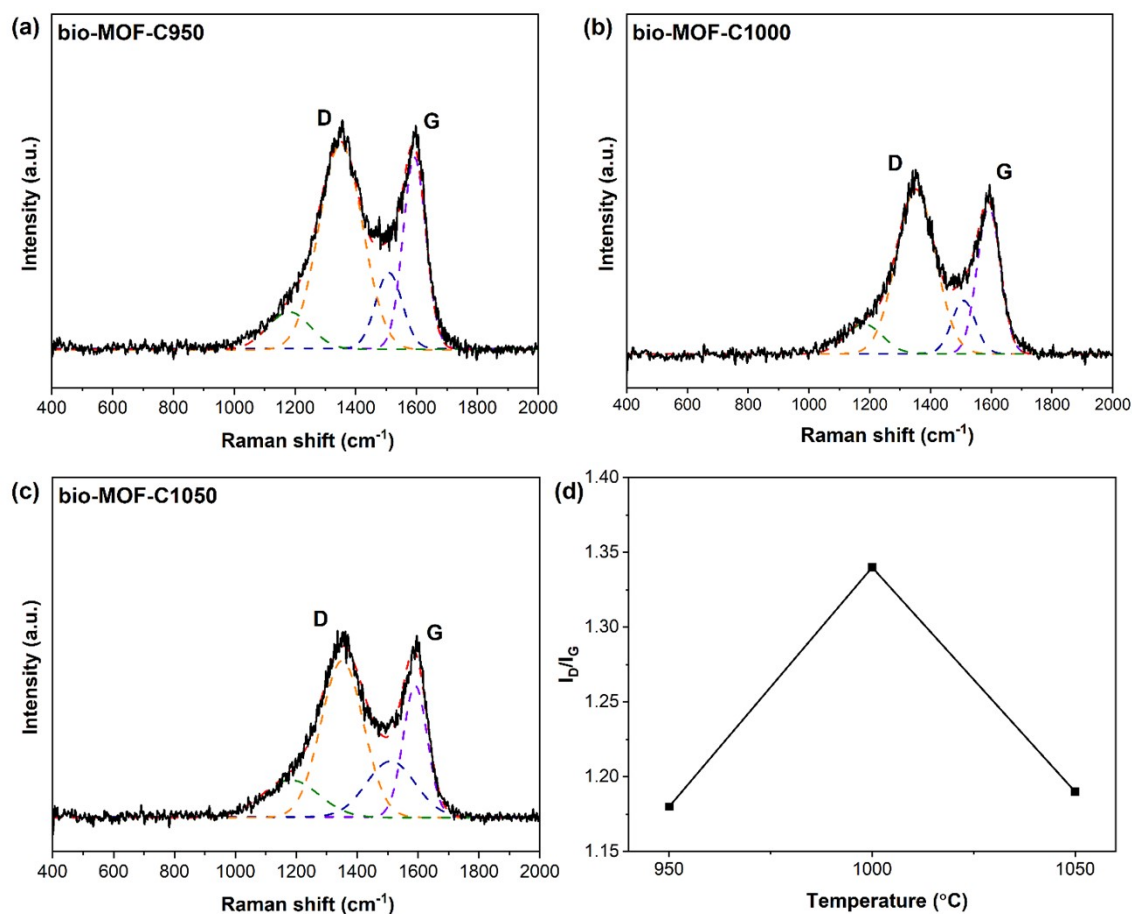
In which  $y_i$  is molar fraction of gas  $i$  ( $i = A, B$ ) in gas mixture.



**Figure S1** Simulated and observed PXRD patterns of bio-MOF-1.

**Table S1** The Zn content of bio-MOF-C.

samples	Zn
<b>bio-MOF-C950</b>	2.74 wt%
<b>bio-MOF-C1000</b>	0.76 wt%
<b>bio-MOF-C1050</b>	0.17 wt%



**Figure S2** Raman curves of bio-MOF-C.

**Table S2** Elemental composition of bio-MOF-1 and all the carbon samples.

	C	N	H
<b>bio-MOF-1</b>	45.03%	11.72%	4.75%
<b>bio-MOF-C950</b>	73.995%	4.53%	2.31%
<b>bio-MOF-C1000</b>	76.34%	2.68%	2.35%
<b>bio-MOF-C1050</b>	74.73%	1.91%	2.26%

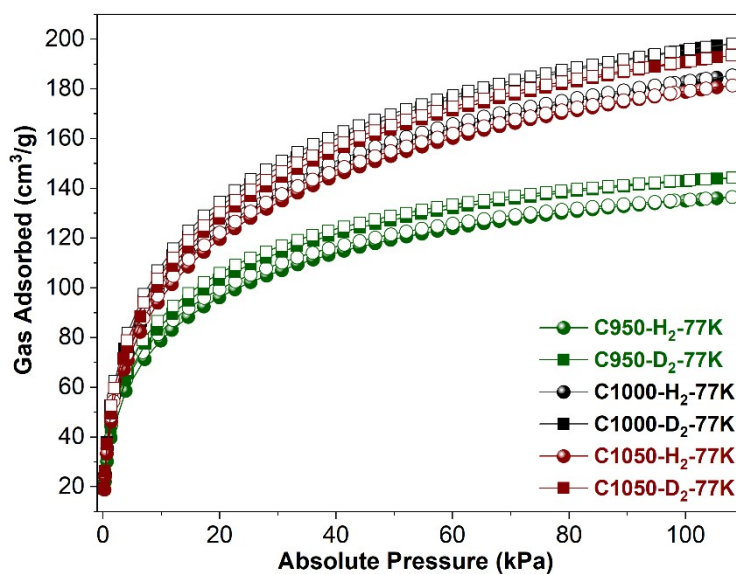
**Table S3** BET surface areas and pore volumes for all the carbon samples.

samples	$S_{\text{BET}}^{\text{a}}$ (m <sup>2</sup> /g)	$V_{\text{t}}^{\text{b}}$ (cm <sup>3</sup> /g)	$V_{\text{m}}^{\text{c}}$ (cm <sup>3</sup> /g)
<b>bio-MOF-C950</b>	729	0.59	0.20
<b>bio-MOF-C1000</b>	1085	0.83	0.32
<b>bio-MOF-C1050</b>	1064	0.82	0.31

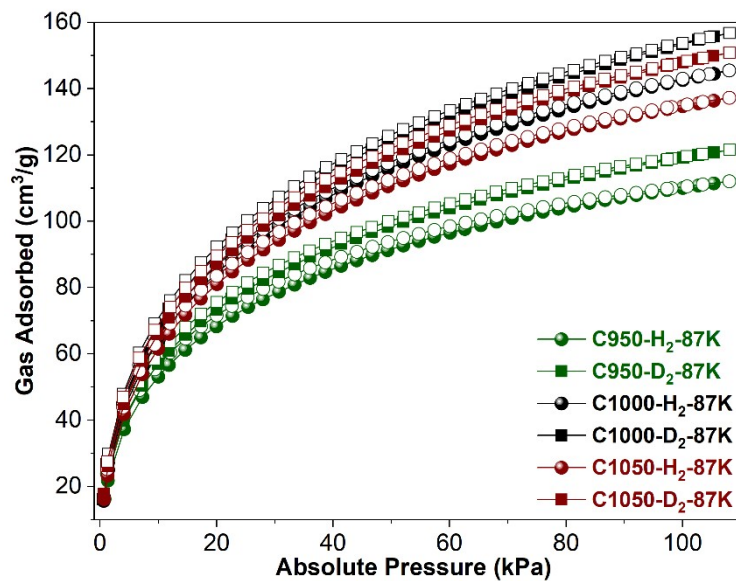
(a) The specific surface area ( $S_{\text{BET}}$ ) was calculated by the Brunauer-Emmet-Teller (BET) method.

(b)  $V_{\text{t}}$  represented the total pore volume.

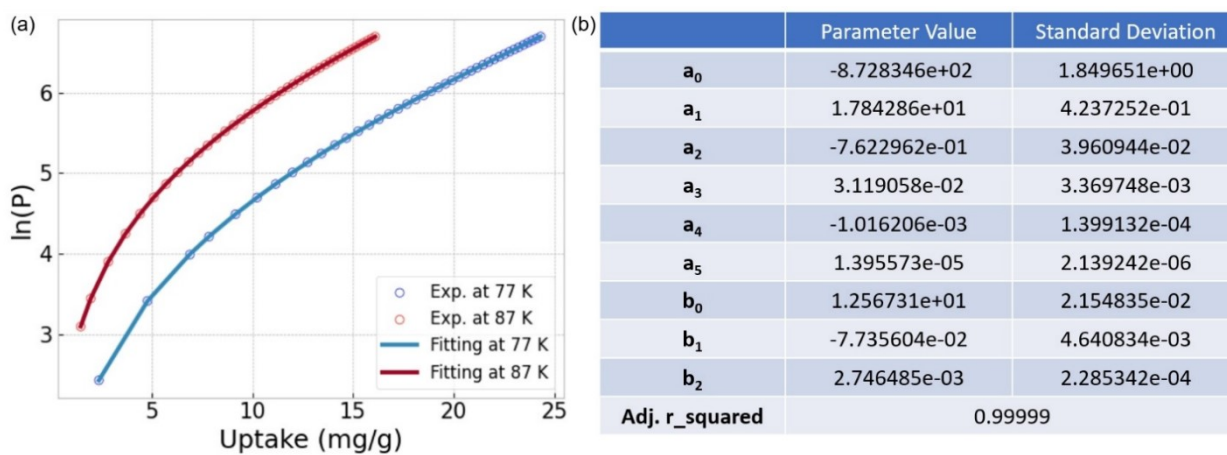
(c)  $V_{\text{m}}$  represented the micropore volume.



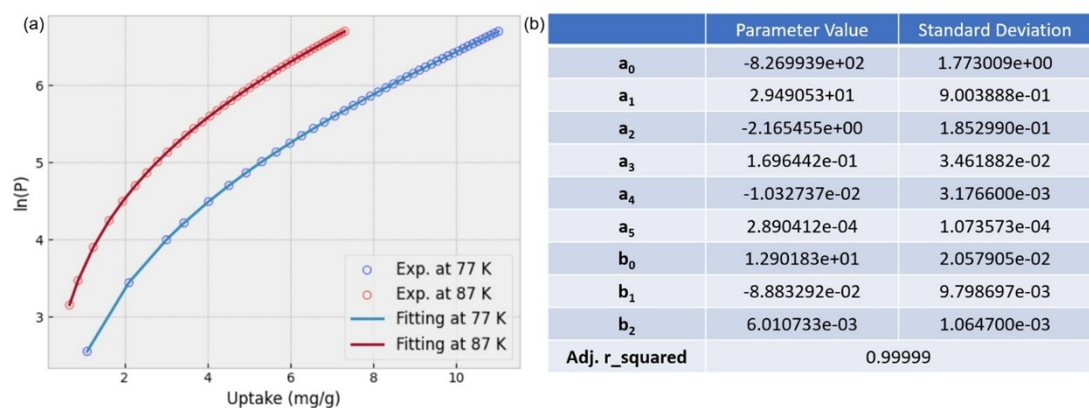
**Figure S3** H<sub>2</sub> and D<sub>2</sub> sorption isotherms of **bio-MOF-C950**, **bio-MOF-C1000** and **bio-MOF-C1050** at 77K. (filled symbols: adsorption; open symbols: desorption).



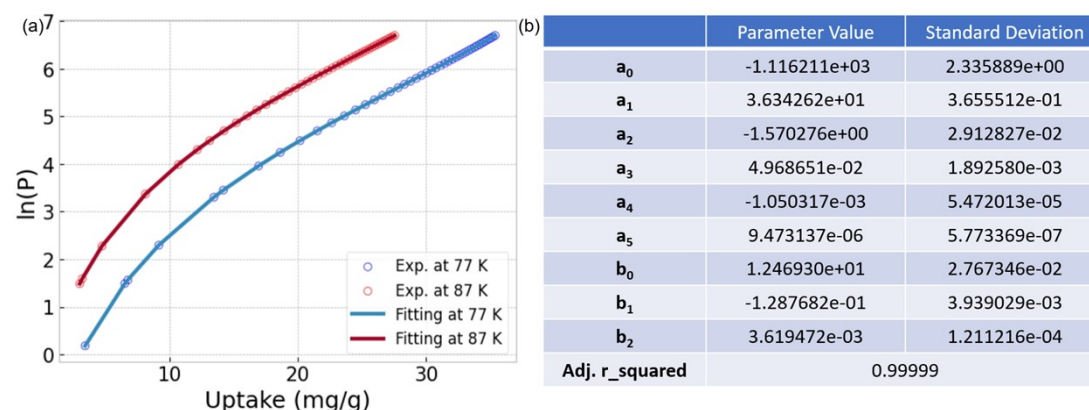
**Figure S4** H<sub>2</sub> and D<sub>2</sub> sorption isotherms of **bio-MOF-C950**, **bio-MOF-C1000** and **bio-MOF-C1050** at 87K. (filled symbols: adsorption; open symbols: desorption).



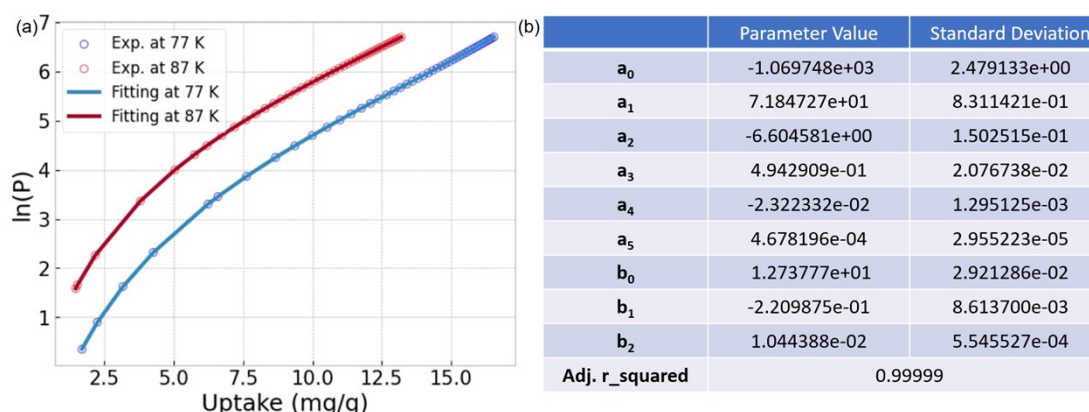
**Figure S5** (a) Virial equation fitting of D<sub>2</sub> adsorption isotherm of bio-MOF-1 at 77 K and 87 K. (b) Relevant fitting parameters for D<sub>2</sub>.



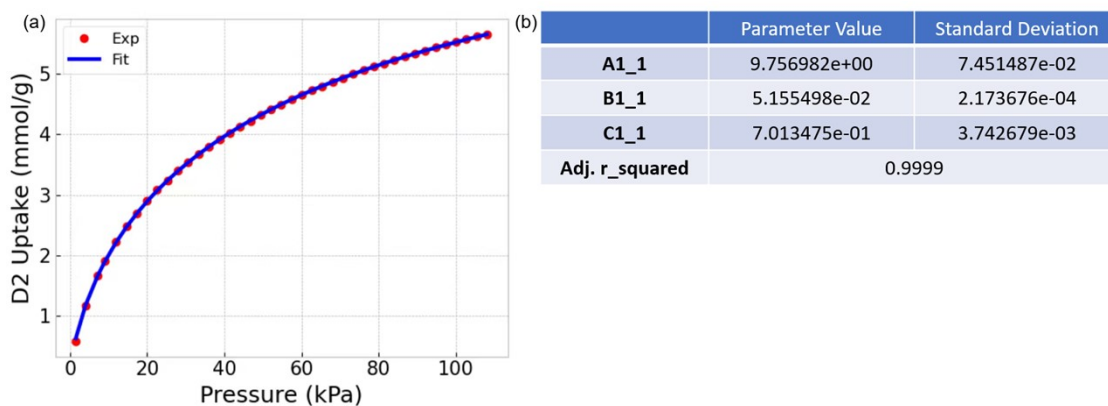
**Figure S6** (a) Virial equation fitting of H<sub>2</sub> adsorption isotherm of bio-MOF-1 at 77 K and 87 K. (b) Relevant fitting parameters for H<sub>2</sub>.



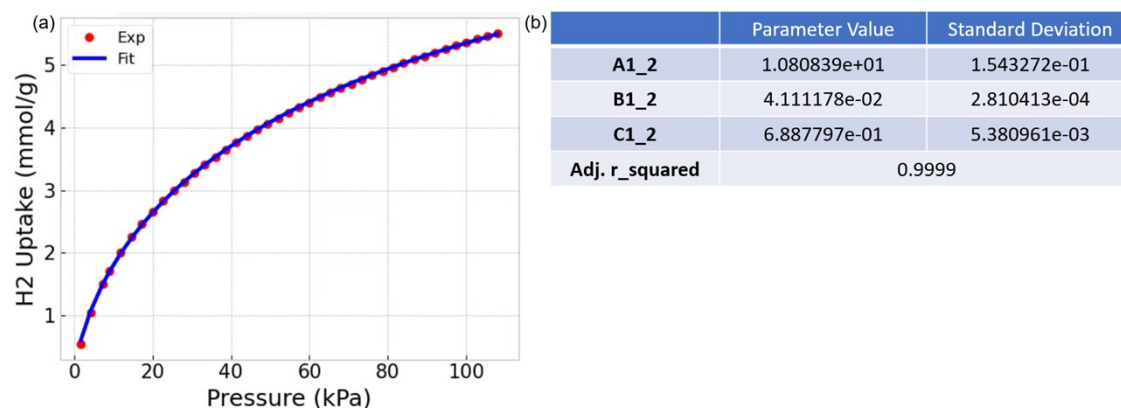
**Figure S7** (a) Virial equation fitting of D<sub>2</sub> adsorption isotherm of bio-MOF-C1000 at 77 K and 87 K. (b) Relevant fitting parameters for D<sub>2</sub>.



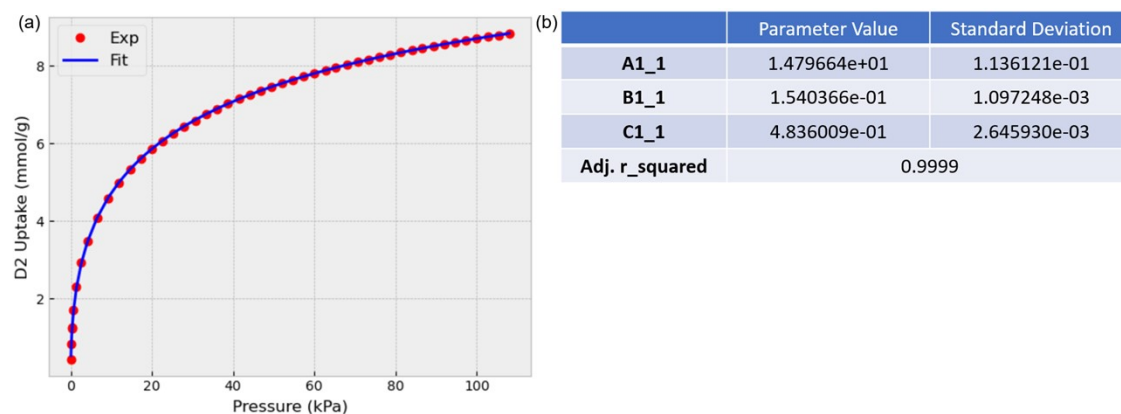
**Figure S8** (a) Virial equation fitting of H<sub>2</sub> adsorption isotherm of bio-MOF-C1000 at 77 K and 87 K. (b) Relevant fitting parameters for H<sub>2</sub>.



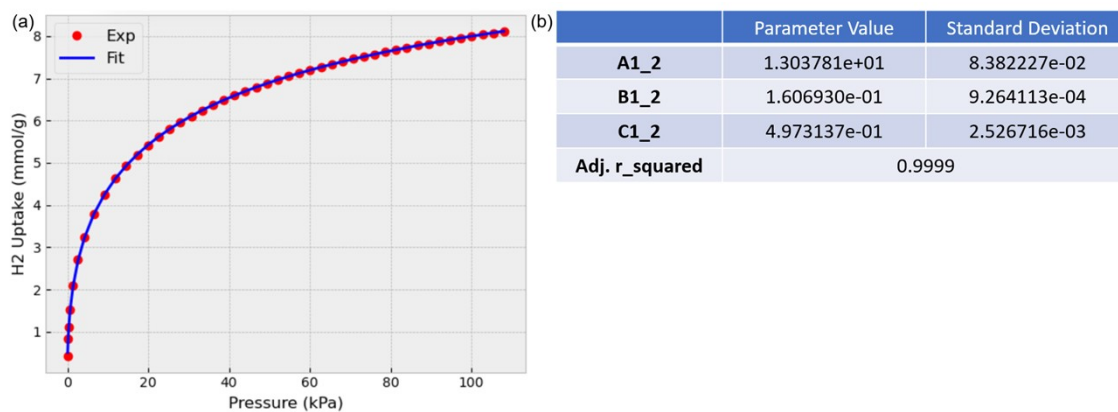
**Figure S9** (a) Langmuir-Freundlich fitting of D<sub>2</sub> adsorption isotherm for bio-MOF-1 at 77 K. (b) Relevant fitting parameters for D<sub>2</sub> at 77 K.



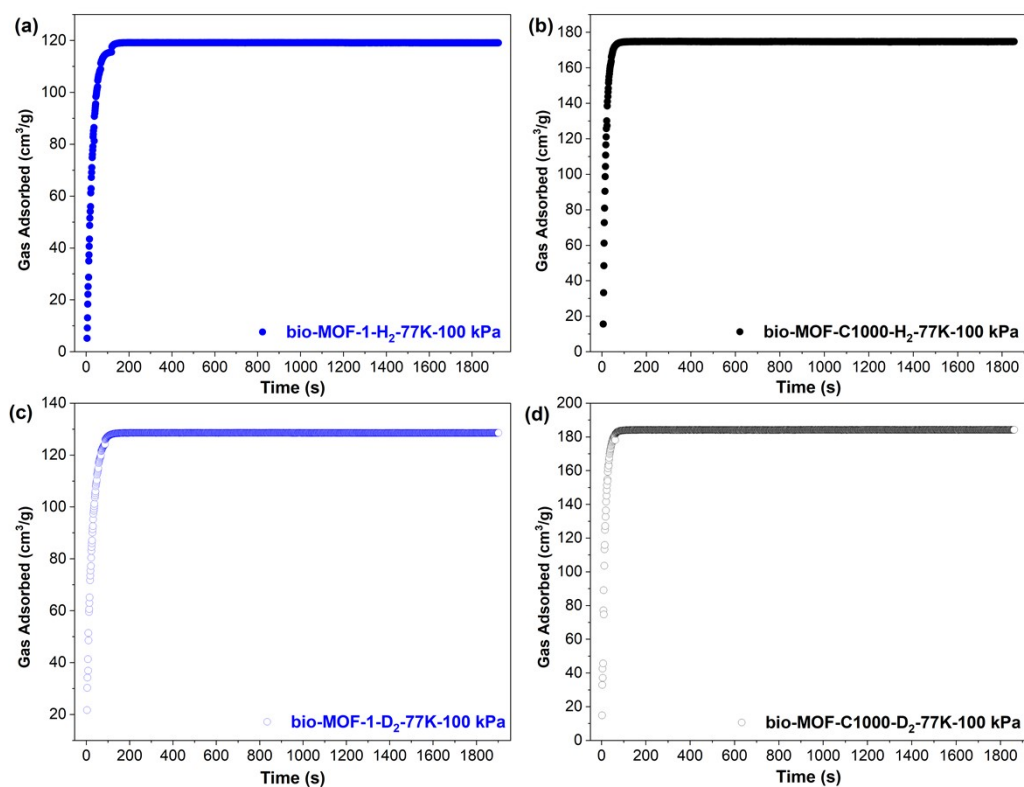
**Figure S10** (a) Langmuir-Freundlich fitting of H<sub>2</sub> adsorption isotherm for bio-MOF-1 at 77 K. (b) Relevant fitting parameters for H<sub>2</sub> at 77 K.



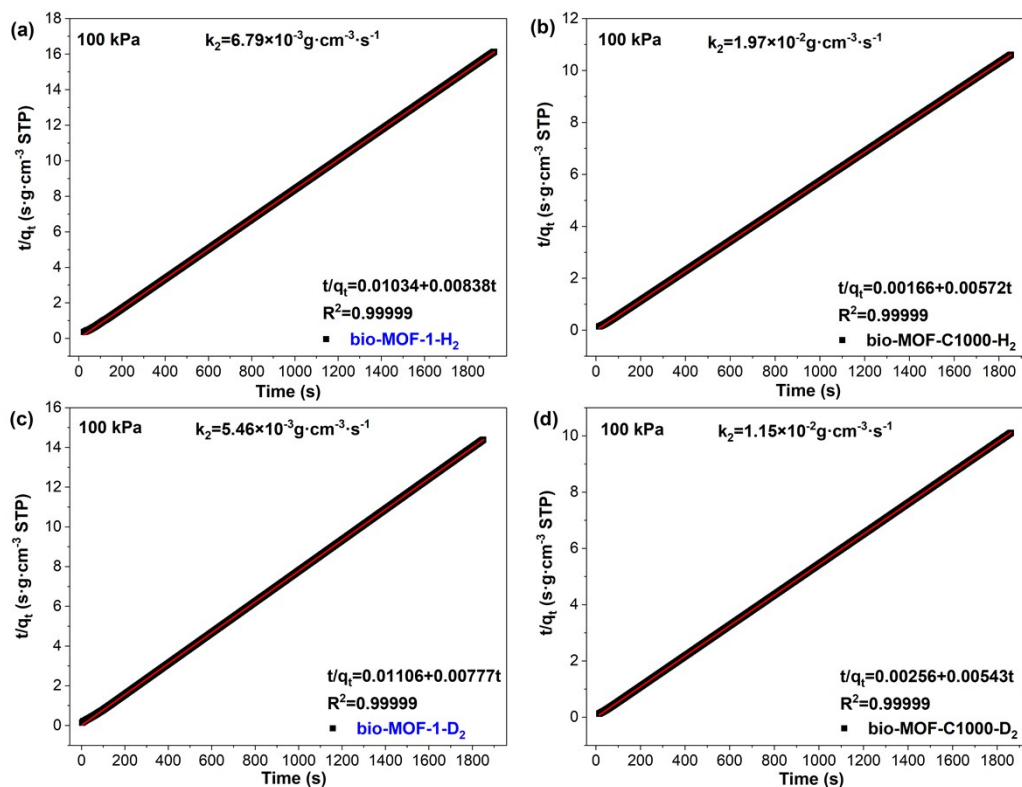
**Figure S11** (a) Langmuir-Freundlich fitting of D<sub>2</sub> adsorption isotherm for **bio-MOF-C1000** at 77 K. (b) Relevant fitting parameters for D<sub>2</sub> at 77 K.



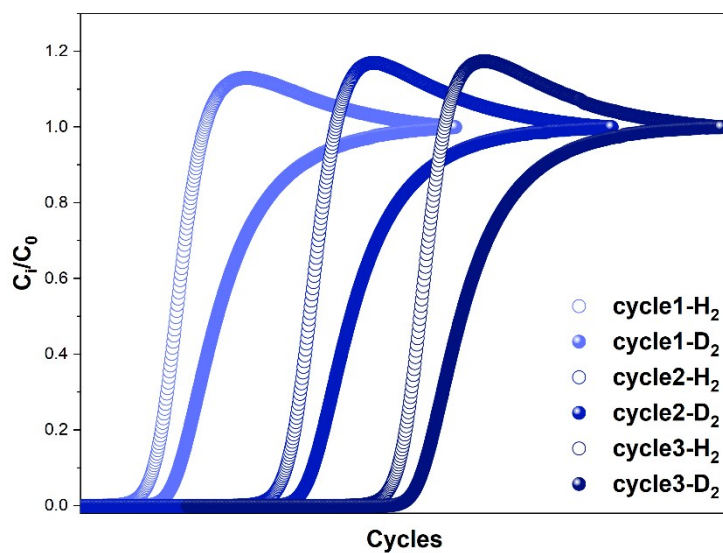
**Figure S12** (a) Langmuir-Freundlich fitting of H<sub>2</sub> adsorption isotherm for **bio-MOF-C1000** at 77 K. (b) Relevant fitting parameters for H<sub>2</sub> at 77 K.



**Figure S13** The kinetic adsorption curves at 100 kPa (a) bio-MOF-1-H<sub>2</sub>; (b) **bio-MOF-C1000-H<sub>2</sub>**; (c) bio-MOF-1-D<sub>2</sub>; (d) **bio-MOF-C1000-D<sub>2</sub>**.



**Figure S14** Fitting of the pseudo-second-order kinetic model at 100 kPa of (a) bio-MOF-1-H<sub>2</sub>; (b) bio-MOF-1-D<sub>2</sub>; (c) bio-MOF-C1000-H<sub>2</sub>; (d) bio-MOF-C1000-D<sub>2</sub>.



**Figure S15** The dynamic breakthrough curves of bio-MOF-C1000 in cycling test.