A Porous Metal-Organic Framework Based on an Asymmetric Angular Diisophthalate for Selective Adsorption of C_2H_2 and CO_2 over CH_4

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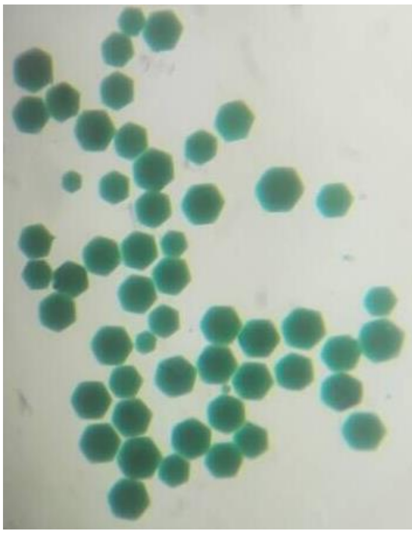


Fig. S1 The photograph of as-synthesized **ZJNU-56**.

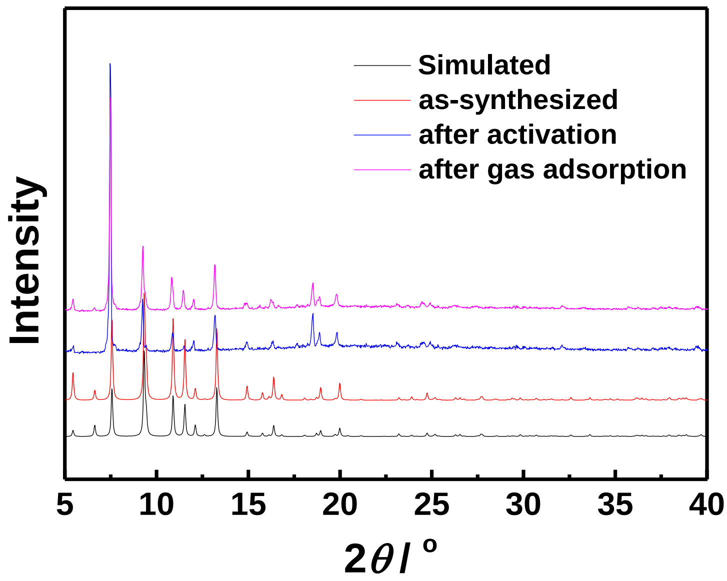


Fig. S2 PXRD patterns of as-synthesized **ZJNU-56** and activated **ZJNU-56a** before and after gas adsorption together with the one simulated from the single-crystal X-ray diffraction data.

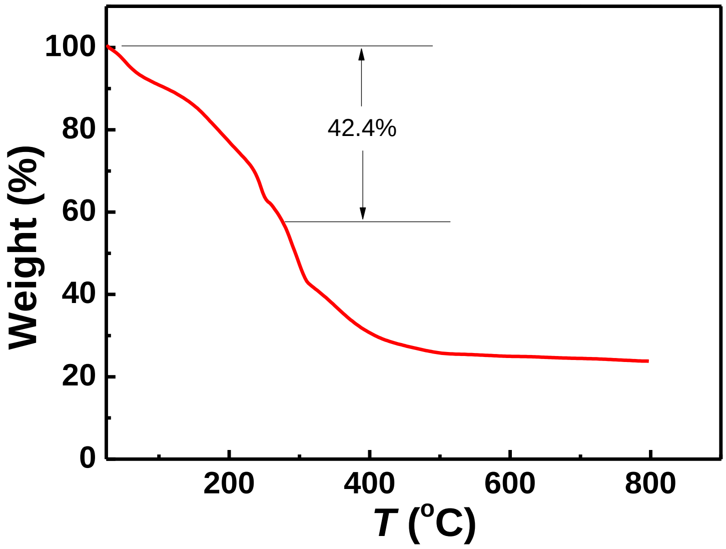


Fig. S3 TGA curve of as-synthesized **ZJNU-56** under N_2 atmosphere.

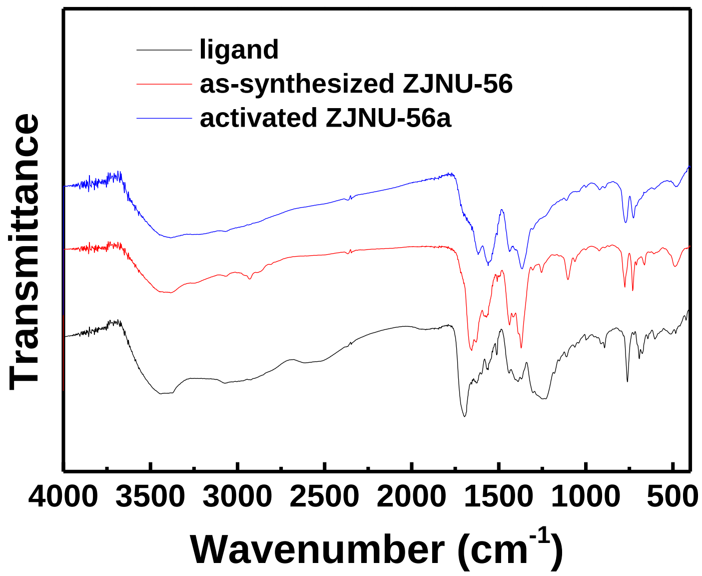


Fig. S4 FTIR spectra of the organic ligand (black), the as-synthesized **ZJNU-56** (red) and the activated **ZJNU-56a** (blue).

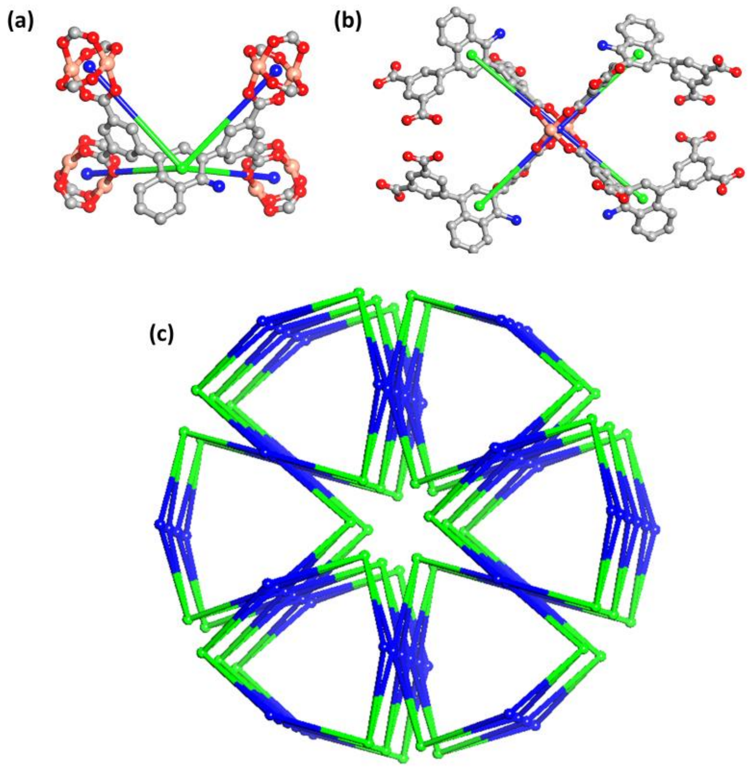
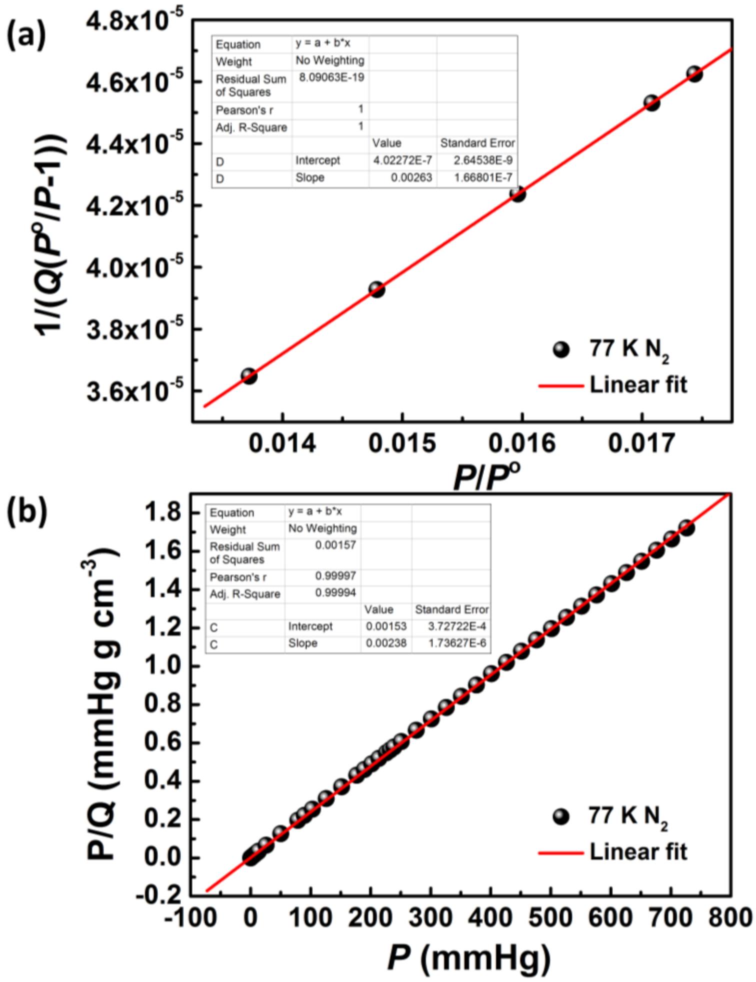


Fig. S5 Views of (a) dinuclear $[Cu_2(COO)_4]$ SBU and (b) the organic linker as 4-connected nodes; (c) the schematic representation of the **ssa** topology.



$S_{\mathrm{BET}} = 1/(\ 4.02272\times10^{-7} + 0.00263)/22414\times6.023\times10^{23}\times0.162\times10^{-18} = 1655\ \mathrm{m^2\ g^{-1}}$

$S_{\mathrm{Langmuir}} = (1/\ 0.00238)/22414\times6.023\times10^{23}\times0.162\times10^{-18} = 1829\ \mathrm{m^2\ g^{-1}}$

Fig. S6 BET (a) and Langmuir (b) plots for **ZJNU-56a**.

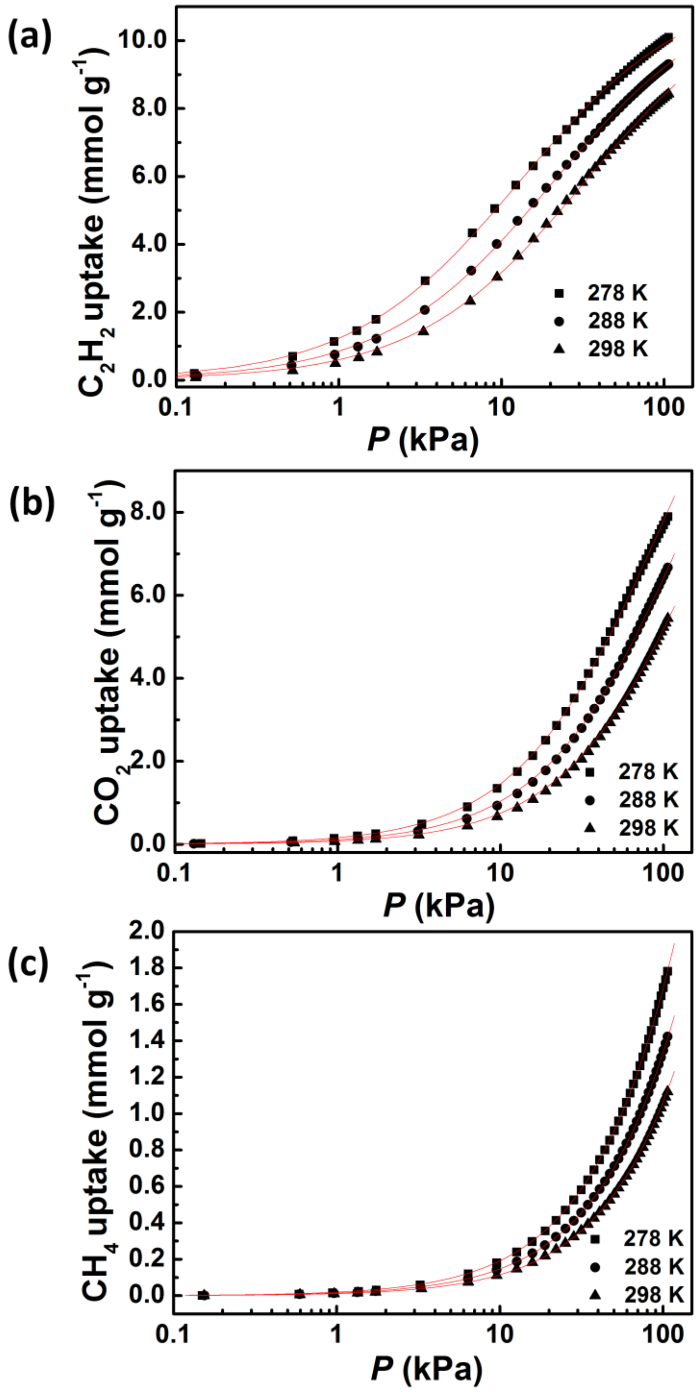


Fig. S7 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-56a** with the fitted isotherms (shown by continuous solid lines) at 278 K, 288 K and 298 K.

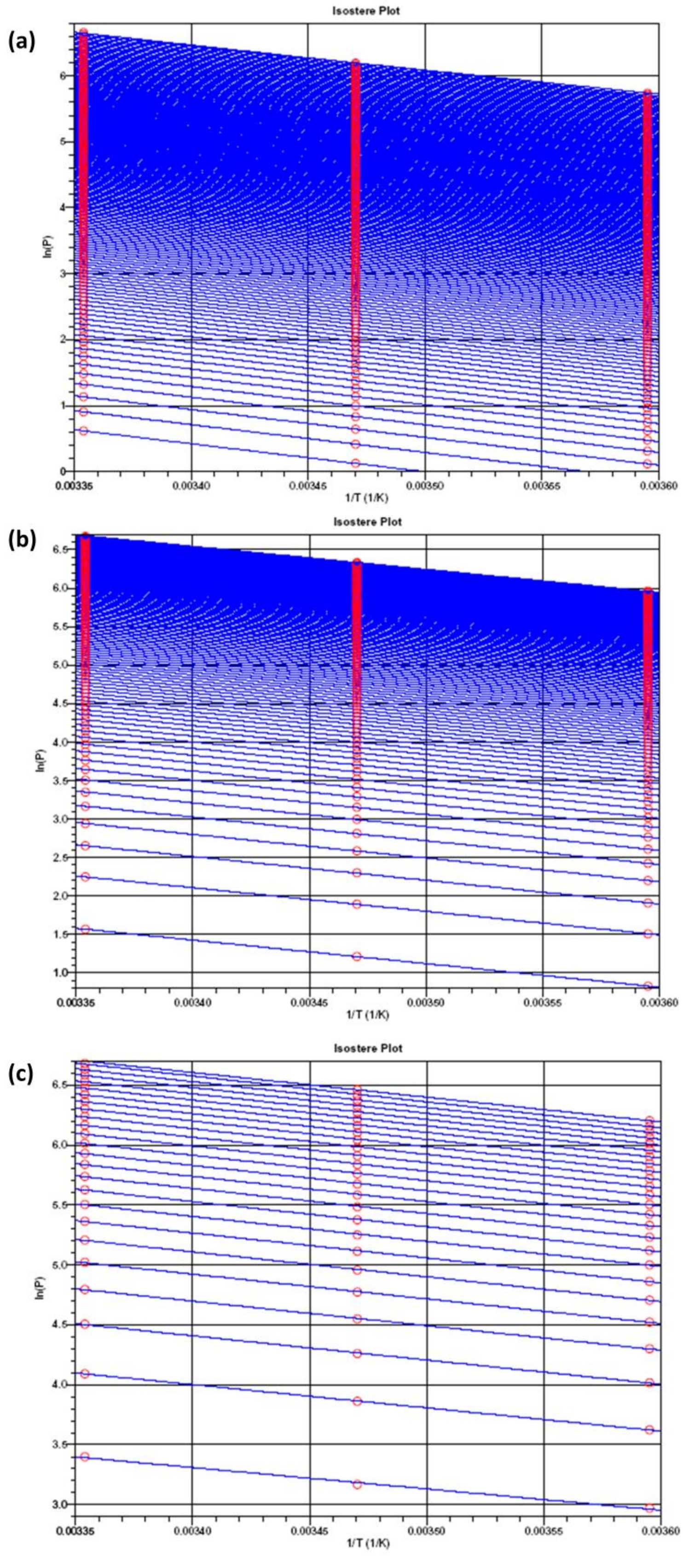
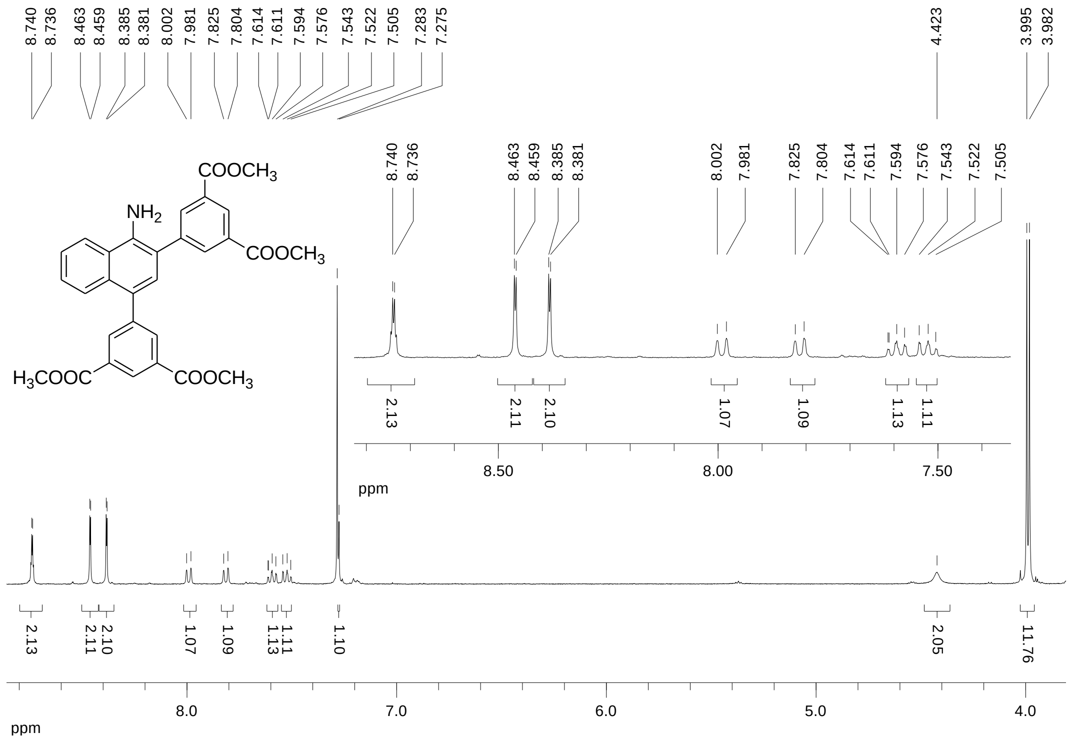
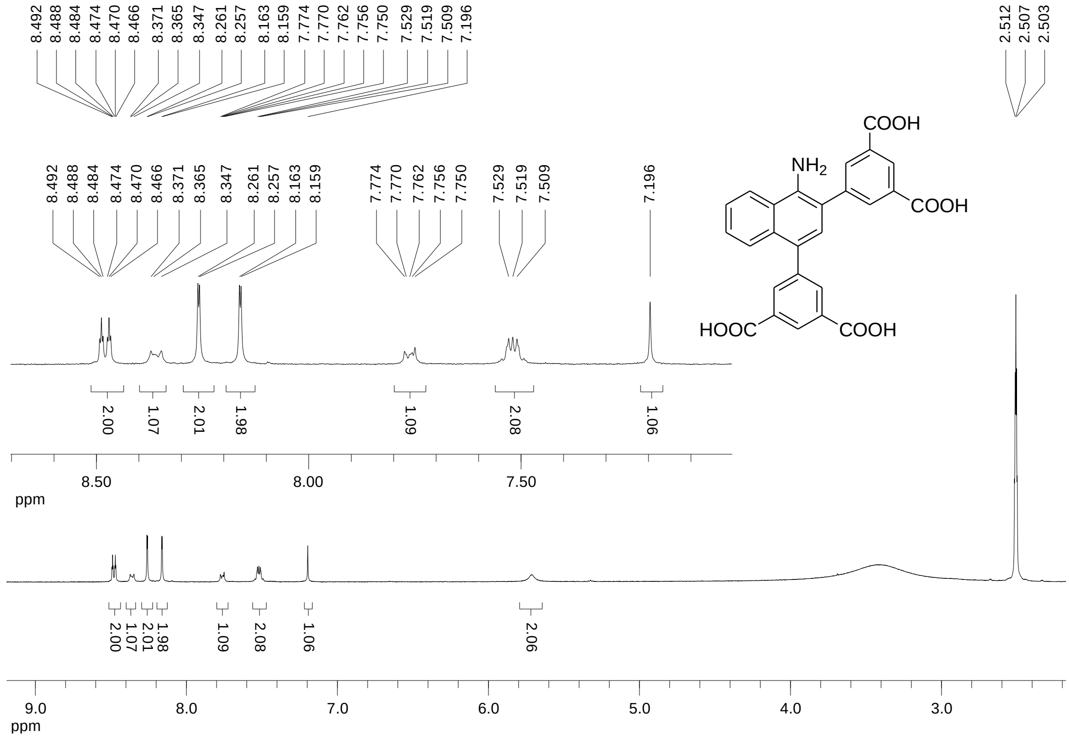


Fig. S8 Isostere plots for C_2H_2 (a), CO_2 (b) and CH_4 (c) adsorption in **ZJNU-56a**.


8.740 8.736 8.463 8.459 8.385 8.381 8.002 7.981 7.825 7.804 7.614 7.611 7.594 7.576 7.543 7.522 7.505 7.283 7.275
4.423
3.995 3.982
COOCH3
NH2
COOCH3
H3COOC
COOCH3
2.13 2.11 2.10 1.07 1.09 1.13 1.11
8.50 8.00 7.50
ppm
2.13 2.11 2.10 1.07 1.09 1.13 1.11 1.10 2.05 11.76
8.0 7.0 6.0 5.0 4.0
ppm


8.492 8.488 8.484 8.474 8.470 8.466 8.371 8.365 8.347 8.261 8.257 8.163 8.159 7.774 7.770 7.762 7.756 7.750 7.529 7.519 7.509 7.196
2.512 2.507 2.503
COOH
NH2
COOH
HOOC
COOH
2.00 1.07 2.01 1.98 1.09 2.08 1.06
8.50 8.00 7.50
ppm
2.00 1.07 2.01 1.98 1.09 2.08 1.06 2.06
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ppm

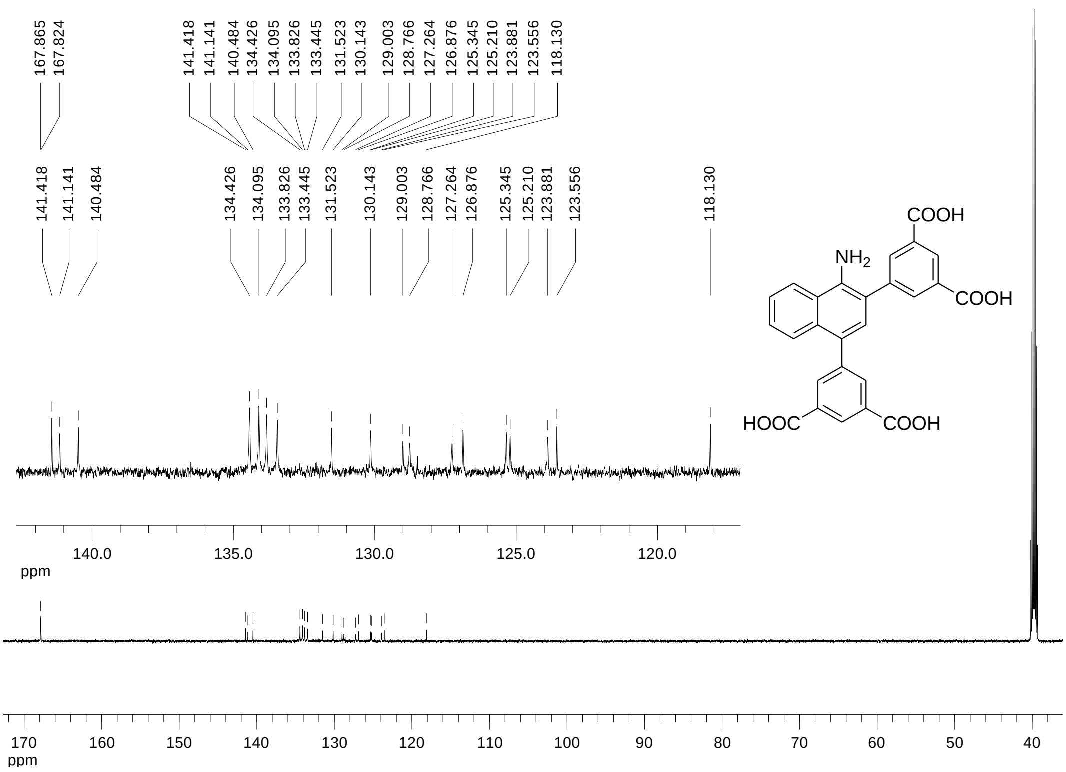


Fig. S9 ^{1}H NMR and ^{13}C NMR spectra of the organic ligand.

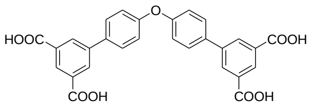
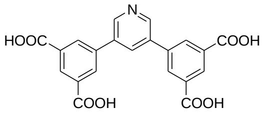
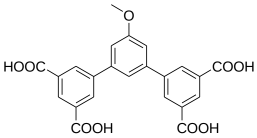
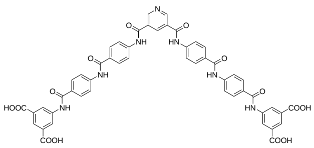
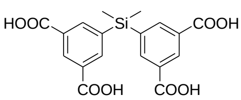
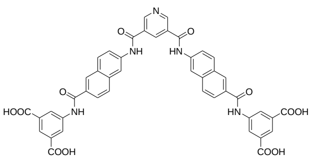
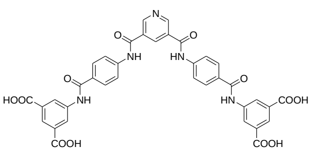
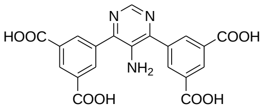
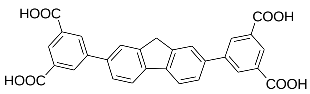
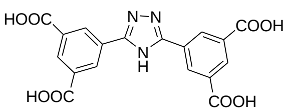
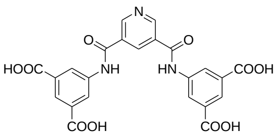
Table S1 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-56a**.

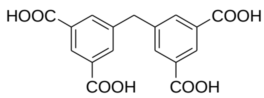
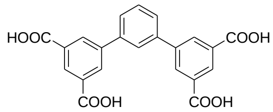
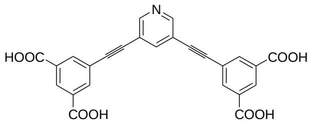
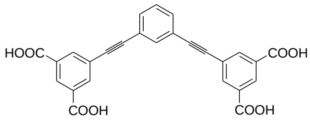
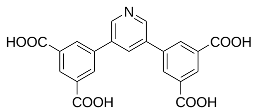
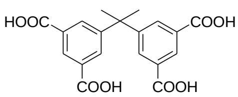
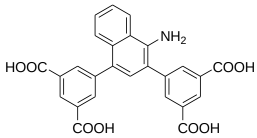
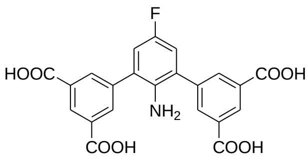
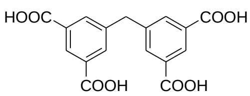
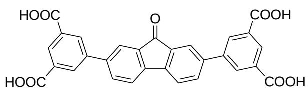
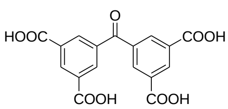
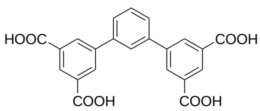
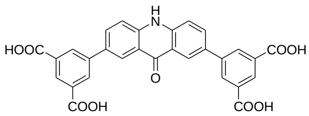
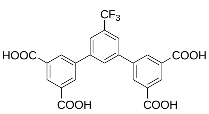
Adsorbate	q_{sat} (mmol g^{-1})	b_0 (kPa)$^{-\nu}$	E (kJ mol^{-1})	ν
C_2H_2	11.69167	1.12338×10^{-6}	26.718	0.83654
CO_2	15.07212	2.53375×10^{-7}	24.619	1
CH_4	12.68405	7.15596×10^{-7}	17.729	1

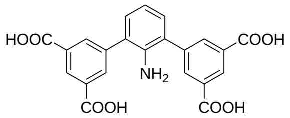
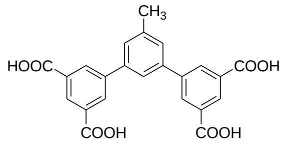
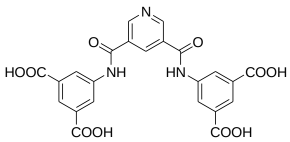
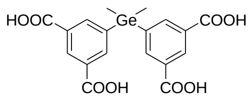
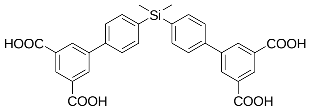
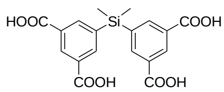
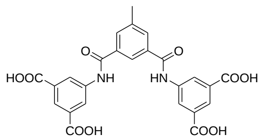
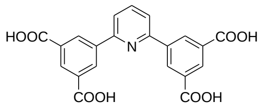
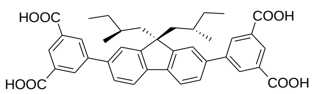
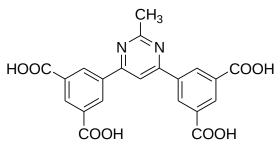
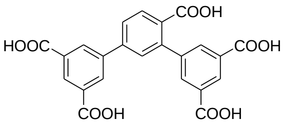
Table S2 Crystal data and structure refinement for **ZJNU-56**.

Empirical formula	$C_{26}H_{17}NO_{10}Cu_2$
Formula weight	630.49
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Hexagonal
Space group	$P\ 6_3/mmc$
Unit cell dimensions	a = 18.7251(3) Å . b = 18.7251(3) Å c = 23.3446(6) Å $\alpha = 90^{o}$ $\beta = 90^{o}$ $\gamma = 120^{o}$
Volume (Å^3)	7088.7(2)
Z	6
Calculated density (g cm^{-3})	0.886
Absorption coefficient (mm^{-1})	0.932
F(000)	1908
Crystal size (mm)	0.30 × 0.20 × 0.15
θ range for data collection (^{o})	1.26 to 25.02
Limiting indices	$-22 \leq h \leq 22$, $-22 \leq k \leq 22$, $-27 \leq l \leq 27$
Reflections collected / unique	117877 / 2361
R_{int}	0.1065
Completeness to θ = 27.60	99.9 %
Max. and min. transmission	0.8728 and 0.7673
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2361 / 122 / 131
Goodness-of-fit on F^2	1.229
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0856, wR_2 = 0.2188
R indices (all data)	R_1 = 0.1074, wR_2 = 0.2399
Largest diff. peak and hole (e·Å^{-3})	1.594 and -1.408
CCDC	1540295

Table S3 BET (Langmuir) surface areas, and selective CO_2 adsorption properties of copper-based MOFs with bent diisophthalates as linkers

MOFs	Ligand structure	$S_{BET}/S_{Langmuir}$ ($m^2\ g^{-1}$)	CO_2 uptake Condition [cm^3 (STP) g^{-1}]	S_{CO_2/CH_4} [a]	Q_{st} ($kJ\ mol^{-1}$)	*Ref.*
FJI-H5		4255/5425	NA	NA	NA	1
NJU-Bai10		2883/3107.9	NA	NA	NA	2
NJFU-3		2531.1/2671.9	95.6 298 K and 1 bar	7.9	24.0	3
NJU-Bai23		2519/5142	49.0 298 K and 1 bar	5.8	25.1	4
UHM-3		2430/NA	NA	NA	NA	5
HHU-1		2290/NA	66.8 298 K and 1 bar	NA	27.7	6
NJU-Bai22		2177/3299	72.9 298 K and 1 bar	6.7	25.6	4
ZJNU-54		2134/2432	120 295 K and 1 atm	6.1	24.7	7
ZJU-25		2124/3304	NA	NA	NA	8
JLU-liu-21		2080/NA	118 298 K and 1 bar	6.9	28	9
NJU-Bai21		1979/NA	115.1 298 K and 1 bar	7.8	25.9	4

PCN-12		1943/2425	NA	NA	NA	10
PCN-306		1927/2929	70.3 297 K and 1 bar	7.5 (273 K)	23.997	11
Cu_2L		1879/2489	63.5 298 K and 1 bar	NA	NA	12
PMOF-3		1840/2020	NA	NA	NA	13
PCN-305		1720/2599	73.8 297 K and 1 bar	7.2	23.847	11
UHM-2		1692/NA	NA	NA	NA	5
ZJNU-56		1655/1829	122 298 K and 1 atm	7.0	25.33	This work
Cu_2L		1580/NA	106 298 K and 1 bar	7.68 (273 K)	39.51	14
PCN-12’		1577/1962	NA	NA	NA	10
ZJU-61		1576/2318	NA	NA	NA	15
Cu_2L		1539/2259	111.3 298 K and 1 bar	4.9-5.4	31.3	16
JLU-Liu22		1487/NA	95 298 K and 1 bar	9.4	30	17
Cu_2L		1475/1736	NA	NA	NA	18
PCN-308		1418/2234	78.4 297 K and 1 bar	7.8	22.215	11

Cu_2L		1410/NA	104.39 298 K and 1 bar	6.95 (273 K)	37.51	19
PCN-307		1376/2235	73.4 297 K and 1 bar	8.8	22.836	11
PCN-124		1372/2002	114 295 K and 1 atm	8-20	26.3	20
UHM-4		1360/NA	NA	NA	NA	5
UHM-6		1164/NA	47 298 K and 1 bar	4	28	21
Cu_2L	 ssa	1145.9/NA	115 298 K and 1 bar	NA	NA	22
HNUST-4		1136/1284	62.9 298 K and 1 bar	NA	27.2	23
Cu_2L		499/569	43.9 298 K and 1 bar	30.8	36.9	24
Cu_2L		467/562	NA	NA	NA	25
ZJNU-55		450.1/508.6	40.6 298 K and 1 atm	13.1	35.44	26
Cu_2L		261.3/365.4	11.6 298 K and 1 bar	2.2	25.4	27

[a] IAST selectivity for the equimolar CO_2/CH_4 mixture at room temperature and 1 atm/bar unless other otherwise noted; NA = not available

Table S4 Summaries of C_2H_2/CH_4 adsorption selectivities in porous MOFs reported in the literature

MOFs	$S_{BET}/S_{Langmuir}$ (m^2 g^{-1})	Henry's Law Selectivity [a]	IAST Selectivity [b]	C_2H_2 uptake Condition [cm^3 (STP) g^{-1}]	Q_{st} (kJ mol^{-1})	*Ref.*
PMOF-3	1378/NA	NA	**156.5**	117.3 296 K and 1 atm	21.9	28
Cu-TDPAT	1938/2608	**127.1**	82	177.7 298 K and 1 atm	42.5	29
Cu-TDPAH	2171/2540	80.9	82	155.7 298 K and 1 atm	23.5	30
FJU-12	136.2/211	31.9	79.7	19.59 296 K and 1 bar	29.2	31
BUT-70A	460/545	NA	66.6	69.5 298 K and 1 atm	23.9	32
ZJU-10	2392/2591	NA	61	174 298 K and 1 bar	39	33
UTSA-90	2273/NA	NA	60.1	214 295 K and 1 bar	36.5	34
UTSA-57	206.5/330.5	NA	58.7	33 296 K and 1 bar	35.0	35
FJI-C4	690/781	NA	51.0	72.5 298 K and 1 bar	27.0-31.7	36
ZJNU-54	2134/2432	NA	45.0	211 295 K and 1 atm	35.4	7
PCP-33	1248/1419.3	NA	40	121.8 298 K and 1 bar	27.5	37
ZJU-72	1184/1750	NA	39.7	167.7 298 K 1 atm	9.7	38
FIR-51	918.6/1400	NA	39.6	141.9 294 K and 1 bar	24.48	39
FJI-C1	1726.3/2392.6	NA	39.3	93.8 298 K and 1 bar	28.9	40
ZJNU-55	450.1/508.6	NA	39.2	56.3 298 K and 1 atm	42.4	26
UPC-2	1725.1/NA	NA	38.1	139.5 295 K and 1 bar	38.8	41
ZJNU-56	1655/1829	NA	35.7	189 298 K and 1 atm	35.19	This work
$[(Et_4N)[Cd_3(ad)_2(ipa)_2Br]$	NA/770.1	NA	32.3	65.5 298 K and 1 bar	41.7	42
ZJNU-38	2291/2516	NA	29.9	153.7 298 K and 1 atm	35.1	43

ZJNU-37	2720/2922	NA	29.5	171.5 298 K and 1 atm	33.6	43
ZJNU-36	2379/2638	NA	29.3	175.8 298 K and 1 atm	37.8	43
ZJNU-35	2591/2827	NA	29.1	179.8 298 K and 1 atm	33.8	43
ZJNU-34	2459/2704	NA	28.9	193.8 298 K and 1 atm	34.2	43
ZJU-199	987/1532	NA	27.3	128 296 K and 1 atm	38.5	44
UTSA-72	173/ NA	21.1	26.5	27.8 296 K and 1 atm	20.2	45
SNNU-23	624.7/NA	17.4	24.9 (273 K)	62.6 298 K and 1 atm	62.2	46
BUT-70B	695/780	NA	23.3	87.1		32
$(H_3O)_4[Ni_6(\mu_3\text{-}O)_2(\mu_2\text{-}OSC_2H_6)_2(SO_4)_2(TATB)_{8/3}]\cdot$	1012.6/1334.6	25.0	22.6	64.1 297 K and 1 bar	29.4	47
SNNU-22	222.9/NA	9.9	20.3 (273 K)	26.6 298 K and 1 atm	39.1	46
Tb(BCB)	716/NA	NA	19.7 (273 K)	60.5 296 K and 1 atm	25.8	48
ZJU-11	2531/2743	NA	19	165 298 K and 1 atm	36.8	49
$Zn_5(BTA)_6(TDA)_2$	414/607	22.3	15.5	44 295 K and 1 atm	37.3	50
$[Zn_2(NH_2\text{-}BTB)(2\text{-nim})]$	893.83/NA	NA	8.0	80 297 K and 1 bar	19.72	51
UTSA-10	1090/1146	8.1	6.2	43.0 296 K and 1 atm	19	52
ZJU-61	1576/2318	74.4	NA	139.23 298 k and 1 atm	23.98	15
UTSA-50	604/933	68.0	NA	90.6 296 K and 1 atm	39.4	53
Cu_2TPTC-Me	2405	60	NA	203 298 K and 1 bar	19.1	54
UTSA-15	553/761	55.6	NA	34 296 K and 1 atm	39.5	55
UTSA-48	285	53.4	NA	40 296 K 1 atm	34.4	56
$Cd(Tipa)Cl_2$	348.8/484.8	39.1	NA	64.13 297 K 1 atm	41.05	57
M'MOF-20	42/62	34.9	NA	21 295 K and 1 atm	33.7	58

MFM-130	2173	34.7	NA	85.9 298 K and 1 bar	33.1	59
UTSA-5	462/712	28.4	NA	59.8 296 K and 1 atm	30.8	60
BUT-52	358/522	23.5	NA	71.6 298 K and 1 bar	35.5	61
$[Zn_4(OH)_2(1,2,4\text{-}BTC)_2]$	408	14.7	NA	53 295 K and 1 atm	28.2	62
UTSA-36	495/806	13.8		56.8 296 K and 1 atm	29.0	63
$[Zn_2(atz)_2(bpydb)$	2340/2393	11	NA	120 298 K and 1 bar	25	64
$[Co_6(\mu_3\text{-}OH)_4(Ina)_8]$	631/739	9.6	NA	64 298 K and 1 bar	27	65
ZJU-30	228	9.58	NA	52.6 298 K and 1 atm	31.3	66
Cu(BDC-OH)	397/584	9.3	NA	43 296 k and 1 atm	25.7	67
Yb(BPT)	515.6	7.8	NA	23.9 296 K and 1 atm	30.4	68
UTSA-38	1090/1690	5.6	NA	63.6 296 K and 1 atm	24.7	69

[a] at 298 K; [b] at 298 K and 1 atm; NA = not available

TDPAT = 2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine

TDPAH = 2,5,8-tris(3,5-dicarboxylphenylamino)-s-heptazine

ad = adenine

ipa = isophthalate

TATB = 4,4’,4’’-s-triazine-2,4,6-triyltribenzoate

BCB = 4,4’,4’’-benzenetricarbonyltribenzoic acid

BTA = 1,2,3-benzenetriazole

TDA = thiophene-2,5-dicarboxylic acid

NH_2-BTB = 1,3,5-(three-benzoic acid)aniline

2-nim = 2-nitroimidazole

TPTC-Me = 2’,5’-dimethyl-[1,1’:4’,1’’-terphenyl]-3,3’’,5,5’’-tetracarboxylate

Tipa = tris(4-(1H-imidazol-1-yl)-phenyl)amine

1,2,4-BTC = Benzene-1,2,4-tricarboxylate

atz = 3-amino-1,2,4-triazole

bpydb = 4,4’-(4,4’-bipyridine-2,6-diyl) dibenzoic acid

Ina = isonicotinate

BDC-OH = 2-hydroxybenzene-1,4-dicarboxylic acid

BPT = biphenyl-3,4’,5-tricarboxylate

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