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Electronic Supplementary Information (ESI)

A Microporous MOF with Polar Pore Surface Exhibiting Excellent Selective Adsorption of CO_2 from CO_2-N_2 and CO_2-CH_4 Gas Mixture with High CO_2 Loading

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Table S1: Crystal data and structure refinements for **IITKGP-5**.

Empirical formula	$C_{21}H_{15}N_2O_6SZn$
Formula weight	488.78
Temperature(K)	298(1)
Radiation	Mo-Kα
Wavelength(λ)	0.71073Å
Crystal system	Triclinic
Space group	$P\bar{1}$
a[Å]	9.1721(8)
b[Å]	11.5764(11)
c[Å]	12.8822(12)
α[°]	79.504(6)
β[°]	72.656(6)
γ[°]	69.425(6)
Volume[Å^3]	1217.8(2)
Z	2
Density (calculated) [Mg/m^3]	1.333
Absorption coefficient [mm^{-1}]	1.129
F(000)	498
Refl. used [$I > 2\sigma(I)$]	3103
Independent reflections	5992
R_{int}	0.1032
Refinement method	full-matrix least squares on F^2
GOF	0.969
Final *R* indices[I>2σ(I)]	R_1= 0.0658 wR_2= 0.1427
R indices (all data)	R_1= 0.1515 wR_2= 0.1710

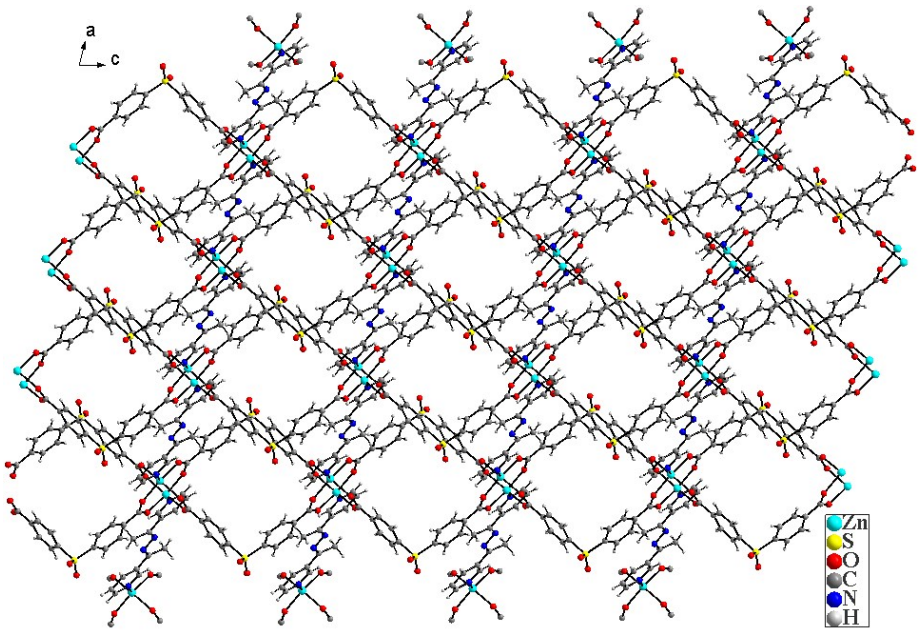

Figure S1: Representation of $-SO_2$ decorated pores of **IITKGP-5** along the crystallographic *b* axis.

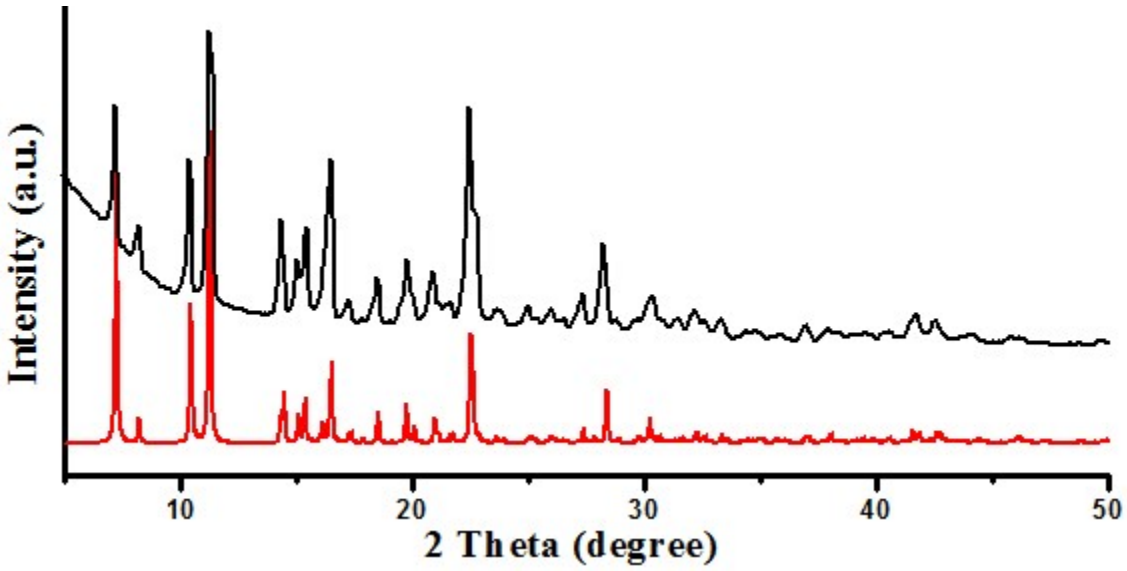

Figure S2: Simulated (red) and as synthesized (black) PXRD pattern of **IITKGP-5**.

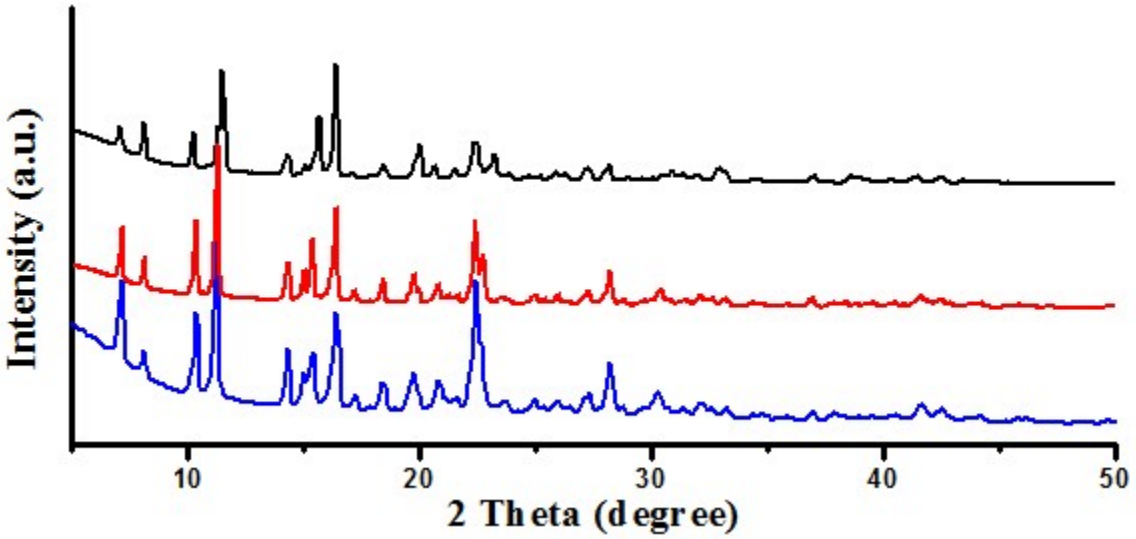

Figure S3: As synthesized (blue), chloroform exchanged (red) and desolvated (black) PXRD pattern.

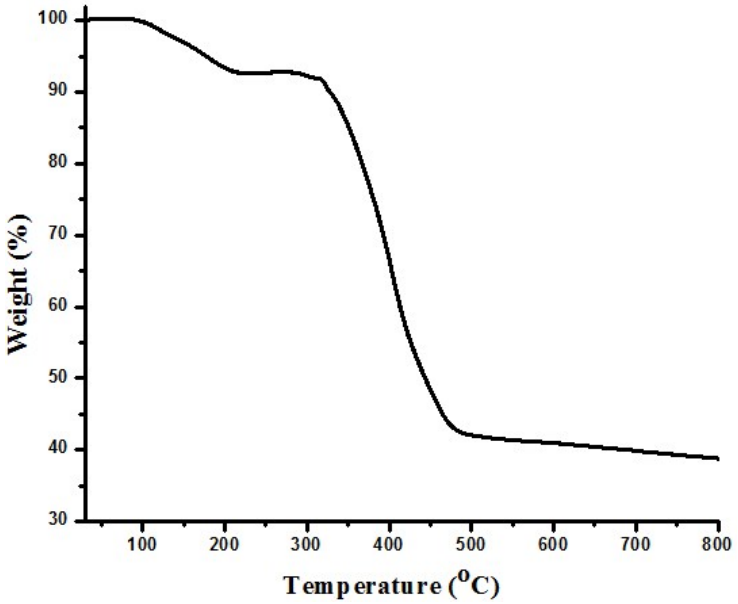

Figure S4: TGA of **IITKGP-5**.

Calculation of Isosteric Heats of Adsorption:

The isosteric heats of adsorption (Q_{st}) were calculated using the Clausius-Clapeyron equation based on pure-component isotherms collected at two different temperatures of 273 K and 295 K. The Q_{st} was defined as

$$Q_{st} = -R\left(\frac{\partial lnx}{\partial\left(\frac{1}{T}\right)}\right)_y$$

Where x is the pressure, T is the temperature, R is the gas constant and y is the adsorption amount. These calculations are done through the "Heat of Adsorption" function embedded in the software supplied by Micromeritics 3- Flex Surface Characterization Analyzer.

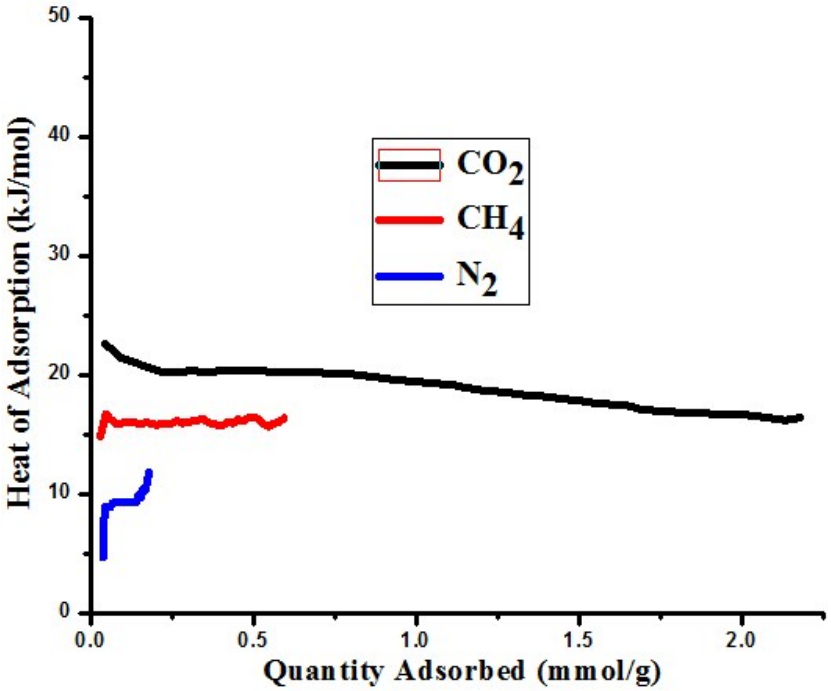

Figure S5: Isosteric heat of CO_2, CH_4 and N_2 adsorption (Q_{st}).

Calculation of CO_2/N_2 and CO_2/CH_4 Selectivity:

IAST Selectivity:

Adsorption isotherms and gas selectivities of mixed CO_2/N_2 (15:85) and CO_2/CH_4 (50:50) at different temperatures were calculated based on the ideal adsorbed solution theory (IAST) proposed by Myers and Prausnitz.[1] In order to calculate the selective sorption performance of **IITKGP-5** toward the separation of binary mixed gases, the parameters fitted from the single-component CO_2, CH_4 and N_2 adsorption isotherms based on the single-site Langmuir−Freundlich model and were used in the IAST calculations as given below in detail.[2]

$$y = \frac{q_m b x^{1/n}}{1 + b x^{1/n}}$$

Where y is the adsorbed amount (mmol/g), q_m is the saturation capacity (mmol/g), x is the equilibrium pressure (kPa) and b and n is the Langmuir and Freundlich constants.

The predicted adsorption selectivity is defined as

$$S = \left(\frac{x_1}{y_1} \middle/ \frac{x_2}{y_2} \right)$$

Where x_i and y_i are the mole fractions of component i (i = 1, 2) in the adsorbed and bulk phases, respectively. The IAST calculations were carried out for a binary mixture containing 15% CO_2 (y_1) and 85% N_2 (y_2), which is typical of flue gases and for a binary mixture containing 50% CO_2 (y_1) and 50% CH_4 (y_2), which is typical of landfill gases.

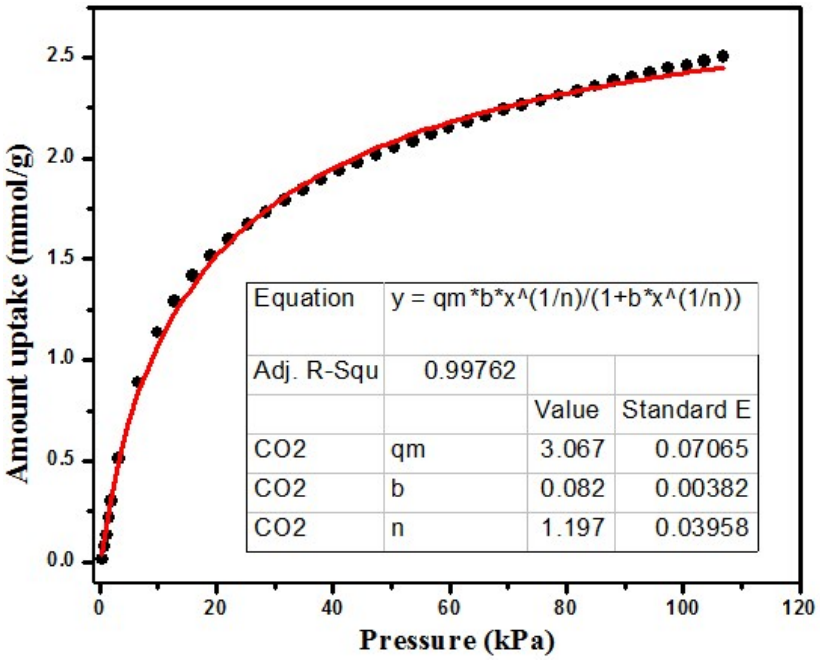

Figure S6: Langmuir-Freundlich fitting (red line) for CO_2 (black circle) isotherms measured at 273 K.

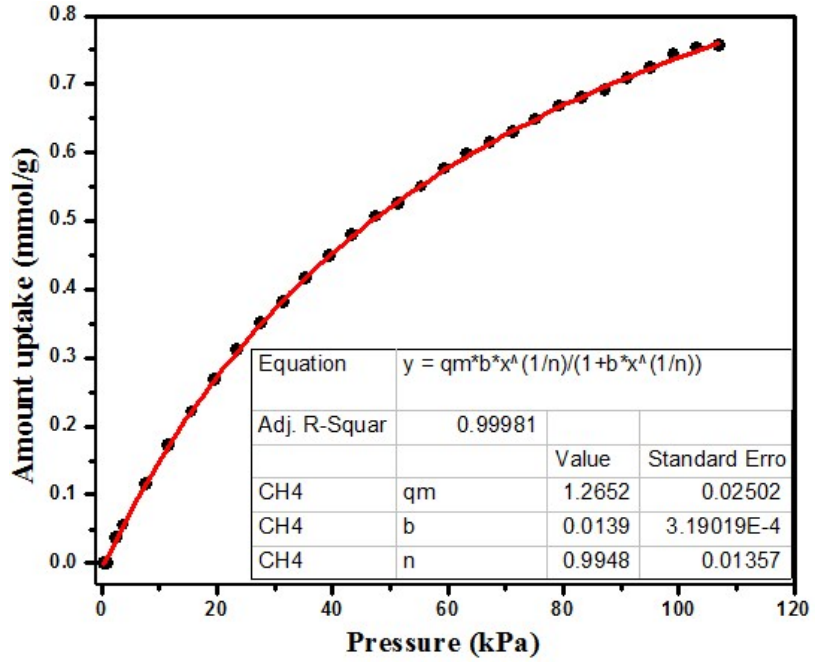

Figure S7: Langmuir-Freundlich fitting (red line) for CH_4 (black circle) isotherms measured at 273 K.

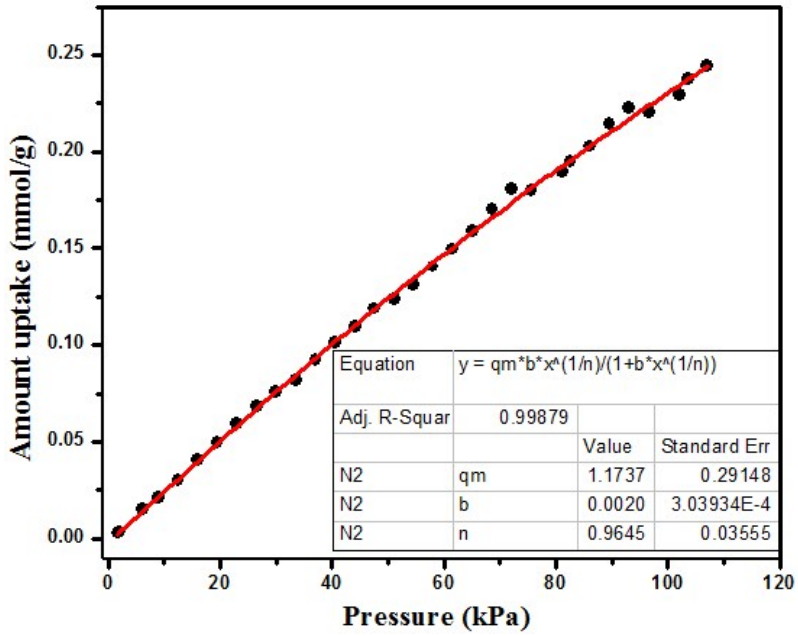

Figure S8: Langmuir-Freundlich fitting (red line) for N_2 (black circle) isotherms measured at 273 K.

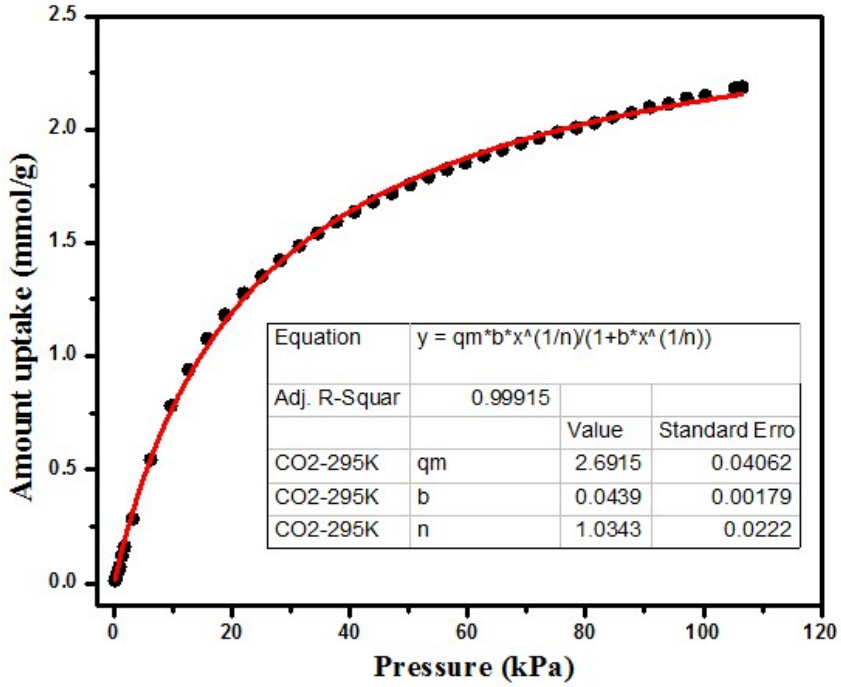

Figure S9: Langmuir-Freundlich fittings (red line) for CO_2 (black circle) isotherms measured at 295 K.

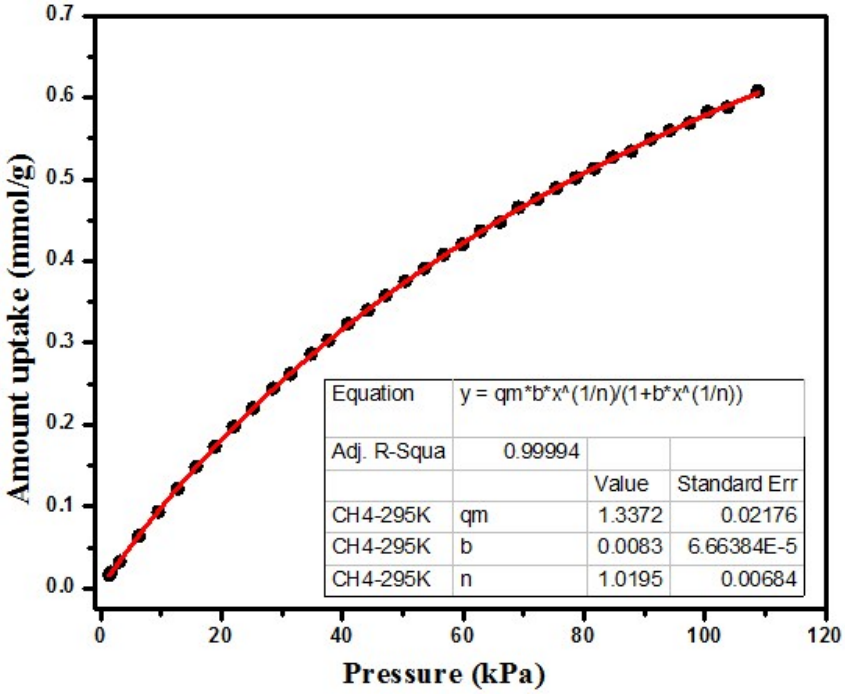

Figure S10: Langmuir-Freundlich fitting (red line) for CH_4 (black circle) isotherms measured at 295 K.

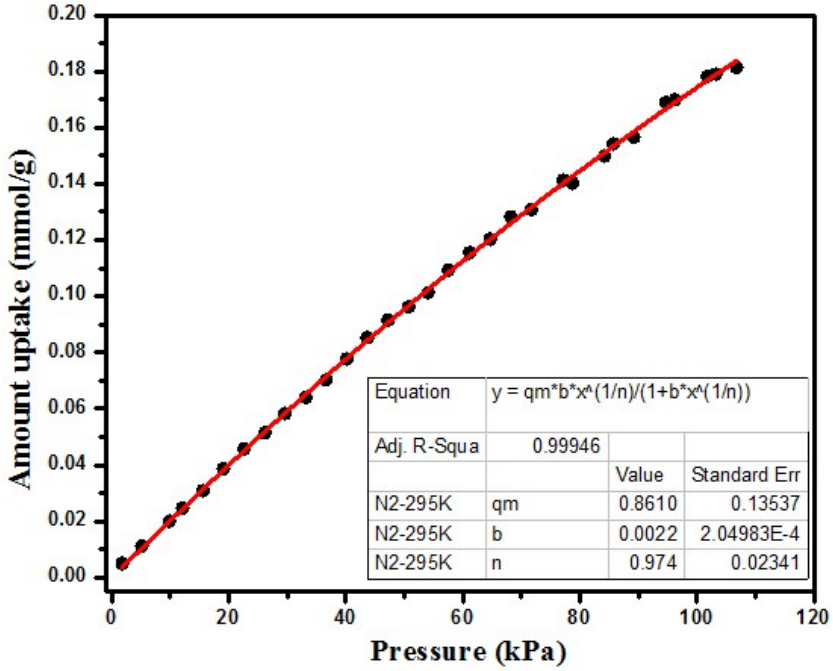

Figure S11: Langmuir-Freundlich fitting (red line) for N_2 (black circle) isotherms measured at 295 K.

Table S2: Selected Bond Distances (Å) and Bond Angles (°) in **IITKGP-5**.

Zn1	O1	2.024(4)	Zn1 O2	2.031(3)	Zn1 N1 2.033(4)
Zn1	O4	2.055(3)	Zn1 O3	2.044(3)	

O1	Zn1	O2	157.27(15)	N1 Zn1 O4	104.48(14)
O1	Zn1	N1	102.39(16)	O1 Zn1 O3	87.11(15)
O2	Zn1	N1	100.35(16)	O2 Zn1 O3	89.74(15)
O1	Zn1	O4	87.13(16)	N1 Zn1 O3	98.03(14)
O2	Zn1	O4	87.23(16)	O3 Zn1 O4	157.47(15)

Table S3: Non-bonding interactions in **IITKGP-5**.

D H…A	d(H…A) (Å)	D(D…A) (Å)	< DHA (°)
C13 H13…O6	2.256(2)	3.169(3)	167.13(13)
C6 H6…O4	2.435(2)	3.280(3)	150.98(11)

Table S4: Adsorption selectivity of reported MOFs for CO_2/N_2 (15:85) and CO_2/CH_4 (50:50) at 1 bar. (a: IAST selectivity; b: selectivity from Henry's Law; c: From slopes of adsorption isotherms at low pressure; d: selectivity at 2 bar).

Compound	CO_2/N_2 adsorption selectivity	CO_2/CH_4 adsorption selectivity	Temperature (K)	Ref.
IITKGP-5	435.5[a]	151.6[a]	273	This work
	147.8[a]	23.8[a], 37.3[d]	295	This work
2	126[a]	26[a]	298	15(a)
	277[a]	35[a]	273	
PCN-88	18[a]	5[a]	296	15(b)
PCN-61	15[a]		298	15(c)
ZJNU-44a	15[a]	5.5[a]	296	15(d)
UTSA-15a		14.2[a,d]	296	6
UTSA-16	314.7[a]	29.8[a,d]	296	6
UTSA-20a		8.3[a,d]	296	6
UTSA-25a		9.4[a,d]	296	6

UTSA-33a		7.0[a,d]	296	6
UTSA-34a		5.1[a,d]	296	6
UTSA-49a	95.8[a]	33.7[a]	298	15(e)
	197.7[a]	34.8[a]	273	
UTSA-72a	48.3[a]	40.7[a]	273	15(f)
	35.6[a]	9.3[a]	296	
UTSA-85a	55[a]	11.4[a]	273	15(g)
	62.5[a]	6.4[a]	296	
SIFSIX-2-Cu	13.7[a]	5.3[a]	298	15(h)
SIFSIX-2-Cu-i	140[a]	33[a]	298	15(h)
SIFSIX-1-Cu	27[a]	11[a]	298	15(h)
TIFSIX-1-Cu	30[a]	11[a]	298	15(i)
SNFSIX-1-Cu	22[a]	12[a]	298	15(i)
HKUST-1	101[b]	7.4[a,d]	293	15(j)
HKUST-1(hydrated)	28[a]	7.5[a]	298	15(k)
Zn-MOF-74	87.7[a]	5[a]	296	6
SNU-M10	98[a]		298	15(l)
$Cu_{24}(TPBTM)_8$	22[a]		298	15(c)
1		16[a]	298	15(m)
PMOF-3a	29.2[a]	8[a]	273	15(n)
	23.4[a]	5.1[a]	296	
JUC-141	21.62[a]	4.20[a]	273	15(o)
	27.60[a]	8.72[a]	298	
Mg-MOF-74	182.1[a]	105.1[a,d]	296	6
ZIF-68	18.7[c]	5[c]	298	15(p)
ZIF-69	19.9[c]	5.1[c]	298	15(p)
ZIF-70	17.3[c]	5.2[c]	298	15(p)
ZIF-78	41.4[a]	10.4[a,d]	296	15(p)
ZIF-78	50.1[c]	10.6[c]	298	15(p)
ZIF-79	23.2[c]	5.4[c]	298	15(p)
ZIF-81	23.8[c]	5.7[c]	298	15(p)
ZIF-82	35.3[c]	9.6[c]	298	15(p)
ZIF-95	18±1.7[c]	4.3±0.4[c]	298	15(p)

ZIF-100	25±2.4[c]	5.9±0.4[c]	298	15(p)
Bio-MOF-11	79.5[a]		296	6
Cu-TDPAT	57.8[a]	13.8[a,d]	296	6
MOF-177	3.6[a]		296	6
Cu-BTTri	21[a]		298	15(q)
en-Cu-BTTri	25[a]		298	15(q)
mmen-Cu-BTTri	327[a]		298	15(r)
mmen-Mg_2(dobpdc)	329[a]		298	15(s)
MIL-101		9.6[a,d]	296	6
1	250[a]	6.4[a]	273	15(t)
		5.6[a]	298	
1		4.1[a]	273	15(u)
		2.3[a]	296	
1		8.9[a]	273	15(v)
		8.1[a]	298	
MAF-66	403[b]	7.5[b]	273	15(e)
	225[b]	5.8[b]	298	
NOTT-202a	26.7[b]	2.9[b]	273K	15(w)
	4.3[b]	1.4[b]	293K	
Cu-SSZ13(zeolite)	67.4[a]		296	6
H-SSZ13(zeolite)	71.3[a]		296	6
NaX zeolite	145.9[a]	60[a,d]	296	6
JBW(zeolite)	524.4[a]	685.5[a,d]	296	6
Zeolite MFI	11.2[a]	2.5[a,d]	296	6

References:

1. A. L. Myers and J. M. Prausnitz, *AIChE J.* 1965, **11**, 121.

2. B. Li, Y. Zhang, R. Krishna, K. Yao, Y. Han, Z. Wu, D. Ma, Z. Shi, T. Pham, B. Space, J. Liu, P. K.Thallapally, J. Liu, M. Chrzanowski and S. Ma, *J. Am. Chem. Soc*. 2014, **136**, 8654.