Electronic Supplementary Material (ESI) for Dalton Transactions.

An Aminopyrimidine-Functionalized Cage-Based Metal-Organic Framework Exhibiting Highly Selective Adsorption of C_2H_2 and CO_2 over CH_4

Jingjing Jiao,[a] Li Dou,[b] Huimin Liu,[a] Fengli Chen,[a] Dongjie Bai,[a] Yunlong Feng,[a] Shunshun Xiong,[*c] De-Li Chen[*b] and Yabing He[*a]

[a] 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

[c] Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, Sichuan 621900, China. E-mail: superssxiong@163.com

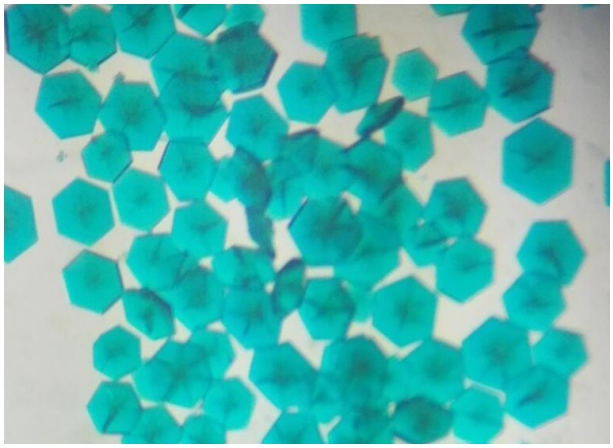


Fig. S1 Photograph of the as-synthesized crystals of **ZJNU-54**.

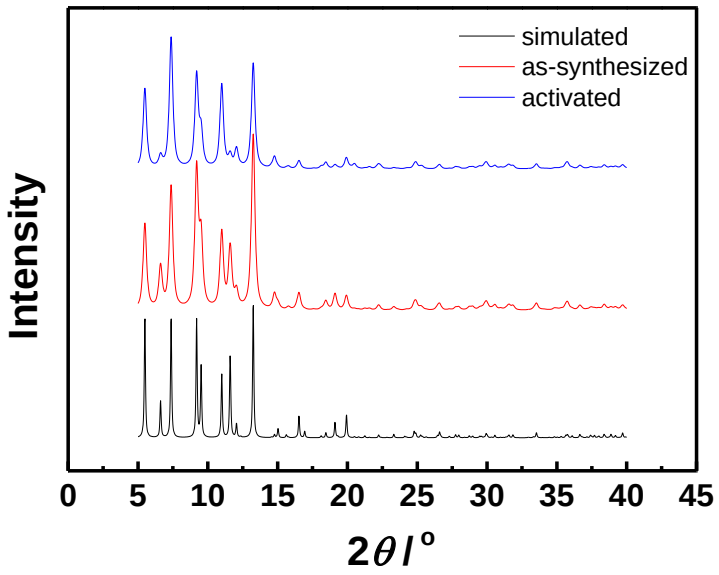


Fig. S2 PXRD patterns.

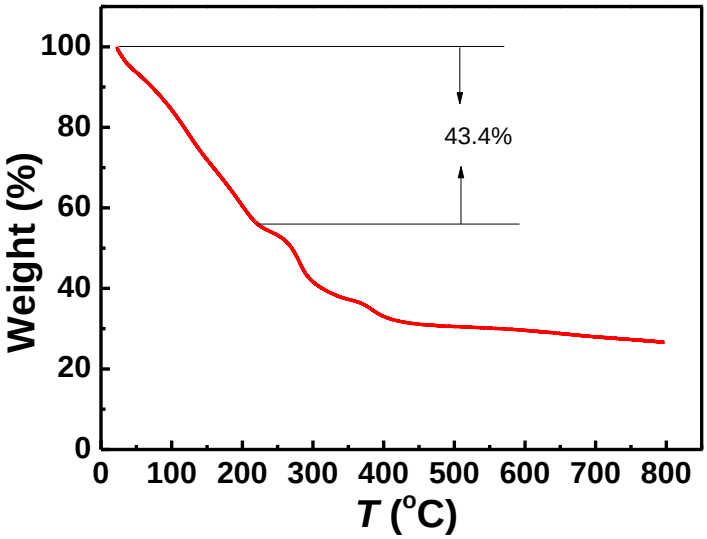


Fig. S3 TGA curve of as-synthesized **ZJNU-54** under a nitrogen atmosphere with a heating rate of 5 K min^{-1}.

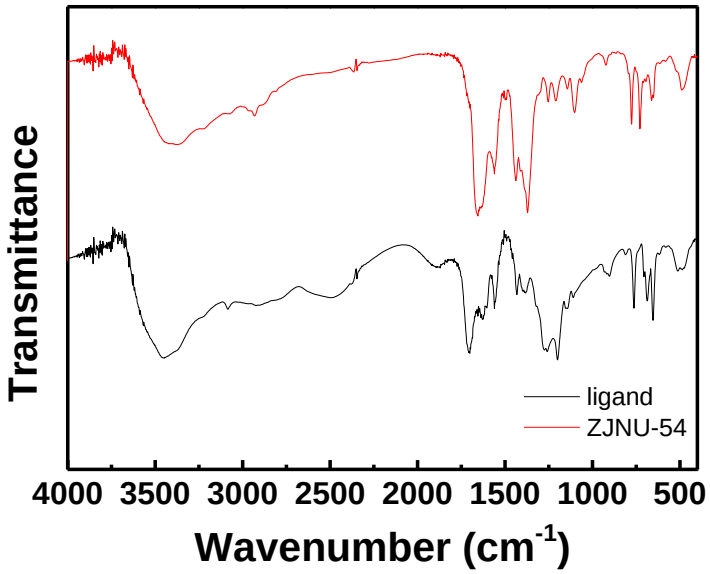


Fig. S4 FTIR spectra of the organic ligand (black) and as-synthesized **ZJNU-54** (red).

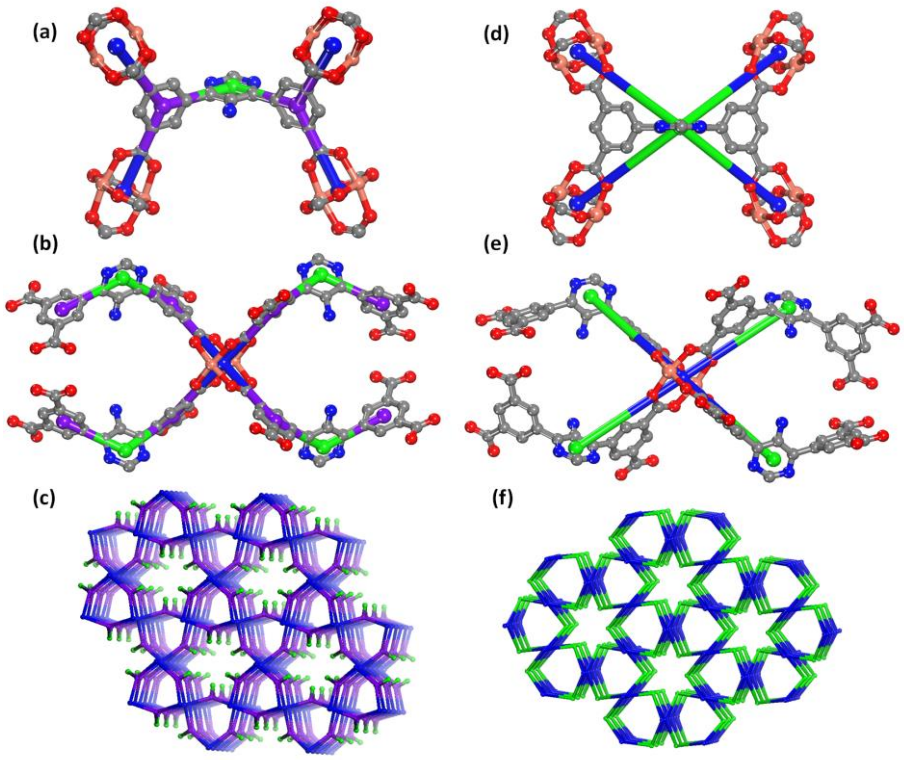
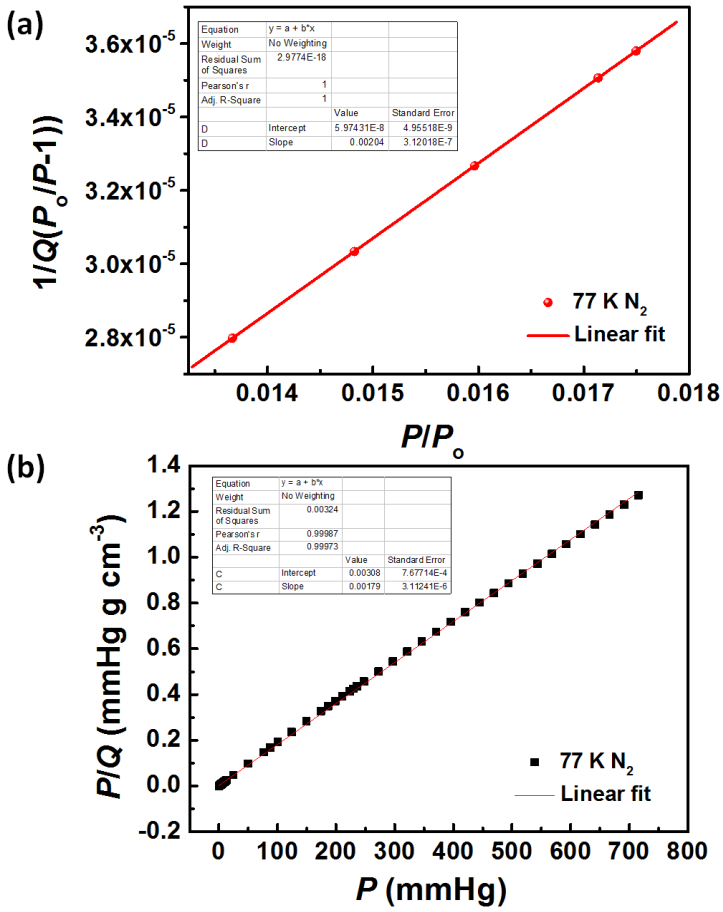


Fig. S5 Topological analysis based on two different simplifications of the organic ligands. If the organic ligand is considered as having a pair of 3-coordinated branch points (a), and the dicopper paddlewheel is regarded as 4-connected node (b), the overall network is a (3,4)-c binodal network with Schläfli symbol of $(6^2\cdot10^4)(6^3)_2$ (c). If the organic ligand and the dicopper paddlewheel are taken as 4-connected nodes (d, e), the overall network is a 4-connected 2-binodal network with the Schläfli symbol of $(4^2\cdot6^4)(4^2\cdot8^4)$ (f).



S_{BET} = 1/(5.97431 ×10^{-8}+0.00204)/22414 ×6.023 ×10^{23} ×0.162 ×10^{-18} = 2134 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00179)/22414 ×6.023 ×10^{23} ×0.162 ×10^{-18} = 2432 m^2 g^{-1}

Fig. S6 BET (a) and Langmuir (b) plots for **ZJNU-54a**.

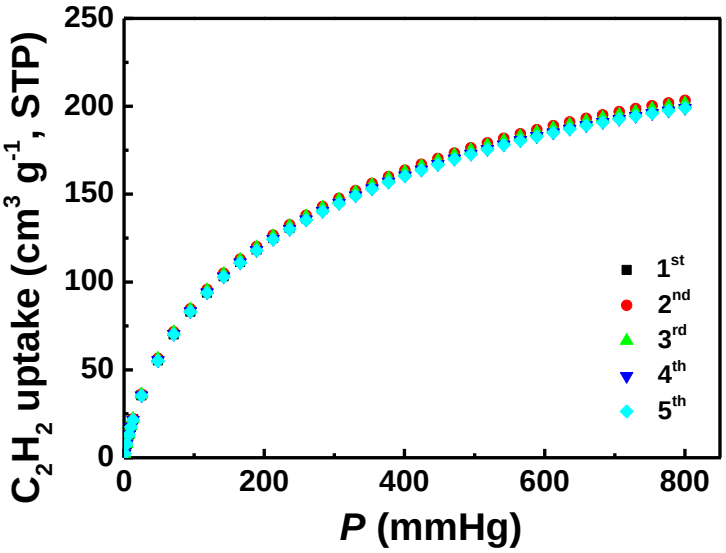


Fig. S7 Five cycles of C_2H_2 adsorption at 298 K in **ZJNU-54a**. Note that the reactivation process was applied between each cycle, which was achieved by heating the sample at 333 K until the degassed rate reached 3 μmHg min^{-1}.

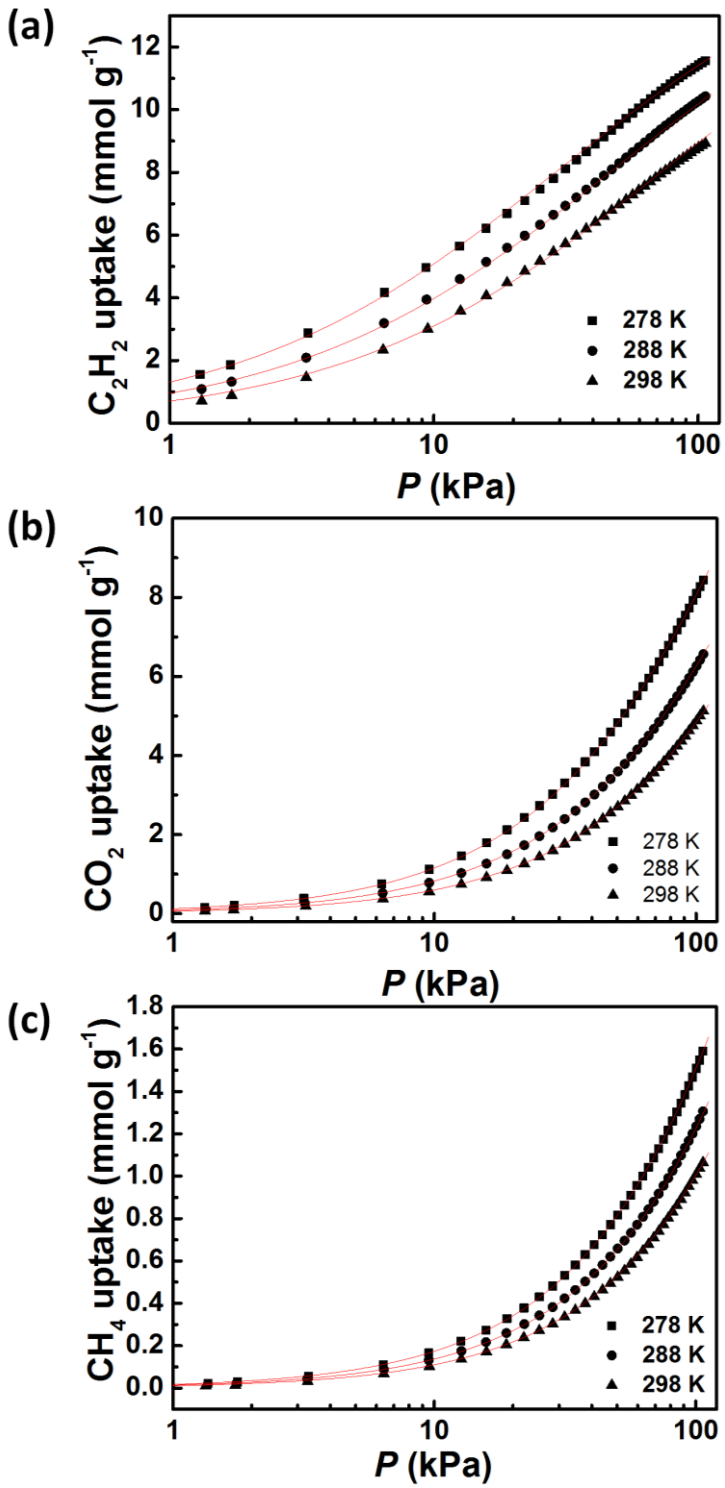


Fig. S8 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-54a** with the fitted isotherms (shown by continuous solid lines) at 278 K, 288 K and 298 K.

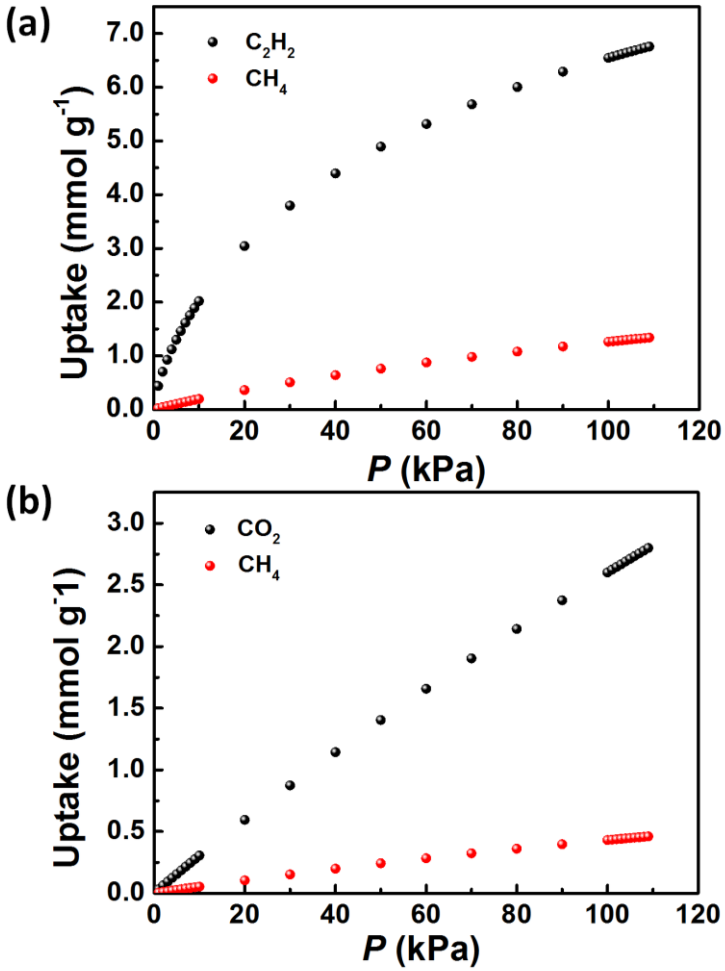


Fig. S9 IAST calculations of mixture adsorption isotherms of **ZJNU-54a** for (a) 50/50 C_2H_2/CH_4 and (b) 50/50 CO_2/CH_4 gas mixtures at 298 K.

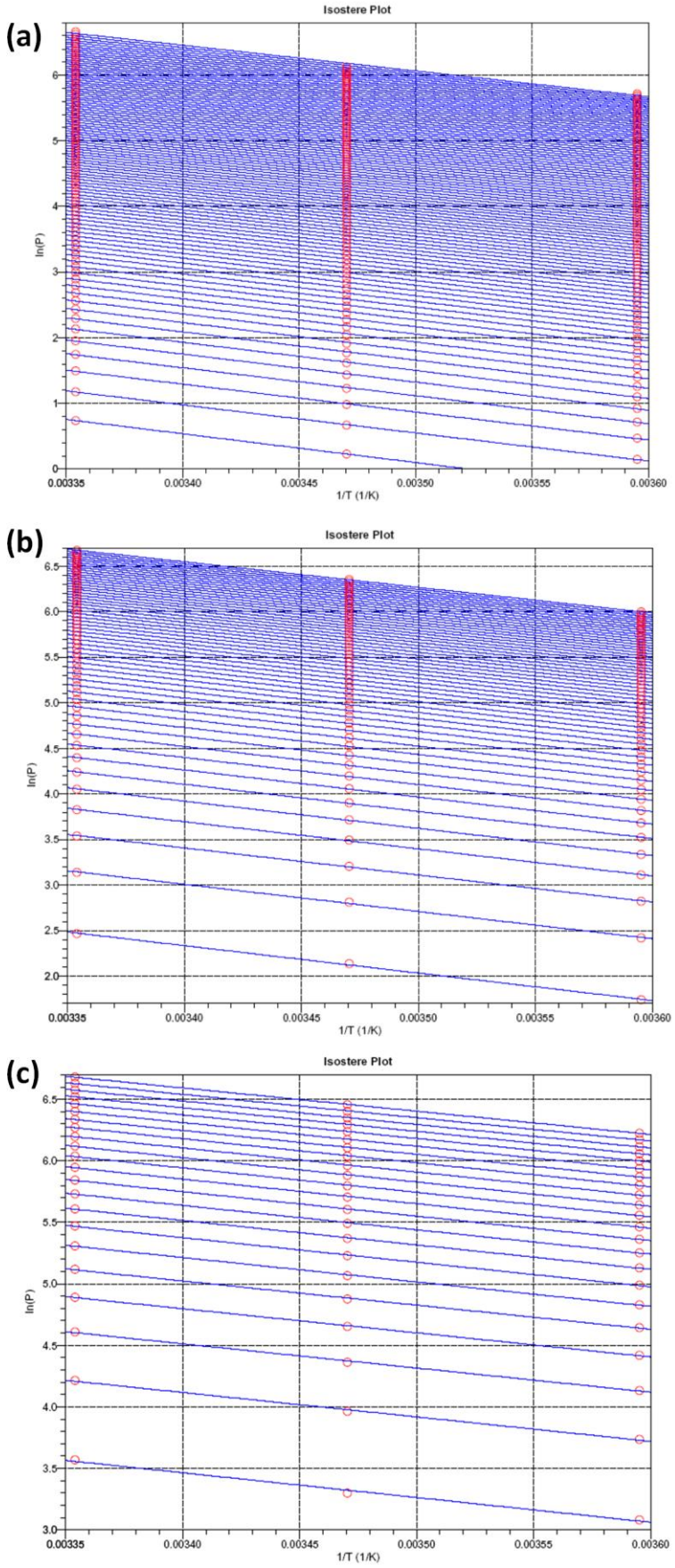
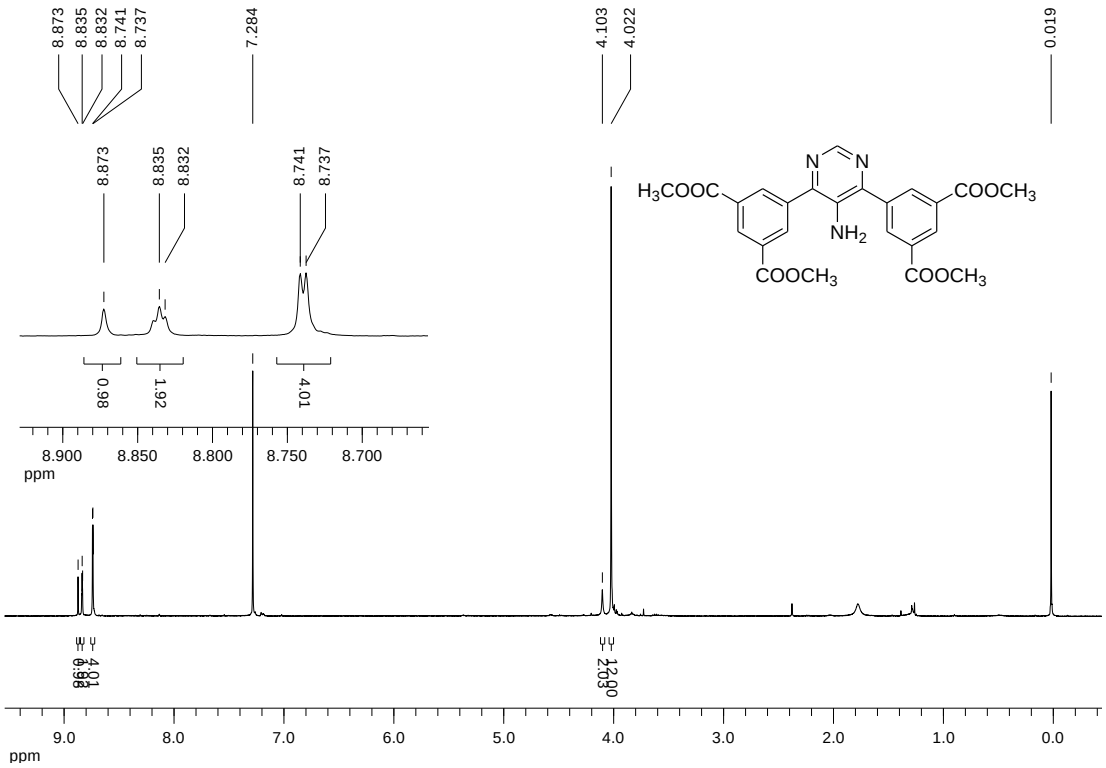
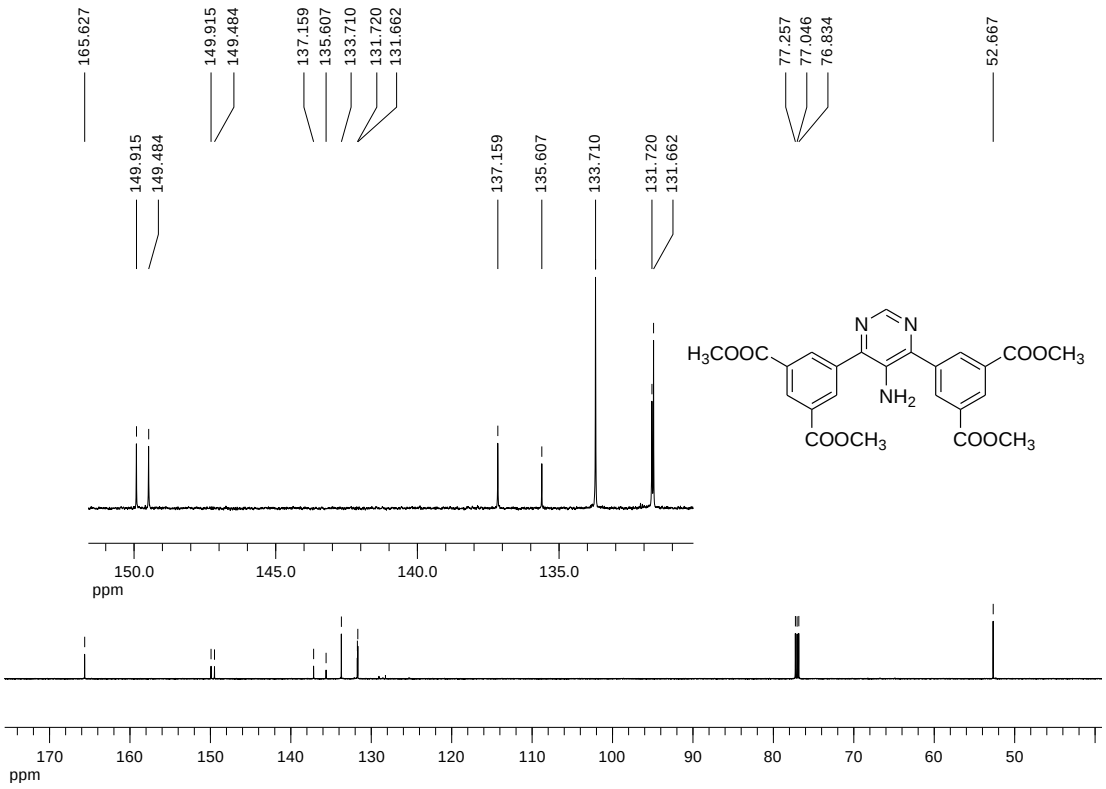


Fig S10 Isostere plots for C_2H_2 (a), CO_2 (b) and CH_4 (c) adsorption in **ZJNU-54a**.


8.873
8.835
8.832
8.741
8.737
7.284
4.103
4.022
0.019
0.98
1.92
4.01
12.00
8.900
8.850
8.800
8.750
8.700
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
N
N
H3COOC
COOCH3
NH2
COOCH3
COOCH3


165.627
149.915
149.484
137.159
135.607
133.710
131.720
131.662
77.257
77.046
76.834
52.667
150.0
145.0
140.0
135.0
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm
N
N
H3COOC
COOCH3
NH2
COOCH3
COOCH3

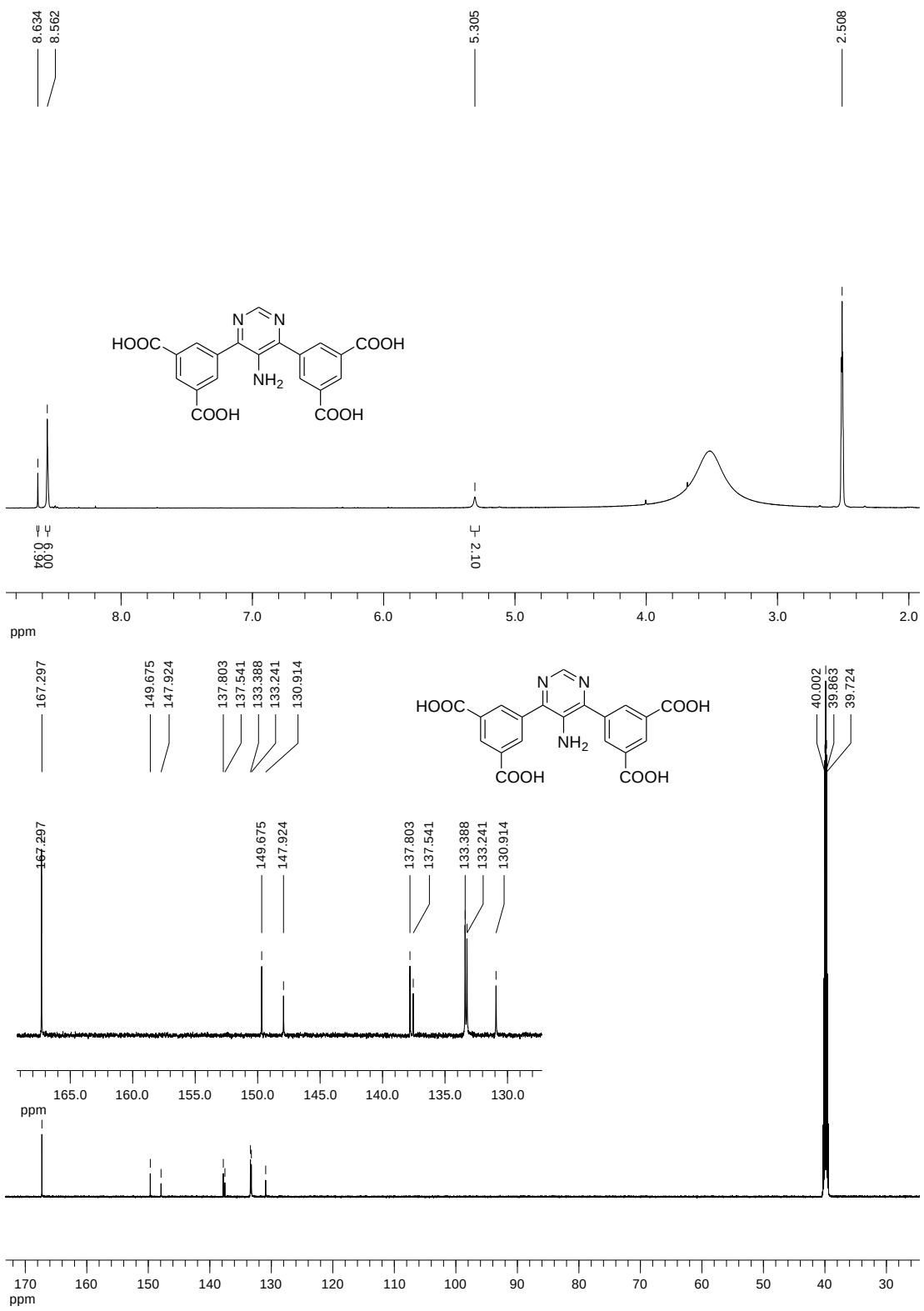


Fig. S11 ^{1}H NMR and ^{13}C NMR spectra.

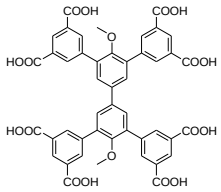
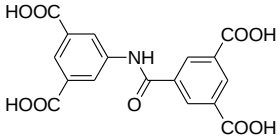
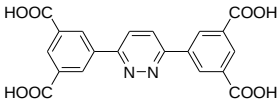
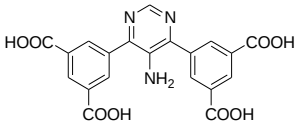
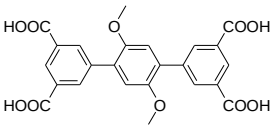
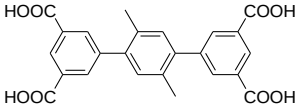
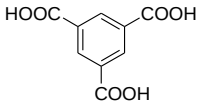
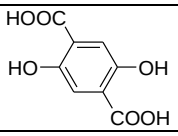
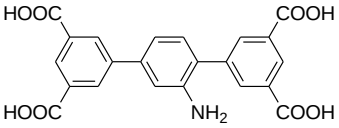
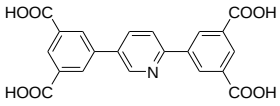
Table S1 Crystal data and structure refinement for **ZJNU-54**.

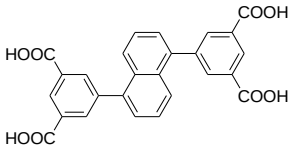
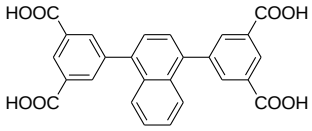
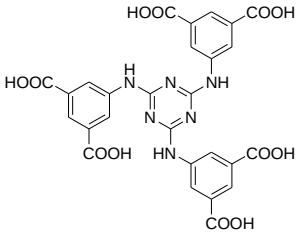
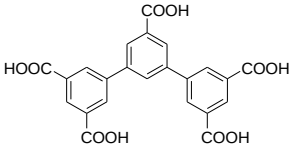
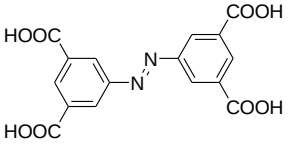
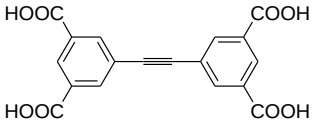
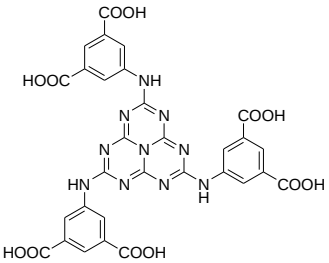
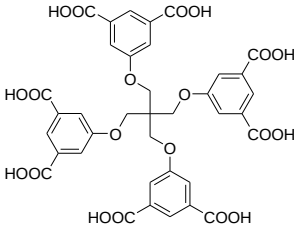
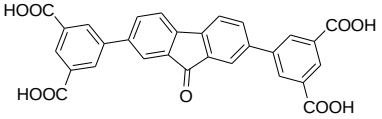
Empirical formula	$C_{20}H_{14}N_3O_{10}Cu_2$
Formula weight	583.44
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Hexagonal
Space group	$P\,6_3/mmc$
Unit cell dimensions	a = 18.5653(6) Å . b = 18.5653(6) Å c = 23.9636(11) Å $\alpha = 90^o$ $\beta = 90^o$ $\gamma = 120^o$
Volume (Å^3)	7153.0(5)
Z	6
Calculated density (g cm^{-3})	0.813
Absorption coefficient (mm^{-1})	0.921
F(000)	1758
Crystal size (mm)	0.24 × 0.21 × 0.09
θ range for data collection (^{o})	1.27 to 27.60
Limiting indices	$-24 \le h \le 24$, $-21 \le k \le 24$, $-31 \le l \le 31$
Reflections collected / unique	115179 / 3099
R_{int}	0.0866
Completeness to θ = 27.60	99.9 %
Max. and min. transmission	0.9217 and 0.8092
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3099 / 0 / 101
Goodness-of-fit on F^2	1.169
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0777, wR_2 = 0.1629
R indices (all data)	R_1 = 0.1024, wR_2 = 0.1774
Largest diff. peak and hole (e.Å^{-3})	0.632 and -0.717
CCDC	1480522

Table S2 Langmuir-Freundich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-54a**

	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v
C_2H_2	16.21986	4.98323×10^{-6}	22.60	0.71494
CO_2	25.96059	2.07758×10^{-7}	23.24	0.98438
CH_4	10.13841	1.78756×10^{-6}	15.91	1.0

Table S3 Comparison of C_2H_2 adsorption in the existing reports.

MOFs	Metal ions	Ligand structure	C_2H_2 uptake	ref
FJI-H8	Cu^{2+}		224 cm^3 (STP) g^{-1} (295 K and 1 atm)	1
NJU-Bai17	Cu^{2+}		222.4 cm^3 (STP) g^{-1} (296 K and 1 bar)	2
ZJNU-47	Cu^{2+}		213 cm^3 (STP) g^{-1} (295 K and 1 bar)	3
ZJNU-54	Cu^{2+}		211 cm^3 (STP) g^{-1} (295 K and 1 atm)	**This work**
Cu_2TPTC-OMe	Cu^{2+}		204 cm^3 (STP) g^{-1} (298 K and 1 bar)	4
Cu_2TPTC-Me	Cu^{2+}		203 cm^3 (STP) g^{-1} (298 K and 1 bar)	4
HKUST-1	Cu^{2+}		201 cm^3 (STP) g^{-1} (295 K and 1 atm)	5
CoMOF-74	Co^{2+}		197 cm^3 (STP) g^{-1} (295 K and 1 atm)	6
ZJU-8	Cu^{2+}		195 cm^3 (STP) g^{-1} (296 K and 1 bar)	7
ZJU-5	Cu^{2+}		193 cm^3 (STP) g^{-1} (298 K and 1 bar)	8

ZJU-9	Cu^{2+}		193 cm^3 (STP) g^{-1} (298 K and 1 atm)	9
ZJU-7	Cu^{2+}		180 cm^3 (STP) g^{-1} (298 K and 1 bar)	10
Cu-TDPAT	Cu^{2+}		177.7 cm^3 (STP) g^{-1} (298 K and 1 atmr)	11
ZJU-72	Cu^{2+}		167.7 cm^3 (STP) g^{-1} (298 K and 1 atm)	12
CPM-200-Fe/Mg	Fe^{3+}, Mg^{2+}		160.8 cm^3 (STP) g^{-1} (298 K and 1 bar)	13
Cu-EBTC	Cu^{2+}		160 cm^3 (STP) g^{-1} (296 K and 1 bar)	14
Cu-TDPAH	Cu^{2+}		155.7 cm^3 (STP) g^{-1} (298 K and 1 atm)	15
Cu-L	Cu^{2+}		154 cm^3 (STP) g^{-1} (296 K and 1 atm)	16
ZJU-61	Cu^{2+}		139.23 cm^3 (STP) g^{-1} (298 K and 1 atm)	17

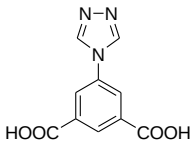
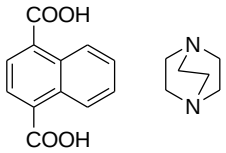
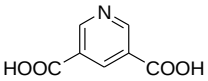
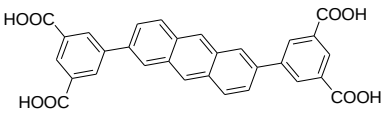
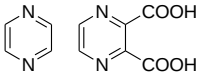
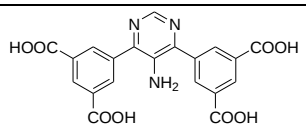
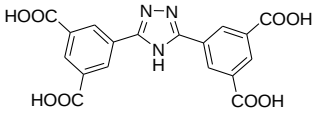
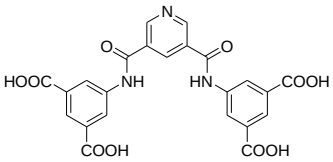
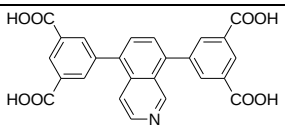
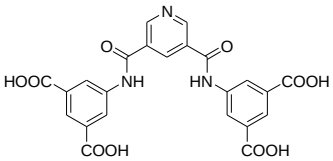
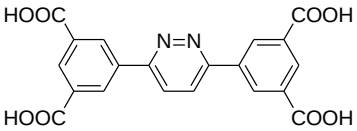
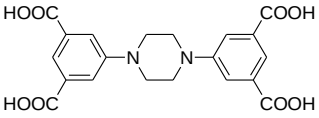
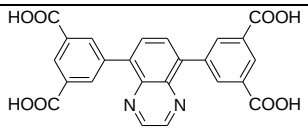
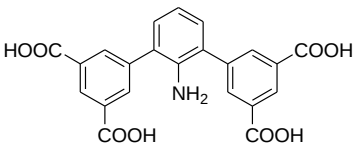
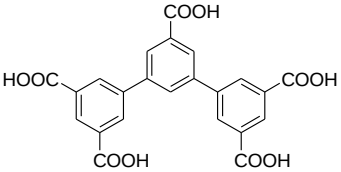
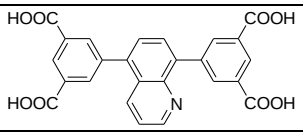
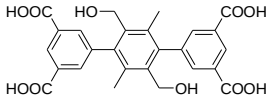
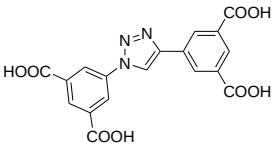
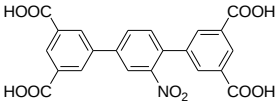
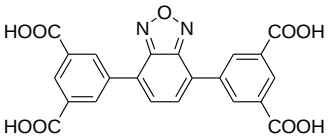
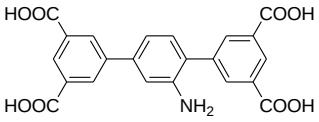
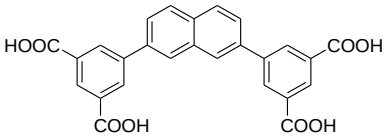
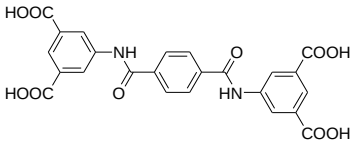
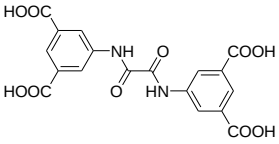
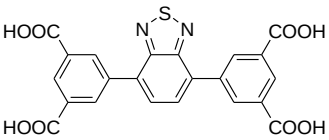
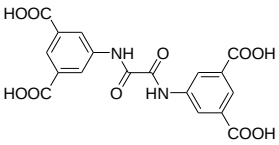
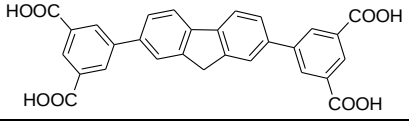
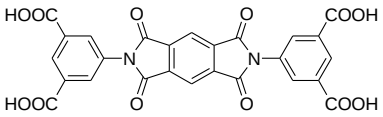
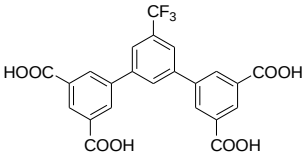
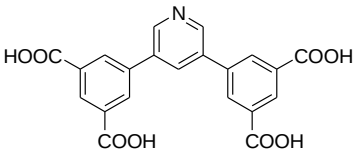
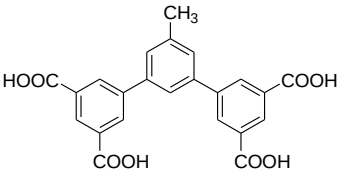
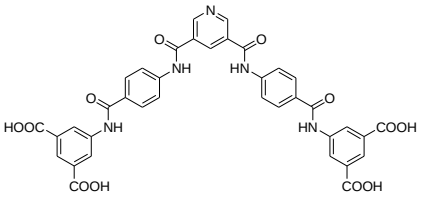
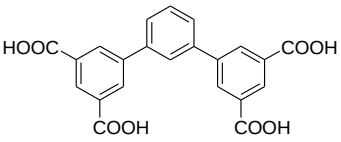
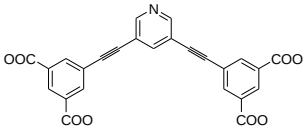
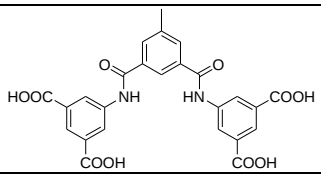
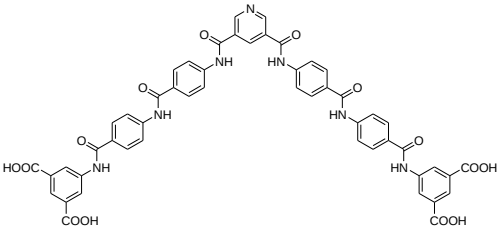
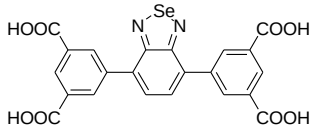
FJU-22a	Cu^{2+}		114.8 cm^3 (STP) g^{-1} (296 K and 1 bar)	18
Zn_2L_2(dabco)	Zn^{2+}		106 cm^3 (STP) g^{-1} (298 K and 1 atm)	19
UTSA-50	Cu^{2+}		91 cm^3 (STP) g^{-1} (296 K and 1 atm)	20
ZJU-26	Cu^{2+}		84 cm^3 (STP) g^{-1} (298 K and 1 atm)	21
$Mg(HCOO)_2$	Mg^{2+}		65.7 cm^3 (STP) g^{-1} (298 K and 1 atm)	22
$Cu_2(pzdc)_2$(pyz)	Cu^{2+}		42 cm^3 (STP) g^{-1}	23

Table S4 Comparison of CO_2 adsorption in copper-based MOFs constructed from diisophthalate ligands.

MOFs	Ligand structure	CO_2 uptake (conditions)	Ref
ZJNU-54		120 cm^3 (STP) g^{-1} (295 K and 1 atm)	**This work**
JLU-Liu21		118 cm^3 (STP) g^{-1} (298 K and 1 bar)	24
NJU-Bai21		115.1 cm^3 (STP) g^{-1} (298 K and 1 bar)	25
ZJNU-44		116 cm^3 (STP) g^{-1} (296 K and 1 atm)	26
PCN-124		114 cm^3 (STP) g^{-1} (295 K and 1 atm)	27
ZJNU-47		108 cm^3 (STP) g^{-1} (296 K and 1 atm)	28
NPC-6		108 cm^3 (STP) g^{-1} (293 K and 1 bar)	29
ZJNU-45		107 cm^3 (STP) g^{-1} (296 K and 1 atm)	26
Cu-L1		104.4 cm^3 (STP) g^{-1} (298 K and 1 bar)	30
ZJU-72		103.9 cm^3 (STP) g^{-1} (298 K and 1 atm)	12

ZJNU-43		103 cm^3 (STP) g^{-1} (296 K and 1 atm)	26
QI-Cu		102 cm^3 (STP) g^{-1} (293 K and 1 bar)	31
NTU-101-Cu		101 cm^3 (STP) g^{-1} (273 K and 1 atm)	32
NJU-Bai14		100 cm^3 (STP) g^{-1} (296 K and 1bar)	33
ZJNU-41		97.4 cm^3 (STP) g^{-1} (298 K and 1 atm)	34
ZJU-8		95 cm^3 (STP) g^{-1} (298 K and 1 bar)	7
PCN-88		94 cm^3 (STP) g^{-1} (296 K and 1 atm)	35
HNUST-1		93 cm^3 (STP) g^{-1} (296 K and 1 bar)	36
NOTT-125		92.6 cm^3 (STP) g^{-1} (298 K and 1 bar)	37
ZJNU-40		85.7 cm^3 (STP) g^{-1} (298 K and 1 atm)	34
HNUST-3		84.5 cm^3 (STP) g^{-1} (298 K and 1bar)	38
ZJU-25		82 cm^3 (STP) g^{-1} (296 K and 1 atm)	39

SNU-50		80 cm^3 (STP) g^{-1} (298 K and 1 bar)	40
PCN-308		78 cm^3 (STP) g^{-1} (297 K and 1 bar)	41
PCN-305		74 cm^3 (STP) g^{-1} (297 K and 1 bar)	41
PCN-307		73 cm^3 (STP) g^{-1} (297 K and 1 bar)	41
NJU-Bai22		72.9 cm^3 (STP) g^{-1} (298 K and 1 bar)	25
PCN-306		70 cm^3 (STP) g^{-1} (297 K and 1 bar)	41
Cu-L		64 cm^3 (STP) g^{-1} (298 K and 1 bar)	42
HNUST-4		62.9 cm^3 (STP) g^{-1} (296 K and 1bar)	43
NJU-Bai23		49.0 cm^3 (STP) g^{-1} (298 K and 1 bar)	25
ZJNU-42		37.6 cm^3 (STP) g^{-1} (298 K and 1 atm)	34

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