

## Supporting Information

### **Polycatenated 2D Hydrogen-Bonded Binary Supramolecular Organic Frameworks (SOFs) with Enhanced Gas Adsorption and Selectivity**

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## DATA AND CALCULATION

**Heats of Adsorption.** The heats of adsorption ( $Q_{st}$ ) were calculated using the Clausius Clapeyron equation (1) for CO<sub>2</sub> for isotherms at 273 K and 298 K and were solved by a virial-type equation (2).

$$\frac{d \ln(p)}{d(1/T)} = -\frac{\Delta H}{R} \quad (1)$$

where  $p$  is pressure;  $T$  is the temperature;  $R$  is the real gas constant;

$$\ln(n/p) = A_0 + A_1n + A_2n^2 + \dots \quad (2)$$

where  $p$  is the pressure,  $n$  is the amount adsorbed,  $A_i$  are virial coefficients, and  $i$  represent the number of coefficients required to adequately describe the isotherms with low uptakes.

*Tóth method* (Table S4)

The non-linear equation:

$$n = n_{\text{sat}} [b^{1/t} / (1 + b^t)]^{1/t} \quad (3)$$

was used, where  $n$  is the uptake in mmol g<sup>-1</sup>,  $n_{\text{sat}}$  is the saturation uptake (mmol g<sup>-1</sup>),  $t$  and  $b$  are parameters which are specific for adsorbate-adsorbent pairs. The value of parameter  $t$  is usually less than unity and is said to characterize the system heterogeneity. The Henry's Law constant  $K_H$  quantifies the extent of the adsorption of a given adsorbate by a solid. For the Tóth isotherm, the Henry's Law constant is defined by the following equation:

$$K_H \lim_{p \rightarrow 0} \left( \frac{dn}{dp} \right) = b^{1/t} n_{\text{sat}} \quad (4)$$

**Quantum chemistry calculations.** All quantum mechanical calculations were performed in the density functional theory (DFT; Table S5) approach with localized basis sets for atomic orbitals,

using the CRYSTAL14 software (version 1.0.4).<sup>S1</sup> The basis sets used for each of the four elements H, C, N and O, can be found at [www.crystal.unito.it/basis-sets.php](http://www.crystal.unito.it/basis-sets.php) (basis sets named **gatti\_94**, also described and used in Ref. S2). The **k**-point meshes used for numerical integrations in reciprocal space were generated using the Pack-Monkhorst method,<sup>S3</sup> with respectively a 2×2×1, a 3×1×2, a 1×1×1, and a 2×1×1 supercell for **SO**F-7, **SO**F-8, **SO**F-9, and **SO**F-10 respectively. The supercell sizes  $N_a \times N_b \times N_c$  in each dimension were chosen in function of the associated cell parameters  $v_i$ , so that  $v_i \times N_i$  is large enough (typically in the range 20–25 Å). The functional used to describe electronic exchange and correlation effects is PBEsol,<sup>S4</sup> a solid-state-adapted functional at the Generalized Gradient Approximation (GGA) level. It was chosen by relaxing structures **SO**F-7 and **SO**F-8 with several functionals (PBE and PBEsol, with and without Grimme’s dispersion corrections<sup>S5</sup>) and comparing the resulting cell parameters with the experimental ones. PBEsol gave the best overall agreement and was thus used for all results reported in this work.

For all geometry optimizations, both cell parameters and atomic coordinates were freely relaxed to minimize the energy, with the only constraint retained being the experimental structure’s space group. We used high-accuracy convergence criteria which are standard for frequency calculations, i.e.  $1.2 \cdot 10^{-4}$  a.u. for root mean square atomic displacements and  $3 \cdot 10^{-5}$  a.u. for root mean square forces.

**Computation of mechanical properties.** The second-order elastic constants  $C_{ij}$  (in Voigt notation, with  $1 \leq i, j \leq 6$ ) were calculated for the materials with the standard strain-stress method implemented in CRYSTAL14 (keyword **ELASTCON**).<sup>S6</sup> For each deformation mode  $i$  (or a subset of the 6 modes, if any are equivalent by symmetry), the calculation of  $C_{ij}$ ’s consists in re-optimizing atomic coordinates after applying small deformations of the unit cell (with strain amplitudes of  $\pm$

0.01) and estimating the resulting changes in energy, forces and stress. Spatially-averaged values of the various moduli correspond to Hill's convention;<sup>S7</sup> bulk moduli ( $B$ ), Young's moduli ( $E$ ), shear moduli ( $G$ ), and Poisson ratio  $\nu$  were calculated with the ELATE online application (Table S6).<sup>S8</sup>

**Analysis of vibration modes.** We analyzed vibration modes (frequencies and mode eigenvectors) within CRYSTAL14 (keyword **FREQCALC**).<sup>S9</sup> Given the large size of the unit cells, modes were computed at the  $\Gamma$ -point (i.e. two atoms with identical coordinates but separated by one lattice vector vibrate in phase). The calculations consist in sequentially performing small displacements for each of the  $3N$  atomic coordinates (or, in practice, a subset of them, thanks to point group symmetries), and after each displacement, estimating the resulting change in energy and forces. From that, the mass-weighted Hessian matrix is calculated in Cartesian coordinates and then diagonalized, giving the vibration frequencies (the eigenvalues) and normal modes (the eigenvectors).

We calculated the thermal expansion coefficient  $\alpha_V(T)$  at  $T = 300$  K as follows:

$$\alpha_V = -V^{-2} (dV/dP) \sum \gamma_i C_V^{(i)}(T) \quad (5)$$

where  $C_V^{(i)}(T) = k_B \exp(-\xi_i) \xi_i^2 [1 - \exp(-\xi_i)]^{-4}$  is the contribution of vibrational mode  $i$  (with frequency  $\omega_i$ ) to the specific heat, and  $\xi_i = (\hbar \omega_i) / (k_B T)$ .

To estimate Grüneisen parameters  $\gamma_i = - (V/\omega_i) (d\omega_i / dV)$ , series of calculations (including geometry optimizations and subsequent vibrational frequencies calculations) were performed at finite pressures  $P = -100$  MPa,  $-50$  MPa,  $+50$  MPa and  $+100$  MPa. The  $(dV/dP)$  term in Eq. (5) was estimated from these relaxed structures, for consistency.

**Table S1** Crystal data and structure refinement for **SOF 8-10**.

Compound	SOF-8	SOF-9	SOF-10
Chemical formula	C <sub>75</sub> H <sub>57</sub> N <sub>13</sub> O <sub>11</sub>	C <sub>95</sub> H <sub>89</sub> N <sub>17</sub> O <sub>15</sub>	C <sub>80</sub> H <sub>76</sub> N <sub>18</sub> O <sub>16</sub>
Formula mass	1316.32	1708.8	1545.55
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	<i>P2<sub>1</sub>/m</i>	<i>Pba2</i>	<i>Pbc2<sub>1</sub></i>
<i>a</i> /Å	8.3560(4)	17.7018(2)	13.6011(3)
<i>b</i> /Å	31.4388(12)	20.5306(2)	20.3271(3)
<i>c</i> /Å	15.2674(8)	21.2452(2)	23.8092(4)
$\alpha$ /°	90	90	90
$\beta$ /°	99.365(4)	90	90
$\gamma$ /°	90	90	90
Cell volume/Å <sup>3</sup>	3957.3(3)	7721.12(16)	6582.6(2)
<i>Z</i>	4	4	4
Reflections collected	25659	28594	35842
Independent reflections	7998	11981	12734
<i>R</i> <sub>int</sub>	0.022	0.015	0.027
Final <i>R</i> <sub>1</sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.102	0.0503	0.0502
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.324	0.142	0.137
Goodness of fit on <i>F</i> <sup>2</sup>	1.22	1.04	1.03

**Table S2** Hydrogen bond lengths (Å) in **SOF 8-10**.

	SOF-8	SOF-9	SOF-10
N···H–O (Å) <sup>a</sup>		1.713 <sup>*</sup> /2.548	1.711/2.547
	1.754 <sup>a</sup> /2.568 <sup>b</sup>	1.763 <sup>*</sup> /2.589	1.786/2.626
	1.753/2.562	1.773/2.611	1.791/2.627
		1.808/2.633	1.822/2.616

<sup>a</sup> The N···H distance.<sup>b</sup> The N···O distance.

<sup>\*</sup> The short N···H distances are due to the partial delocalization of H atoms on the carboxyl groups, which can be confirmed by the smaller C–O/C=O discrepancy (1.272/1.237 Å and 1.284/1.230 Å) comparing with localized carboxyl groups (1.335/1.206 Å and 1.309/1.210 Å).

**Table S3** CO<sub>2</sub> adsorption data for porous organic molecular solids with comparable surface area and SOF-n series materials.

	Surface Area (m <sup>2</sup> g <sup>-1</sup> )	V (CO <sub>2</sub> ) (mmol g <sup>-1</sup> )			
		273 K 1 bar	298 K 1 bar	273 K 20 bar	298 K 20 bar
<b>HOF-8d</b> <sup>S10</sup>	--	--	2.55	--	--
<b>TTBI</b> <sup>S11</sup>	2796 <sup>[b]</sup>	3.61	--	--	--
<b>SOF-7a</b> <sup>S12</sup>	900 <sup>[a]</sup>	2.85	1.49	7.07	5.48
<b>SOF-10a</b>	221 <sup>[a]</sup>	2.11	1.29	5.11	4.44
<b>TTP</b> <sup>S13</sup>	--	--	0.98	--	--
<b>SOF-1a</b> <sup>S14</sup>	474 <sup>[d]</sup>	1.34	0.71	4.06 <sup>[e]</sup>	3.08 <sup>[e]</sup>
<b>TBC[4]DHQ</b> <sup>S15,S16</sup>	230 <sup>[b]</sup>	--	--	--	1.56 <sup>[c]</sup>
<b>SOF-9a</b>	182 <sup>[a]</sup>	0.93	0.55	2.27	1.58

[a] calculated from CO<sub>2</sub> isotherm at 273 K; [b] Determined by N<sub>2</sub> sorption at 77 K with data points in the range for P/P<sub>0</sub> between 0.01 and 0.04; [c] measured at 35 bar; [d] measured at 30 bar; [e] calculated from N<sub>2</sub> adsorption at 125 K and 1 bar; [e] measured at 16 bar.

**Table S4** Tóth fitting parameters and Henry's Law constants

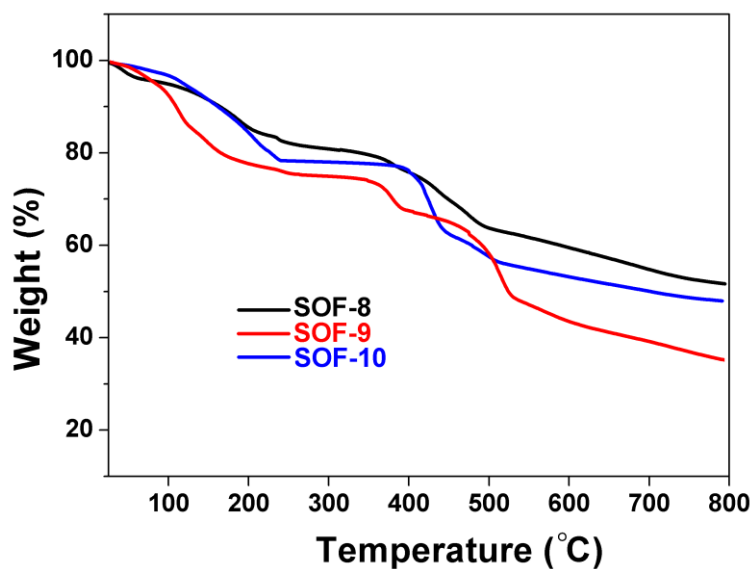
		$N_{\text{sat}}$	$b$	$t$	$R^2$	$K_H$	Selectivity
<b>SOF-9a</b>							
CO <sub>2</sub>	273 K	1.26	5.49	1.39	0.9994	4.29	<b>7.19<sup>a</sup></b>
	298 K	0.91	2.02	1.38	0.9992	1.51	
CH <sub>4</sub>	273 K	0.55	0.37	1.34	0.9997	0.26	<b>6.75<sup>b</sup></b>
	298 K	0.46	0.44	1.05	0.9992	0.21	
<b>SOF-10a</b>							
CO <sub>2</sub>	273 K	6.09	0.29	0.94	0.9996	1.63	<b>6.27<sup>a</sup></b>
	298 K	5.79	0.31	0.95	0.9994	1.69	
CH <sub>4</sub>	273 K	3.58	0.09	0.98	0.9997	0.31	<b>5.25<sup>b</sup></b>
	298 K	1.37	0.08	1.33	0.9998	0.25	
<b>SOF-1a<sup>S13</sup></b>							
CO <sub>2</sub>	273 K	6.07	0.66	0.60	0.99965	3.07	<b>5.60<sup>a</sup></b>
	298 K	4.68	0.31	0.76	0.99994	1.01	
CH <sub>4</sub>	273 K	3.62	0.27	0.69	0.99973	0.55	<b>4.24<sup>b</sup></b>
	298 K	3.38	0.13	0.77	0.99992	0.24	
<b>SOF-7a<sup>S14</sup></b>							
CO <sub>2</sub>	273 K	8.05	0.55	0.97	0.9993	4.32	<b>14.2<sup>a</sup></b>
	298 K	8.25	0.26	0.91	0.9996	1.84	
CH <sub>4</sub>	273 K	3.57	0.09	0.98	0.9997	0.31	<b>9.13<sup>b</sup></b>
	298 K	1.37	0.08	1.33	0.9998	0.20	

<sup>a</sup> Selectivity at 273 K.<sup>b</sup> Selectivity at 298 K.**Table S5** DFT-optimized structures of **SOF 7-10**, cell parameters, and binding energies.

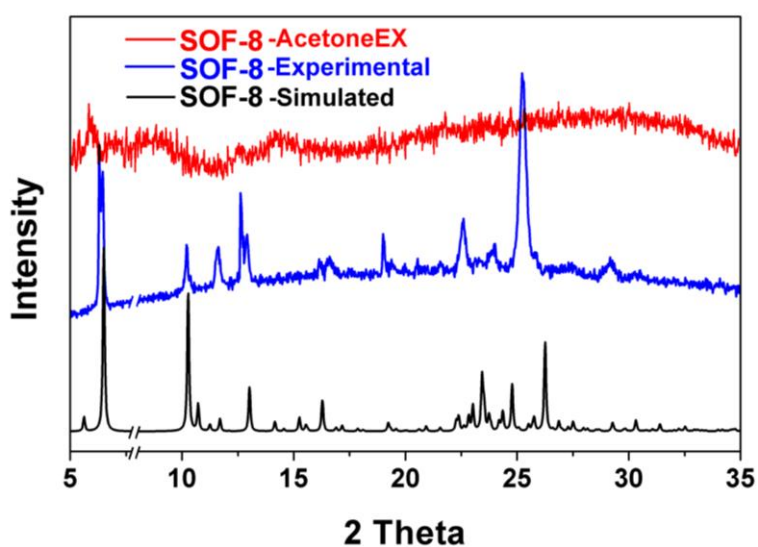
Compound	<b>SOF-7</b>	<b>SOF-8</b>	<b>SOF-9</b>	<b>SOF-10</b>
Space group	<i>C2/c</i>	<i>P2<sub>1</sub>/m</i>	<i>Pba2</i>	<i>Pbc2<sub>1</sub></i>
<i>a</i> /Å	8.1989	8.3720	18.0423	13.5790
<i>b</i> /Å	29.6603	31.5143	20.4842	20.2541
<i>c</i> /Å	34.4522	15.2746	21.3114	24.0043
$\beta$ /°	101.161	98.588	90	90
Binding energy (kJ mol <sup>-1</sup> ; per constituent <b>3</b> , <b>4</b> or <b>5</b> )	-438.0	-432.2	-429.1	-436.6
Cell volume/Å <sup>3</sup>	8219.8	3984.9	7876.3	6601.9

**Table S6** Mechanical properties of SOF compounds (all values in GPa)

Compound	SOF-7	SOF-8	SOF-9	SOF-10
Bulk modulus $B$	8.96	9.09	9.5	8.99
Young's modulus $E$	5.81	7.97	--	8.98
Shear modulus $G$	2.09	2.94	--	3.36
Minimal Young's modulus $E_{\min}$	0.60	1.04	--	2.69
Minimal shear modulus $G_{\min}$	0.21	0.41	--	1.20

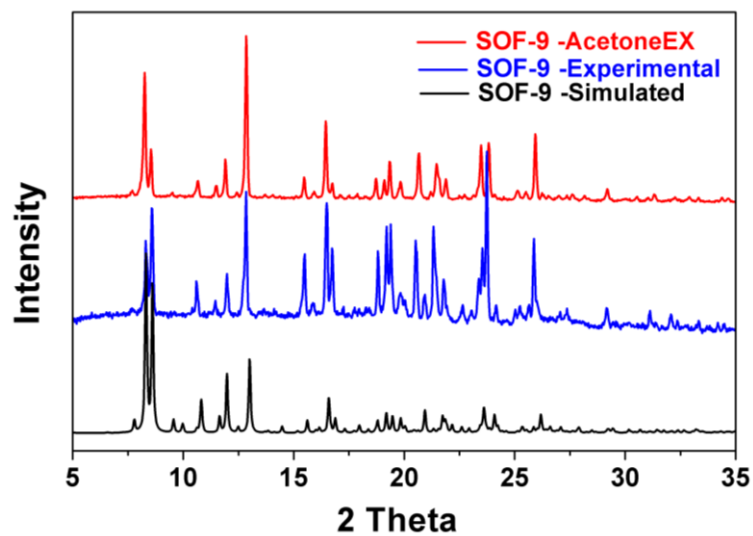


**Figure S1** TGA curves of SOF 8-10.

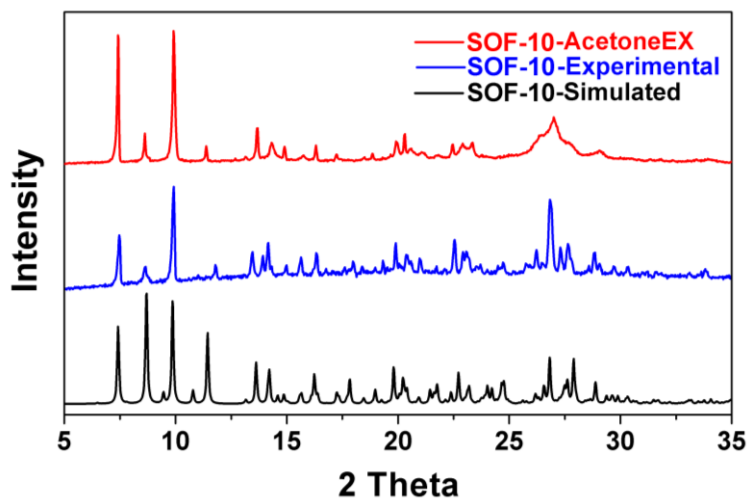


**Figure S2** PXRD patterns of as-synthesized (Experimental; blue), acetone-exchanged (AcetonEX; red), and simulated from single crystal data (Simulated; black) for SOF-8.

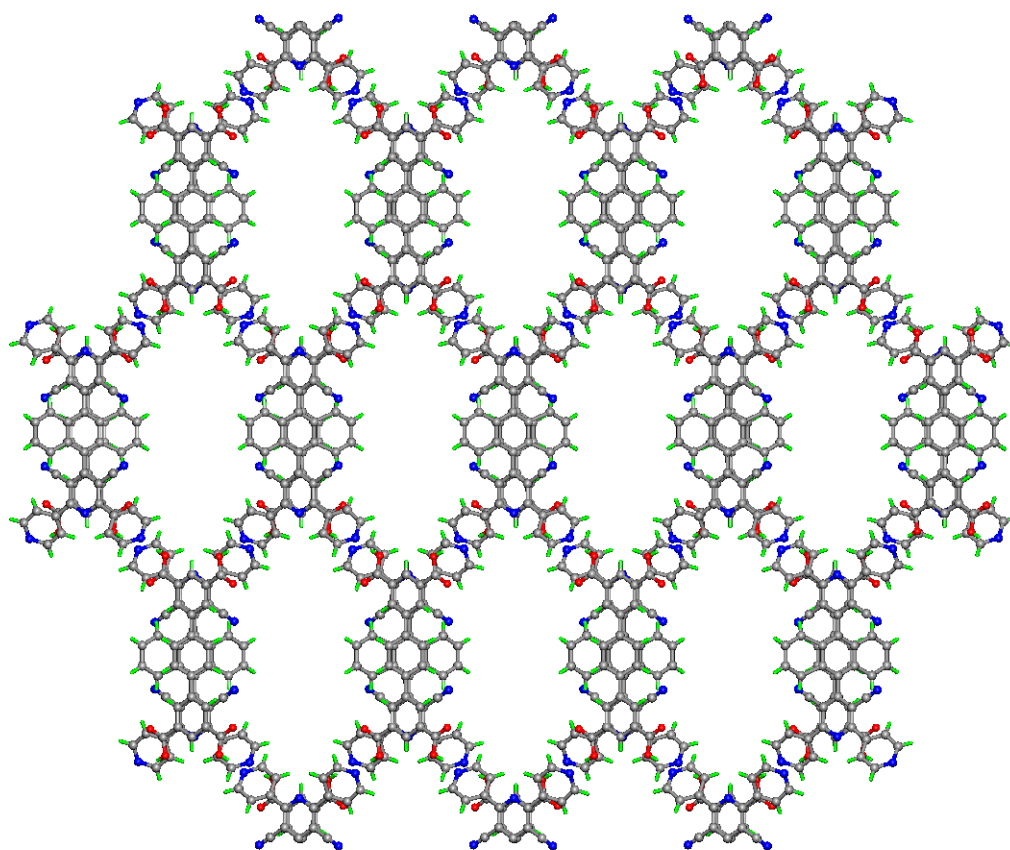




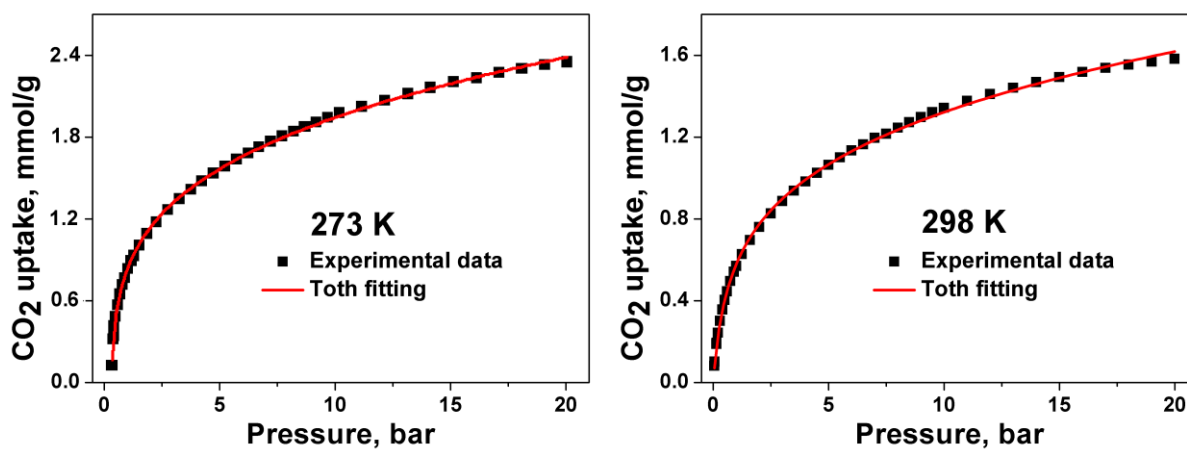
**Figure S3** PXRD patterns of as-synthesized (Experimental; blue), acetone-exchanged (AcetonEX; red), and simulated from single crystal data (Simulated; black) for **SOF-9**.



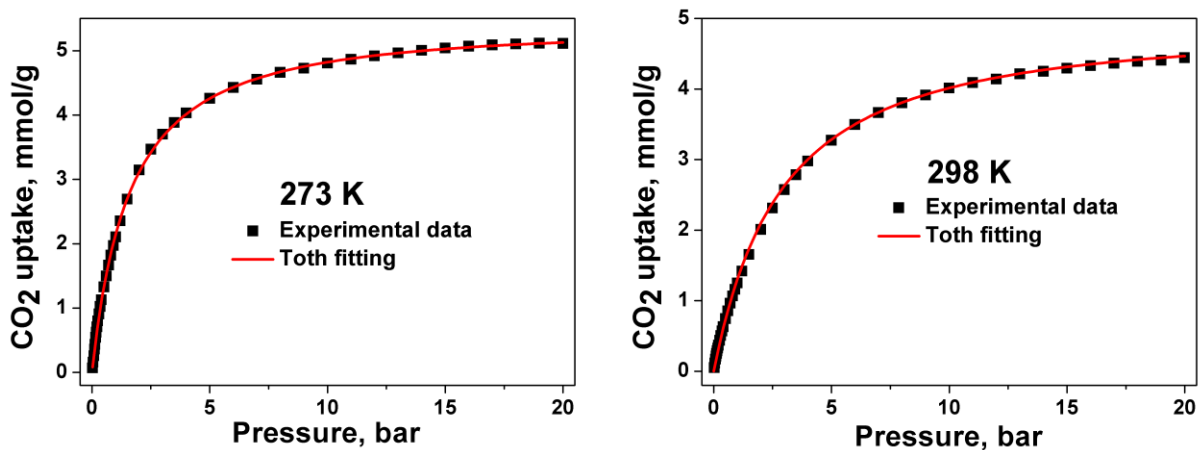
**Figure S4** PXRD patterns of as-synthesized (Experimental; blue), acetone-exchanged (AcetonEX; red), and simulated from single crystal data (Simulated; black) for **SOF-10**.



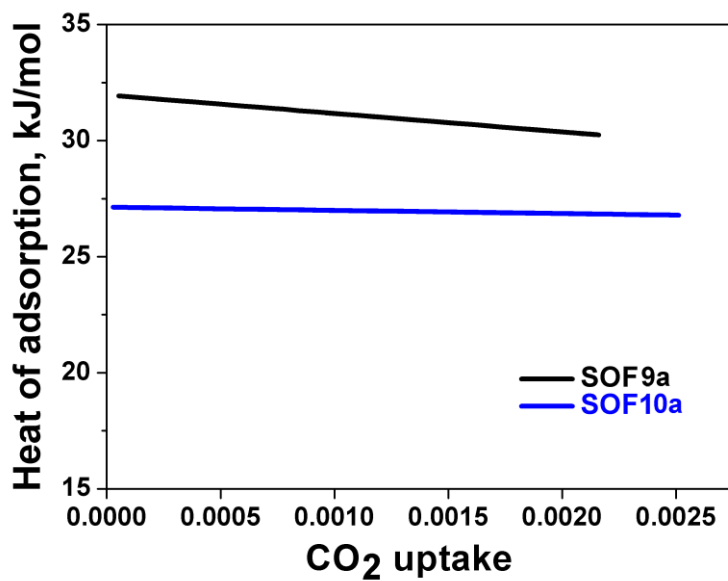
**Figure S5** Packing patterns of SOF-8.



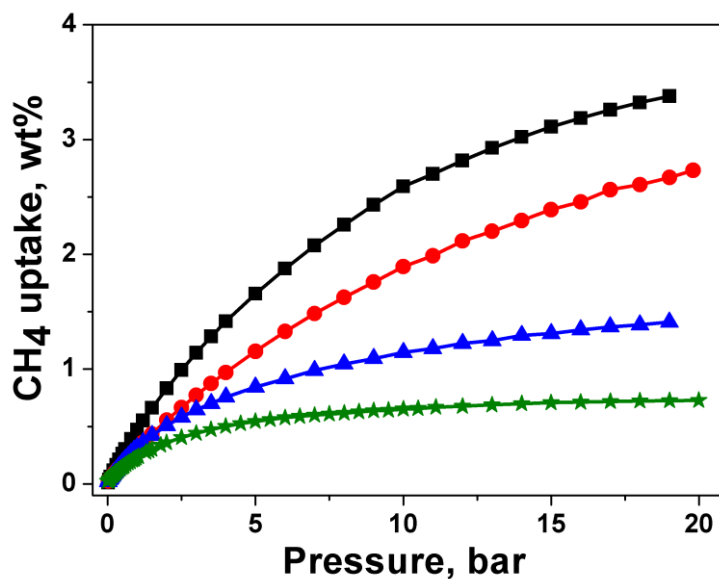
**Figure S6** Isotherms for CO<sub>2</sub> uptake in SOF-9 at 273 K and 298 K, black squares: experimental data fitted using Toth model (red line).



**Figure S7** Isotherms for CO<sub>2</sub> uptake in **SOF-10** at 273 K and 298 K, black squares: experimental data fitted using Tóth model (red line).



**Figure S8** Heat of adsorption for CO<sub>2</sub> uptake in **SOF-9a** and **SOF-10a**.



**Figure S9** Isotherms for CH<sub>4</sub> uptake in **SOF-9a** (at 273 K, blue; 298 K, green) and **SOF-10a** (at 273 K, black; 298 K, red).

## References

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