Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Size exclusion propyne/propylene separation in a ultramicroporous yet hydrophobic metal-organic framework

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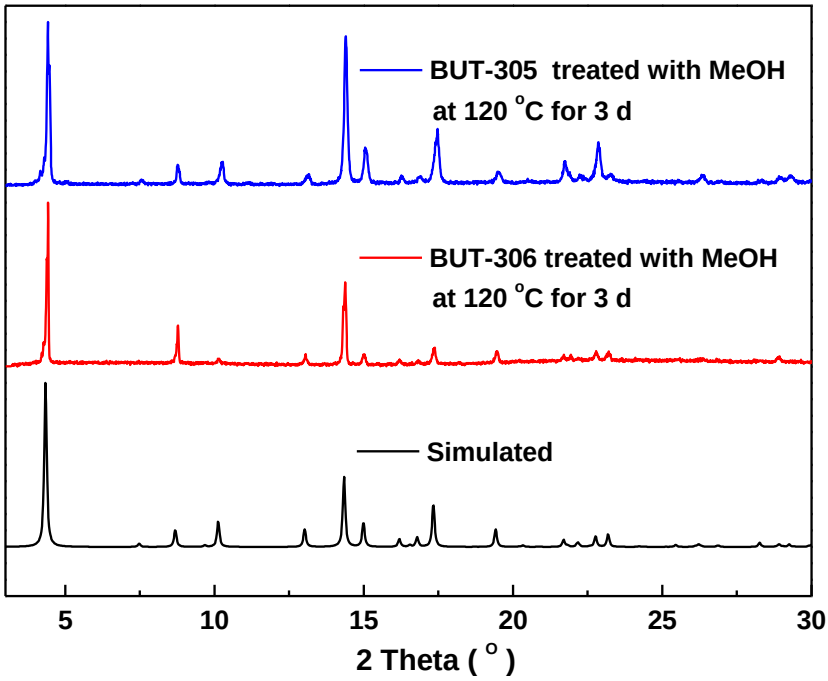

Fig. S1 The PXRD patterns of **BUT-305** and**-306** treated with MeOH at 120 ℃ for 3 days.

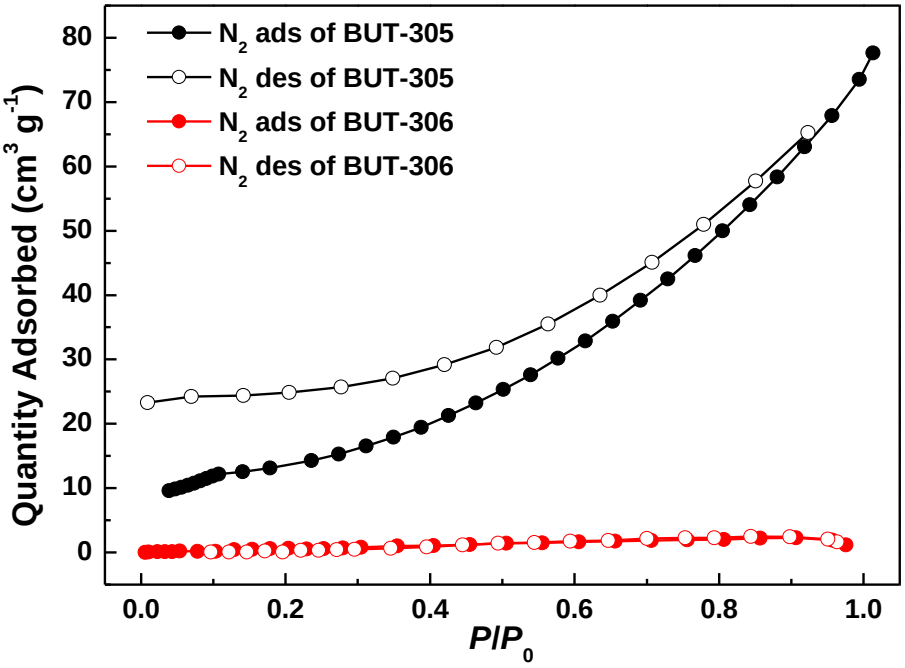

Fig. S2 N_2 adsorption isotherms of **BUT-305** and **-306** at 77 K.

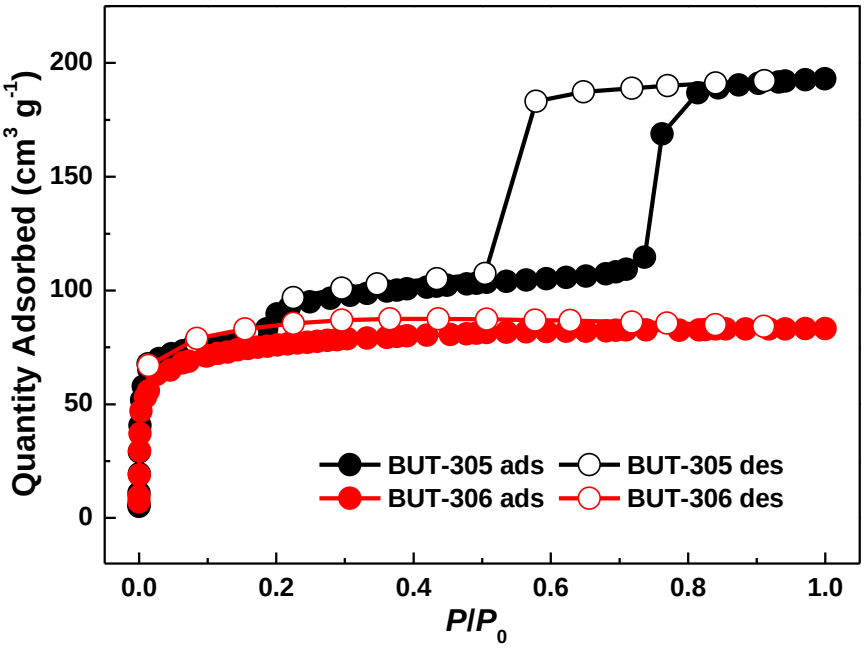

Fig. S3 The CO_2 adsorption isotherms of **BUT-305** and **-306** at 195 K.

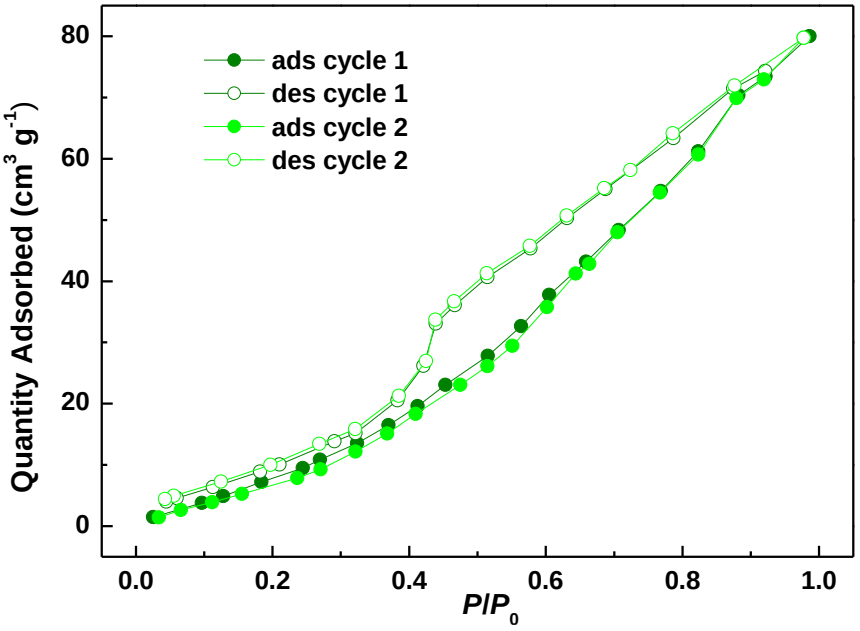

Fig. S4 Two repeated measurements of H_2O adsorption isotherms of **BUT-306** at 298 K.

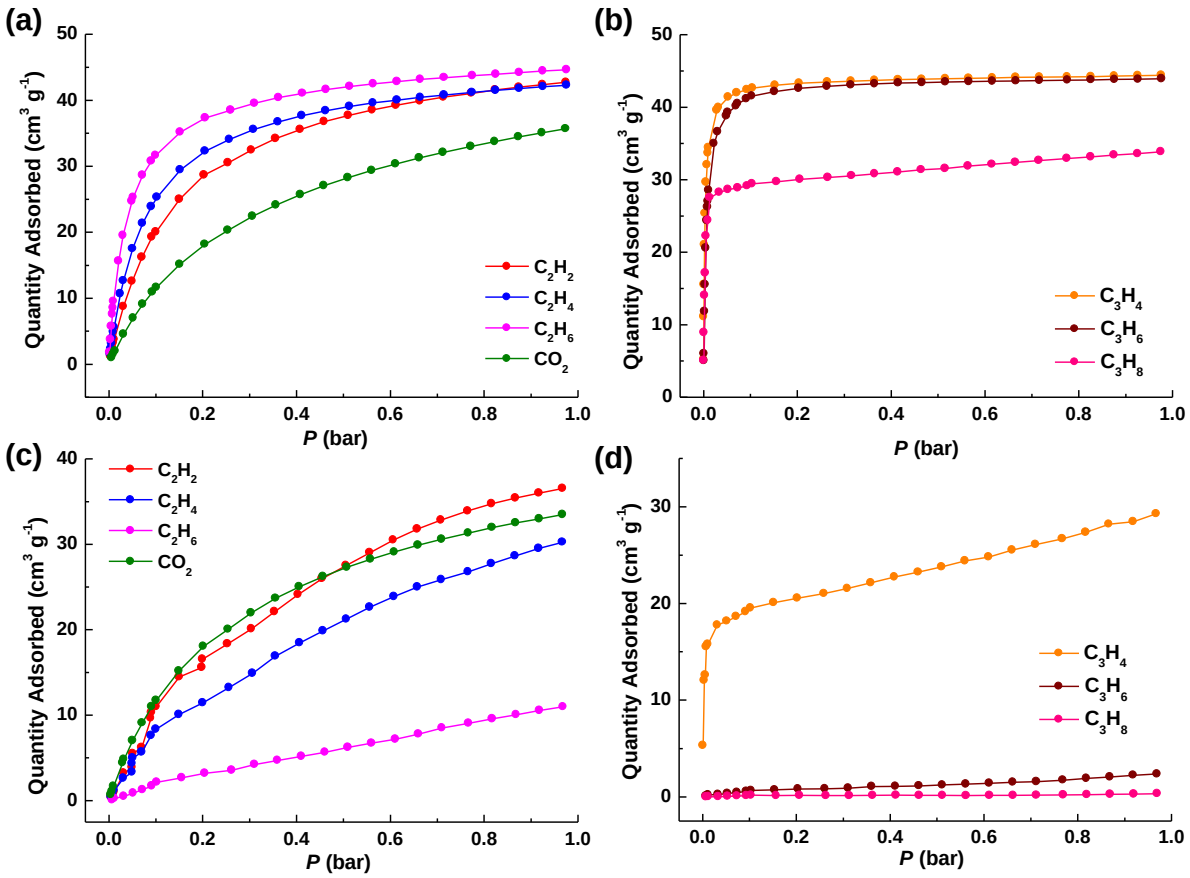

Fig. S5 Single-component gas adsorption isotherms (CO_2, C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_3H_6, and C_3H_8) of (a, b) **BUT-305** and (c, d) **BUT-306** recorded at 298 K.

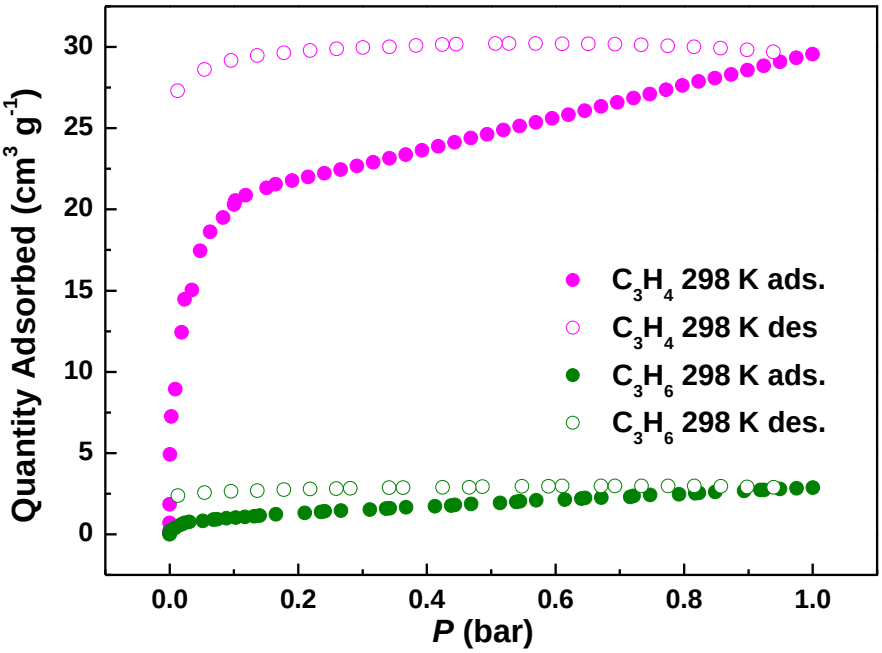

Fig. S6 C_3H_4, C_3H_6 adsorption and desorption isotherms of **BUT-306** measured at 298 K.

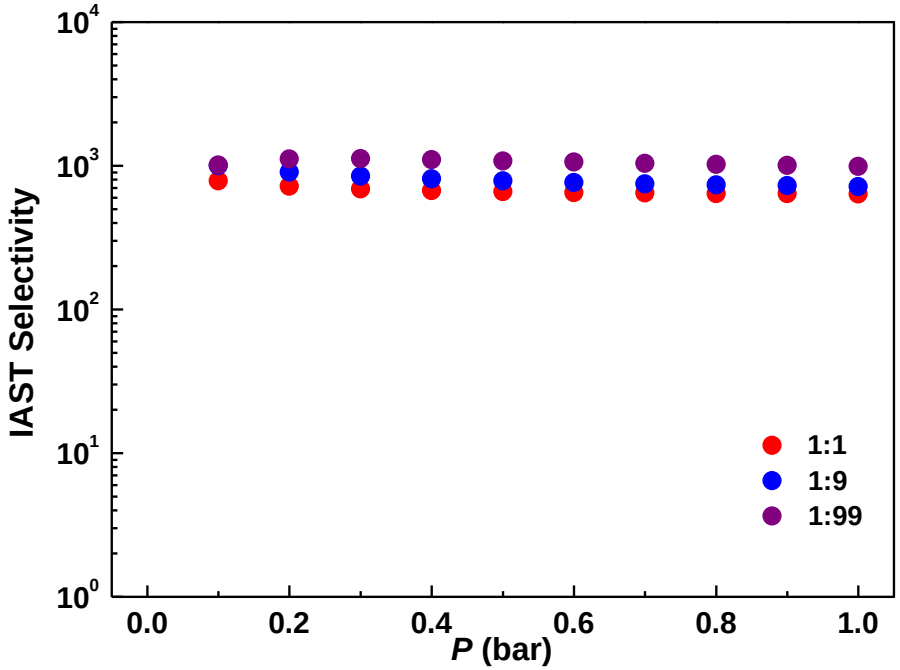

Fig. S7 IAST selectivities of **BUT-306** for 1:1, 1:9 and 1:99 (*v*/*v*) C_3H_4/C_3H_6 gas mixtures at 298 K calculated from single-component gas adsorption isotherms.

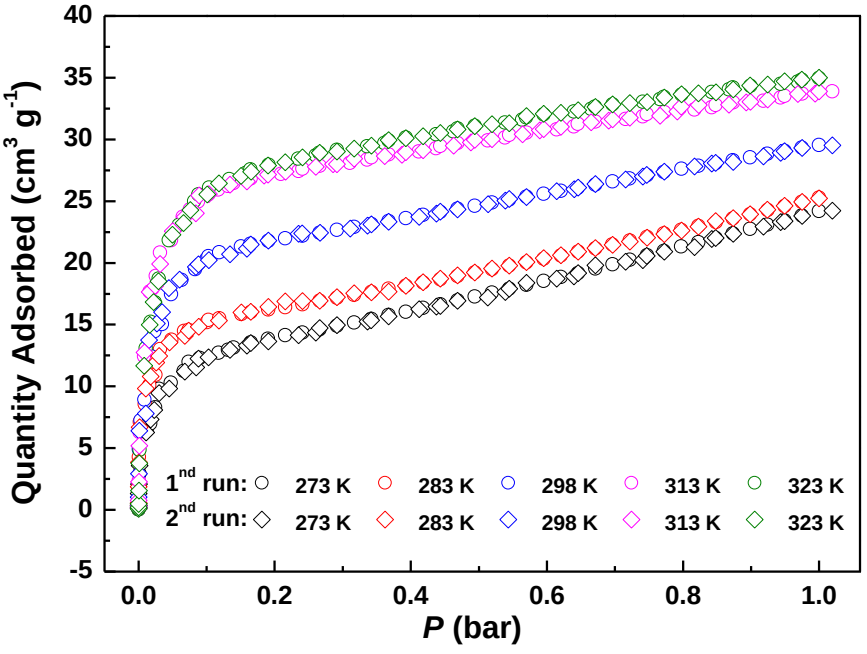

Fig. S8 The C_3H_4 adsorption isotherms of **BUT-306** recorded at 273, 283, 298, 313, and 323 K, respectively. The measurements were repeated to verify the data.

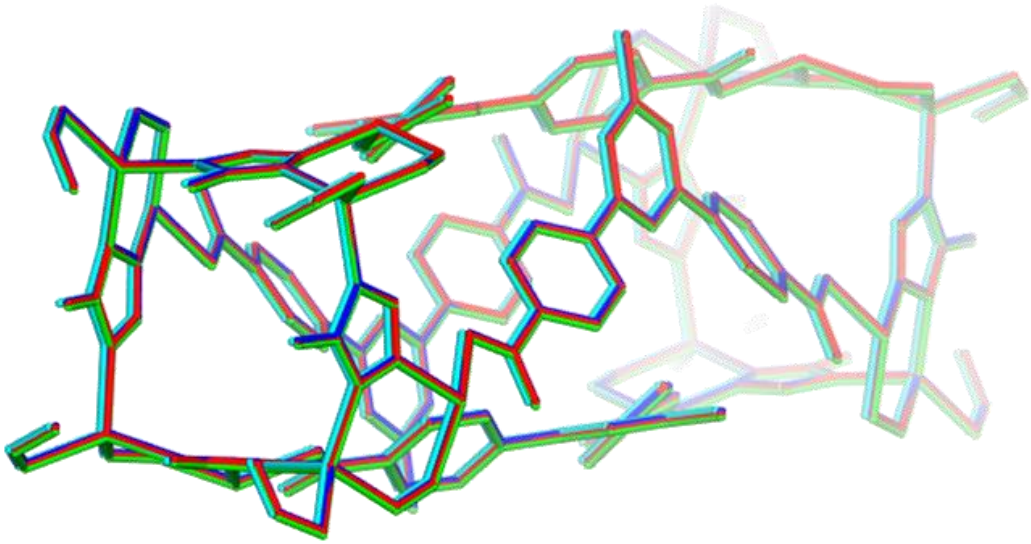

Fig. S9 Overlapping of the framework structures **BUT-306** recorded at 273 K (blue), 298 K (red), and 313 K (green) and that of C_3H_4-loaded **BUT-306** recorded at 200 K (turquoise).

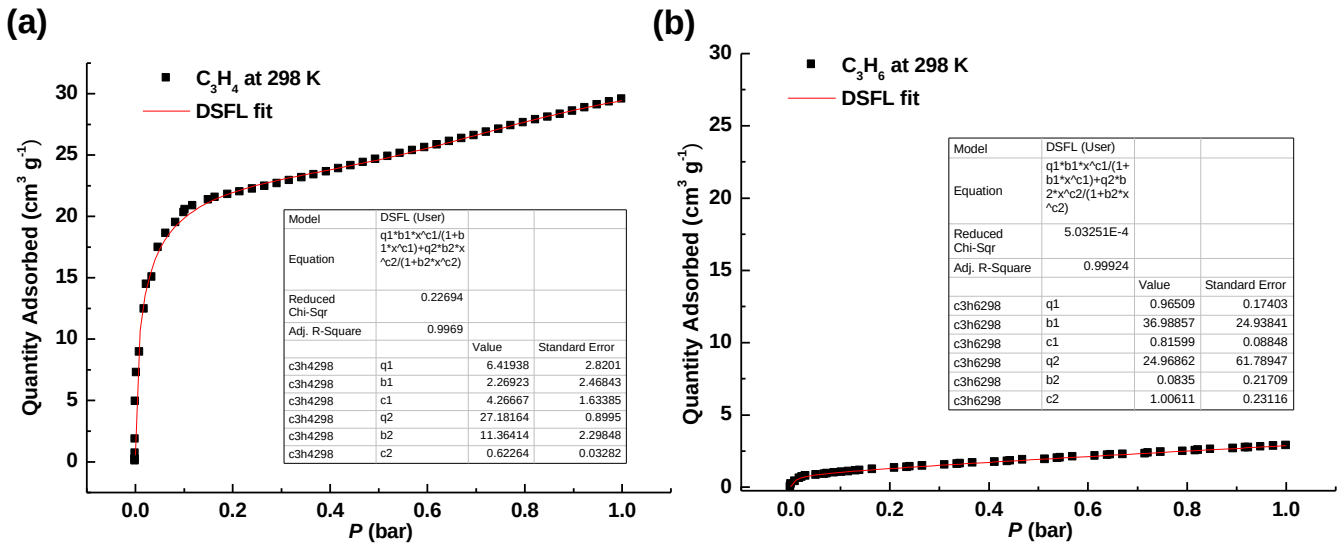

Fig. S10 C_3H_4 and C_3H_6 adsorption isotherms of **BUT-306** measured at 298 K and its double-site Langmuir-Freundlich fits.

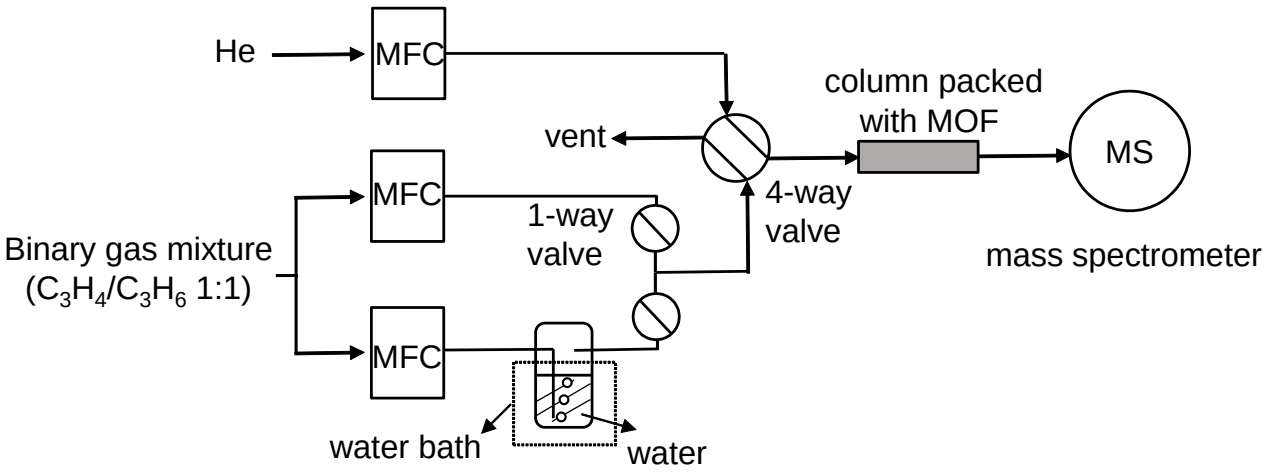

Fig. S11 Schematic diagram of column breakthrough experiment device.

Table S1 Crystal data and structure refinement parameters for **BUT-306** at 273, 298 and 313 K, and C_3H_4-loaded **BUT-306** at 200 K.

	BUT-306	**BUT-306**	**BUT-306**	C_3H_4-loaded **BUT-306**
Temp. (K)	273	298	313	200
Formula	$C_{12.5}H_{10}N_4O_2Zn$	$C_{12.5}H_{10}N_4O_2Zn$	$C_{12.5}H_{10}N_4O_2Zn$	$C_{12.73}H_{10.2}N_4O_2Zn$
Crystal system	tetragonal	tetragonal	tetragonal	tetragonal
Space group	*I*4/*m*	*I*4/*m*	*I*4/*m*	*I*4/*m*
a (Å)	12.3290(2)	12.3420(2)	12.3425(2)	12.3020(10)
c (Å)	40.6790(6)	40.6826(9)	40.6799(5)	40.7025(5)
α (°)	90	90	90	90
V (Å^3)	6183.4(2)	6197.0(2)	6197.1(2)	6159.9(13)
Z	16	16	16	16
D_c (g cm^{-3})	1.348	1.345	1.345	1.365
F (000)	2544.0	2544.0	2544.0	2569.0
Reflections collected	11595	11499	11532	11249
Unique reflections	2364	2343	2326	3109
GOF	1.031	1.031	1.020	1.060
R_1[a] [I > 2σ(*I*)]	0.0424	0.0588	0.0425	0.0371
wR_2[b] (all data)	0.1243	0.1192	0.1263	0.1048
CCDC deposition number	2168051	2168052	2168053	2168054

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]w$R_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$

Table S2 Pawley refinement parameters for the PXRD pattern of **BUT-305**.

Formula	$Zn_2(ATZ)_2(TPDC)$
crystal system	tetragonal
space group	*I*4/*m*
a / Å	12.38096(0.00647)
c / Å	40.65355(0.02070)
R_{wp} / %	8.62
R_p / %	6.05
U	0.34090(0.18549)
V	-0.14615(0.07521)
W	0.02189(0.01621)
NA	0.28626(0.01743)
NB	0.01061(0.00102)
Zero Point / º	0.37865(0.00167)
Shift #1	-0.48957(0.00097)
Shift #2	0.10628(0.03413)
*P*1	-0.20988(0.00230)
*P*2	-0.11320(0.00109)
*P*3	0.21332(0.00475)
*P*4	0.18014(0.00218)

Table S3 Comparison of C_3H_4 and C_3H_6 uptake (mmol/g, mmol/cm^3 and cm^3/cm^3) from gas adsorption isotherms at various pressures, and the C_3H_4/C_3H_6 uptake ratio at 0.01/0.01 bar and 0.01/0.99 bar for various reported MOFs at 298 K.

MOFs	**C_3H_4 adsorption mmol g^{-1}**			**C_3H_6 adsorption mmol g^{-1}**			**C_3H_4/C_3H_6 adsorption ratio**		**Ref.**
	0.01 bar	0.1 bar	0.99 bar	0.01 bar	0.1 bar	0.99 bar	0.99/0.99	0.01/0.99	
UTSA-200	2.99	3.3	3.58	0.02	0.33	1.2	2.98	2.49	Ref. [32] in maintext
SIFSIX-3-Ni	2.56	2.73	2.85	0.15	2.42	2.72	1.05	0.98	
ZU-62	2.19	3.01	3.64	0.17	2.26	2.67	1.36	0.82	
SIFSIX-2-Cu-i	1.96	3.22	3.77	0.15	2.19	2.63	1.43	0.74	
SIFSIX-1-Cu	2.57	6.79	8.63	0.3	4.92	5.88	1.47	0.44	
ELM-12	1.82	2.54	2.77	0.19	1.11	1.43	1.94	1.27	
ZJUT-1	0.4	1.07	2.24	0.06	0.54	0.84	2.67	0.47	
Mg-MOF-74	2.71	7.32	9.4	2.03	6.07	6.49	1.33	0.42	
Co-MOF-74	2.85	5.8	7.47	1.27	5.64	5.95	1.26	0.48	
Ni-MOF-74	1.8	4.68	5.51	1.53	4.5	4.78	1.15	0.38	
Fe-MOF-74	2.18	6.67	7.94	1.67	6.25	6.63	1.20	0.33	
Cu-BTC	1.47	8.17	10.47	1.36	7.9	8.33	1.26	0.18	
Fe-BTT	1.74	6.87	12.41	1.52	8.03	8.74	1.42	0.2	

Cr-BTT	1.08	4.42	7.28	0.76	5.04	5.85	1.24	0.18	
MIL-100(Cr)	1.52	4.98	14.51	0.63	4.53	6.25	2.32	0.24	
MIL-100(Fe)	1.34	4.74	17.14	0.52	4.52	6.96	2.46	0.19	
UIO-66	1.58	5.29	10.23	0.36	2.7	3.33	3.07	0.47	
ZIF-8	0.13	1.44	6.27	0.08	3.15	4.07	1.54	0.03	
UTSA-74-Zn	0.33	2.13	7.43	0.09	2.47	5.07	1.45	0.06	
UTSA-100	1.87	4	5.35	1.34	2.68	3.04	1.76	0.62	
Co-gallate	1.61	2.4	3.21	0.09	0.5	1.49	2.15	1.08	
Mg-gallate	1.65	2.7	3.75	0.08	1.0	1.50	2.50	1.10	Ref. [51] in maintext
Ni-gallate	1.1	1.9	2.65	0.18	0.4	0.9	2.94	1.22	
NKMOF-1	1.78	2.10	2.90	0.65	0.75	1.50	1.93	1.19	Ref. [52] in maintext
BUT-306	**0.44**	**0.89**	**1.29**	**0.02**	**0.04**	**0.12**	**10.75**	**3.67**	**this work**