Electronic Supplementary Information (ESI)

Self-assembly of two robust 3D supramolecular organic frameworks from a geometrically non-planar molecule for high gas selectivity performance

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1. Syntheses and preparations^[1]



Scheme S1. Synthetic route for M5 (TMBTI)

Synthesis of 3,5-dicarboxyethylester-phenylboronic acid (M2):

(3,5-dimethylphenyl)boronic acid (15.0 g, 0.1 mol) and NaOH (12.0 g, 0.3 mol) were dissolved in a mixture of tert-butanol/water (v/v = 1:1, 600 mL), which was heated to 60 °C with stirring, then a small amount of KMnO₄ (120 g) was added to the mixture. When the solution starts to fade, the other portion of KMnO₄ (120 g) was added with stirring and the mixture was heated at 70 °C for 4 h. The resulting mixture was filtered, and then the MnO₂ residue was washed with excess boiling deionized water. The filtrate was concentrated under reduced pressure, and then acidified with concentrated hydrochloric acid. The formed precipitate was filtrated and washed with deionized water to give 5-boronoisophthalic acid (**M1**), as a white powder. Then, the concentrated sulfuric acid (5 mL) was added gradually into ethanol solvent (300 mL) containing **M1** (10.5 g, 50 mmol) with stirring, and the mixture was refluxed for 12 h. Excess ethanol was removed by rotary evaporation, the residue was dropped into deionized water (300 mL), and then collected by filtration and washed with deionized water. The white product **M2** was obtained after being dried under vacuum (11.57 g, 69 %). ¹H NMR (300 MHz, DMSO-*d*₆, 25 °C) δ (ppm): 8.64 (s, 2H), 8.51 (s, 3H), 4.38 (q, *J* = 21.3 Hz, 4H), 1.36 (t, *J* = 14.1 Hz, 6H).

Synthesis of 1,3,5-tribromo-2,4,6-trimethylbenzene (M3):

Iron powder (2.79 g, 50.0 mmol) was added to a three-neck flask containing bromine (45 mL, 0.88 mol), and then 1,3,5-trimethylbenzene (18.03 g, 0.15 mol) was added slowly to the mixture over 4 h with stirring at room temperature. After 3 days, a reddish brown sludge was generated, which was filtered to give crude product. Finally, the precipitate was recrystallized from CHCl₃ and colorless needles of **M3** were achieved (41.29 g, 81 %). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 2.65 (s, 9H).

Synthesis of 2,4,6-trimethyl benzene-1,3,5-triyl-isophthalate (M4):

M3 (5.35 g, 15 mmol), K₃PO₄ (25.2 g, 120 mmol) and Pd(PPh₃)₄ (0.69 g, 0.6 mmol) were dissolved in a 1000 mL round-bottom flask containing 1,4-dioxane (400 mL) under nitrogen atmosphere. Then, **M2** (15.96 g, 60 mmol) was introduced into the system, and the reaction mixture was stirred and heated under reflux for 3 days. The resulting mixture was filtered and washed with CH₂Cl₂, and then the filtrate was removed by rotary evaporation. The crude product was purified by column chromatography (SiO₂: light petroleum / EtOAc, 5:1) to give the white product (7.14 g, 61 %). ¹H NMR (300 MHz, CDCl₃, 25 °C) δ (ppm): 8.69 (t, *J* = 3.3 Hz, 3H), 8.10 (d, *J* = 1.8 Hz, 6H), 4.44 (q, *J* = 21.3 Hz, 12H), 1.68 (s, 9H), 1.43 (t, *J* = 14.1 Hz, 18H).

Synthesis of 2,4,6-trimethyl benzene-1,3,5-triyl-isophthalic acid (M5, TMBTI):

The reaction mixture containing the solutions of **M4** (15.62 g, 20 mmol) in a mixture of tetrahydrofuran (200 mL) and ethanol (200 mL), and of NaOH (8 g, 0.2 mol) in deionized water (100 mL) was stirred and heated under reflux for 15 h. The mixture was concentrated by rotary evaporation to remove solvent, and the residue was diluted into deionized water and then acidified with concentrated hydrochloric acid. The precipitate was collected by filtration, washed with deionized water, and dried under vacuum to give the final product **M5** (TMBTI) (11.03 g, 90 %). ¹H NMR (300 MHz, DMSO-*d*₆, 25 °C) δ (ppm): 13.33 (s, 6H), 8.49 (t, *J* = 3.3 Hz, 3H), 8.02 (d, *J* = 1.8 Hz, 6H), 1.62 (s, 9H).



Fig. S1 ¹H NMR spectrum of TMBTI.



Fig. S2 FT-IR spectrum of TMBTI.

2. Experimental and theoretical pore volumes calculations

The value of experimental pore volume was obtained from the N₂ sorption isotherms (77 K) at $P/P_o \approx 1$. The theoretical value was calculated based on the porosity estimated using PLATON^[2] and the density of the crystal structure. The equation was given as follows^[3] and corresponding values were listed in **Table S1**:

 $V_{\text{p(theory)}} = V_{\text{cell}} * \text{Porosity} / W_{\text{cell}} = V_{\text{cell}} * \text{Porosity} / (V_{\text{cell}} * \text{Density}) = \text{Porosity} / \text{Density}$

in which $V_{p(\text{theory})}$: theoretical pore volume [cm³ g⁻¹]; V_{cell} : volume of unit cell [nm³];

 W_{cell} : mass of unit cell [g]; Density [g cm⁻³]

Table S1. Experimental and theoretical pore volumes for JLU-SOF2 and JLU-SOF3.

Samples	Samples $ \frac{V_{p(experiment)}}{[cm^3 g^{-1}]} $		Density [g cm ⁻³]	$V_{ m p(theory)}$ [cm ³ g ⁻¹]
JLU-SOF2	0.47	43.7	0.769	0.47
JLU-SOF3	0.63	51.3	0.927	0.63

3. Material characterizations



Fig. S3 Ball-and-stick and space-filling models of **JLU-SOF2** along the x-axis (a and c) and y-axis (b and d).



Fig. S4 Simplified organic building block as a combination of 3-connected node (green ball) and 4-connected nodes (blue ball) based on the molecular structure and hydrogen-bonding interactions and the (3,4)-connected network topology (a), and topological features of this network displayed by tiles (b) for **JLU-SOF2**.



Fig. S5 Ball-and-stick and space-filling models of JLU-SOF3 along the z-axis.



Fig. S6 Space-filling model of the three-fold interpenetrated net of JLU-SOF3 along the z-axis.



Fig. S7 The C-H··· π interaction between the H atoms and the centroids of phenyl rings of the isophthalic acid groups for **JLU-SOF3**.



Fig. S8 Ball-and-stick and space-filling models of the single net of JLU-SOF3 along the z-axis.



Fig. S9 Simplified organic building block as 3-connected nodes (green and blue balls) based on the molecular structure and hydrogen-bonding interactions and the (3,3)-connected network topology for the single net of **JLU-SOF3**.



Fig. S10 TGA curves for as-synthesized and CH_3CN -exchanged JLU-SOF2 (a) and JLU-SOF3 (b).



Fig. S11 PXRD patterns of JLU-SOF2 heated under variable-temperature for 2 hours.



Fig. S12 PXRD patterns of simulated (a-i), as-synthesized (a-ii), exchanged in CH_3CN for one week (a-iii), regenerated after recrystallization of dissolved SOFs (a-iv), after CO_2 adsorption (a-v), and heated under variable-temperature for 2 hours (b) for **JLU-SOF3**.



Fig. S13 N₂ sorption isotherms for **JLU-SOF2**, **JLU-SOF3**, **JLU-SOF2R** and **JLU-SOF3R** at 77 K.



Fig. S14 N₂ sorption isotherms for different temperature heated JLU-SOF2 samples.



Fig. S15 N₂ sorption isotherms for different temperature heated JLU-SOF3 samples.

The total pore volumes of these materials were not detracted obviously following the temperature increase and a significant decrease appeared for the micro pore volumes at 300 and 350 °C (Tables S8 and S9). These results indicate that mesopore was formed after treated at high temperature.



Fig. S16 SEM images of JLU-SOF2 and JLU-SOF3 after N_2 sorption at 100 °C (a and c) and 350 °C (b and d).

The materials heated at 100 °C display complete morphology substantially, while the morphology is irregular and particle sizes decrease after heated at 350 °C. The changing of these materials maybe induces the formation of mesopore and alters the orientation of crystal.



Fig. S17 Photographs of as-synthesized (a and d), and 350 °C (b and e) and 380 °C heated (c and f) **JLU-SOF2** and **JLU-SOF3** for 2 hours, the inset profiles display the solubility of corresponding samples.



Fig. S18 ¹H NMR spectra of 350 °C heated JLU-SOF2 (a) and JLU-SOF3 (b).



Fig. S19 PXRD patterns of JLU-SOF2 (a) and JLU-SOF3 (b) heated at 380 °C for 2 hours.

As shown in Fig. S17, the color of **JLU-SOF2** and **JLU-SOF3** turns into light yellow and brown at 350 °C, and changes to dark brown after further heated to 380 °C. The inset profiles indicate that the 350 °C heated materials can be dissolved in DMF (6 mg/mL), while 380 °C treated samples remain in powder despite decreasing the concentration to 1 mg/mL. At the meantime, ¹H NMR spectra of 350 °C heated **JLU-SOF2** and **JLU-SOF3** indicate that the TMBTI blocks retain intact (Fig. S18). PXRD patterns indicate that 380 °C heated materials are probably transformed into an amorphous phase (Fig. S19).



Fig. S20 N₂ sorption isotherms for JLU-SOF2 and JLU-SOF3 at 273 and 298 K under 1 bar.



Fig. S21 Q_{st} of CO₂ for JLU-SOF2 (a) and JLU-SOF3 (b).



Fig. S22 Nonlinear curves fitting at 273 and 298 K under 1 bar and Q_{st} of N₂ for **JLU-SOF2** (a and b) and **JLU-SOF3** (c and d).



Fig. S23 CO_2 (a), CH_4 (b), C_2H_6 (c), and C_3H_8 (d) adsorption isotherms at 273 and 298 K for JLU-SOF2R and JLU-SOF3R.



Fig. S24 CH₄, C_2H_6 , and C_3H_8 adsorption isotherms at 298 K under 1 bar along with DSLF fits (a) and the adsorption selectivity of equimolar binary mixtures of C_2H_6/CH_4 and C_3H_8/CH_4 (b) for **JLU-SOF2**.



Fig. S25 CO_2 and CH_4 adsorption isotherms at 298 K along with the DSLF fits (a and c) and the adsorption selectivity of the binary mixtures predicted by IAST (b and d) for JLU-SOF2 and JLU-SOF3.

Compounds	JLU-SOF2	JLU-SOF3
formula	$C_{41}H_{40}O_{16}$	$C_{41}H_{40}O_{16}$
formula weight	788.73	788.73
temperature (K)	293	153
wavelength (Å)	0.71073	0.71073
crystal system	trigonal	hexagonal
space group	<i>P</i> -31 <i>c</i>	P-62 <i>c</i>
<i>a</i> (Å)	12.2358(17)	22.670(3)
<i>b</i> (Å)	12.2358(17)	22.670(3)
<i>c</i> (Å)	33.860(7)	16.778(3)
α (°)	90	90
β (°)	90	90
γ (°)	120	120
volume (Å ³)	4390.2(12)	7468(2)
$Z, D_c (Mg/m^3)$	4, 1.193	6, 1.052
<i>F</i> (000)	1656	2484
θ range (deg)	1.20-25.05	1.04-25.72
reflns collected/unique	26951/2575	35337/4886
R _{int}	0.0330	0.0513
data/restraints/params	2575/0/136	4886/24/244
GOF on F^2	1.076	1.112
$R_1, wR_2 (I \ge 2\sigma(I))$	0.0609, 0.1758	0.0726, 0.2186
R_1 , wR_2 (all data)	0.0734, 0.1863	0.0897, 0.2360

Table S2. Crystal data and structure refinement for JLU-SOF2 and JLU-SOF3.

 $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \ w R_2 = [\sum [w (F_o^2 - F_c^2)^2] / \sum [w (F_o^2)^2]]^{1/2}$

Table S3. Hydrogen-bonding data for JLU-SOF3.

D- H····A	d(D-H)	d(H····A)	d(D····A)	<(DHA)
O(1)-H(1)····O(2)#2	0.82	1.79	2.605(2)	174.9
O(3)-H(3)····O(6)#3	0.82	1.80	2.615(7)	177.2
O(3')-H(3')···O(6')#3	0.82	1.81	2.630(6)	174.3
O(5)-H(5)····O(4)#4	0.82	1.82	2.628(3)	170.9

Symmetry codes: #1 x,y,-z+1/2; #2- x,-x+y,-z+1; #3 -x+1,-x+y+1,-z+1; #4 -x+1,-x+y,-z+1.

Table S4. Hydrogen-bonding data for JLU-SOF2.

D-H···A	d(D-H)	d(H···A)	d(D····A)	<(DHA)
O(2)-H(2)···O(1)#3	0.82	1.84	2.6606(19)	174.4
O(4)-H(4)····O(3)#4	0.82	1.84	2.642(2)	165.5

Symmetry codes: #1 -y+1,x-y,z; #2 -x+y+1,-x+1,z; #3 x-y,x,-z; #4 -x+y,y,-z+1/2.

Samples	Uptake [mmol/g]	S _{BET} [m ² g ⁻¹]	$\begin{array}{c} S_{Lang.} \\ [m^2 g^{-1}] \end{array}$	V _{p(experiment)} [cm ³ g ⁻¹]	V _{p(theory)} [cm ³ g ⁻¹]
JLU-SOF2	13.71	937	1258	0.47	0.47
JLU-SOF3	18.05	1141	1538	0.63	0.63

Table S5. N_2 sorption data of JLU-SOF2 and JLU-SOF3 measured at 77 K.

Table S6. Comparison of BET surface area for SOF/HOF materials.

SOFs/HOFs	SA _{BET} ^[a] [m ² g ⁻¹]	Ref.	SOFs/HOFs	SA _{BET} [m ² g ⁻¹]	Ref.
TTBI	2796	[4]	SOF-7a	900 ^[c]	[12]
PFC-1	2122	[5]	FDM-15	749	[13]
HOF-TCBP	2066	[6]	CPHAT-1a	649 ^[b]	[14]
CBPHAT-1 a	1288	[7]	SOF-1a	474 ^[d]	[15]
TPZ	1159	[8]	JLU-SOF1-R	460	[16]
JLU-SOF3	1141	This work	HOF-1a	359 ^[b]	[17]
HOF-5a	1101	[9]	HOF-9a	286 ^[b]	[18]
tcpb	1095	[10]	HOF-2a	238 ^[b]	[19]
IISERP-HOF1	1025 ^[b]	[11]	HOF-3a	165 ^[b]	[20]
JLU-SOF2	937	This work	HOF-7a	124 ^[b]	[21]

[a] Determined by N_2 sorption at 77 K; [b] Calculated from CO_2 sorption at 196 K; [c] Calculated from CO_2 sorption at 273 K; [d] Determined by N_2 adsorption at 125 K.

Ta	ble	S7.	Co	mpariso	n of a	as-syı	nthes	sized	l and	reused	materials	s for	different	gas a	adsorr	otion.
						2								$\boldsymbol{\omega}$		

Samples	JLU-SOF2	JLU-SOF2R	JLU-SOF3	JLU-SOF3R
SA _{BET} [m ² g ⁻¹]	937	884	1141	1005
V(CO ₂ -273) [mmol/g]	4.25	3.99	4.49	4.51
V(CO ₂ -298) [mmol/g]	1.98	2.11	2.34	2.37
V(CH ₄ -273) [mmol/g]	1.67	1.63	1.73	1.69
V(CH ₄ -298) [mmol/g]	0.96	0.89	1.05	0.98
V(C ₂ H ₆ -273) [mmol/g]	5.10	5.31	5.79	5.35
V(C ₂ H ₆ -298) [mmol/g]	4.04	3.73	4.41	4.11
V(C ₃ H ₈ -273) [mmol/g]	4.45	4.71	5.51	5.27
V(C ₃ H ₈ -298) [mmol/g]	4.11	4.13	4.70	4.55

	Uptake	S _{BET}	V _{p(total)}	$V_{ m p(micro)}$
Samples	[mmol/g]	[m ² g ⁻¹]	[cm ³ g ⁻¹]	[cm ³ g ⁻¹]
JLU-SOF2-100°C	13.70	937	0.47	0.41
JLU-SOF2-200°C	13.06	942	0.45	0.41
JLU-SOF2-250°C	14.57	929	0.45	0.41
JLU-SOF3-300°C	13.87	492	0.48	0.21
JLU-SOF2-350°C	12.43	406	0.43	0.17

Table S8. Comparison of adsorption capacity and pore volumes based on N_2 sorption datameasured at 77 K for different temperature heated JLU-SOF2.

Table S9. Comparison of adsorption capacity and pore volumes based on N_2 sorption datameasured at 77 K for different temperature heated JLU-SOF3.

	Uptake	S _{BET}	V _{p(total)}	$V_{ m p(micro)}$
Samples	[mmol/g]	$[m^2 g^{-1}]$	[cm ³ g ⁻¹]	[cm ³ g ⁻¹]
JLU-SOF3-100°C	18.05	1141	0.63	0.49
JLU-SOF3-200°C	16.84	1030	0.58	0.41
JLU-SOF3-250°C	14.57	949	0.50	0.38
JLU-SOF3-300°C	10.52	607	0.36	0.27
JLU-SOF3-350°C	13.70	527	0.47	0.22

SOFs/HOFs	V(CO ₂) [mmol/g]			Qst	Ref.
	195 K	273 K	298 K	[kJ mol ⁻¹]	
JLU-SOF3	15.18	4.51	2.32	21.8	This work
JLU-SOF2	13.75	4.24	1.96	24.5	This work
CBPHAT-1 a	13.62	N.A.	N.A	N.A	[7]
T12-apo	13.17	N.A.	N.A	N.A	[22]
TPZ	12.05	N.A.	N.A	N.A	[8]
HOF-1a	~10.09	N.A.	N.A	N.A	[17]
JLU-SOF1-R	9.51	3.39	2.37	34.3	[16]
HOF-11a	~8.66	2.19	1.34 ^[a]	21	[23]
IISERP-HOF1	6.29	4.82	2.90 ^[b]	31	[11]
SOF-1a	5.58	1.34	0.71	27.6	[15]
HOF-9a	~4.15	~2.46	~1.79 ^[a]	23.5	[18]
HOF-7a	~3.13	0.85	0.54 ^[a]	32	[21]
ТРР	2.70	N.A.	0.94	N.A.	[24]
HOF-3a	~2.23	1.38	0.94 ^[a]	~42	[20]
HOF-5a	N.A.	5.23	4.02 ^[a]	22.8	[9]
tcpb	N.A.	2.95	N.A	22	[10]
SOF-7a	N.A.	2.85	1.49	21.6	[12]
HOF-6a	N.A.	1.04	0.54 ^[a]	21.5	[25]

Table S10. Comparison of CO_2 uptakes for SOF/HOF materials at different temperature.

N.A.: Not Available. [a] Measured at 296 K and 1 bar, [b] Measured at 303 K and 1 bar.

~ .	SA _{BET}	V(CO ₂) [mmol/g]	
Samples	[m ² g ⁻¹]	273 K	298 K	Ref.
Mg-MOF-74	1525	10.2	6.7	[26]
Zeolite 13X	790	N.A.	5.8	[27]
JLU-Liu47	1800	8.57	4.82	[28]
rht-MOF-7	2170	6.52	4.38	[29]
NOTT-125	2471	9.1	4.2	[30]
JLU-SOF3	1141	4.51	2.32	This work
CB[6](hexagonal)	210	~2.77	2.2	[31]
P5-SOF	97	2.37	2.01	[32]
JLU-SOF2	937	4.24	1.96	This work
Activated carbon	1727	N.A.	1.89	[33]
JLU-MOF50	1101	2.95	1.56	[34]
IGO	283	2.1	1.4	[27]
SWCNT	790	N.A.	1.1	[27]
ZIF-100	595	1.7	0.96	[35]
HGO	36	0.97	0.81	[27]
PPF-3	419	2.09	N.A.	[36]

Table S11. Comparison of BET surface areas and CO_2 uptakes for porous materials.

Table S12. Comparison of CO_2/N_2 selectivity for SOF/HOF materials under different conditions.

SOFs/HOFs	Selectivity	Ref.	SOFs/HOFs	Selectivity	Ref.
HOF-7a	40 ^[a]	[21]	JLU-SOF3	22.8 ^[b]	This work
JLU-SOF1-R	31.2 ^[b]	[16]	HOF-5a	22.4 ^[e]	[9]
JLU-SOF2	30.0 ^[b]	This work	HOF-6a	21.9 ^[a]	[25]
JLU-SOF1-R	29.3 ^[c]	[16]	HOF-9a	17.8 ^[e]	[18]
JLU-SOF2	29.1 ^[c]	This work	HOF-11a	15.1 ^[a]	[23]
HOF-9a	25.1 ^[d]	[18]	HOF-11a	$13.1^{[f]}$	[23]
JLU-SOF3	23.6 ^[c]	This work			

[a] Predicted at 273 K and 1 bar for a 15:85 mixture; [b] Calculated at 298 K and 1 bar for a 15:85 mixture; [c] Predicted at 298 K and 1 bar for a 10:90 mixture; [d] Calculated at 273 K and 1 bar for a 10:90 mixture; [e] Measured at 296 K and 1 bar for a 10:90 mixture; [f] Calculated at 296 K and 1 bar for a 15:85 mixture.

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