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An Anionic Metal-Organic Framework Based on an Angular Tetracarboxylic Acid and Mononuclear Copper Ion for Selective Gas Adsorption

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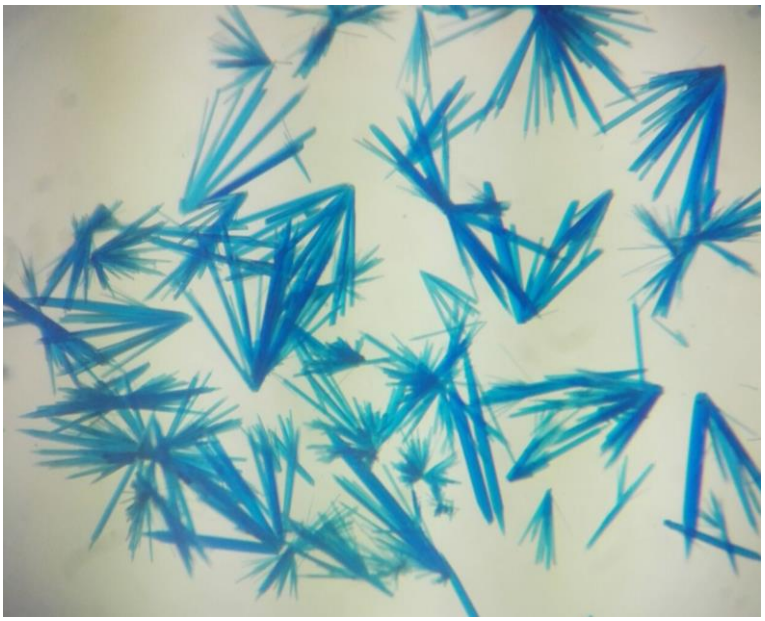


Fig. S1 Photograph of the as-synthesized **ZJNU-55**.

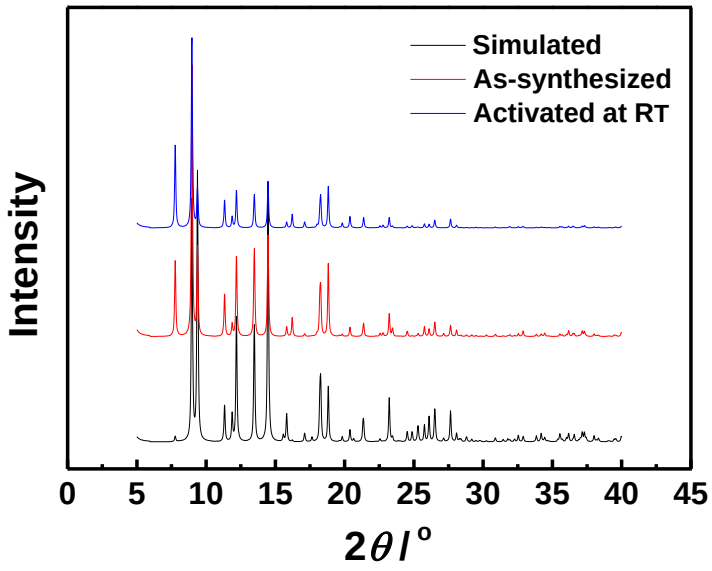


Fig. S2 PXRD patterns.

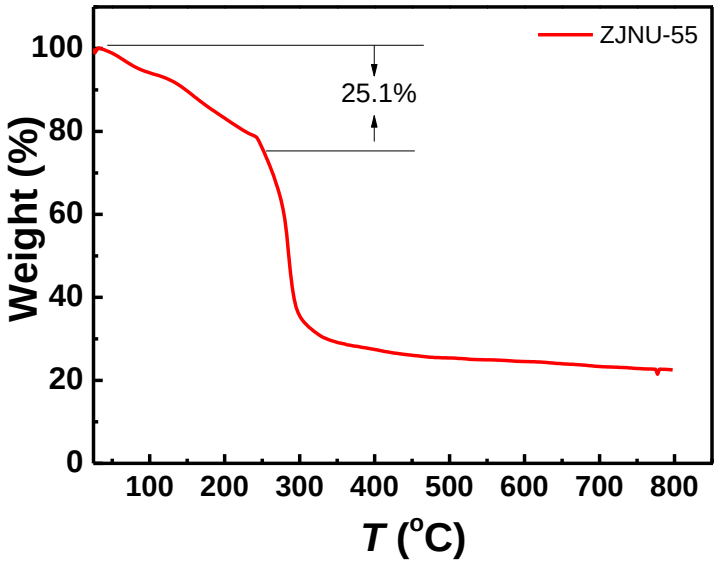


Fig. S3 TGA curve of the as-synthesized **ZJNU-55** under a nitrogen atmosphere.

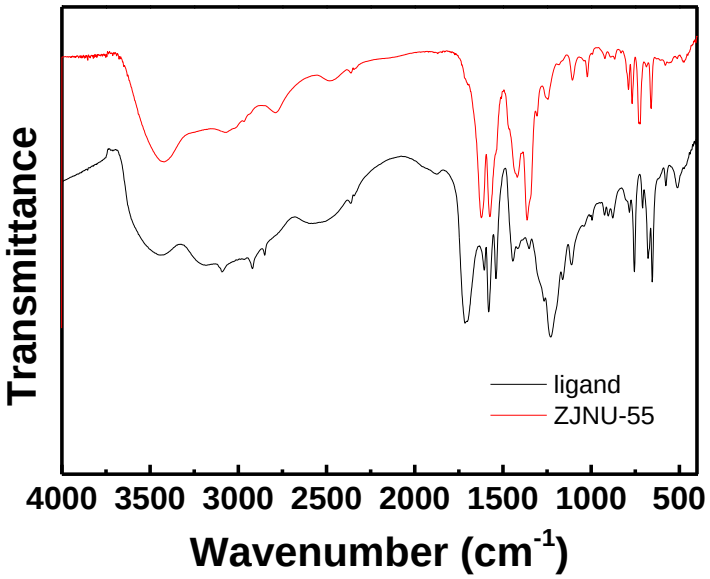
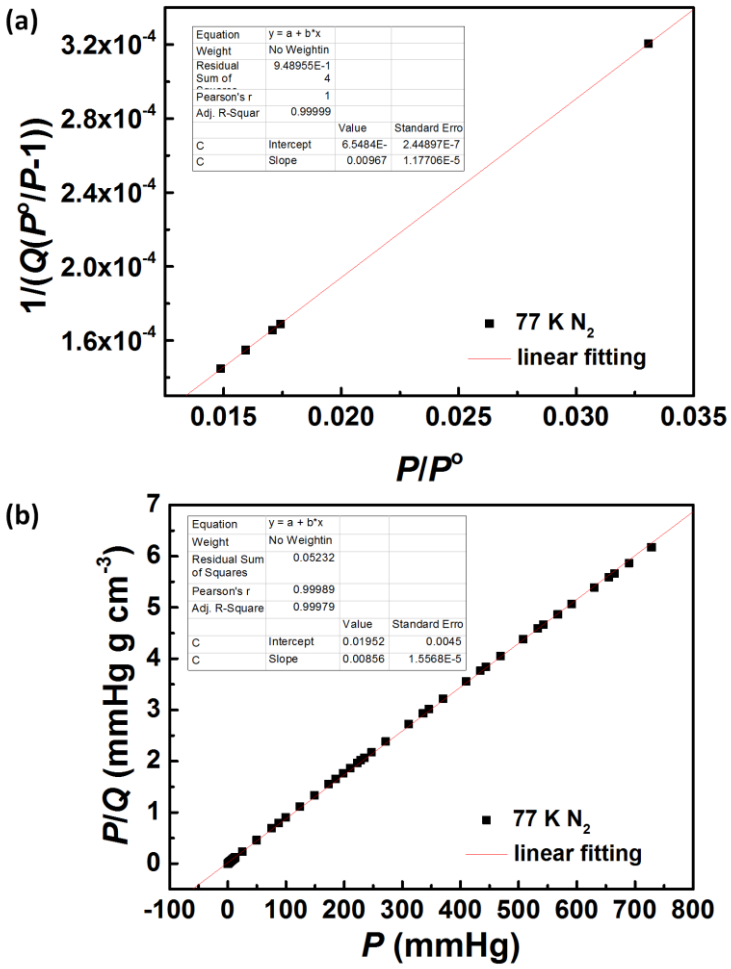


Fig. S4 FTIR spectra of the organic ligand and as-synthesized **ZJNU-55**.



S_{BET} = (1/(6.5484×10^{-7}+0.00967))/22414×6.023×10^{23}×0.162×10^{-18} = 450.1 m^2 g^{-1}

$S_{Langmuir}$ = (1/(0.00856)/22414×6.023×10^{23}×0.162×10^{-18} = 508.6 m^2 g^{-1}

Fig. S5 (a) BET and (b) Langmuir plots for **ZJNU-55a**.

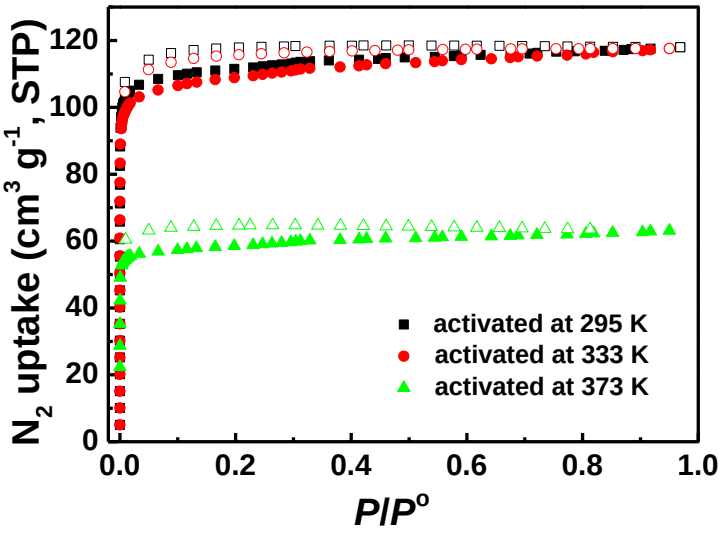


Fig. S6 N_2 adsorption-desorption isotherms of **ZJNU-55** activated at different temperatures. Solid and open symbols represent adsorption and desorption, respectively.

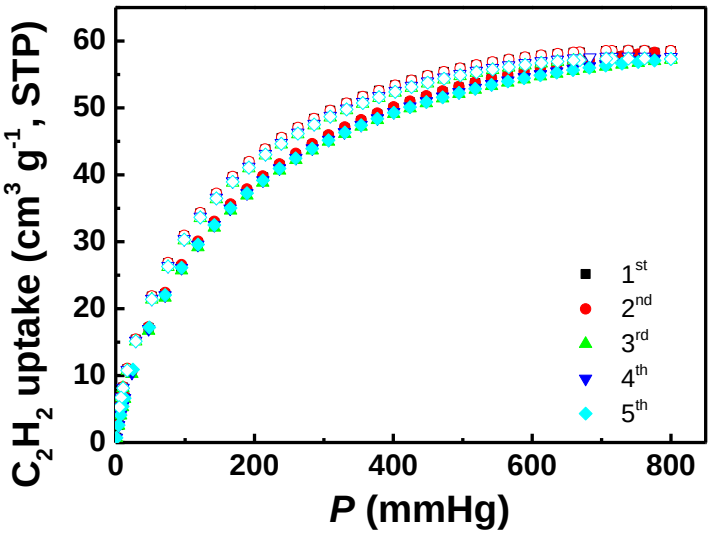


Fig. S7 Five cycles of C_2H_2 adsorption-desorption isotherms at 298 K. Solid and open symbols represent adsorption and desorption, respectively.

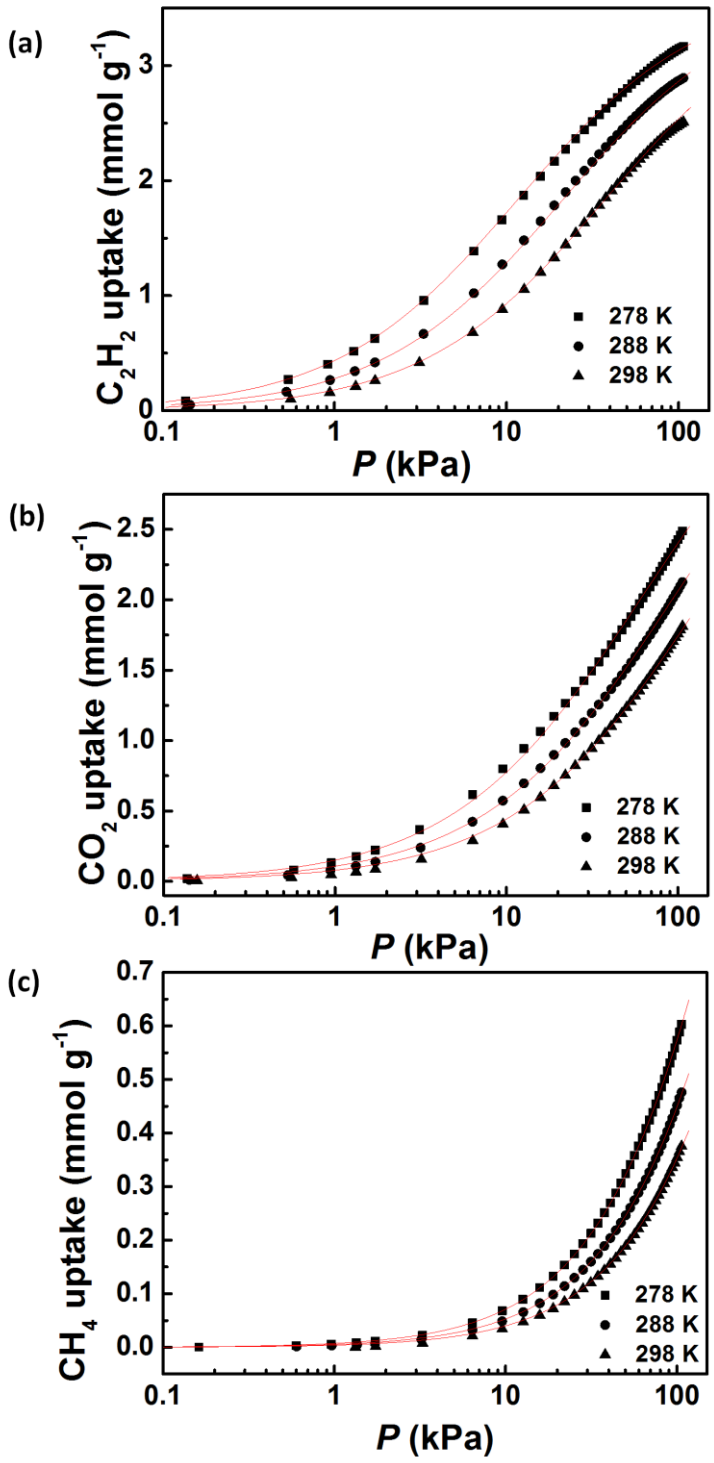


Fig. S8 Comparison of the pure-component (a) C_2H_2, (b) CO_2 and (c) CH_4 isotherm data with the fitted isotherms.

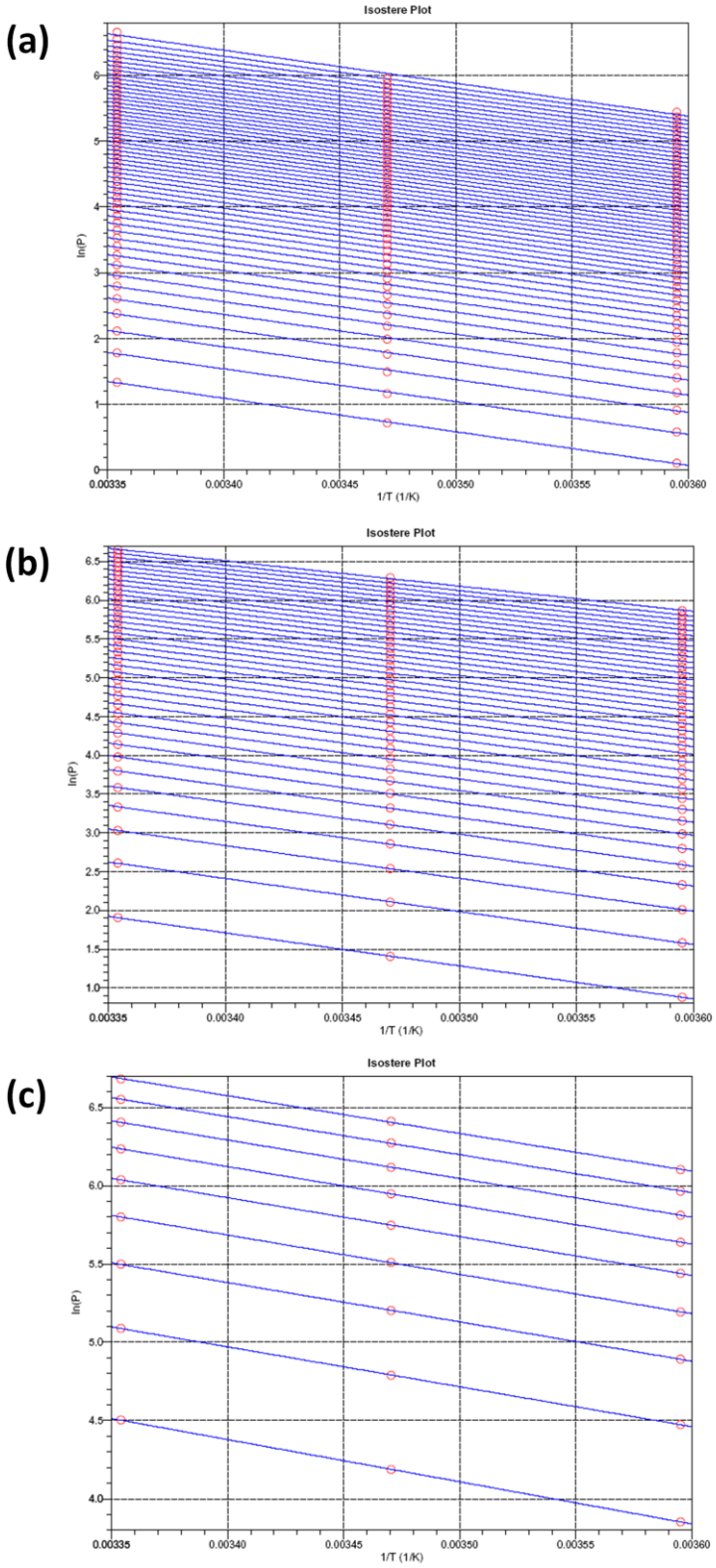
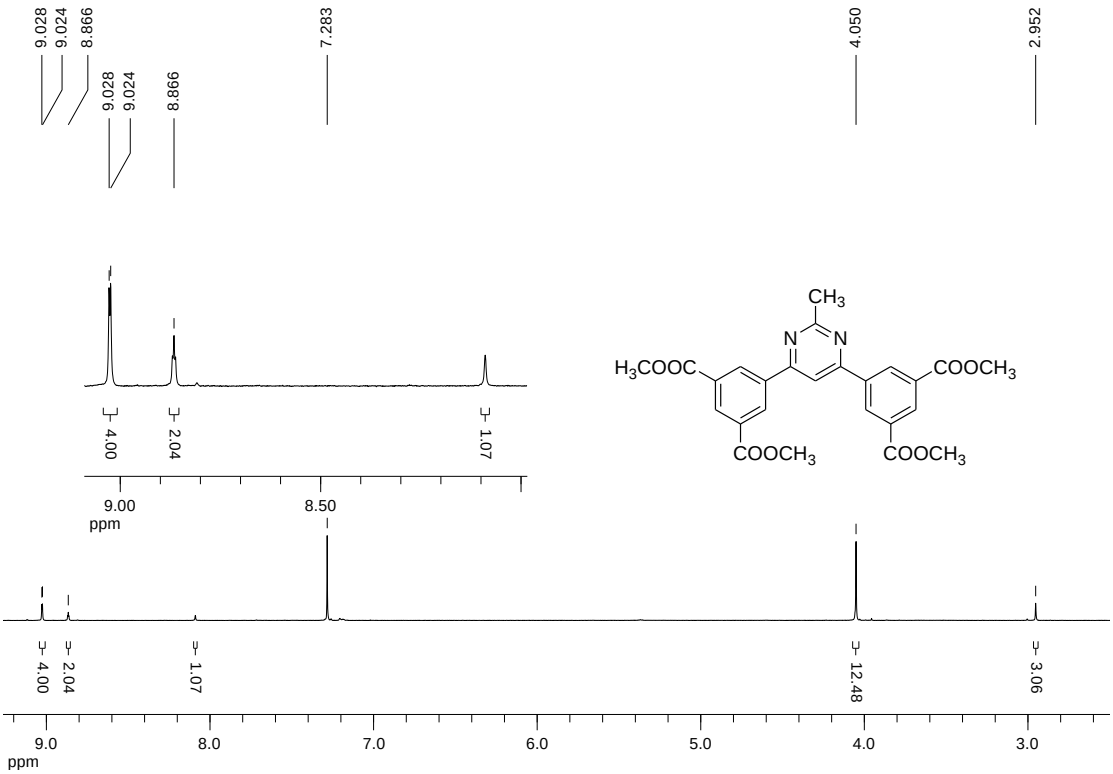


Fig. S9 Isosteric plots for (a) C_2H_2, (b) CO_2 and (c) CH_4 adsorption.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9.028
9.024
8.866
7.283
4.050
2.952
4.00
2.04
1.07
9.00
ppm
8.50
CH3
N
N
H3COOC
COOCH3
COOCH3
COOCH3
4.00
2.04
1.07
12.48
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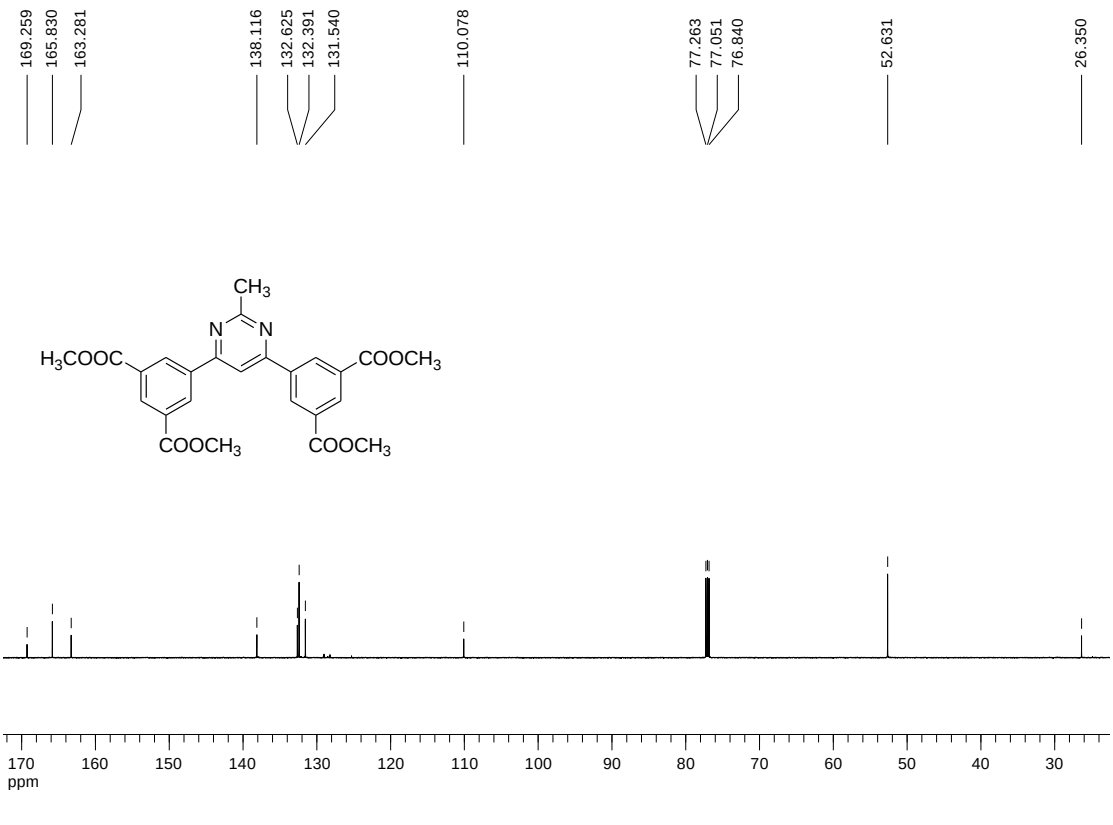
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm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132.625
132.391
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77.051
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26.350
CH3
N
N
H3COOC
COOCH3
COOCH3
COOCH3
170
160
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140
130
120
110
100
90
80
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60
50
40
30
ppm

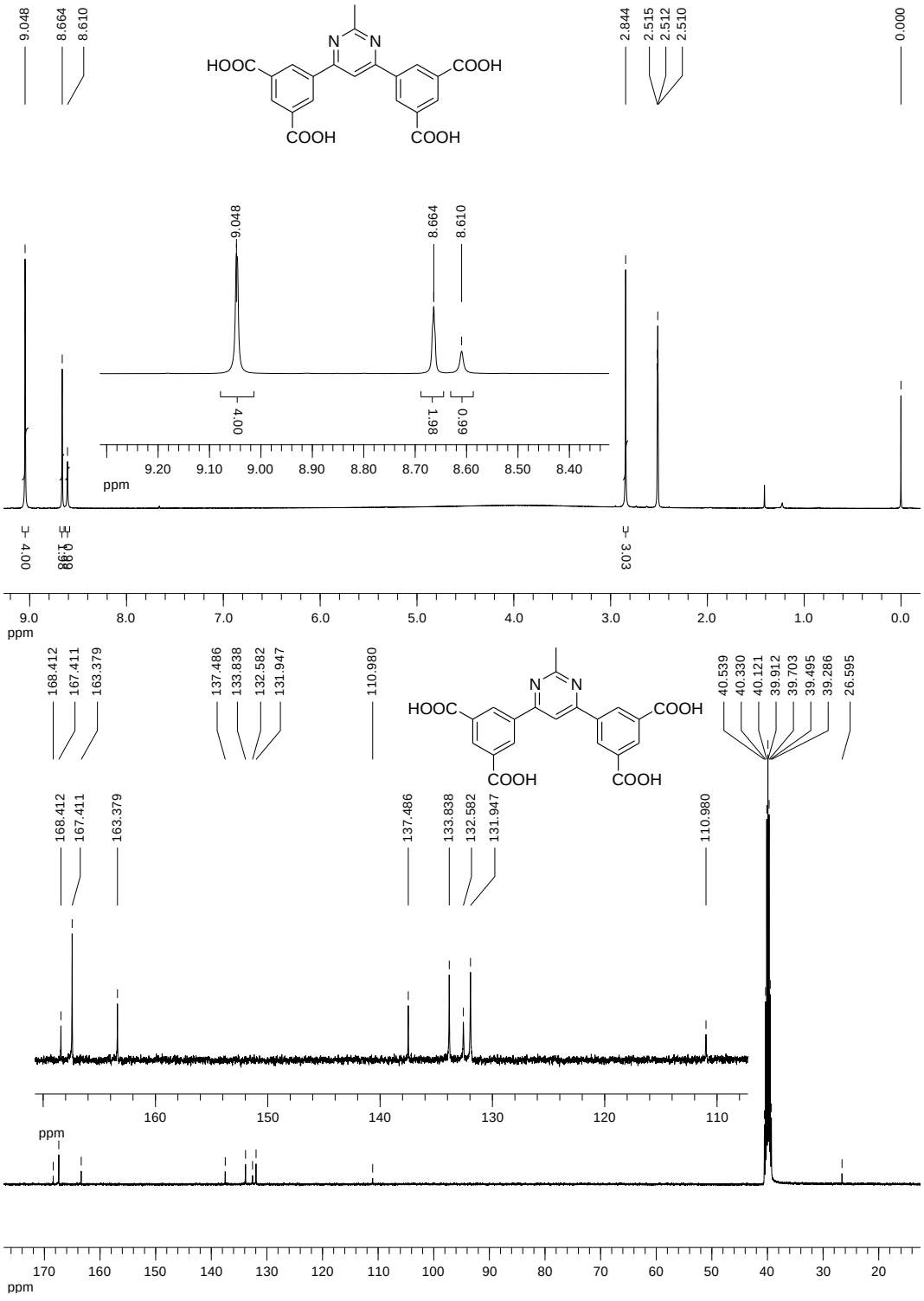

Fig. S10 ^{1}H and ^{13}C NMR spectra.

Table S1 Crystal data and structure refinement for **ZJNU-55**.

Empirical formula	$C_{21}H_{10}CuN_2O_8$
Formula weight	481.86
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Hexagonal
Space group	$P6_2$
Unit cell dimensions	a = 22.7393(15) Å . b = 22.7393(15) Å c = 10.7316(10) Å $\alpha = 90^o$ $\beta = 90^o$ $\gamma = 120^o$
Volume (Å^3)	4805.6(8)
Z	6
Calculated density (g cm^{-3})	0.999
Absorption coefficient (mm^{-1})	0.715
F(000)	1458
Crystal size (mm)	0.270 ×0.160 ×0.110
θ range for data collection (^{o})	2.610 to 27.540
Limiting indices	$-24 \le h \le 29$ $-29 \le k \le 29$ $-13 \le l \le 13$
Reflections collected / unique	51818 / 7386
R_{int}	0.0684
Completeness to θ = 25.242	99.9%
Absorption correction	Empirical
Max. and min. transmission	0.925 and 0.830
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7386 / 23 / 278
Goodness-of-fit on F^2	1.038
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0992, wR_2 = 0.2992
R indices (all data)	R_1 = 0.1148, wR_2 = 0.3149
Absolute structure parameter	0.5
Extinction coefficient	0
Largest diff. peak and hole (e·Å^{-3})	1.447 and -0.547
CCDC	1492066

Table S2 Langmuir-Freundich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-55a**.

guest	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v
C_2H_2	3.67137	8.66196×10^{-8}	32.95	0.81845
CO_2	4.05461	2.18764×10^{-6}	22.60	0.78765
CH_4	2.64787	4.46682×10^{-7}	20.18	1

Table S3 C_2H_2 uptakes and the Henry's Law adsorption selectivities of C_2H_2/CH_4 in the reported MOFs.

MOFs	C_2H_2 uptakes [cm^3 (STP) g^{-1}]	C_2H_2/CH_4 selectivities	Q_{st} (kJ mol^{-1})	*Ref*
Cu-TDPAT	177.7	127.1	42.5	[1]
Cu-TDPAH	155.7	80.9	23.5	[2]
ZJU-61	139.23	74.4	23.98	[3]
UTSA-50	90.6	68.0	39.4	[4]
Cu_2TPTC-Me	203	60.01	19.1	[5]
ZJNU-47a	213.8	58.5	35.0	[6]
UTSA-15	34	55.6	39.5	[7]
ZJNU-54a	210.5	50.5	35.4	[8]
Cu_2TPTC-OMe	204	46.14	20.1	[5]
ZJU-26	84	45.9	32.7	[9]
Cd-Tipa	64.13	39.1	41.05	[10]
ZJNU-55a	56.3	35.5	42.4	This work
M'MOF-20	21	34.9	33.7	[11]
$Zn_5(BTA)_6(TDA)_2$	44	22.3	37.3	[12]
UTSA-72a	27.8	21.1	20.2	[13]
Ni-TATB	64.1	16.3	NA	[14]
UTSA-36a	56.8	16.1	29.0	[15]
$[Zn_4(OH)_2(1,2,4\text{-BTC})]$	53	14.7	28.1	[16]
ZJNU-61a(Ho)	48.0	9.9	23.9	[17]
ZJU-30a	52.6	9.58	31.3	[18]
Cu(BDC-OH)	43	9.3	25.7	[19]
UTSA-10a	43.0	8.1	19	[20]
Yb-BPT	23.9	7.8	30.4	[21]
UTSA-28a-Cu	75.5	6.9	25.4	[22]
Cu-BBTC	84	5.74	37.64	[23]
UTSA-38a	63	5.6	24.7	[24]
FIR-51	141.9	NA	24.48	[25]
$InAg(na)_4$	98.14[a]	NA	24.79	[26]
ZJU-48a	57.07	NA	15.6	[27]

TDPAT = 2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine;
TDPAH = 2,5,8-tris(3,5-dicarboxylphenylamino)-*s*-heptazine;
na = nicotinic acid;
BBTC = 1, 1'-butadiynebenzene-3,3',5,5'-tetracarboxylate;
Tipa = tris(4-(1H-imidazol-1-yl)phenyl)amine;
TATB = 4,4',4''-*s*-triazine-2,4,6-triyltribenzoate;
1,2,4-BTC = benzene-1,2,4-tricarboxylate;
HBTA = 1,2,3-benzenetriazole;
H_2TDA = thiophene-2,5-dicarboxylic acid;

H_2BDC-OH = 2-hydroxy-benzenedicarboxylic acid.
NA = not available
[a] cm^3 (STP) cm^{-3}.

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