Supporting Information

Halogen-modified Metal−Organic Frameworks for Efficient Separation of Alkane from Natural Gas

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IAST adsorption selectivity

The selectivity of DMOF-X for CH_4, C_2H_6, and C_3H_8 was calculated using the ideal adsorption solution theory. The adsorption selectivity is defined by the following equation:

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$

In the formula, q_1 and q_2 are the adsorption capacity of component 1 and component 2 at equilibrium, and p_1 and p_2 are the gas partial pressures of component 1 and component 2.

Isosteric heat of adsorption

The adsorption enthalpies of CH_4(at 273 and 298K), C_2H_6 (at 273 and 298K) and C_3H_8 (at 273 and 298K) on DMOF-X were calculated using the Virial method. The steps are as follows: First, calculate the empirical constant a_i and b_i based on the adsorption data at different temperatures, and then calculate it using the following equation:

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

Among them, N is the gas intake (mg g^{-1}), P is the pressure (mmHg), T is the temperature (K), a and b are empirical constants, m and n are the number of coefficients required to adequately describe the isotherm. Then the following expression evaluates Q_{st}:

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

where R is the gas constant.

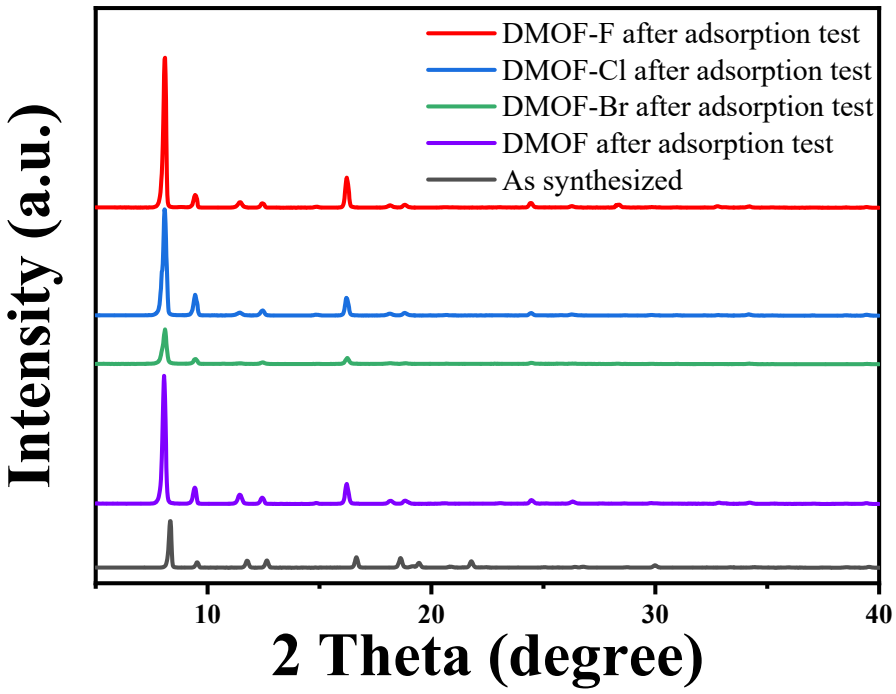

Figure S1. As-synthesized and after adsorbed PXRD patterns for DMOF-X.

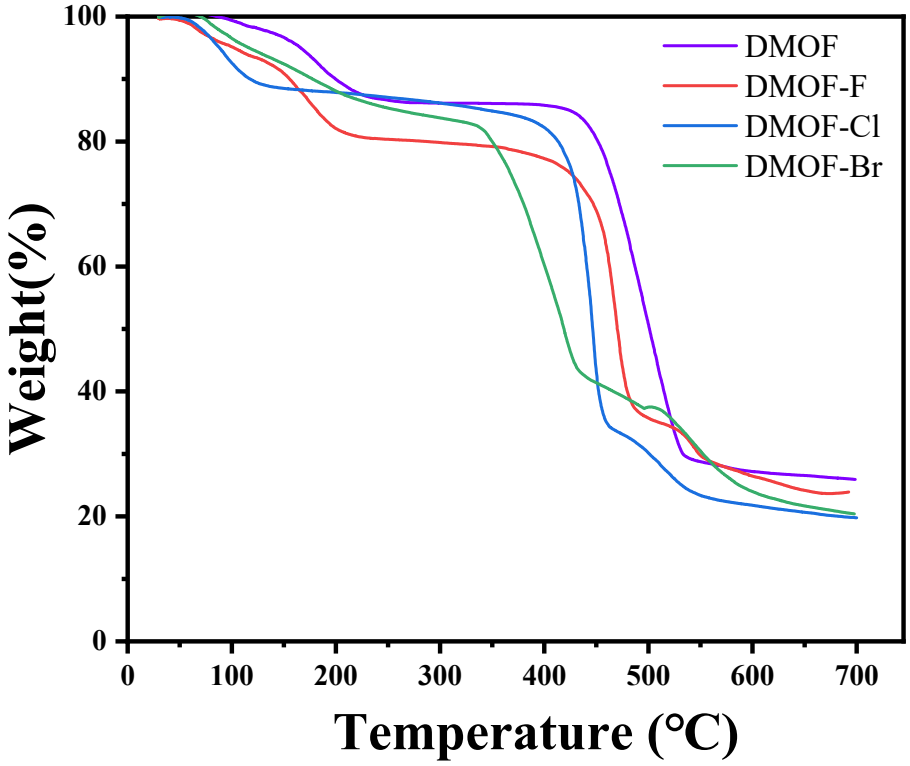

Figure S2. TGA curve of DMOF and DMOF-X under N_2.

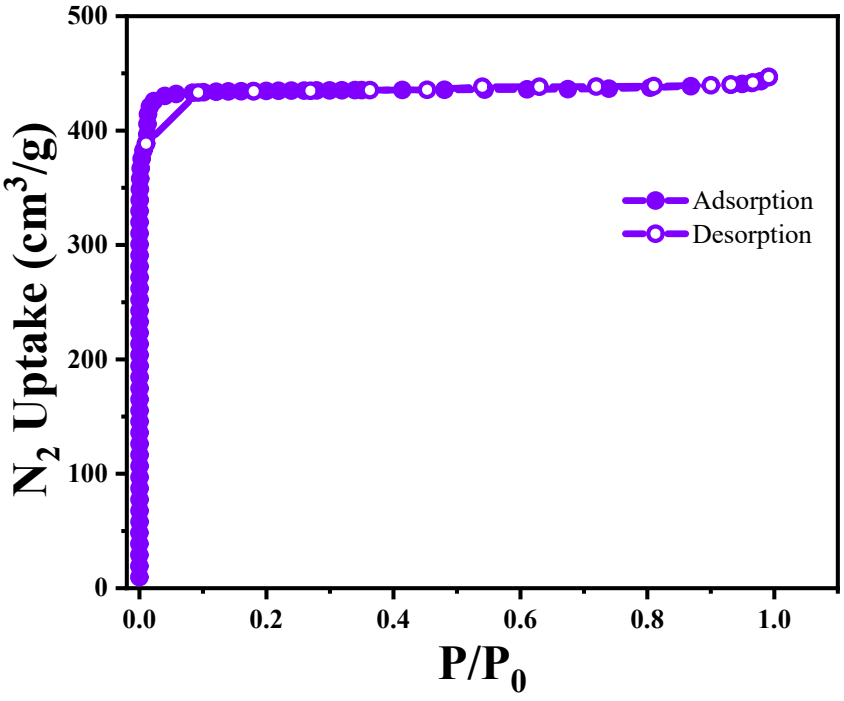

Figure S3. Nitrogen sorption isotherms at 77 K for DMOF.

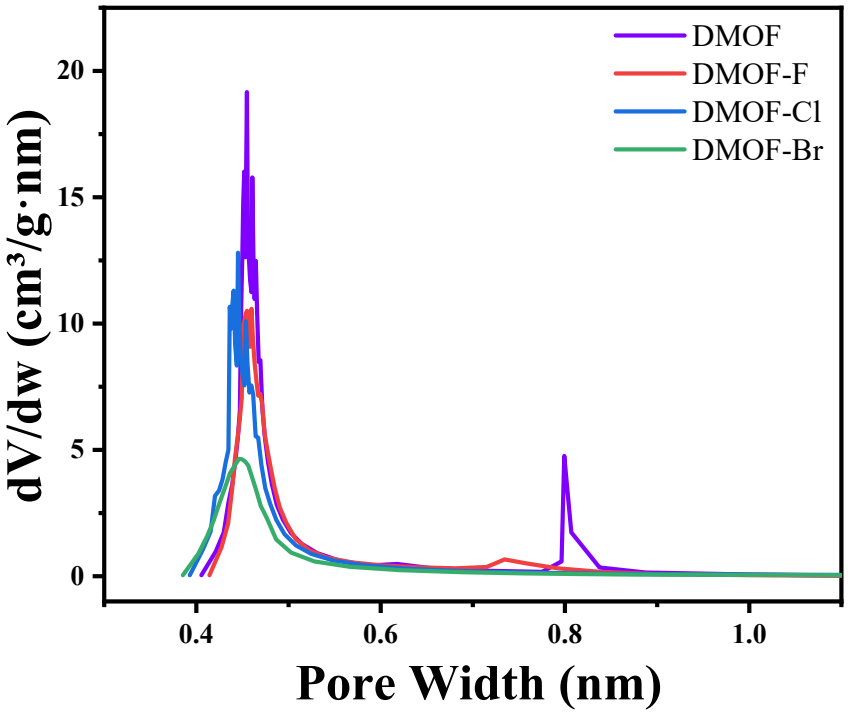

Figure S4. corresponding pore size distribution of DMOF-X calculated by DFT method.

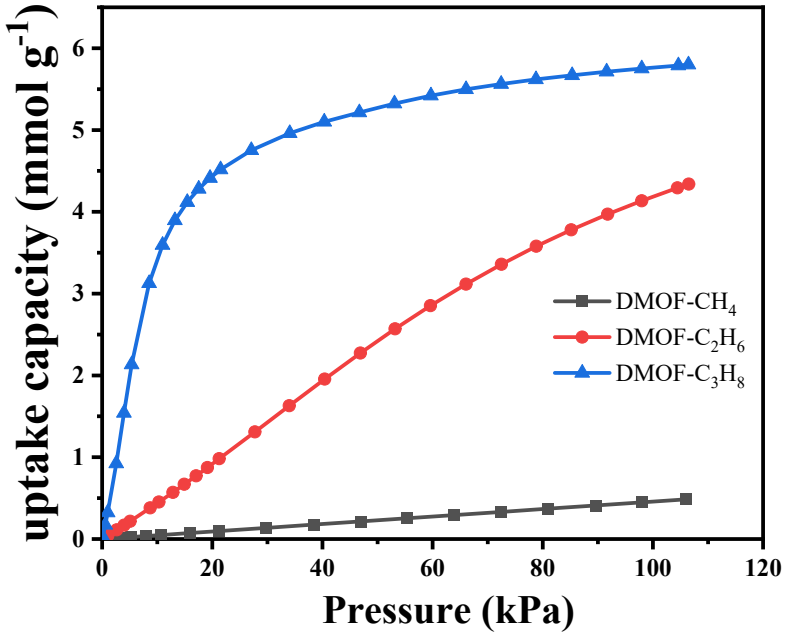

Figure S5. Single-component isotherms of CH_4, C_2H_6, and C_3H_8 for DMOF at 298 K.

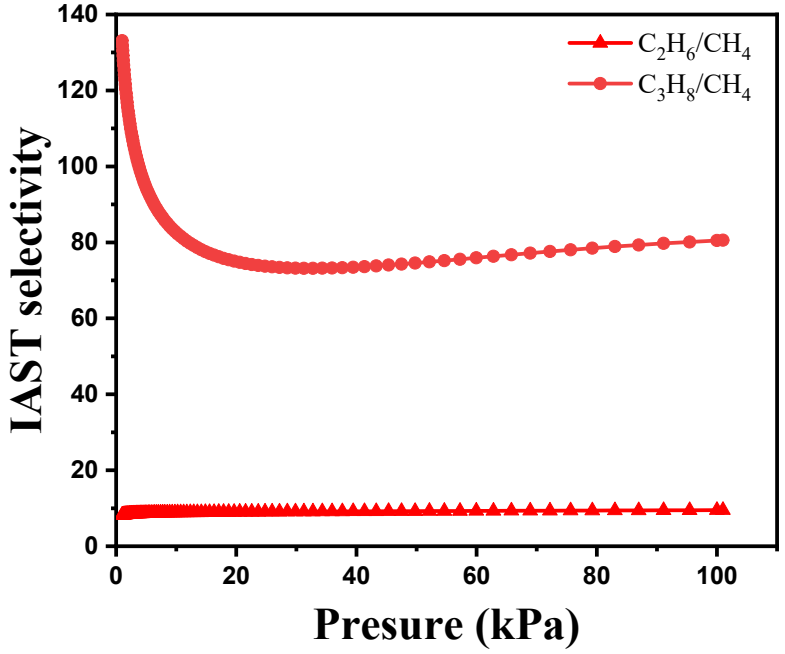

Figure S6. IAST selectivity of the DMOF.

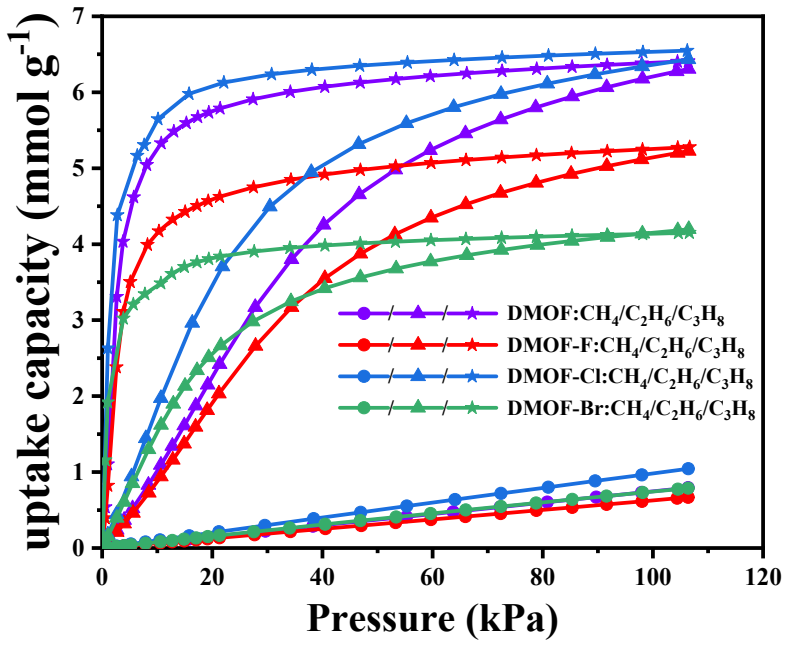

Figure S7. CH_4, C_2H_6, and C_3H_8 adsorption isotherms of DMOF-X at 273 K.

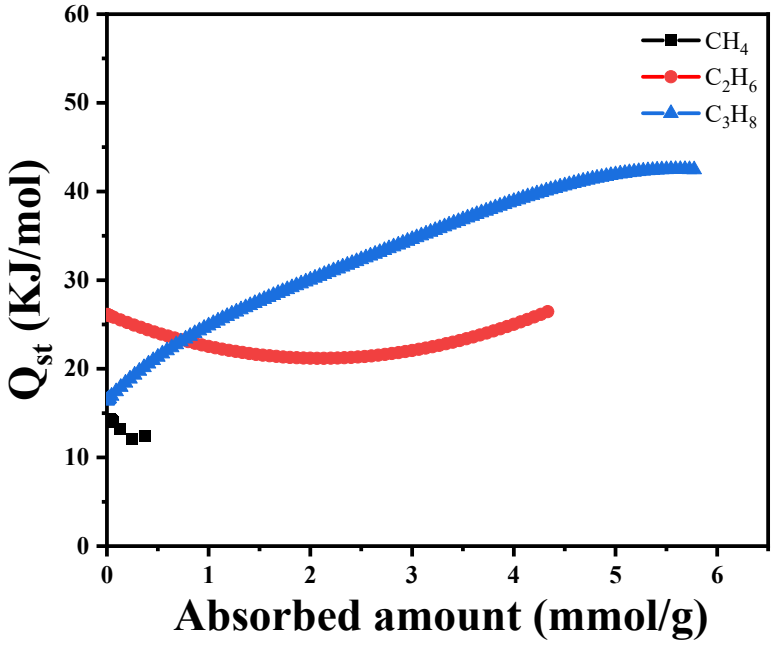

Figure S8. Isosteric heats of C_3H_8, C_2H_6, and CH_4 on DMOF.

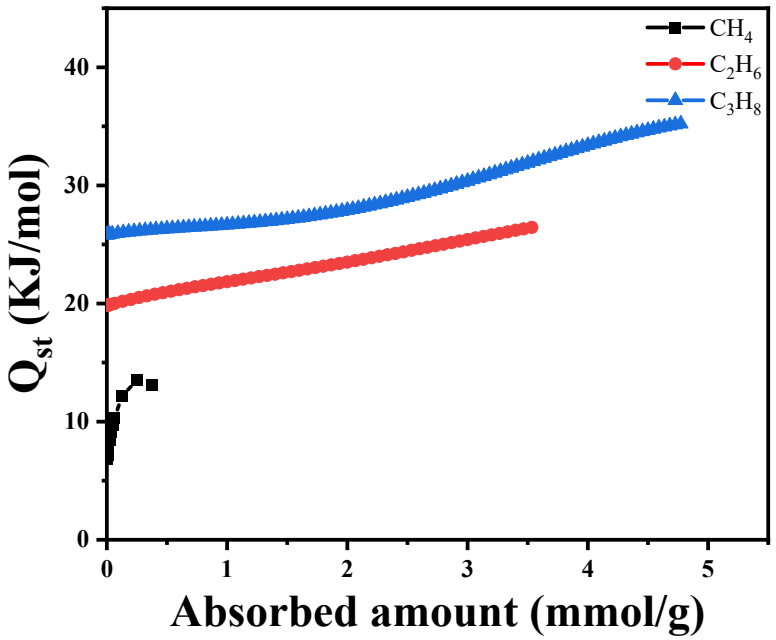

Figure S9. Isosteric heats of C_3H_8, C_2H_6, and CH_4 on DMOF-F.

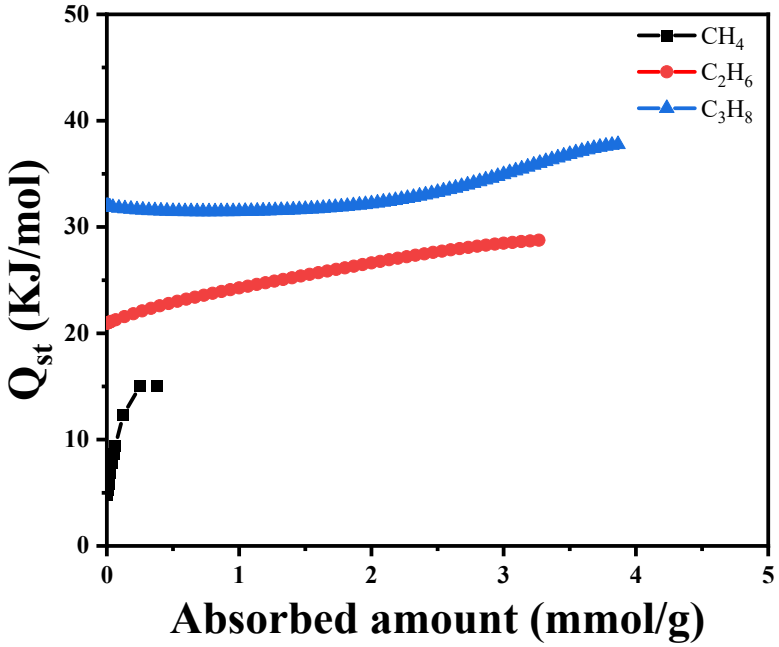

Figure S10. Isosteric heats of C_3H_8, C_2H_6, and CH_4 on DMOF-Br.

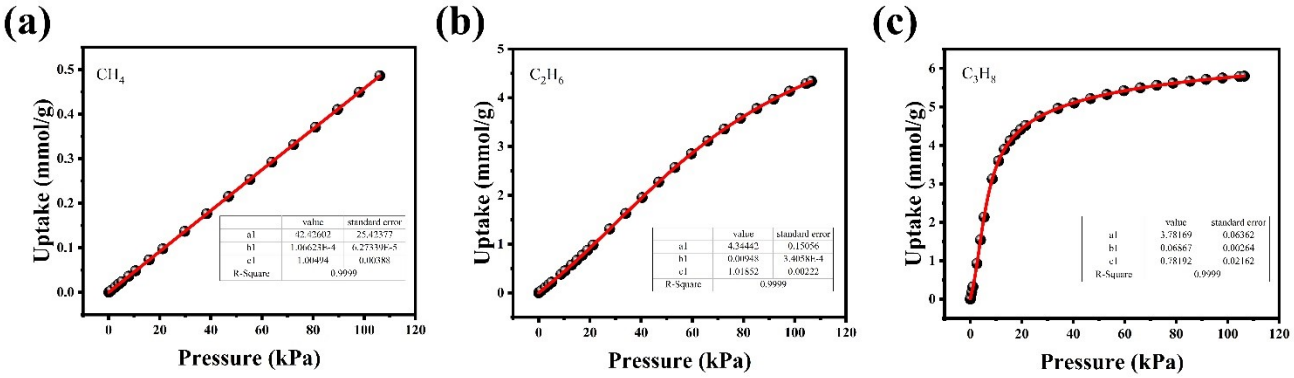

Figure S11. The fitting parameters for Single Sites Langmuir-Freundlich isotherms model for DMOF at 298K (a) CH_4 (b) C_2H_6 (C) C_3H_8.

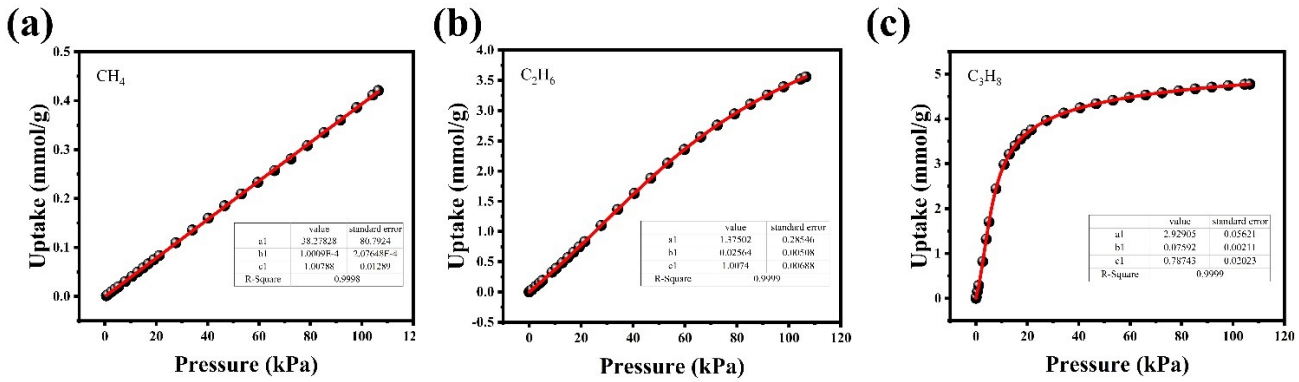

Figure S12. The fitting parameters for Single Sites Langmuir-Freundlich isotherms model for DMOF-F at 298K (a) CH_4 (b) C_2H_6 (C) C_3H_8.

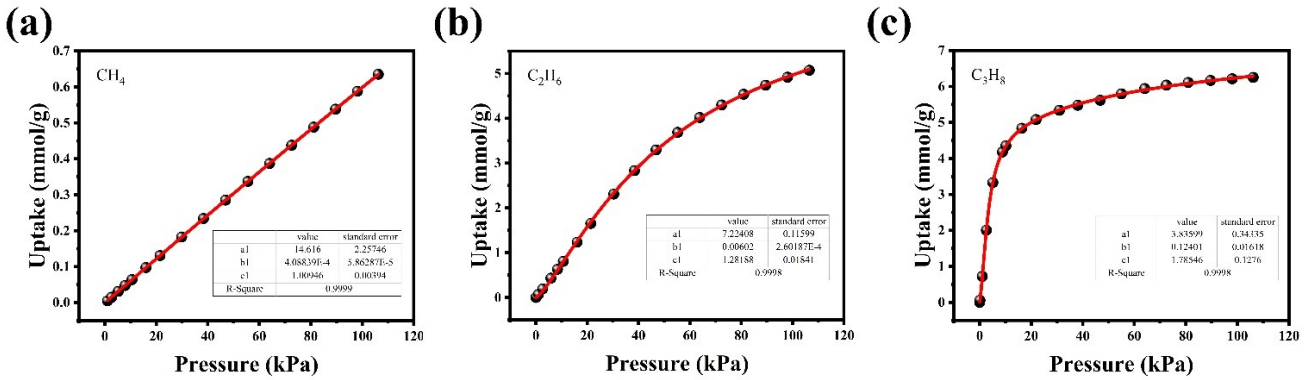

Figure S13. The fitting parameters for Single Sites Langmuir-Freundlich isotherms model for DMOF-Cl at 298K (a) CH_4 (b) C_2H_6 (C) C_3H_8.

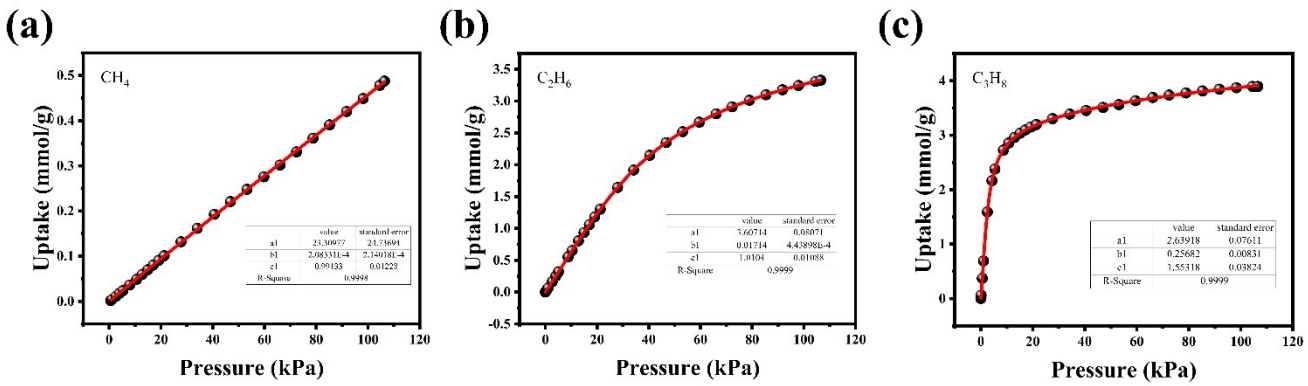

Figure S14. The fitting parameters for Single Sites Langmuir-Freundlich isotherms model for DMOF-Br at 298K (a) CH_4 (b) C_2H_6 (C) C_3H_8.

Table S1. Summary of CH_4, C_2H_6, and C_3H_8 adsorption capacities and C_3H_8/CH_4 and C_2H_6/CH_4 selectivities in various porous materials.

Materials	C_3H_8 uptake	C_2H_6 uptake	CH_4 uptake	C_3H_8/CH_4 selectivity	C_2H_6/CH_4 selectivity	Ref.
	mmol/g	mmol/g	mmol/g	(5/85)	(10/85)	
DMOF-Cl	**6.25**	**5.07**	**0.63**	**130.9**	**12.5**	**This work**
DMOF-F	**4.78**	**3.56**	**0.42**	**80.8**	**9.5**	**This work**
DMOF-Br	**3.90**	**3.33**	**0.49**	**133.8**	**13.8**	**This work**
DMOF	**5.80**	**4.34**	**0.49**	**80.5**	**9.5**	**This work**
MIL-101-Cr	3.35	1.59	0.49	84.3	22.5	[1]
MIL-101-Fe	3.29	1.25	0.45	24.9	15.4	[1]
MIL-101-Fe-NH_2	3.32	1.35	0.46	42.5	11.6	[1]
ZUL-C1	2.72	2.95	-	158	28	[2]
ZUL-C2	2.52	2.82	-	741	82	[2]
Cu-MOF	5.98	3.22	-	203.6	9.3	[3]
MOF-303	4.74	4.96	0.86	5114	26	[4]
MIL-160	5.08	4.65	0.94	174	20	[4]
Ni(TMBDC)(DABCO)$_{0.5}$	5.54	5.81	-	274	29	[5]

Zn-BPZ-SA	2.73	2.97	0.64	65.7	10.9	[6]
RT-MIL-100(Fe)	6.78	2.22	0.36	33.3	6.0	[7]
LIFM-ZZ-1	4.06	2.80	0.39	338	16	[8]
PAN-m1	3.42	2.53	0.63	222.8	23.1	[9]
PAN-m3	4.01	2.72	0.71	296.3	17.4	[9]
Cu-IPA	3.10	2.57	0.81	296	35	[10]

References

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