

Electronic Supporting Information for:

**A robust *etb*-type metal-organic framework showing
polarity-exclusive adsorption of acetone over methanol for
their azeotropic mixture**

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1. Materials and General Procedures.

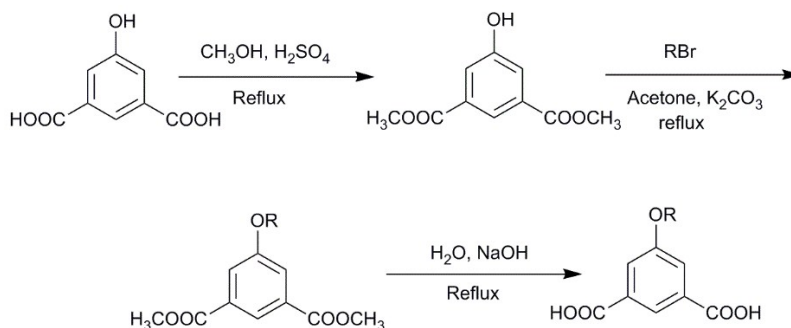
All reagents were purchased from commercial sources and used without further purification. Thermogravimetric (TGA) analyses were investigated on a Mettler Toledo TGA/SDTA 851 analyzer under N₂ flow from room temperature to 800 °C with a heating rate of 10 °C·min⁻¹. Elemental analysis was measured on an Elementar Vario EL III microanalyzer. Powder X-ray diffraction (PXRD) patterns were measured using a Bruker D8 powder diffractometer at 40 kV, 40 mA for Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at air atmosphere, with a scan speed of 0.2 s/step and a step size of 0.05 °(2 θ). Diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) was performed on a Nicolet 6700 FTIR spectrometer equipped with an *in situ* reaction cell (Harrick Scientific Products, INC). The absorbance spectra were obtained by collecting 120 scans at 4 cm⁻¹ resolution. Before measurement, sample was activated at 473 K for 4 h, then cooled to 298 K. After the collection of background spectrum, the sample was exposed to the corresponding vapor for 1 h under different pressure. The components of liquid after pervaporation separation was analyzed on Thermo Focus DSQII gas-chromatography-mass spectrometer equipment using HP-Innowax (30 m \times 0.25 mm \times 0.25 μ m) column with a split ratio of 30:1, along with electrospray ionization (EI) method for mass spectrometric detection. The temperature program consisted of the following steps: holding 60 °C for 2 min, then ramping to 250 °C with a heating rate of 30 °C·min⁻¹ and holding for 10 min.

Volumetric nitrogen adsorption/desorption were measured on Micromeritics ASAP 2020 at 77 K. Before measurement, about 120 mg sample was activated (473 K in

vacuum condition) for 8 hours. Vapor sorption of CH_3OH and CH_3COCH_3 was respectively carried out on HIDEN IGA-002 adsorption apparatus. The temperature was controlled by an external water bath. Virial fittings and adsorption enthalpy plot were obtained using virial method, which is discussed in Calculation Method section. Dual-site Quadratic fittings and necessary equations for selective gas adsorption by using ideal adsorbed solution theory (IAST) method are given in IAST Calculation section.

Experiment methods

The H₂eoip and H₂poip were synthesized according to the route shown in below, which was modified according to a reported method. [1]

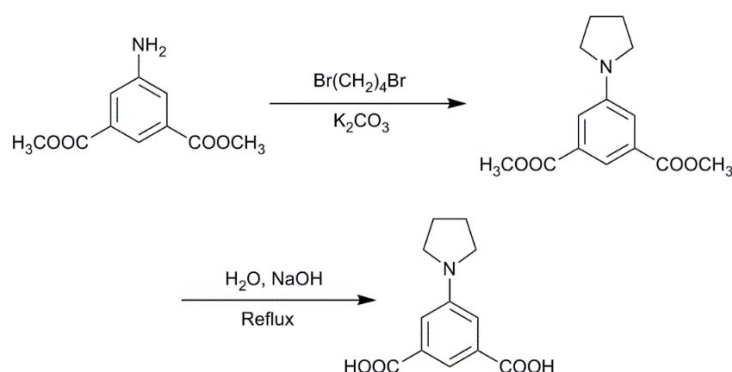


Synthesis of H₂eoip (H₂L1). A mixture of 5-Hydroxyisophthalic acid (3.65 g, 20 mmol) and concentrated sulfuric acid (10 mL) in methanol (100 mL) was heated to reflux for 5 h. The reaction solution was poured into water (500 mL) and the white product was filtered off after modulating pH value to 7 using NaHCO₃. Dimethyl 5-hydroxyisophthalate (2.1 g, 10 mmol), bromoethane (1.64 g, 15 mmol) and K₂CO₃ (1.4 g, 10 mmol) in acetone (50 mL) was heated to reflux for 20 h. After removing dissolution, the white product was then dissolved by ethyl acetate and washed by saturated NaHCO₃ solution and deionized water for 3 times respectively. Product by rotary evaporation, NaOH (4 g) and water (50 mL) was added in a round-bottomed flask and stirred for 24 h. The solution was acidified with HCl (4 mmol/L). White precipitate was collected, washed by distilled water and recrystallized from distilled water. ¹H NMR (400 MHz, DMSO-*d*₆) δ ppm: 8.07 (s, 1H), 7.62 (s, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 6.8 Hz, 3H).

Synthesis of H₂poip (H₂L2). The synthesis procedure of H₂poip was similar to that of H₂eoip, except replacing bromoethane by bromopropane. ¹H NMR (400 MHz, DMSO-*d*₆) δ ppm: 8.07 (s, 1H), 7.65 (s, 2H), 4.04 (t, *J* = 6.4 Hz, 2H), 1.76 (m, 2H), 0.99 (t, *J* =

7.2 Hz, 3H).

The H₂pyip was synthesized according to the route shown below:



Synthesis of H₂pyip (H₂L3). A mixture of dimethyl 5-aminoisophthalate (4.18 g, 20 mmol), 1,4-dibromobutane (25.9 g, 120 mmol) and K₂CO₃ (16.8 g, 120 mmol) in ethanol (100 mL) and water (25 mL) mixture solution was heated to reflux for 20 h. After rotary evaporation, the product was purified by silica-gel column chromatography to afford 5-(pyrrolidin-1-yl)isophthalate. The product was added in a round-bottomed flask with NaOH (4 g) and water (50 mL) and stirred for 24 h. The solution was acidified with HCl (4 mmol/L). White precipitate was collected, washed by distilled water and recrystallized from distilled water. ¹H NMR (400 MHz, CDCl₃) δ ppm: 7.95 (s, 1H), 7.38 (s, 2H), 3.37 (t, *J* = 7.2 Hz, 4H), 2.06 (m, 4H).

Synthesis of [Zn₂(eoip)₂·H₂O]_n (1). Zn(OAc)₂·2H₂O (0.025 g, 0.1 mmol) and H₂eoip (0.021 g, 0.1 mmol) was added to the mixed solution of water (8 mL) and methanol (2 mL). Then the mixture was stirred at room temperature for 2 hours, and then the white mixture was transformed into Teflon-lined stainless steel autoclave (15 mL) and heated at 140 °C for 3 days, followed by cooling down to room temperature. Colorless rod-like crystals were collected by filtration. Yields: 55 % based on H₂eoip. Elemental analysis calc. (%) C 42.51, H 3.21, Found (%) C, 42.50, H 3.23.

Synthesis of $[\text{Zn}_2(\text{poip})_2 \cdot \text{H}_2\text{O}]_n$ (2). The synthesis procedure of **2** was similar to that of **1**, except replacing H_2eoip with H_2poip . Colorless rod-like crystals were collected by filtration. Yields: 62 % based on H_2poip . Elemental analysis calc. (%) C 44.70, H 3.41, Found (%) C, 44.68, H 3.45.

Synthesis of $[\text{Zn}(\text{pyip})]_n$ (3). The synthesis procedure of **3** was similar to that of **1**, except replacing H_2eoip with H_2pyip . Colorless rod-like crystals were collected by filtration. Yields: 77 % based on H_2pyip . Elemental analysis calc. (%) C 48.27, H 3.71, N 4.69. Found (%) C, 42.25, H 3.74, N 4.71.

Fabrication of MOF/membrane. The metal-organic frameworks / polyvinylidene fluoride (MOF/PVDF) composite membranes were fabricated by a one-step immersion co-precipitation method reported before. Activated **1** and PVDF, polyvinylpyrrolidone (PVP) were primarily degassed and dried at 110 °C for 8 h to remove residual water in polymer and frameworks. PVDF (17 wt.%), PVP (4 wt.%) and dimethylacetamide (DMAC, 79 wt.%) were added to a flask and stirred by mechanical agitation at 250 rpm for 24 h under 70°C to form uniform solvent. Then different amounts of the synthesized **1** (1-5 wt.%) were added into the polymer solution with 31 wt.% DMAC and then stirred for 24 h. The solution was smeared onto a smooth glass sheet with a JFA-II film applicator to form membrane with uniform thickness, and then the glass sheet was immersed into deionized water/ethanol solution with a volume ratio of 1:1. After immersed in the solution for 60 s, the generated membrane was peeled off from the glass substrate and airing at room temperature for 1 h. Finally, the obtained membrane was thoroughly washed with deionized water to remove residual solvent and dried at

room temperature. The obtained membranes with different contents of the MOF (1, 2, 3, 4, 5 wt.% based on the casting solution weight) are denoted as MOF/PVDF-1, 2, 3, 4, 5, respectively. For comparison, neat PVDF membrane without fillers was also prepared.

Measurement of Membrane Separation Selectivity. The synthesized MOF/PVDF membranes were cropped as small wafers to fix the detachable filter. Then the collected methanol/acetone azeotrope was added in a round-bottomed flask connected to a cold trap with the loaded detachable filter as junction. Then a pump connected to the cold trap was used to obtain low pressure at 0.3 bar. Resulted mixture was collected in the cold trap after the low pressure maintained for 10 minutes and then analyzed on Thermo Focus DSQII gas-chromatography-mass spectrometer equipment using biphenyl as interior standard substance.

Performance of Separation. The main parameters to measure the performance of membranes are permeation flux (J) and separation factor (α). The parameters can be calculated by the following equations:

$$J = \frac{\Delta G}{S \cdot \Delta t}$$

In this equation, ΔG is the amount of penetration in mg during the penetration time Δt in s, S is the area of membrane in cm^2 .

$$\alpha_{i/j} = \frac{Y_i/Y_j}{X_i/X_j}$$

In this equation, X and Y represents the fraction of methanol and acetone, respectively.

The subscript i and j represents the fraction in crude solution and resulted solution, respectively.

2. X-ray Crystallographic Study

Data collection for **1** and **3** were carried out on a Bruker Apex II diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature, while data collection for **2** was carried out on a Bruker Apex Duo diffractometer with graphite monochromated Ga K α radiation ($\lambda = 1.34139 \text{ \AA}$). Data reduction was performed with SAINT, and empirical absorption corrections were applied by SADABS program. Structures were solved by direct method using SHELXS program and refined with SHELXL program.^[2] Heavy atoms and other non-hydrogen atoms were directly obtained from difference Fourier map. Final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2 . C-bonded H atoms were placed geometrically and refined as riding modes. Crystallographic data are listed in Table S1, for detailed bond length and angles, please see in CIFs.

3. The calculation of enthalpy and IAST

Calculation of adsorption enthalpy

Before calculation of adsorption enthalpy, the isotherms of methanol were fitted using dual-site Quadratic models as given below:

$$n_i^0(P) = M_1 \frac{(K_{A1} + 2K_{B1}P)P}{1 + K_{A1}P + K_{B1}P^2} + M_2 \frac{(K_{A2} + 2K_{B2}P)P}{1 + K_{A2}P + K_{B2}P^2}$$

Where n corresponds to the adsorbed amount in mmol/g, P is the pressure in bar, M_i is the number of adsorption sites of type i , K_{Ai} (units: pressure⁻¹) and K_{Bi} (units: pressure⁻²) are constants.

The isotherms of acetone for **1** were fitted using Freundlich model given below:

$$n(P) = Q \frac{(a \times P)^{1/b}}{(1 + a \times P)^{1/b}}$$

Where n corresponds to the adsorbed amount in mmol/g, P is the pressure in bar, Q , a and b are constants.

The virial method was employed to calculate the enthalpies of the adsorption for methanol and acetone (298 K) on compound **1**, **2** and **3**. In each case, the data were fitted using the following equation:

$$\ln P = \ln N + 1/T \sum_{i=0}^m a_i N^i + \sum_{i=0}^m b_i N^i$$

In this equation, P is the pressure in mbar, N is the adsorbed amount in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, m and n are the number of coefficient required to describe the isotherms. The adsorption enthalpy is calculated using the following equation:

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

Where R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and Q_{st} is the adsorption enthalpy.

IAST calculation

Proposed by Myers and Prausnitz in 1965, ^[3] ideal adsorbed solution theory (IAST) is widely used to predict multi-component adsorption isotherms from respective pure-component adsorption isotherms at the same pressure. IAST simulation is based on the assumption that the adsorbed species form an ideal mixture, which is a reasonable approximation in many systems. In this case, we utilized a python package, pyIAST, developed by Simon and Smit, ^[4] to perform IAST calculations to predict azeotropic mixture adsorption of methanol and acetone from respective pure-component adsorption isotherms. Before calculation of the sorption and separation properties, the isotherms of methanol and acetone for **1**, **2** and **3** were fitted using dual-site Quadratic models discussed above.

Table S1. Crystal structure parameter and refinement data of **1**, **2** and **3**.

	1	2	3
Empirical formula	C ₂₀ H ₁₈ O ₁₁ Zn ₂	C ₂₂ H ₂₀ O ₁₁ Zn ₂	C ₁₂ H ₁₁ NO ₄ Zn
Formula weight	565.08	591.12	298.59
Crystal system	Trigonal	Trigonal	Trigonal
Space group	<i>R</i> -3	<i>R</i> -3	<i>R</i> -3m
<i>a</i> / Å	27.684(5)	27.660(7)	28.868(7)
<i>b</i> / Å	27.684(5)	27.660(7)	28.868(7)
<i>c</i> / Å	18.006(5)	17.978(5)	8.261(3)
<i>V</i> / Å ³	11951(5)	11912(7)	5962(4)
<i>Z</i>	18	18	18
<i>D</i> _{calc} / g·cm ⁻³	1.413	1.483	1.497
μ / mm ⁻¹	1.855	1.779	1.858
<i>F</i> (000)	5148	5400	2736
Data / restraints / parameters	4788 / 27 / 307	5186 / 99 / 354	1271 / 0 / 87
GOF on <i>F</i> ²	1.018	1.101	1.175
<i>R</i> ₁ ^a / w <i>R</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0408 / 0.1162	0.0421 / 0.1227	0.0336 / 0.1092
<i>R</i> indices (all data)	0.0496 / 0.1205	0.0492 / 0.1287	0.0406 / 0.1111
$\Delta\rho_{\max}$ / $\Delta\rho_{\min}$	0.658 / -0.635	0.933 / -0.529	0.687 / -0.294
CCDC	1898403	1898404	1898405

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = [\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}]^{1/2}$$

Table S2. Theoretical surface area calculated by solvent surface simulation for **1**, **2** and **3** (1.84 Å as radius for probe atom, 2 × 2 × 2 supercell).^[5]

	Accessible Surface Area (Å ² /cell)	D _{calc} (g/cm ³)	Volume (Å ³)	Theoretical Surface Area (m ² /g)
1	781.02	1.413	11951	475.84
2	349.63	1.483	11912	197.91
3	230.74	1.497	5962	258.51

$$\text{Theoretical Surface Area} = \text{Accessible Surface Area} / (D_{\text{calc}} \times \text{Volume}) \times 10^4 \text{ m}^2/\text{g}$$

Figure S1. (a) Structural motif of **1** (hydrogen atoms are omitted for clarity), symmetry code: A: $1/3-x, 1/3-y, 1/3-z$; B: $4/3-x+y, 2/3-x, -1/3+z$; C: $-1/3+x-y, -2/3+x, 1/3-z$; (b) 1D helical chain formed by Zn and carboxylate groups in **1**; (c) Connolly surface simulation for porous structure of **1** (1.84 Å as radius for probe atom, $2 \times 2 \times 2$ supercell, the blue surface shows the Connolly surface).

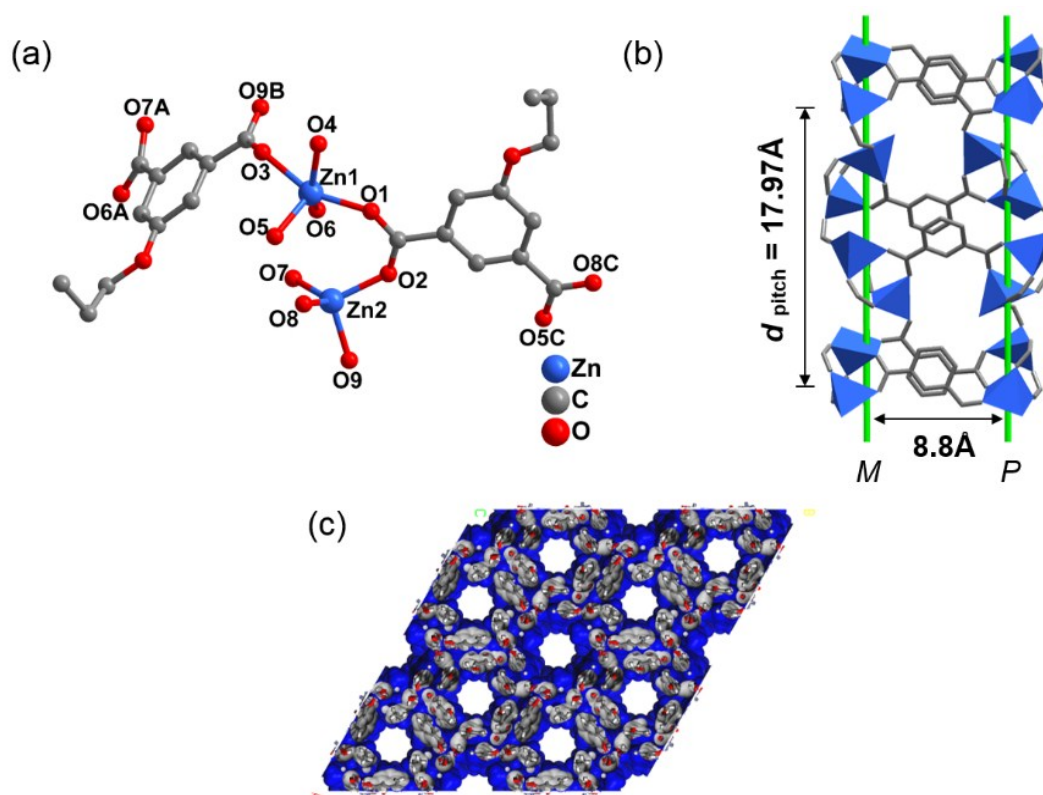


Figure S2. (a) The temperature-dependent PXRD patterns for **1**; (b) The TG curve of **1** (black for as-made sample, red for sample after degassing); (c) The PXRD patterns for **1** soaked in water.

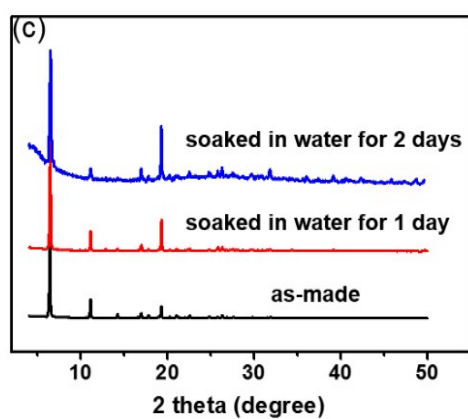
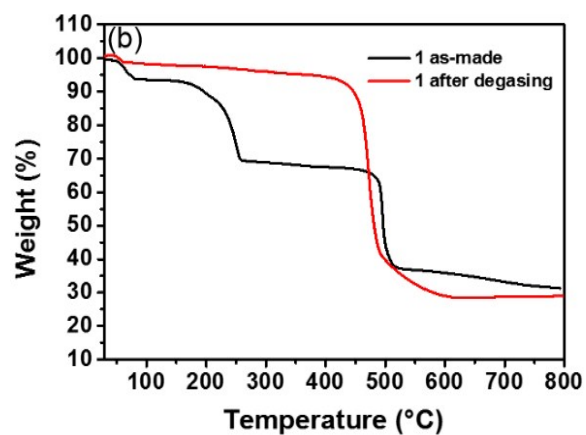
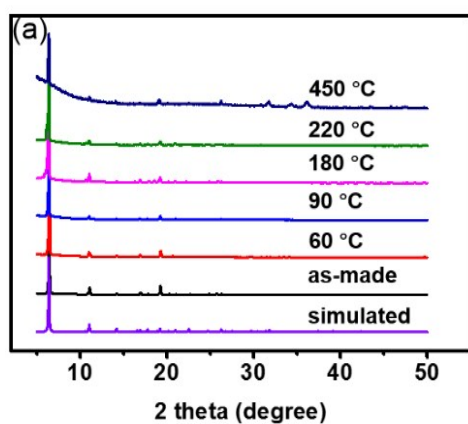
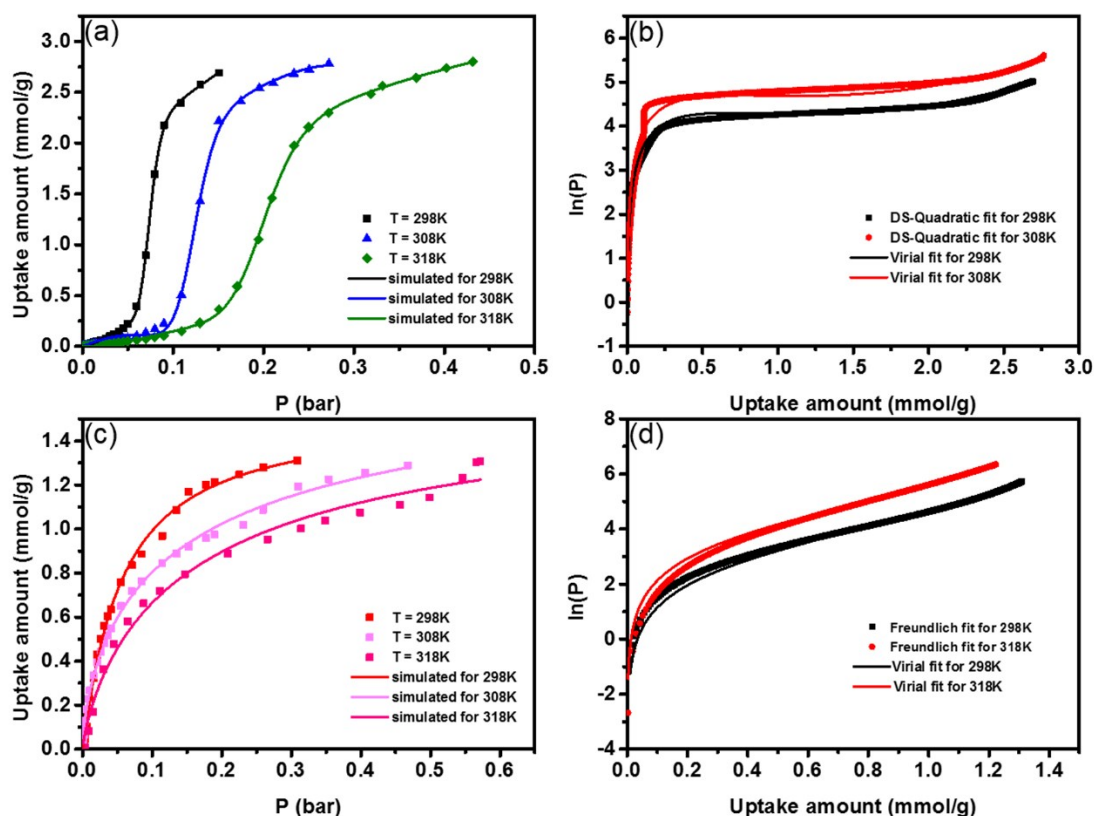


Figure S3. (a) Simulation of methanol adsorption isotherms for **1** at 298 K, 308 K and 318 K; (b) Virial fit for methanol adsorption isotherms for **1** at 298K and 308K; (c) Simulation of acetone adsorption isotherms for **1** at 298 K, 308 K and 318 K; (d) Virial fit for acetone adsorption isotherms for **1** at 298 K and 318 K.



Methanol							
	R ²	M ₁	M ₂	K _{A1}	K _{A2}	K _{B1}	K _{B2}
298K	0.99974	0.18389	1.6308	-25.90666	3.08	181.10449	79.54837
308K	0.99917	-2.16319	0.23916	-3.3135	-15.1859	3.77465	63.57021
318K	0.99979	0.19649	1.67293	-9.38151	1.09507	24.3759	10.43562

Acetone				
	R ²	Q	a	b
298K	0.99650	1.62396	17.97584	0.94424
308K	0.99718	1.88015	6.49211	1.47082
318K	0.99489	1.30513	11.35711	1.00099

Q _{st}						
	R ²	a ₀	a ₁	a ₂	a ₃	b
methanol	0.94301	-3297.2391	-733.8598	228.2068	-14.15872	17.08409
acetone	0.99088	-4679.6834	365.8138	-123.3275	159.75512	19.0331

Figure S4. IAST calculation for **1** at different pressure and different molar fraction for methanol (red for azeotropic mixture).

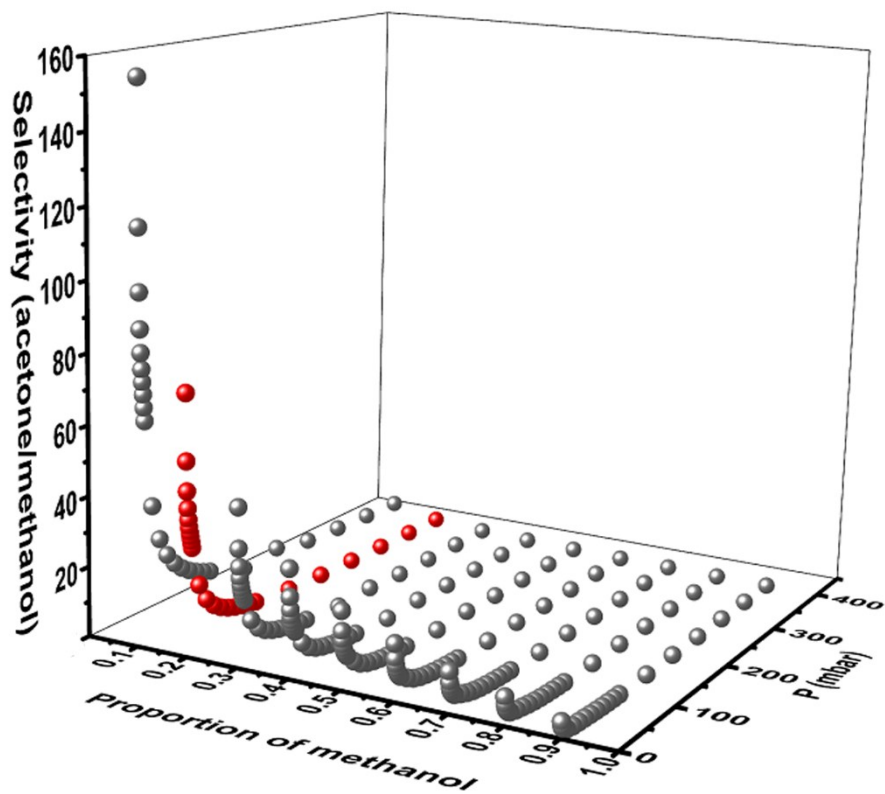


Figure S5. (a) Structural motif of **2** (hydrogen atoms are omitted for clarity) symmetry code: A: $1-x, 2-y, 1-z$; B: $1/3-x+y, 5/3-x, -1/3+z$; C: $1+x-y, x, 1-z$; (b) 1D channel of **2** along c axis; (c) 3D structure of **2** showing the pore surface decorated with flexible propoxy group (in olive space filling model); (d) Connolly surface simulation for porous structure of **2** (1.84 \AA as radius for probe atom, $2 \times 2 \times 2$ supercell, the blue surface shows the Connolly surface).

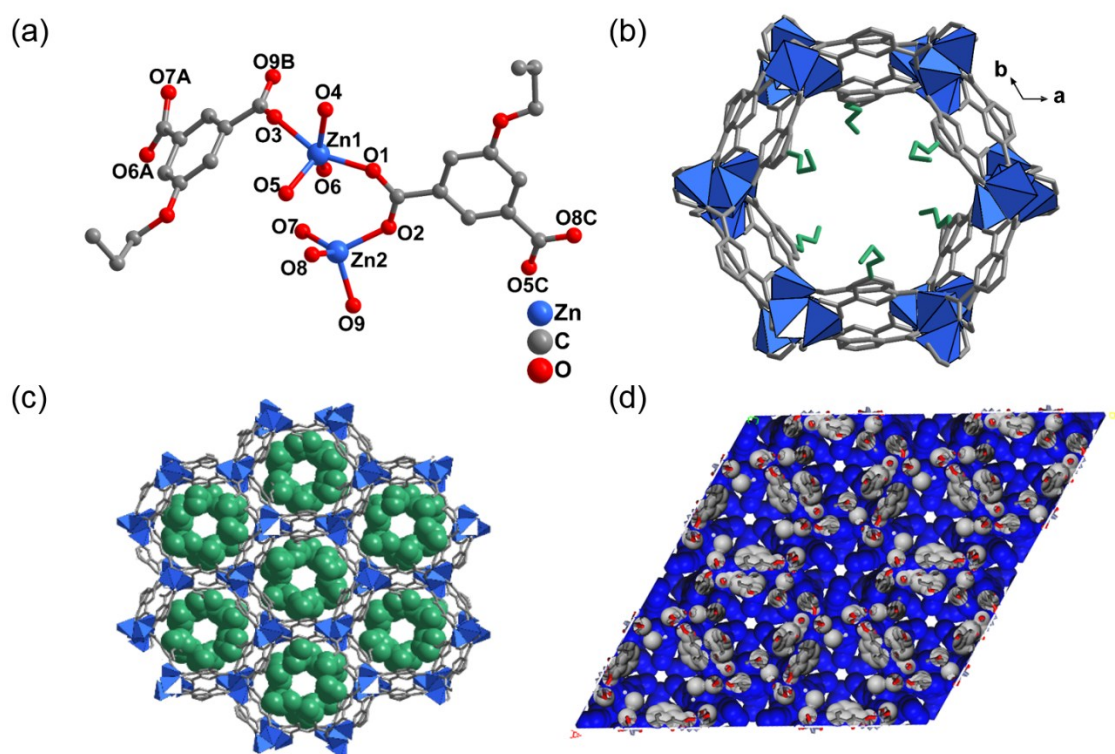


Figure S6. (a) The temperature-dependent PXRD patterns for **2**; (b) The TG curve of **2**.

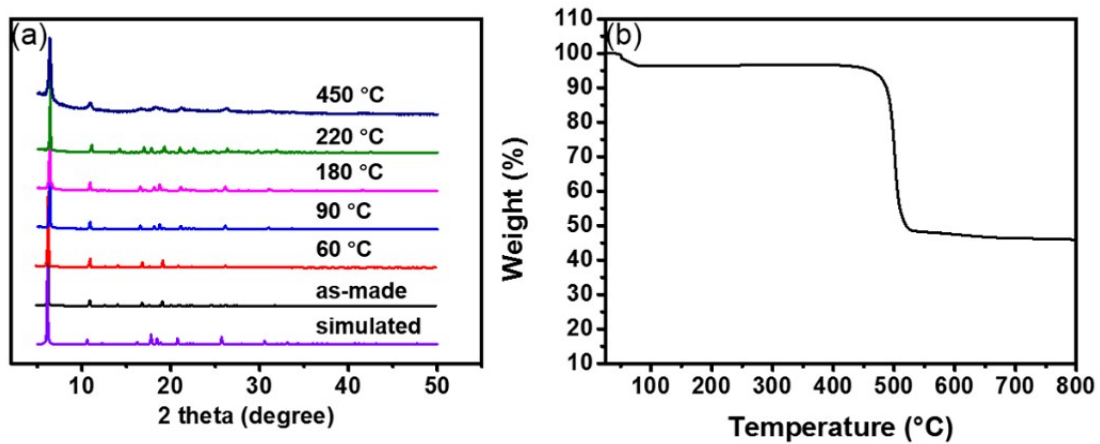


Figure S7. Methanol (black) and acetone (red) adsorption isotherms for **2** at 298 K.

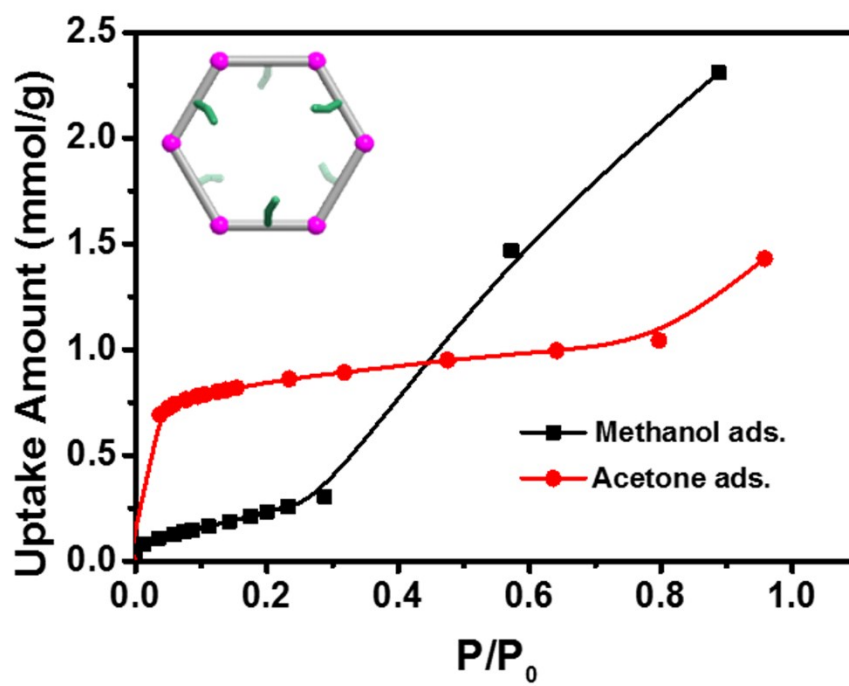


Figure S8. (a) Structural motif of **3** (hydrogen atoms are omitted for clarity) symmetry code: A: $2/3-x, 1/3-x+y, 4/3-z$; B: $2/3-x+y, 1/3-x, 1/3+z$; C: $x-y, -y, 1-z$; D: $x, x-y, z$; (b) 1D channel of **3** along c axis; (c) 3D structure of **3** showing the pore surface decorated with robust pyrrolidinyll group (in orange space filling model); (d) Connolly surface simulation for porous structure of **3** (1.84 \AA as radius for probe atom, $2 \times 2 \times 2$ supercell, the blue surface shows the Connolly surface).

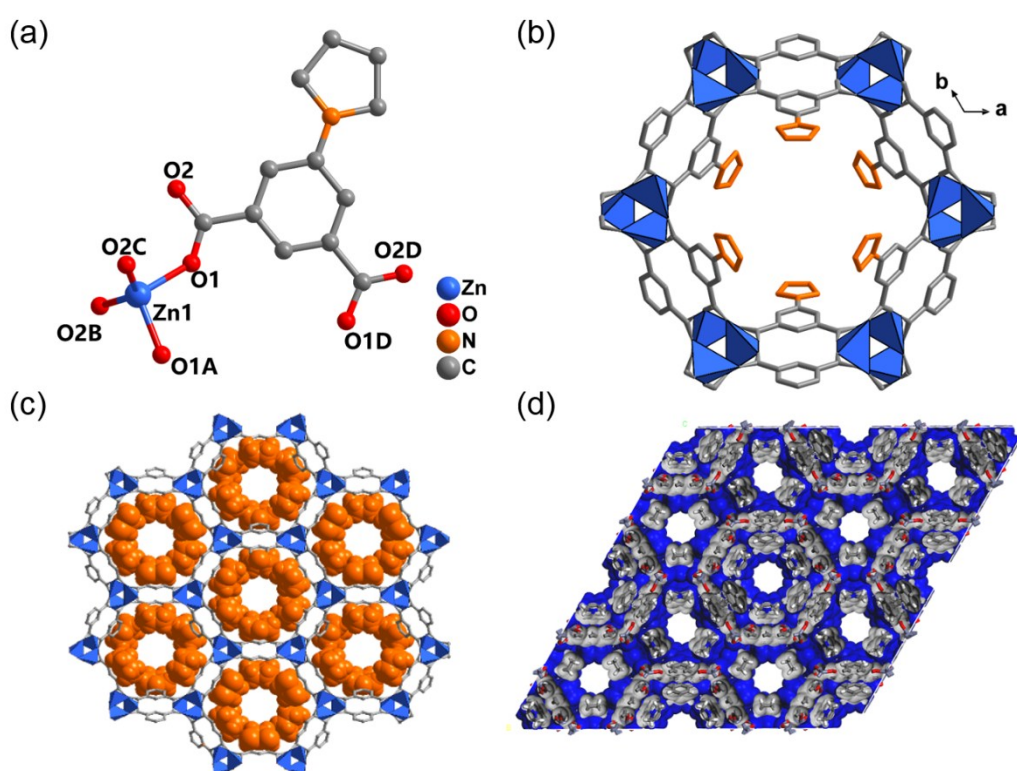


Figure S9. (a) The temperature-dependent PXRD patterns for **3**; (b) The TG curve of **3**.

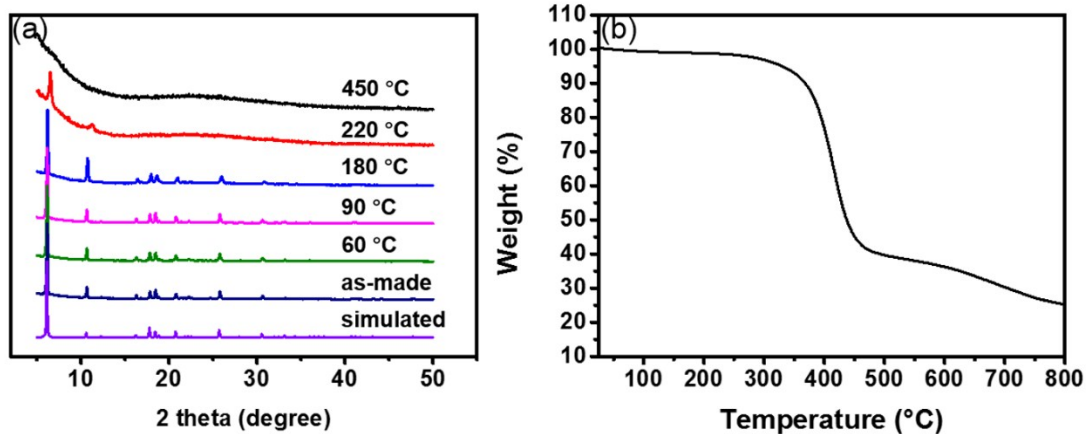


Figure S10. Methanol (black) and acetone (red) adsorption isotherms for **3** at 298 K.

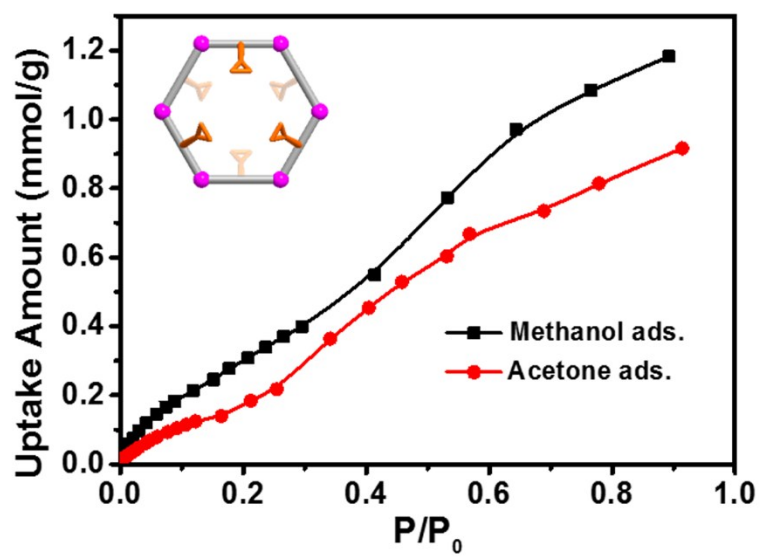
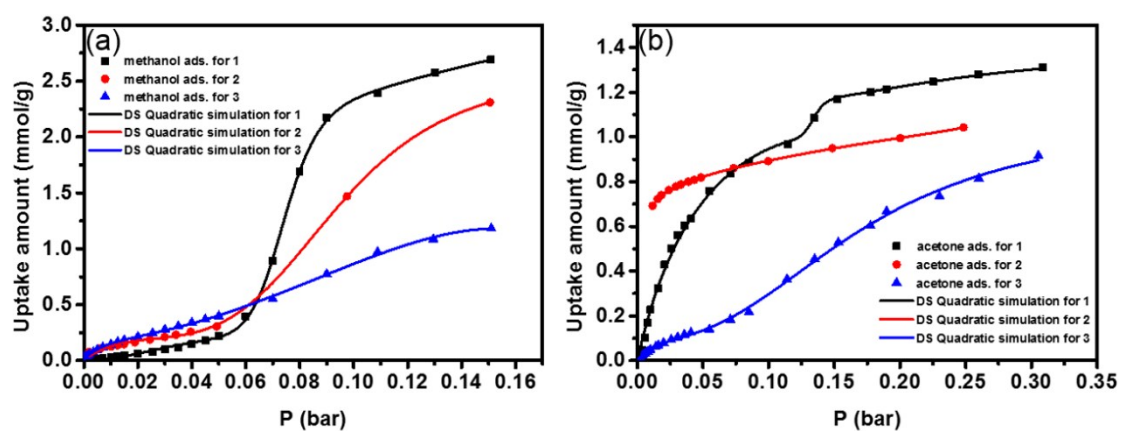


Figure S11. DS Quadratic simulation for methanol and acetone adsorption isotherms for 1, 2 and 3 at 298 K.



Methanol							
	R^2	M_1	M_2	K_{A1}	K_{A2}	K_{B1}	K_{B2}
1	0.9997	1.63099	0.18392	3.08245	-25.9067	79.5167	181.10673
2	0.99943	0.62537	0.62974	-5.48408	48.09472	111.1063	321.40965
3	0.9983	1.95859	0.31842	-0.37606	101.36216	28.08449	-466.29371
Acetone							
1	0.99766	0.00602	1.55208	-14.83591	17.32673	55.68038	-0.81905
2	0.99979	-0.00129	0.78015	28.64326	563.0548	-118.781	1103.25628
3	0.99858	0.39772	0.1828	-3.69637	54.74454	33.97595	53.13611

Figure S12. Optical photograph of (a) neat PVDF membrane and (b) MOF/PVDF membrane with 5 wt.% loading amount; SEM images of (c) neat PVDF membrane and (d) MOF/PVDF membrane with 5 wt.% loading amount (MOF particles mounted in the sponge-like membrane).

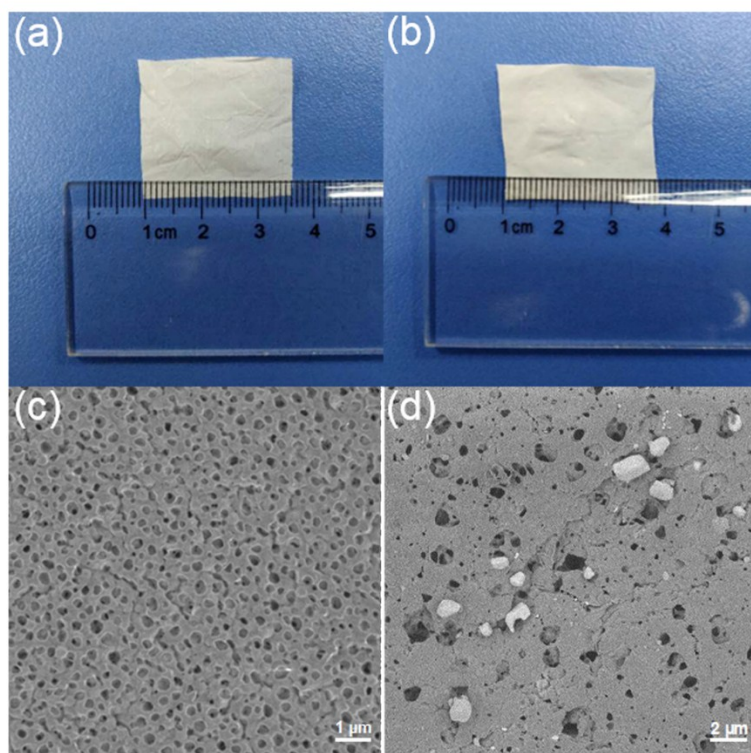
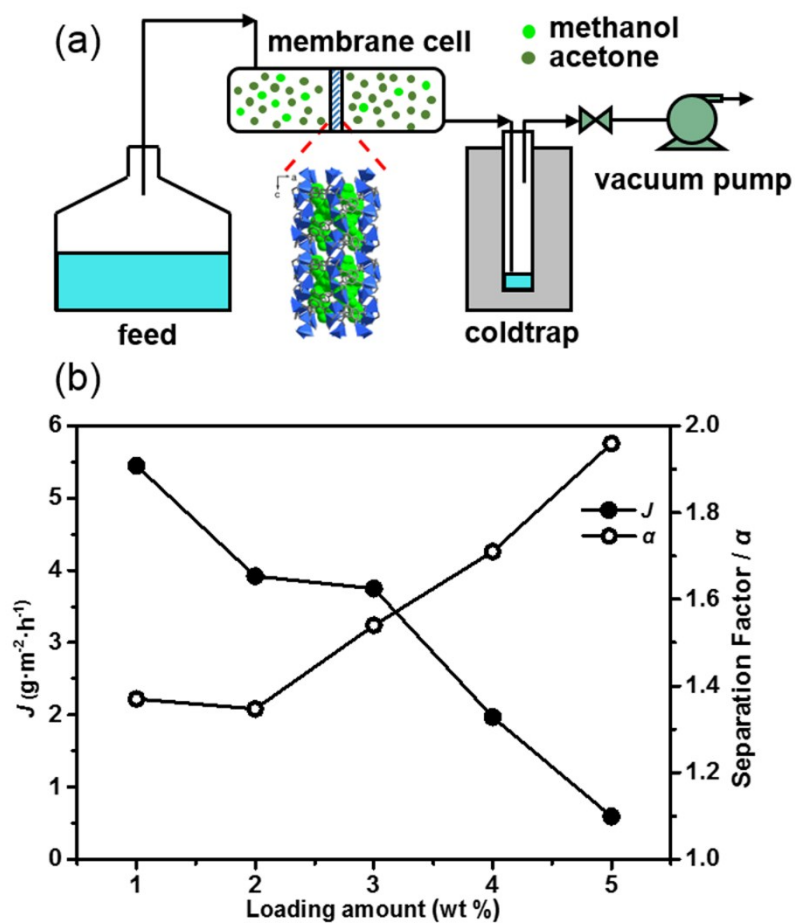


Figure S13. (a) Process of pervaporation separation taking **1** as filler in membrane; (b) the permeate flux (J) and separation factor (α) of MOF/membrane (loading amount = 1-5 wt.%) at 298 K.



Reference

- [1] Y.-F. Sha, S.-Z. Bai, J.-Y. Lou, D. Wu, B.-Z. Liu and Y. Ling, *Dalton Trans.*, 2016, **45**, 7235-7239.
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