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Supporting Information

Solvent controlled self-assembly of π-stacked/H-bonded supramolecular organic frameworks from a C_3-symmetric monomer for iodine adsorption

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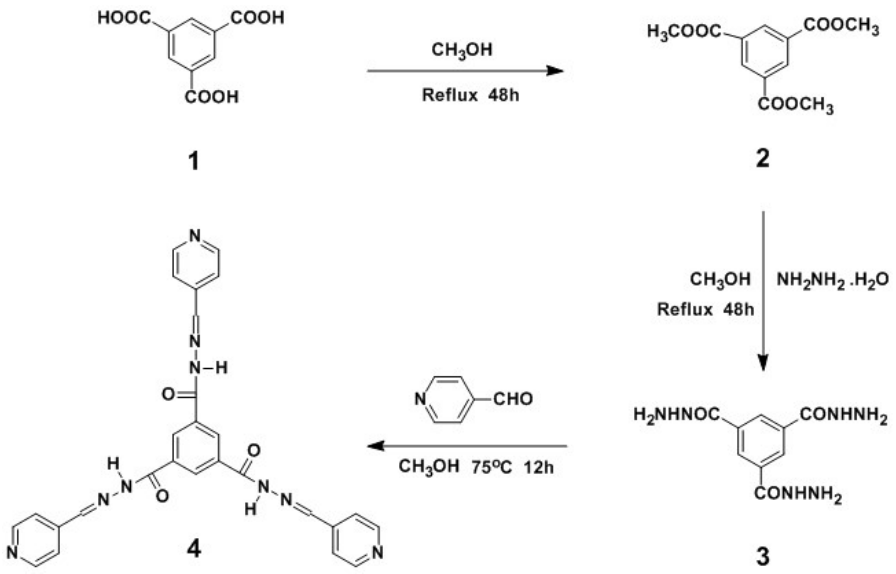
Contents

1. Synthesis



Scheme S1 General synthetic routes.

1.1 Synthesis of trimethyl benzene-1,3,5-tricarboxylate (**2**)

1 (2 g) and TsOH (100 mg) were added into 200 ml CH_3OH, then heated to reflux for 48 h under N_2 atmosphere. Last, the reaction was quenched with a saturated aqueous $NaHCO_3$ solution and the resulting mixture was extracted with diethylether.[1] The organic layer was washed with water and brine, then dried over Na_2SO_4. After that, the solvent were evaporated in vacuo, yielding **2** (2 g) as a white powder. ^1H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 1.5 Hz, 1H), 3.98 (s, 3H).

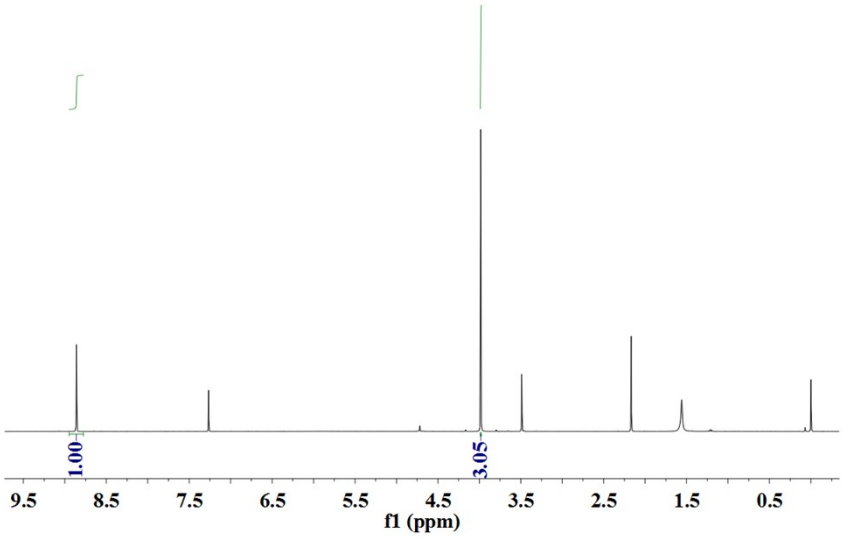


Fig. S1 ^{1}H NMR spectrum of trimethyl benzene-1,3,5-tricarboxylate (**2**).

1.2 Synthesis of benzene-1,3,5-tricarbohydrazide (**3**)

Hydrazine monohydrate (5 ml) was added in portions to a solution of **2** (1 g) in methanol. The mixture was stirred for 48 h under reflux, then filtered and washed with methanol, yielding **3** as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.83 (s, 1H), 8.32 (s, 1H), 4.58 (s, 2H).

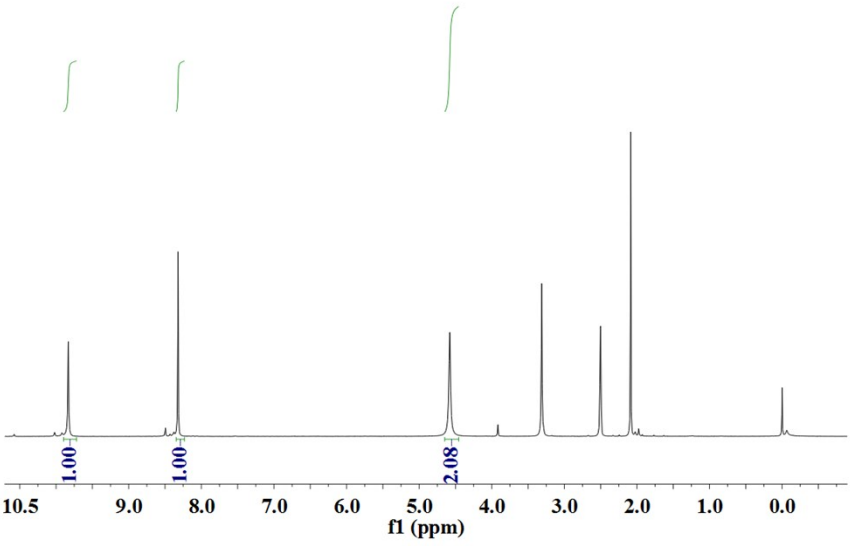


Fig. S2 ^{1}H NMR spectrum of benzene-1,3,5-tricarbohydrazide (**3**).

1.3 Synthesis of N1',N3',N5'-tris((pyridin-4-yl)methylene)benzene-1,3,5-tricarbohydrazide (**4**)

3 (502 mg) and 4-pyridine aldehyde (800 mg) were dispersed in 100 ml methanol, , then the mixture was stirred at boiling temperature for 12 h. Afterwards, filtered and washed with methanol, yielding **4** as a flavescent powder.[2] ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.47 (s, 1H), 8.70 (s, 2H), 8.51 (s, 1H), 7.72 (s, 2H). ^{13}C NMR (400 MHz, DMSO-d_6, ppm): 121.09, 133.87, 141.32, 146.37, 150.31,162.33 ppm.

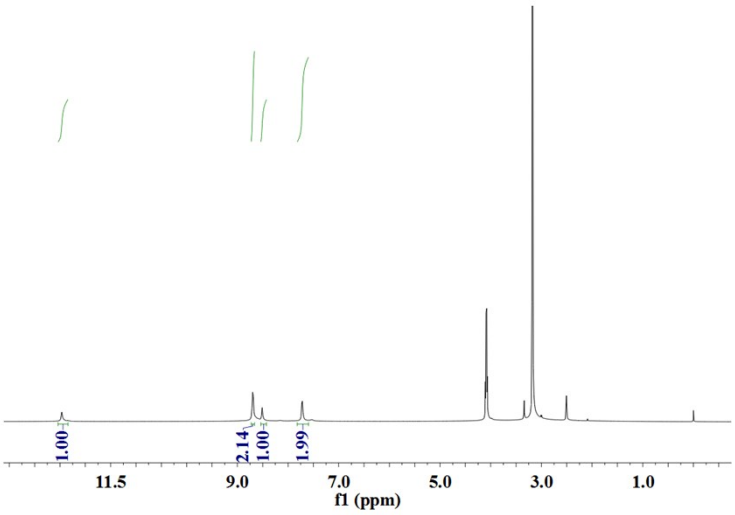


Fig. S3 ^{1}H NMR spectrum of N1',N3',N5'-tris((pyridin-4-yl)methylene)benzene-1,3,5-tricarbohydrazide (**4**).

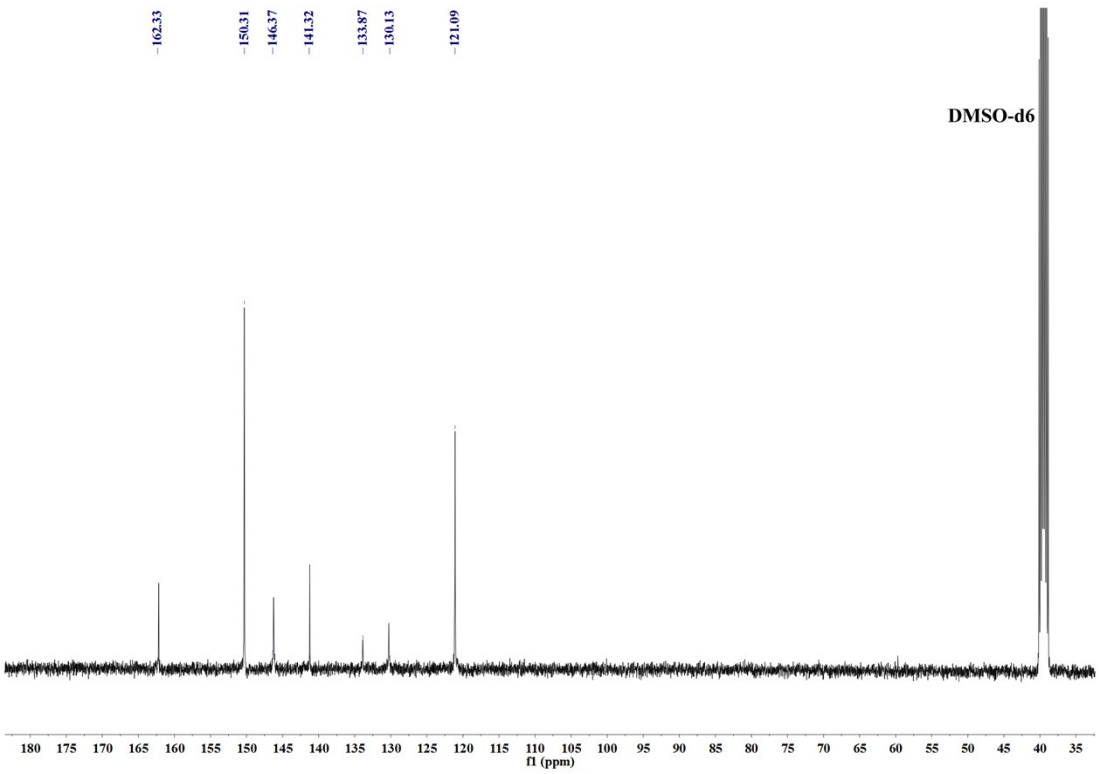


Fig. S4 ^{13}C NMR spectrum of N1',N3',N5'-tris((pyridin-4-yl)methylene)benzene-1,3,5-tricarbohydrazide (**4**).

2. PXRD patterns

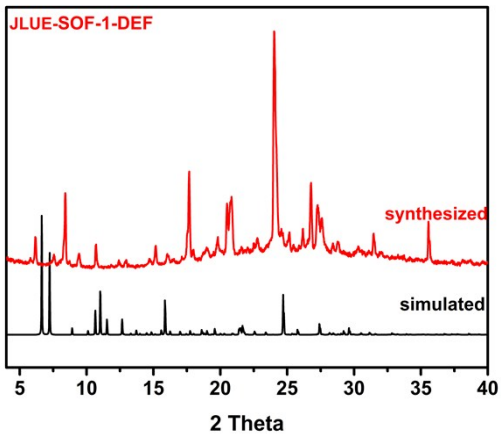


Fig. S5 Simulated and synthesized PXRD patterns of JLUE-SOF-1-DEF.

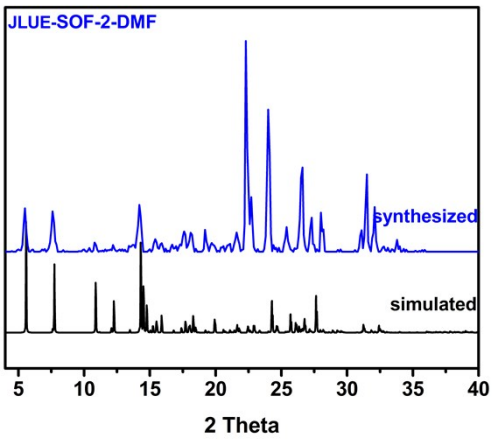


Fig. S6 Simulated and synthesized PXRD patterns of JLUE-SOF-2-DMF.

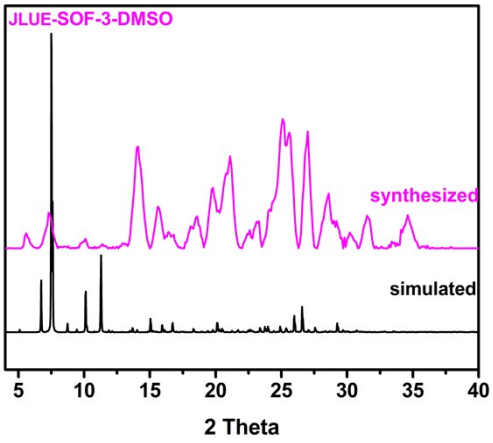


Fig. S7 Simulated and synthesized PXRD patterns of JLUE-SOF-3-DMSO.

3. TGA curves

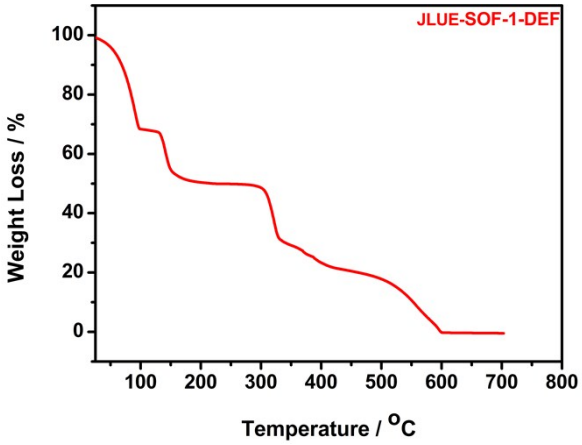


Fig. S8 TGA curve of JLUE-SOF-1-DEF.

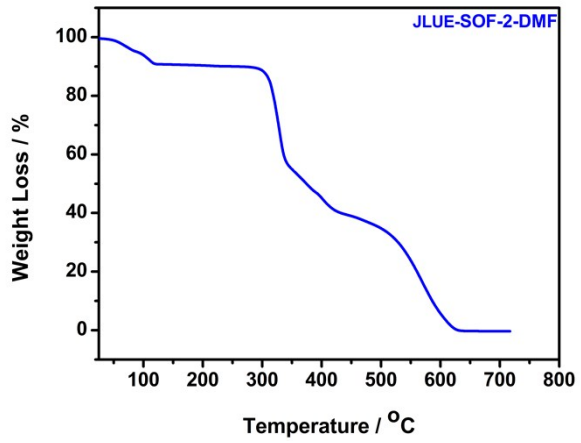


Fig. S9 TGA curve of JLUE-SOF-2-DMF.

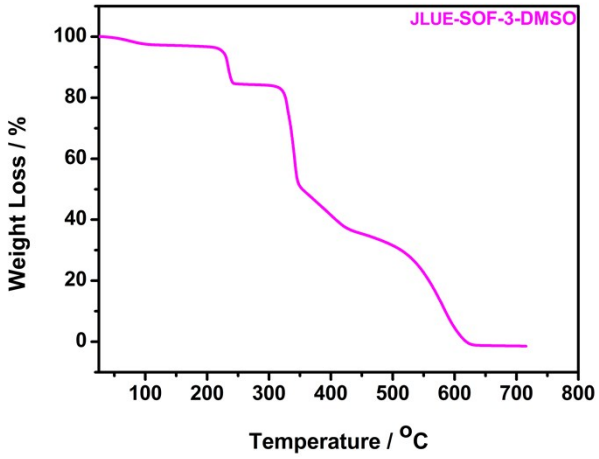


Fig. S10 TGA curve of JLUE-SOF-3-DMSO.

4. FT-IR spectra

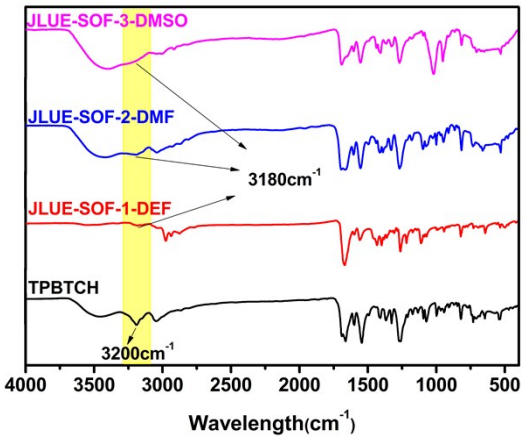


Fig. S11 FT-IR spectra of the TPBTCH monomer, JLUE-SOF-1-DEF, JLUE-SOF-2-DMF and JLUE-SOF-3-DMSO.

5. N_2 adsorption isotherms and pore size distribution

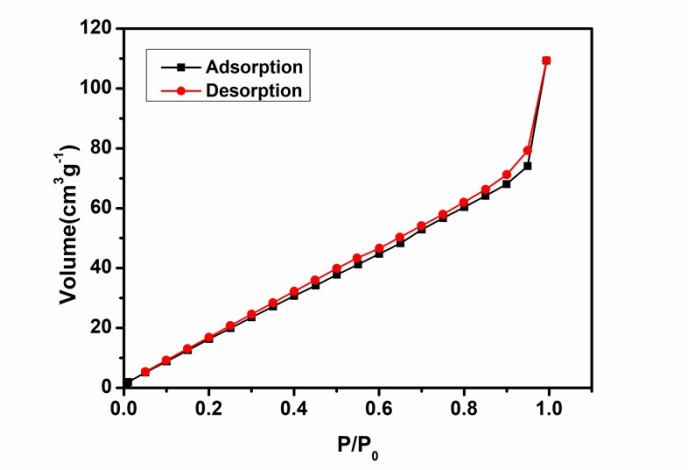


Fig. S12 Nitrogen adsorption and desorption isotherms of JLUE-SOF-3-DMSO measured at 77 K.

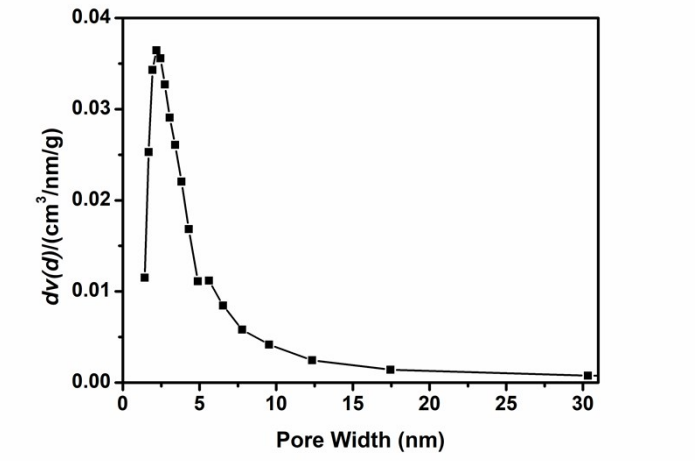


Fig. S13 Pore size distribution of JLUE-SOF-3-DMSO.

6. Crystallographic Data and Hydrogen Bond Data.

Table S1 Crystal data and structure refinement for JLUE-SOFs.

Compound	JLUE-SOF-1-DEF	JLUE-SOF-2-DMF	JLUE-SOF-3-DMSO
Formula	$C_{27}H_{21}N_9O_3(C_5NO_4)$	$C_{27}H_{21}N_9O_3(O_4)$	$C_{27}H_{21}N_9O_3(C_6O_5S)$
F.w.	657.59	583.53	703.65
T (K)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P-1*	*P-1*	*P-1*
a (Å)	10.1382(11)	7.4872(6)	11.9851(17)
b (Å)	12.7716(14)	12.4001(10)	12.2632(17)
c (Å)	13.5128(4)	17.0797(13)	13.7369(19)
α (°)	79.967(2)	109.166(2)	94.016(2)
β (°)	89.142(2)	99.619(2)	112.728(2)
γ (°)	76.356(2)	93.273(2)	103.896(2)
V (Å^3)	1673.7(3)	1466.1(2)	1777.6(4)
Z	2	2	2
Dc (g/cm^3)	1.305	1.322	1.315
μ (mm^{-1})	0.096	0.099	0.153
Data collected/uniq. (R_{int})	8458 / 4783 (0.0239)	8084 / 5692 (0.0626)	8773 / 6144 (0.0310)

R^a, R_w^b [$I > 2\sigma(I)$]	**0.0719, 0.2265**	**0.0654, 0.2061**	**0.0889, 0.2729**
GOF	**1.086**	**1.033**	**1.057**

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b] $R_w=[\Sigma_w(F_o^2-F_c^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$.

Table S2 Hydrogen Bond Data for JLUE-SOF-2-DMF.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(7)-H(7)...O(2)#1	**0.86**	**2.02**	**2.8320(16)**	**157.0**

Symmetry codes: #1 -x+1,-y+1,-z+2.

Table S3 Hydrogen Bond Data for JLUE-SOF-3-DMSO.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4A)...N(9)#1	**0.86**	**2.21**	**3.022(2)**	**157.0**
N(7)-H(7)...O(2)#2	**0.86**	**2.06**	**2.8990(17)**	**164.8**

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

7. Iodine adsorption experiments

The adsorption related fundamental functions 1 and 2 were as shown below [3]:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

where q_e (mg/g) represents the adsorbed amount of iodine, C_0 (mg/L) represents the initial iodine concentration, C_e (mg/L) represents the final equilibrium iodine concentration, m (g) represents the quantity of JLUE-SOF-3-DMSO used, V (L) represents the volume of hexane treated, E (%) represents the removal efficiency for iodine by JLUE-SOF-3-DMSO.

7.1 Adsorption dynamics analysis

The experimental data for JLUE-SOF-3-DMSO towards iodine adsorption were processed by pseudo-first-order kinetic model, pseudo-second-order kinetic model and intraparticle diffusion model according to the following functions [4]:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

$$q_t = k_i t^{1/2} + C \tag{5}$$

where q_t (mg/g) and q_e (mg/g) represent the adsorbed iodine amounts at regular intervals and equilibrium time, respectively; k_1 (1/h) and k_2 ((g/mg/h) represent the pseudo-first-order kinetic rate constant and the pseudo-second-order kinetic rate constant, respectively; k_i (mg/g/h$^{1/2}$) represents the intraparticle diffusion rate constant, and C (mg/g) represents the intercept.

7.2 Adsorption isotherms analysis

In order to understand the adsorption mechanism of iodine by the JLUE-SOF-3-DMSO, the two most familiar adsorption isothermal models, i.e., Langmuir isotherm and Freundlich isotherm, corresponding with monolayer adsorption process and multilayer adsorption process, respectively, were adopted to analyze the isothermal curves [1]:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L} \tag{6}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

Where q_e (mg/g) and C_e (mg/L) represent the same meaning as above, K_L (L/g) and a_L (L/mg) represent the Langmuir adsorption isotherm constants, K_F and n represent the Freundlich adsorption isotherm constants.

Additionally, known as the unit-less equilibrium parameter, the values of separation factor "R_L" can be used to predict the shape of the adsorption isotherm using the following equation[5]:

$$R_L = \frac{1}{1 + a_L C_0} \quad (8)$$

Where C_0 (mg/L) and a_L (L/mg) represent the initial iodine concentration and the Langmuir binding constant. Accordingly, $R_L > 1$ (unfavourable), $R_L = 1$ (linear), $0 < R_L < 1$ (favourable) or $R_L = 0$ (irreversible).

Table S4 Kinetic parameters of iodine adsorption by JLUE-SOF-3-DMSO.

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Removal Efficiency (%)	Pseudo-first order kinetics			Pseudo-second order kinetics		
			k_1 (1/h)	$q_{e1,cal}$ (mg/g)	R^2	k_2 (g/mg/h)	$q_{e2,cal}$ (mg/g)	R^2
75	74.9	99.8	0.359	48.4	0.95	0.006	89.3	0.99
100	89.4	89.4	0.296	76.7	0.98	0.005	103.0	0.99
125	111.1	88.8	0.199	99.5	0.98	0.003	124.8	0.99
150	131.4	87.6	0.157	116.7	0.98	0.002	138.1	0.99

Table S5 Intraparticle diffusion model parameters for the adsorption of iodine by JLUE-SOF-3-DMSO.

C_0 (mg/L)	Intraparticle diffusion model					
	$k_{i,1}$ (mg/g/h$^{1/2}$)	C_1 (mg/g)	R^2	$k_{i,2}$ (mg/g/h$^{1/2}$)	C_2 (mg/g)	R^2
75	24.3	9.6	0.96	0.5	72.1	0.93
100	27.9	8.8	0.98	2.30	78.3	0.90
125	33.9	3.7	0.99	5.6	81.5	0.83
150	36.3	3.6	0.99	8.8	82.3	0.98

Table S6 Langmuir and Freundlich isotherm parameters for iodine adsorption by JLUE-SOF-3-DMSO.

	Temperature (K)	Q_m	K_F	K_L	1/n	R_L	R^2
Langmuir isotherm	298	207	——	28.6	——	0.028~0.134	0.99
Freundlich isotherm	298	——	50.2	——	0.31	——	0.95

Table S7 Iodine adsorption properties of porous materials.

No.	Adsorbent	Temperature [°C]	S_{BET} [m^2/g]	Equilibrium Time [h]	Adsorption Capacity [mg/g]	References
1.	JLUE-SOF-3-DMSO	25	81	8	207	This work
2.	UiO-66	25	1015	24	401	[6]
3.	pha-COP-1	25	217	120	833	[7]
4.	UiO-66-PYDC	25	1030	24	1250	[6]

8. Solubility Table

Table S8 Solubility of TPBTCH monomer in different solvents.

No.	Solvent	Temperature [°C]	Solubility [mg/mL]
1.	DEF	25	10
2.	DMF	25	20
3.	DMSO	25	50

9. Reference

[1] J. Dong, F. F. Xu, Z. J. Dong, Y. S. Zhao, Y. Yan, H. Jin and Y. X. Li, *RSC Adv.,* 2018, **8**, 19075–19084.

[2] C. He, Z. Lin, Z. He, C. Duan, C. Xu, Z. Wang and C. Yan, *Angew. Chem. Int. Ed.*, 2008, **47**, 877–881.

[3] L. Merí-Bofí, S. Royuela, F. Zamora, M. L. Ruiz-González, J. L. Segura, R. Muñoz-Olivas and M. J. Mancheño, *J. Mater. Chem. A*, 2017, **5**, 17973–17981.

[4] R. Wen, Y. Li, M. C. Zhang, X. H. Guo, X. Li, X. F. Li, J. Han, S. Hu, W. Tan, L. J. Ma and S. J. Li, *J. Hazard. Mater.*, 2018, **358**, 273–285.

[5] D. D. Lu, Q. L. Cao, X. J. Cao and F. Luo, *J. Hazard. Mater.*, 2009, **166**, 239–247.

[6] Z. Wang, Y. Huang, J. Yang, Y. S. Li, Q. X. Zhuang and J. L. Gu, *Dalton Trans.,* 2017, **46**, 7412–7420.

[7] L. Lin, H. D. Guan, D. L. Zou, Z. J. Dong, Z. Liu, F. F. Xu, Z. G. Xie and Y. X. Li, *RSC Adv.,* 2017, **7**, 54407–54415.