An aromatic-rich cage-based MOF with inorganic chloride ions decorating the pore surface displaying the preferential adsorption of C_2H_2 and C_2H_6 over C_2H_4

Zhenzhen Jiang,[a] Lihui Fan,[a] Ping Zhou,[a] Tingting Xu,[a] Simin Hu,[a] Jingxian Chen,[a] De-li Chen*[b] and Yabing He*[a]

[a] Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, China. E-mail: heyabing@zjnu.cn

[b] Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China. E-mail: chendl@zjnu.cn

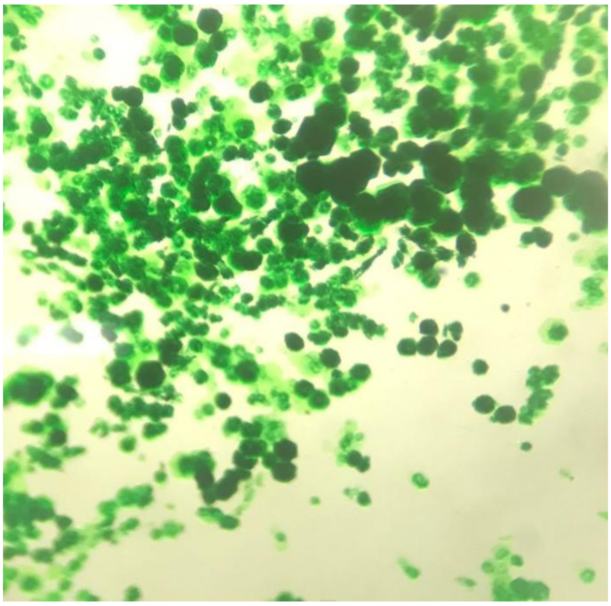


Fig. S1 The electronic photograph of as-synthesized **ZJNU-7**.

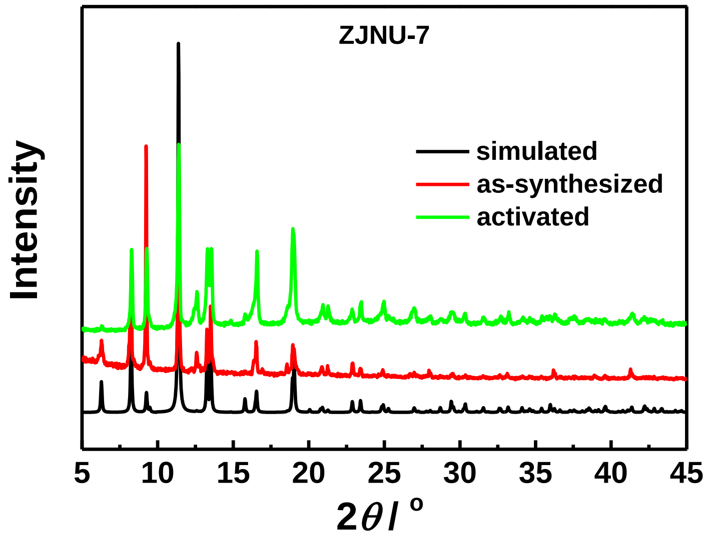


Fig. S2 Comparison of experimental and simulated PXRD patterns of **ZJNU-7**.

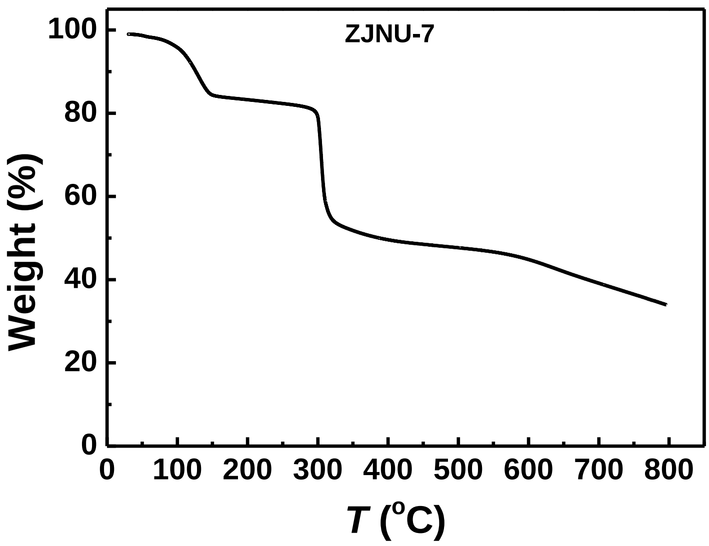


Fig. S3 TGA profile of as-synthesized **ZJNU-7** under N_2 atmosphere.

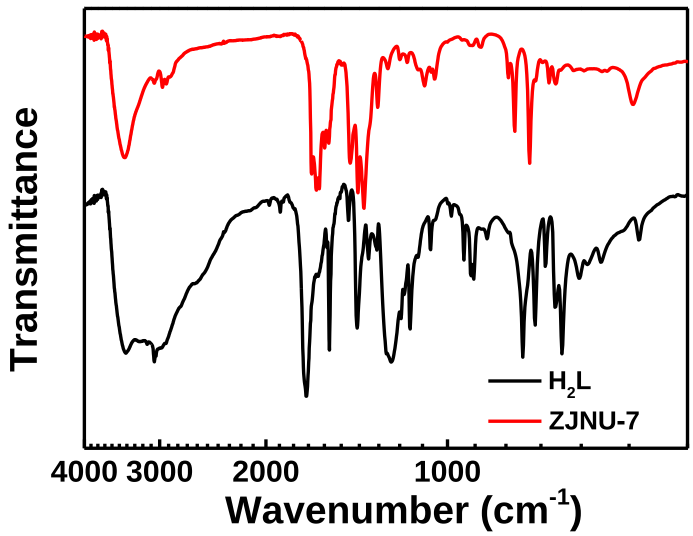
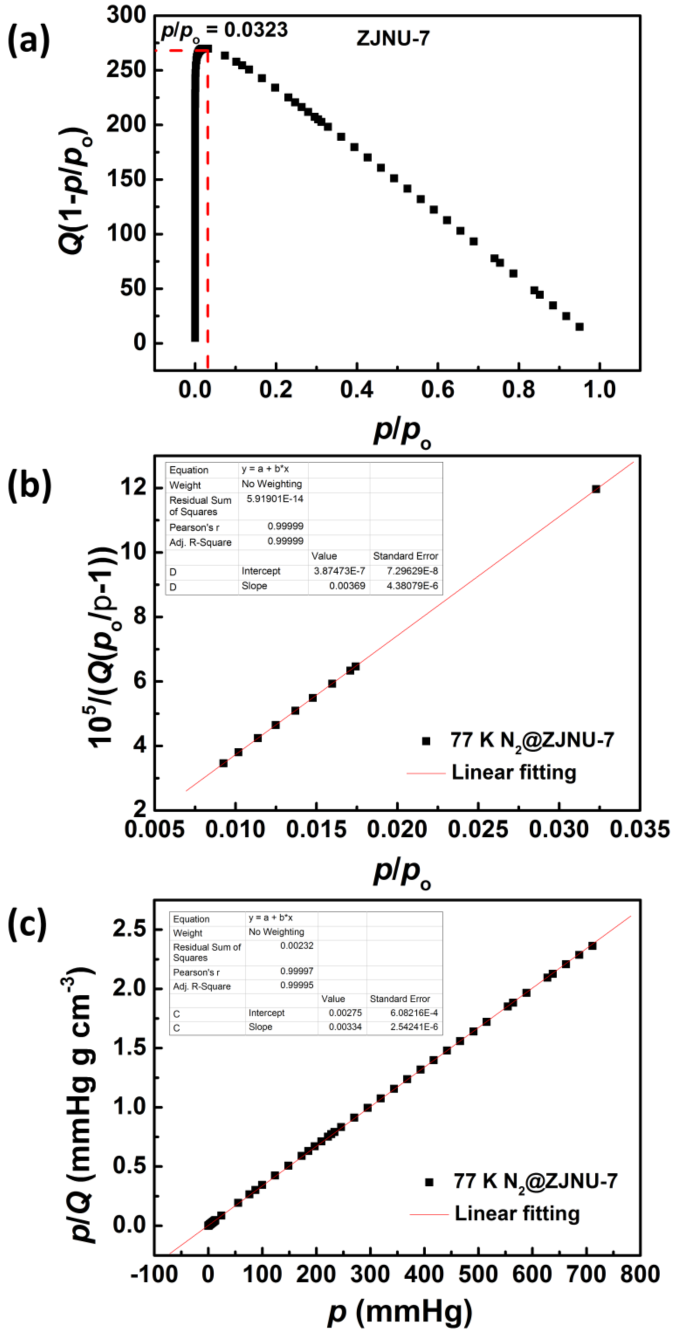


Fig. S4 Comparison of FTIR spectra of as-synthesized **ZJNU-7** and its organic ligand



$S_{\mathrm{BET}} = 1/(3.87473\times10^{-7} + 0.00369)/22414 \times 6.023 \times 10^{23} \times 0.162 \times 10^{-18} = 1180\ \mathrm{m^2\ g^{-1}}$

$S_{\mathrm{Langmuir}} = (1/0.00334)/22414 \times 6.023 \times 10^{23} \times 0.162 \times 10^{-18} = 1303\ \mathrm{m^2\ g^{-1}}$

BET constant $C = 1 + 0.00369/3.87473\times10^{-7} = 9524$

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.010143$$

Fig. S5 The consistency plot (a), BET surface area plot (b), and Langmuir surface area plot (c) for **ZJNU-7**.

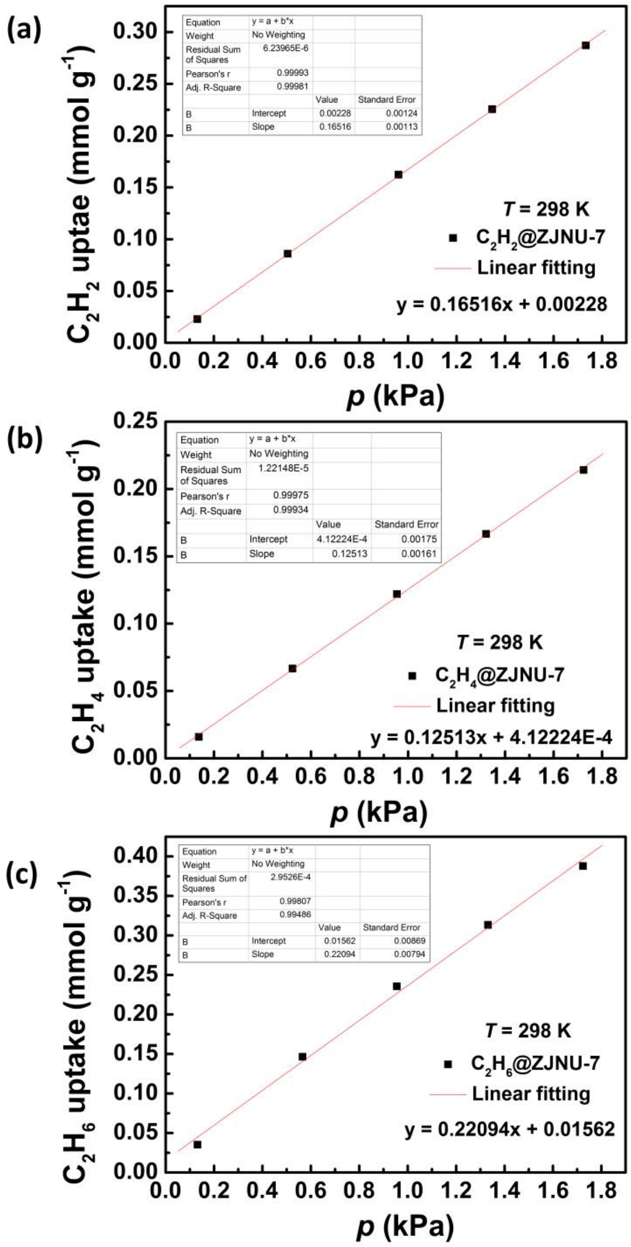


Fig. S6 Calculations of Henry constants for (a) C_2H_2, (b) C_2H_4 and (c) C_2H_6 adsorption in **ZJNU-7**. Note that Henry constant equals to the slope of gas isotherm at low pressure region.

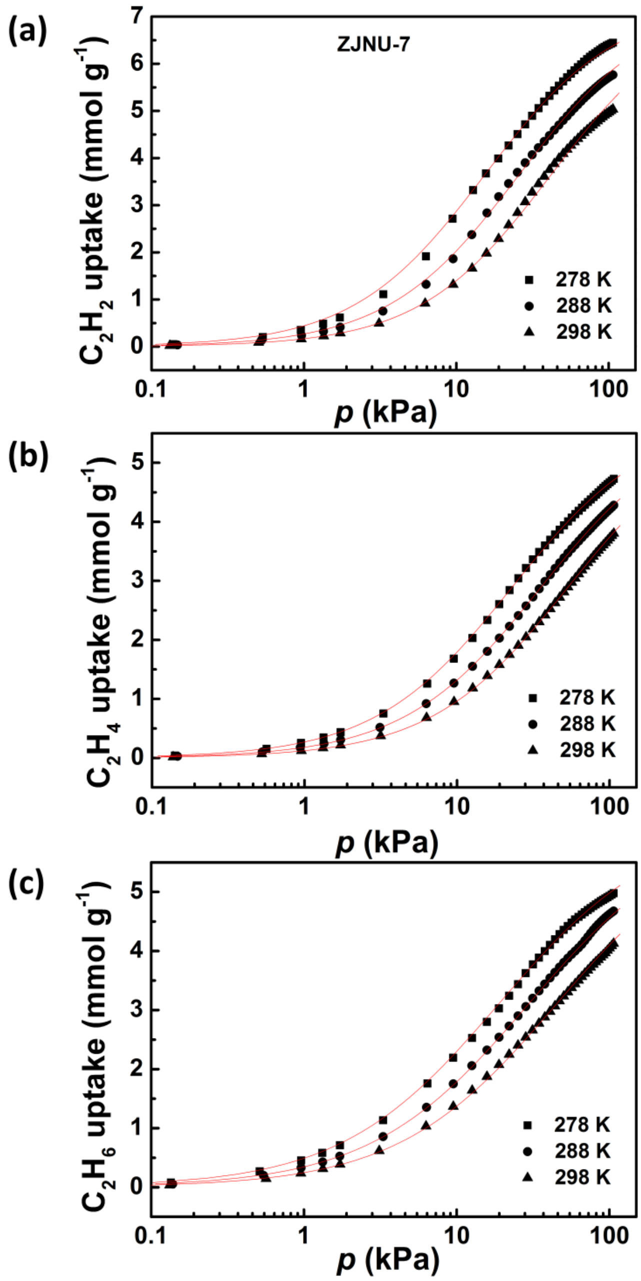


Fig. S7 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) C_2H_4, and (c) C_2H_6 in **ZJNU-7** with the fitted isotherms at 278 K, 288 K, and 298 K.

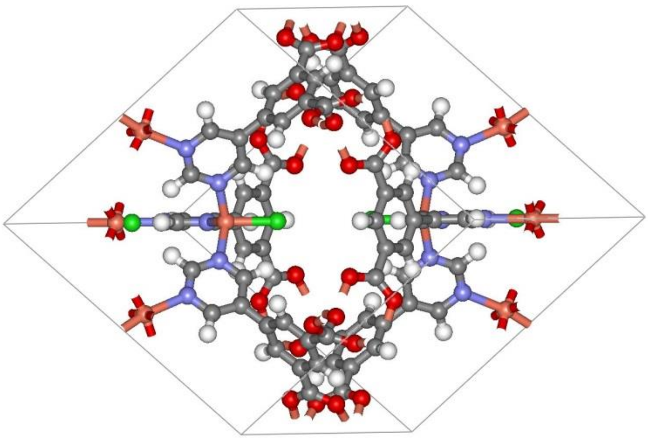
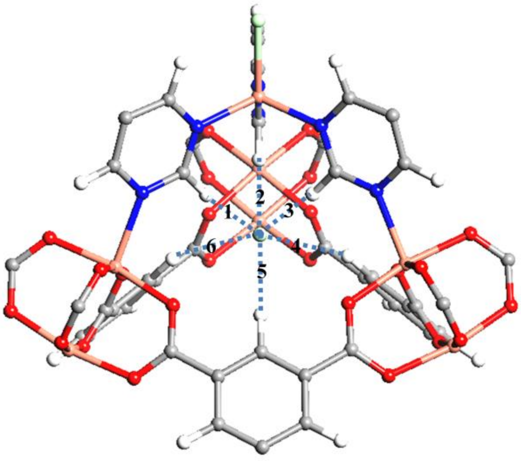


Fig. S8 The calculated stable structure of **ZJNU-7**.



1	2.291
2	2.285
3	2.285
4	3.068
5	3.085
6	3.063

Fig. S9 DFT optimization results about the couteranion (Cl^-) position. The unit of interatomic distances shown in the inset Table is Å.

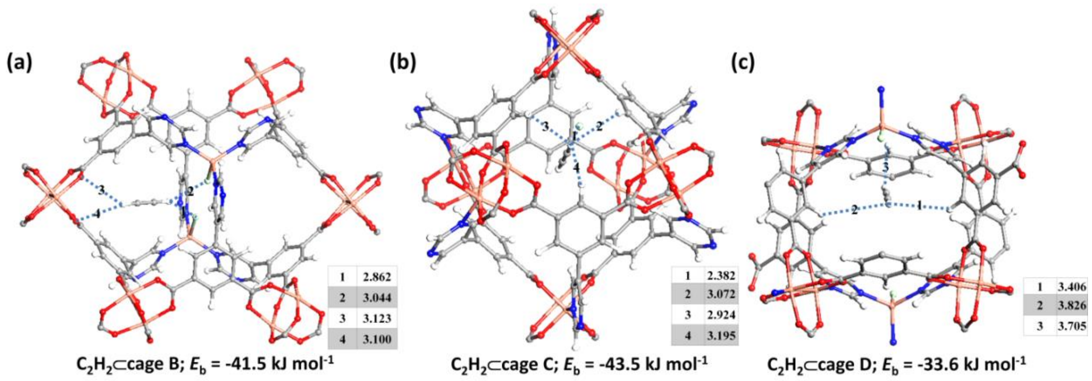


Fig. S10 The adsorption sites of C_2H_2 in (a) cage B, (b) cage C, and (c) cage D, and the corresponding binding energies. The unit of interatomic distances shown in the inset Table is Å.

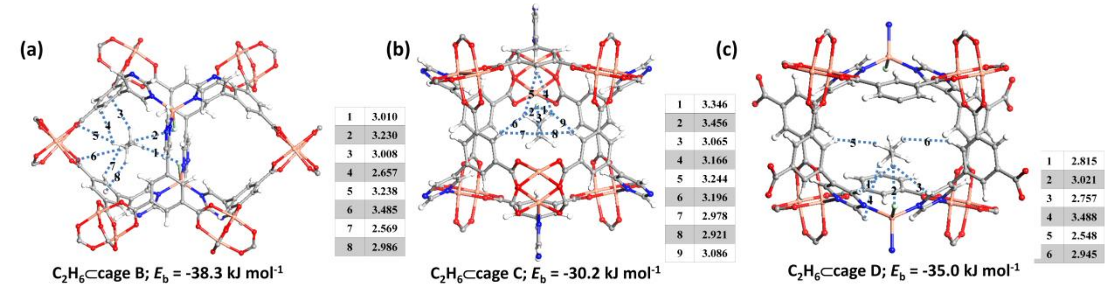
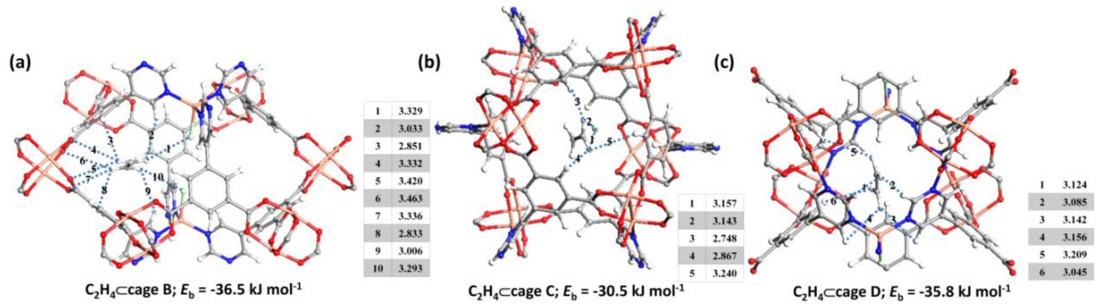


Fig. S11 The adsorption sites of C_2H_6 in (a) cage B, (b) cage C, and (c) cage D, and the corresponding binding energies. The unit of interatomic distances shown in the inset Table is Å.

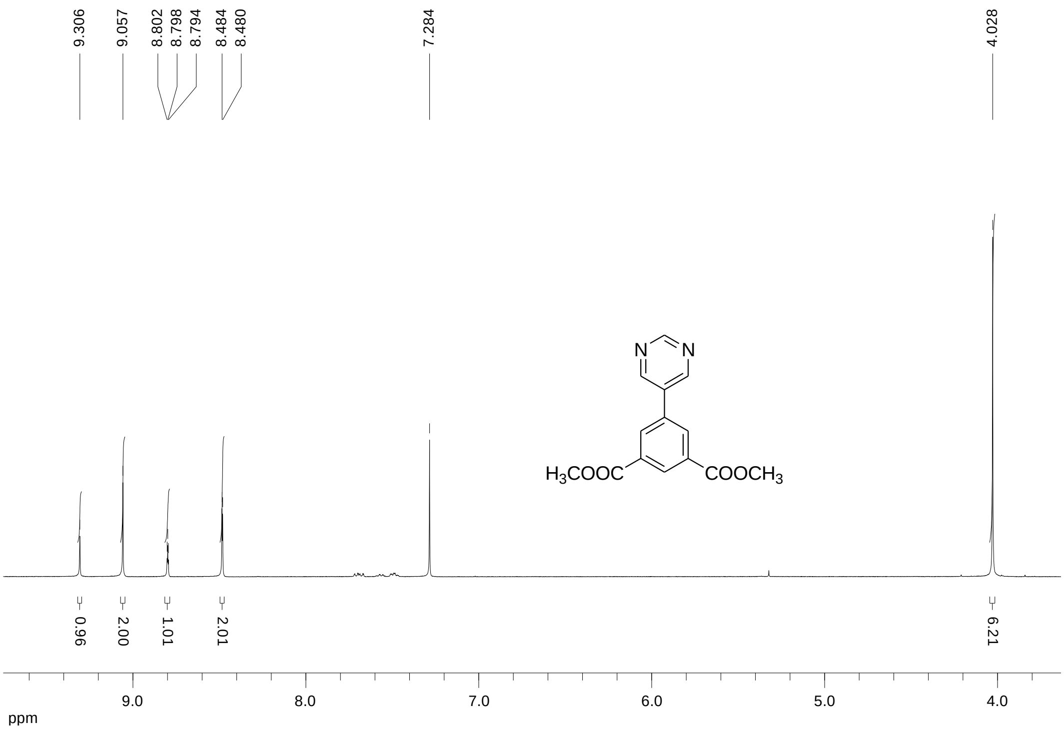


1	3.329
2	3.033
3	2.851
4	3.332
5	3.420
6	3.463
7	3.336
8	2.833
9	3.006
10	3.293

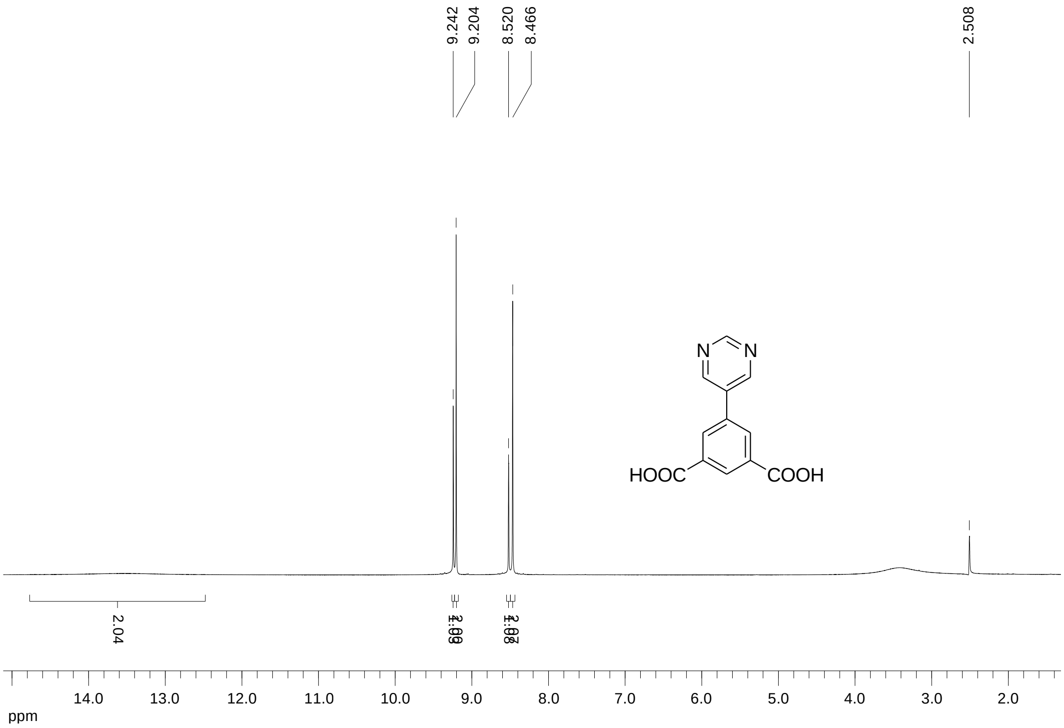
1	3.157
2	3.143
3	2.748
4	2.867
5	3.240

1	3.124
2	3.085
3	3.142
4	3.156
5	3.209
6	3.045

Fig. S12 The adsorption sites of C_2H_4 in (a) cage B, (b) cage C, and (c) cage D, and the corresponding binding energies. The unit of interatomic distances shown in the inset Table is Å.



9.306
9.057
8.802
8.798
8.794
8.484
8.480
7.284
4.028
H3COOC
COOCH3
0.96
2.00
1.01
2.01
6.21
9.0
8.0
7.0
6.0
5.0
4.0
ppm



9.242
9.204
8.520
8.466
2.508
HOOC
COOH
2.04
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm

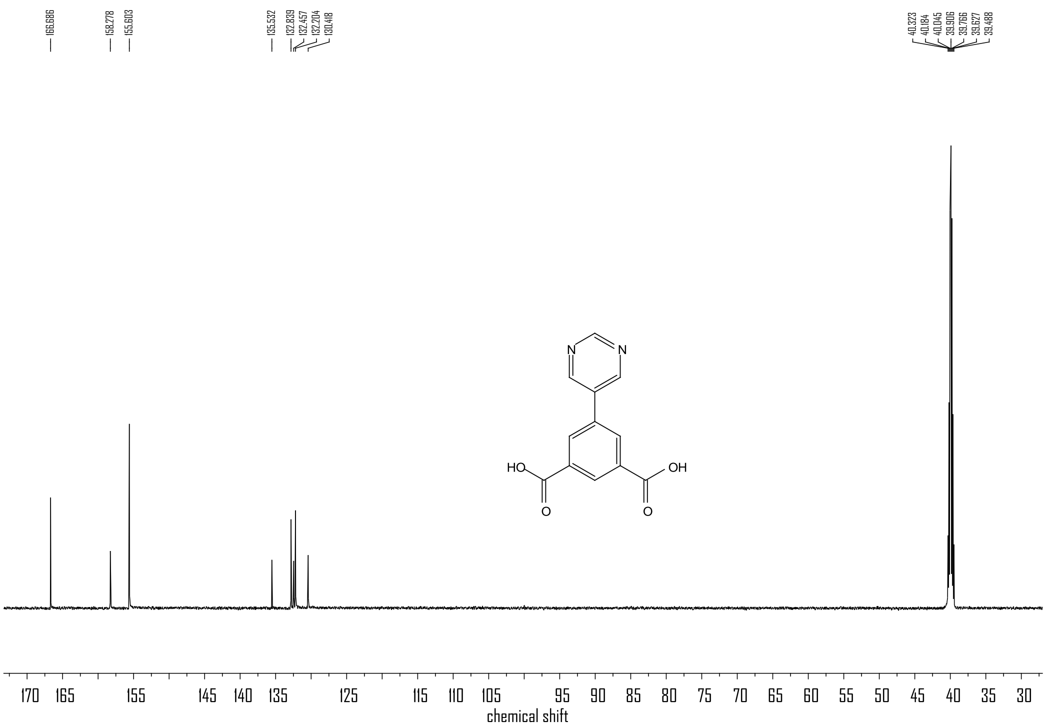


Fig. S13 ^{1}H and ^{13}C NMR spectra

Table S1 Summarizes of physical parameters of C_2H_2, C_2H_4, C_2H_6, CO_2, and CH_4

Adsorbates	BP (K)	T_c (K)	p_c (bar)	Kinetic diameter (Å)	Molecular dimension (Å)	Polarizability ($\times 10^{25}$ cm^3)	Dipole moment ($\times 10^{18}$ esu cm)	Quadruple moment ($\times 10^{26}$ esu cm^2)
C_2H_2	188.40	308.30	61.14	3.3	3.32×3.34×5.70	33.3-39.3	0	+7.5
C_2H_4	169.42	282.34	50.41	4.163	3.28×4.18×4.84	42.52	0	+1.50
C_2H_6	184.55	305.32	48.72	4.443	3.81×4.08× 4.82	44.4-44.7	0	+0.65

BP: normal boiling point; T_c: critical temperature; p_c: critical pressure

Table S2 Crystal data and structure refinement for **ZJNU-7**.

MOF	**ZJNU-7**
Empirical formula	$C_{36}H_{18}ClCu_4N_6O_{12}$
Formula weight	1016.17
Temperature (K)	150(2)
λ (Å)	0.71073
Crystal system	Trigonal
Space group	*R-3m:H*
Unit cell dimensions	a = 18.6356(4) Å b = 18.6356(4) Å c = 28.6177(7) Å $\alpha = 90^{o}$ $\beta = 90^{o}$ $\gamma = 120^{o}$
V (Å^3)	8607.0(4)
Z	6
D_c (g cm^{-3})	1.176
μ (mm^{-1})	1.557
F(000)	3030
θ range for data collection (^{o})	3.056 to 27.490
Limiting indices	$-23 \leq h \leq 24$ $-24 \leq k \leq 24$ $-37 \leq l \leq 36$
Reflections collected / unique	17821 / 2396
R_{int}	0.0289
Max. and min. transmission	0.898 and 0.879
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2396 / 0 / 106
Goodness-of-fit on F^2	1.549
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0387 wR_2 = 0.1735
R indices (all data)	R_1 = 0.0420 wR_2 = 0.1766
Largest diff. peak and hole (e$\cdot$Å^{-3})	0.649 and -1.779
CCDC	2032687

Table S3 Langmuir-Freundlich fitting parameters for adsorption of C_2H_2, C_2H_4, and C_2H_6 in **ZJNU-7**.

Adsorbates	q_{sat} (mmol g^{-1})	b_0 (kPa)$^{-v}$	E (kJ mol^{-1})	v	R^2
C_2H_2	7.29633	1.99792×10^{-8}	34.635	1.00346	0.99824
C_2H_4	5.78088	2.70808×10^{-7}	27.982	0.96256	0.99988
C_2H_6	6.22563	1.66603×10^{-6}	25.073	0.83471	0.99938

Table S4 Summaries of gas adsorption properties of **ZJNU-7.**

ZJNU-7		298 K	288 K	278 K
Uptake capacity[a] (cm^3 g^{-1}, STP)	C_2H_2	112.8	129.2	144.5
	C_2H_4	85.2	95.9	105.9
	C_2H_6	92.5	104.8	111.6
IAST adsorption selectivity[a]	C_2H_2/C_2H_4 (1:99)	2.31	2.01	1.77
	C_2H_2/C_2H_4 (1:1)	2.51	2.13	1.85
	C_2H_6/C_2H_4 (1:1)	1.56	1.56	1.57
	C_2H_6/C_2H_4 (1:9)	1.58	1.57	1.58
	C_2H_6/C_2H_4 (1:15)	1.58	1.57	1.58
Q_{st}[b] (kJ mol^{-1})	C_2H_2	34.1		
	C_2H_4	29.3		
	C_2H_6	29.7		

[a] at 1 atm; [b] at near zero surface coverage

Table S5 Summary of the adsorption properties of MOFs reported for C_2H_2/C_2H_4 separation

MOFs	C_2H_2 uptake ($cm^3\ g^{-1}$, STP)	C_2H_4 uptake ($cm^3\ g^{-1}$, STP)	C_2H_2/C_2H_4 IAST selectivity	Q_{st} (kJ mol^{-1})	*ref*
UTSA-300 $Zn(dps)_2(SiF_6)$	76.4	0.92	>10^4	57.6	1
ELM-11 Cu(4,4'-bipy)$_2$$(BF_4)_2$	78.96	NA	>10^4	23.8	2
ELM-13 Cu(4,4'-bipy)$_2$$(CF_3BF_3)_2$	60.17	NA	>10^4	31	2
NCU-100/UTSA-300-Cu $Cu(dps)_2(SiF_6)$	102.4	7.2	7291	60.5	3
UTSA-200 SIFSIX-14-Cu-i	81.8	14.1	6320	40	4
ZU-33 GeFSIX-14-Cu-i	119 cc/cc	22 cc/cc	>1100	43.6	5
$Ni_3(pzdc)_2(7Hade)_2$	52.9	33.1	168	44.5	6
$[Ni_2(BTEC)(bipy)_3]$	76.8	8.0	104	26.5	7
ZU-32 GeFSIX-2-Cu-i	116 cc/cc	64 cc/cc	67	42.6	5
TIFSIX-2-Cu-i	91.8	56	55	46.3	8
NKMOF-1-Ni	61.0	47.3	49	60.3	9
SIFSIX-2-Cu-i	90.0	49.1	44.54	41.9	10
Ni-gallate	80.4	44.2	43.7	46	11
NbOFFIVE-2-Ni-i ZU-62-Ni	67.2	17.9	37.2	43	12
CPL-1	46.4	6.9	26.8	40.2	13
FJU-22	114.8^{a}	85.8^{a}	25.8^{b}	23	14
ZJU-74	85.7^{d}	NA	24.2	45	15
M'MOFs-3a	42.0^{c}	9.2^{c}	24.03	27.1	16
ZU-12-Ni TIFSIX-2-Ni-i	94.3	54.2	22.7	40	17
Mg-gallate	98.4	67.9	20.9	33	11
$\{[Mn_3(bipy)_3(H_2O)_4][Mn(CN)_6]_2$	59^{a}	0	16	32.4	18
Co-gallate	87.1	75.5	15.0	47	11
ELM-12	57.3	22.5	14.8	25.4	19
M'MOF-4	30.1^{d}	9.4^{d}	14.31	35	20
MECS-5	86.2	25.5	12.6	26	21
CPL-2	70.1	41.7	12.0	30.8	13
TIFSIX-4-Cu-i	96.3	33.6	11	40.8	8
UTSA-100	95.6	37.2	10.72	22	16
SIFSIX-1-Cu	190.4	92.1	10.63	30	10

UTSA-220	76.2	56.7	10	29.0	[22]
SIFSIX-3-Zn	81.5	50.2	8.82	21	[10]
M'MOF-7	14.4	5.1	7.43	47	[20]
M'MOF-6	37.9	14.3	7.42	29	[20]
BSF-4	53.3	34.9	7.3	35	[23]
SIFSIX-2-Cu	120.5	45.2	6.0	26.3	[10]
CPL-5	67.4	41.2	6.0	31.3	[13]
NbU-1	81.5	46.4	5.9	38.3	[24]
UTSA-60	70	46	5.5	36	[25]
Ni-DCPTP	146.4	100.4	5.5	38.9	[26]
SIFXIX-3-Ni	73.9	39.2	5.03	30.5	[10]
M'MOF-5	30.5	11.8	4.94	49	[20]
Mg-CUK-1	61.6	39.2	3.13[e]	21	[27]
M'MOFs-2a	43.4	28.7	3.12	37.7	[16]
UPC-98	30.2	17.6	3.1	22.8	[28]
BSF-1	52.6	36.6	2.3	31	[29]
NOTT-300	142[f]	95.9[f]	2.17	32	[30]
FeMOF-74	152.3[g]	136.6[g]	2.08	47	[31]
TJT-100	127.7[e]	98.1[e]	1.8	31	[32]

[a] 296 K; [b] based on breakthrough experiments; [c] 295 K; [d] 296 K; [e] 273 K; [f] 293 K; [g] 318 K

Table S6 Summary of MOFs reported for C_2H_6/C_2H_4 separation

MOFs	C_2H_6 uptake ($cm^3\ g^{-1}$, STP)	C_2H_4 uptake ($cm^3\ g^{-1}$, STP)	C_2H_6/C_2H_4 IAST selectivity	Q_{st} ($kJ\ mol^{-1}$)	*Ref.*
NIIC-20-Bu	55	31.7	24	24.1/22.9	33
$Fe_2(O_2)$dobdc	74.3	NA	4.4	66.8	34
$Cu(Qc)_2$	41.5	17.5	3.4	29	35
ZJU-120	110	88	2.74	27.6	36
MAF-49	38.7	38.0	2.7	60	37
Ni(TMBDC) $(DABCO)_{0.5}$	122.1	112.4	1.985	39	38
ZIF-4	52.0	49.5	2.15	NA	39
MUF-15	105 (293K)	93 (293K)	1.96	29.2/28.2	40
ZIF-71	31.7	24.5	1.91	NA	41
PCN-250	116.7	94.5	1.9	23.6	42
MIL-53(Al)-FA	82.9 (308K)	NA	1.9	34	43
Ni(bdc)$(ted)_{0.5}$	107.5	73.7	1.85	29	44
Co(bdc)$(ted)_{0.5}$	92.5	62.0	1.83	29	44
Cu(bdc)$(ted)_{0.5}$	82.4	56.7	1.82	29	44
Ni(bdc)$(ted)_{0.5}$	112	76.2	1.8	21.5	45
Ni(bdc)$(ted)_{0.5}$	115	76	1.80	21	36
PCN-245	3.27	2.39	1.8	23.0	46
IRMOF-8	112.5	107.5	1.8	NA	47
CPM-81-Co	123.5	113.5	1.8	24.2/24.1	64
MIL-53(Al)-BDC	NA	NA	1.8	22.5	48
ZIF-8	53.8	30.2	1.8	NA	49
NUM-7	63.9	58.6	1.757	35.8/30.0	50
Co_2V-bdc-tpt (CPM-733)	159.6	142.7	.1.75	23.4	51
Zn(bdc)$(ted)_{0.5}$	99.7	70.8	1.73	31	44
ZIF-8	45.4	34.2	1.7		
Ca(H_2tcpb)	62.3	59.8	1.7	35.1/26.8	52
DUT-8(Ni)	77.3	43.0	1.65	25.5	53
Mg_2V-bdc-tpt (CPM-233)	166.8	146.1	1.64	27.3	51
Ni(BDC) $(DABCO)_{0.5}$	97.7	68.1	1.619	NA	38
JNU-2	92	81	1.6	29.4/26.7	63
Mg_2Ti-bdc-tpt (CPM-223)	154.8	142.1	1.57	25.4	51
Mg_2Ti-bdc-tpbz (CPM-223-tpbz)	154.2	140.0	1.51	21.9	51
ZJU-121	69	71	1.51	47.1	36
MIL-142A	85.1	65.0	1.5	27.3	54
Ni(HBTC)(bipy)	147.8	6.0	1.5	33.6	55
ZIF-7	41.1	40.4	1.5	NA	56

Co_2Ti-bdc-tpt (CPM-723)	154.7	149.4	1.50	21.7	[51]
Co_2V-ndc-tpt (CPM-736)	90.2	86.9	1.48	30.4	[51]
Azole-Th-1	100.2	80.7	1.44	28.6	[57]
Mg_2V-dmbdc-tpt (CPM-238)	124.6	117.6	1.43	24.7	[51]
DUT-8(Cu)	3.96	2.27 (303K)	1.43	25.8	[53]
Zn-PNMI	36.5	32.7	1.42	24.5	[58]
Co_2V-dmbdc-tpt (CPM-738)	104.6	102.1	1.42	27.9	[51]
In-soc-MOF-1	4.04	3.72	1.4	28.4	[59]
UTSA-33	62.0	61.0	1.4	33	[60]
UTSA-35	54.5	48.5	1.4	NA	[61]
$Ni_2(HBTC)_2(bipy)_{0.6}(dabco)_{1.4}$	4.8mmol/g	4.6	1.4	33.5	[55]
ZIF-9	54.9	54.0	1.39	NA	[41]
Mn-PNMI	61.8	45.3	1.38	23.5	[58]
Cd-PNMI	41.9	31.6	1.27	19.4	[58]
$Cu(ina)_2$	44.7	42.7	1.3	26.5	[35]
HCP-1.5	56	50.4	1.3	NA	[62]
Mg_2Ti-bdc-tppy (CPM-223-tppy)	160.6	164.5	1.28	25.0	[51]
TJT-100	NA	NA	1.2	29	[32]

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