Electronic Supplementary Material (ESI) for Materials Advances.

Electronic Supplementary Information

A microporous, amino acid functionalized Zn(II)-organic framework nanoflower for selective CO_2 capture and solvent encapsulation†

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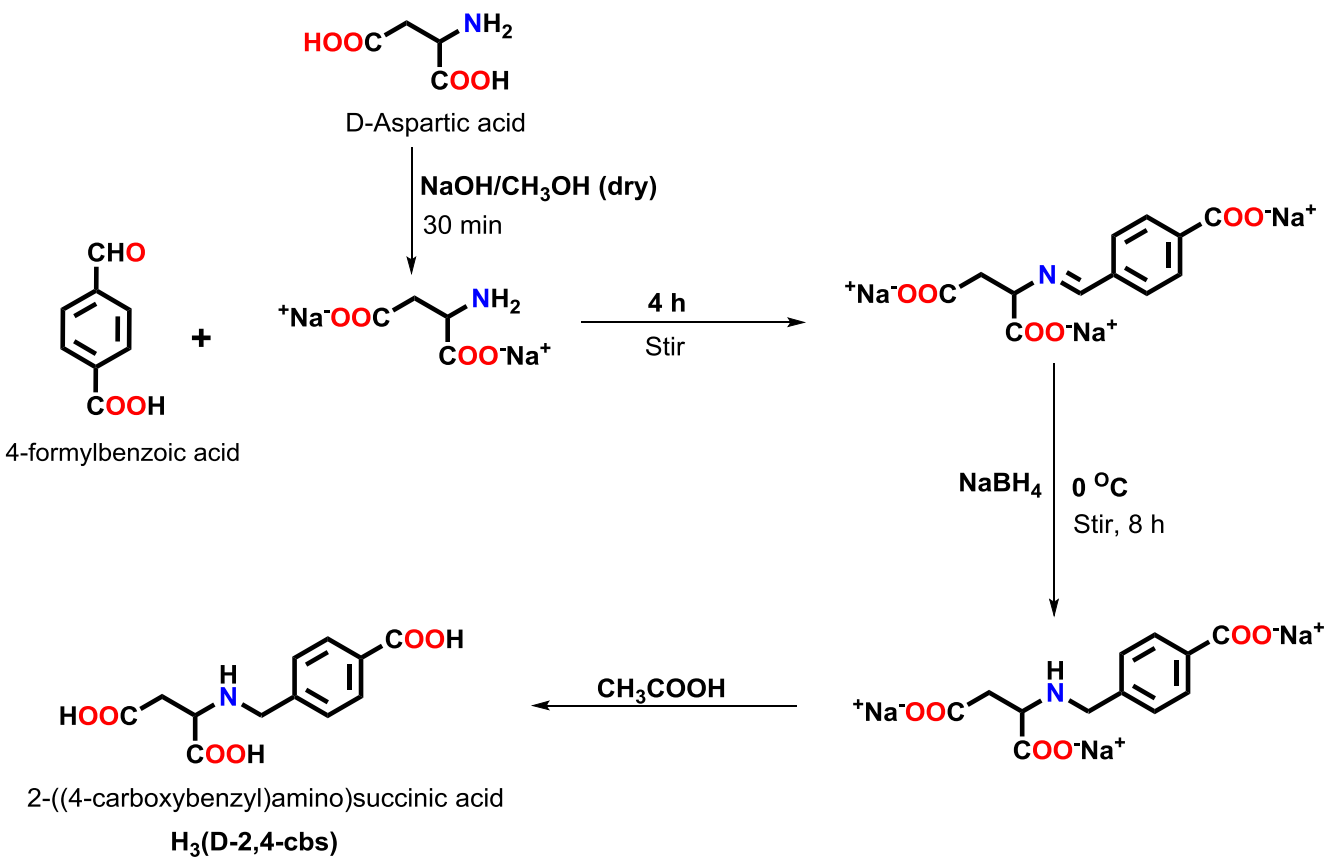


Scheme S1. Synthesis of H_3(D-2,4-cbs).

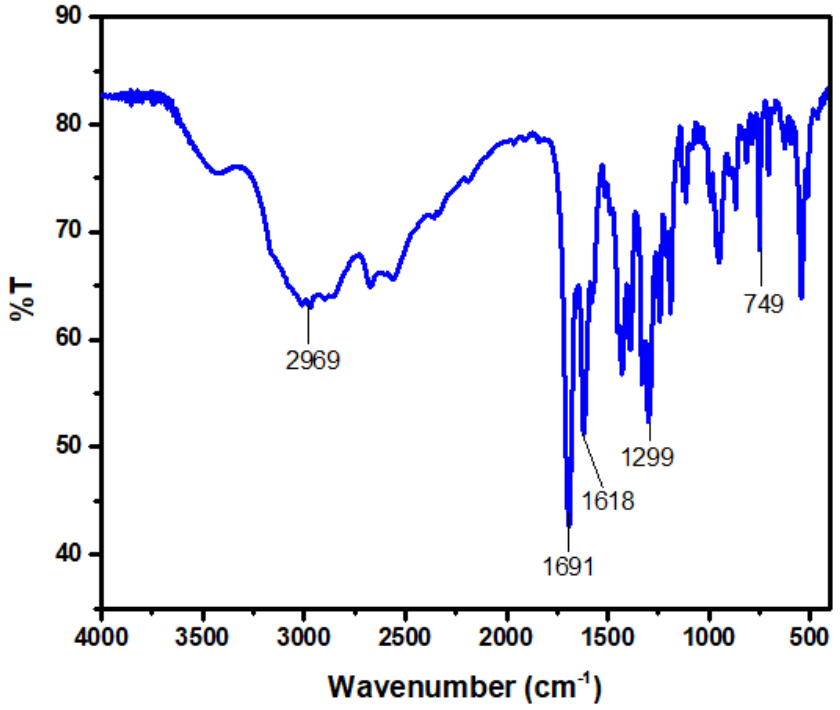


Fig. S1 FTIR spectrum of H_3(D-2,4-cbs).

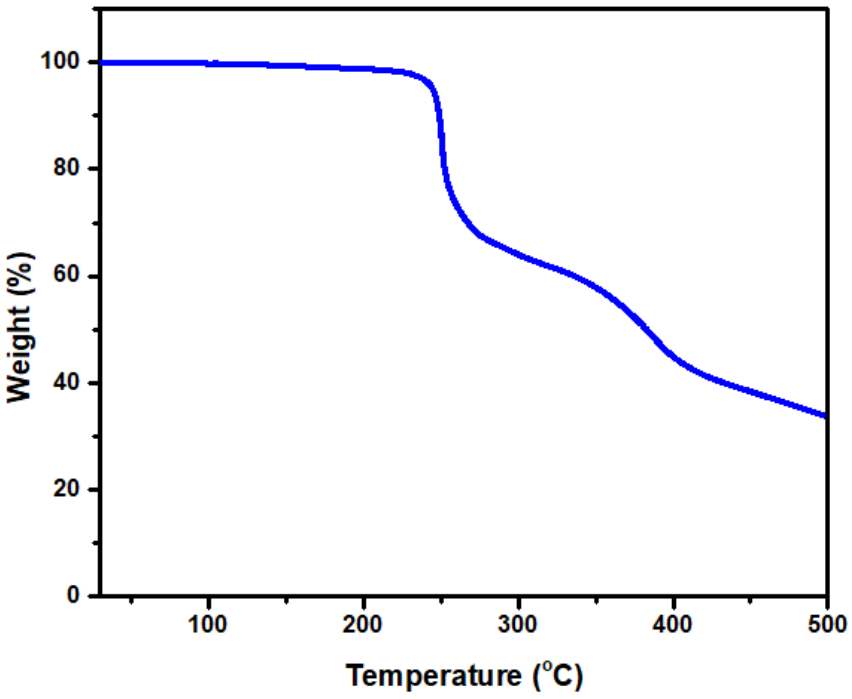


Fig. S2 TGA profile of H_3(D-2,4-cbs).

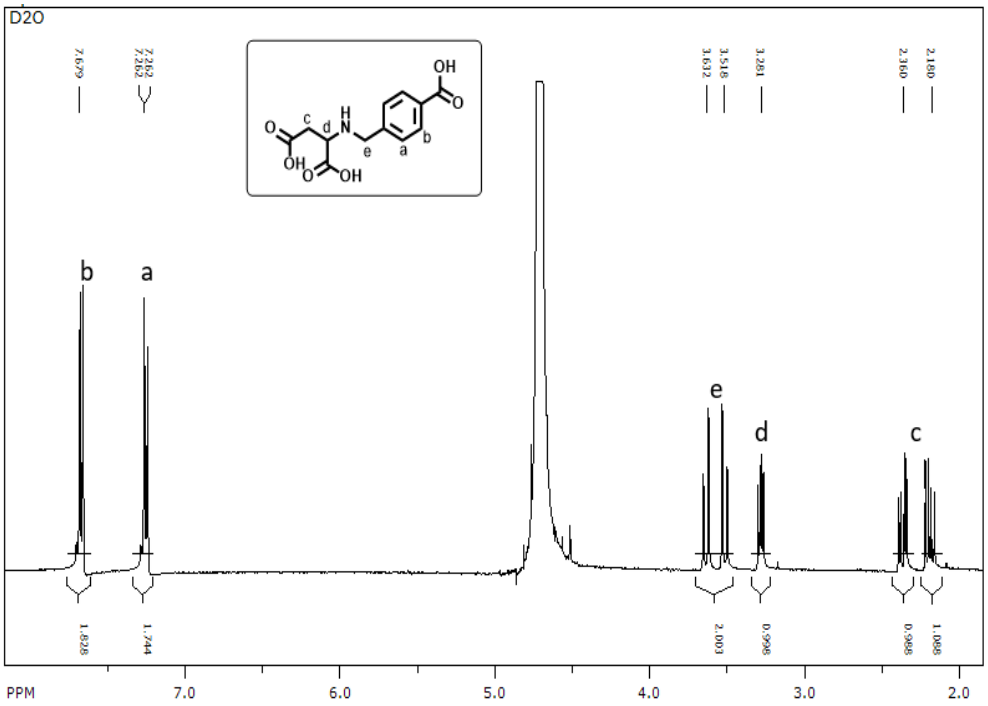


Fig. S3 ^{1}H NMR spectrum of H_3(D-2,4-cbs) in D_2O.

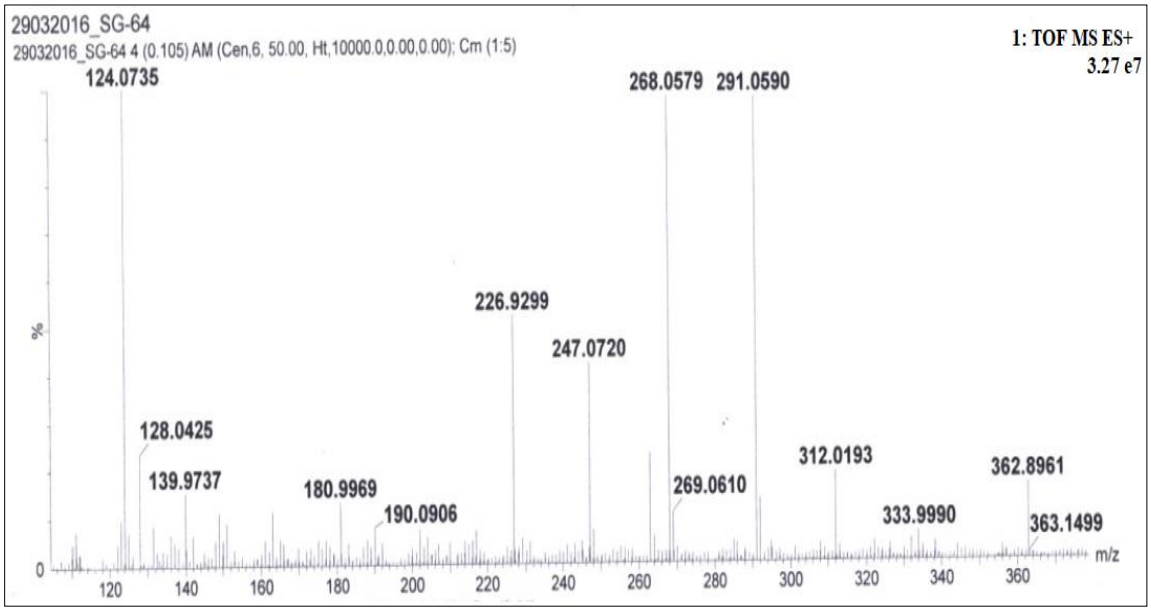


Fig. S4 HRMS of H_3(D-2,4-cbs).

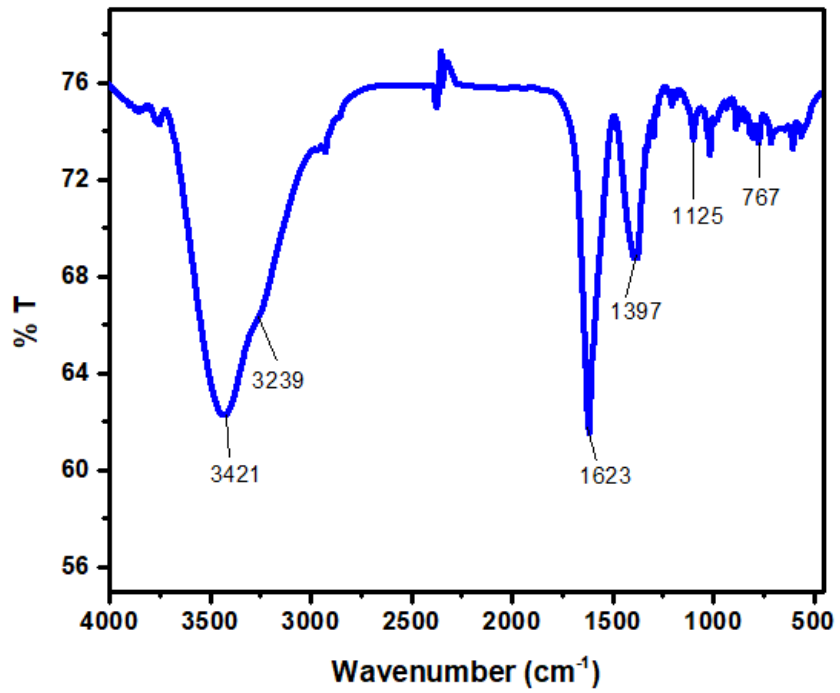


Fig. S5 FTIR spectrum of **Zn-CBS**.

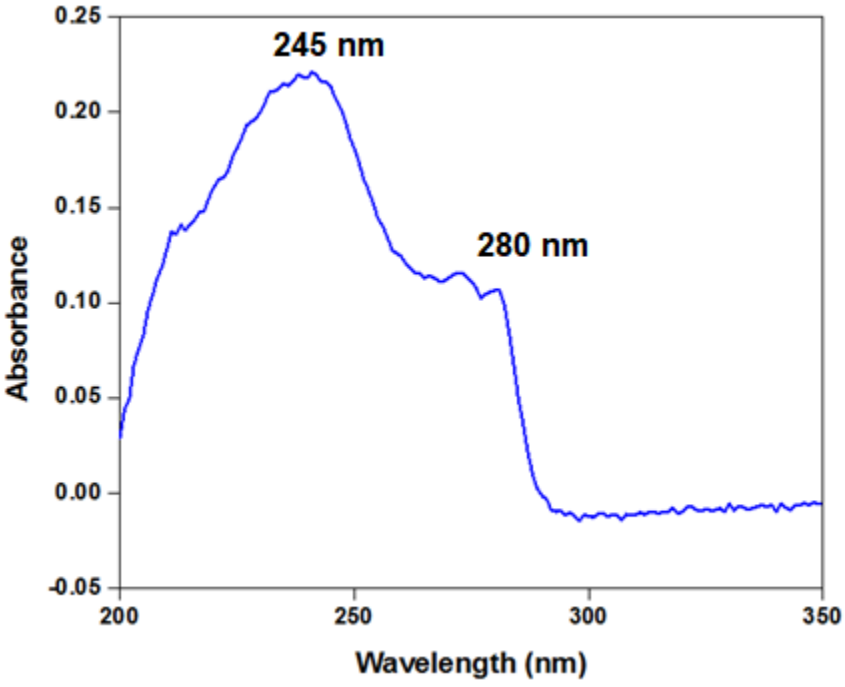


Fig. S6 Solid State diffuse reflectance spectrum of **Zn-CBS**.

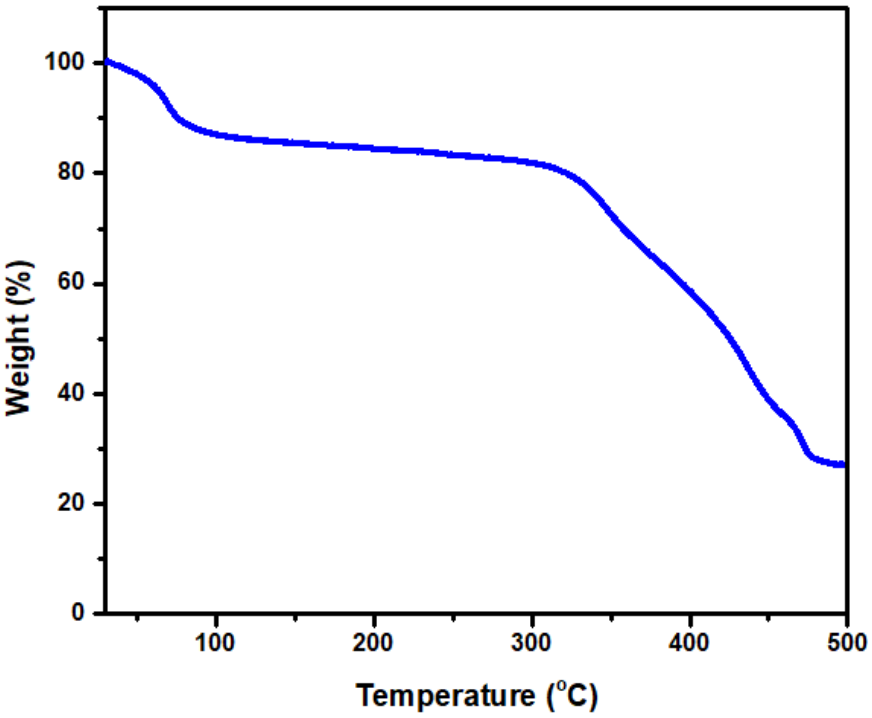


Fig. S7 TGA profile of **Zn-CBS**.

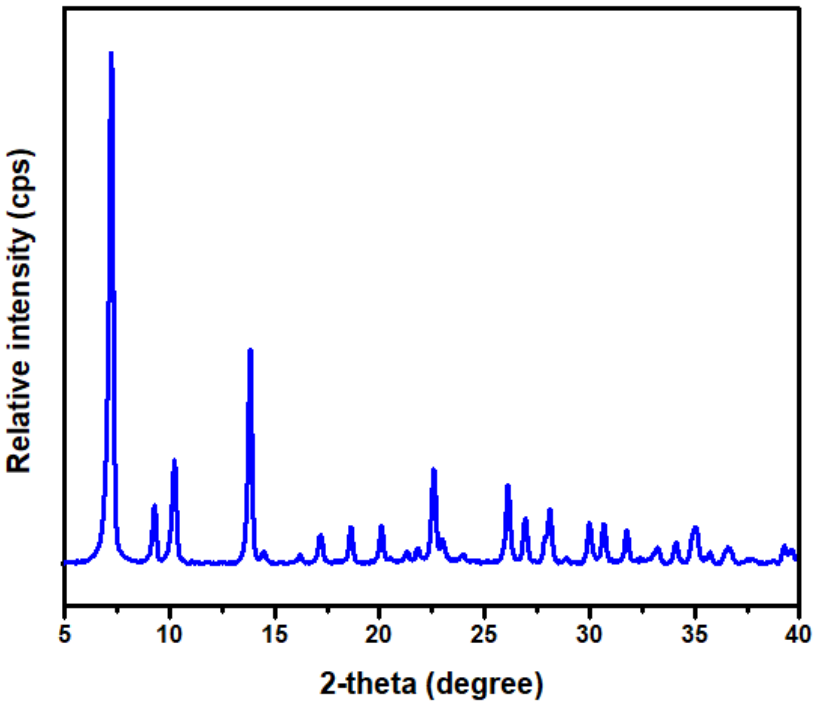


Fig. S8 PXRD pattern of **Zn-CBS**.

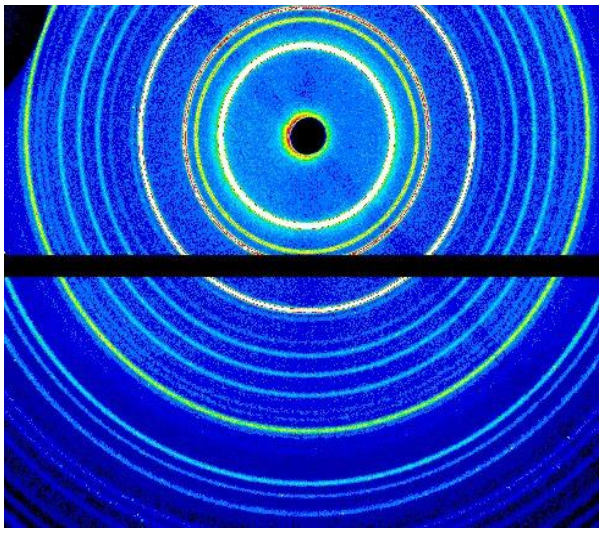
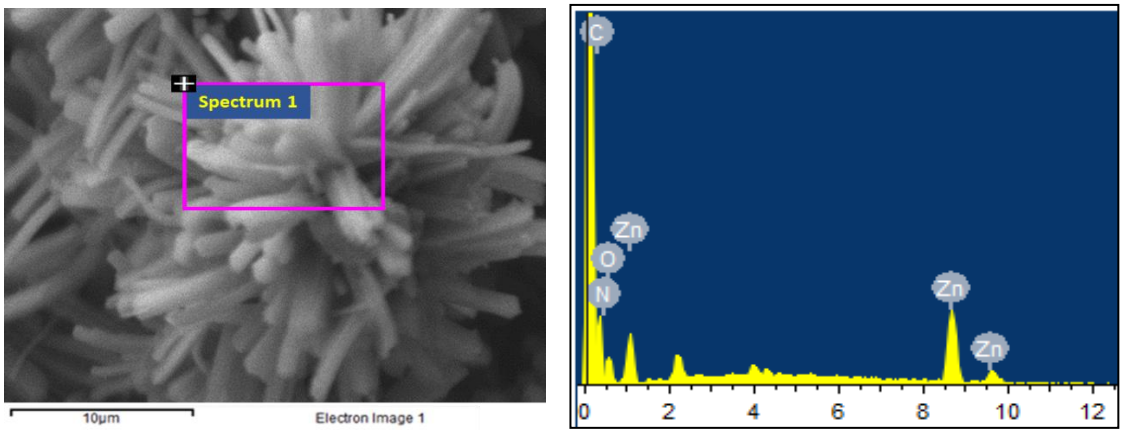


Fig. S9 2D WAX Map of **Zn-CBS**.



Element	Weight (%)	Atomic (%)
C K	33.5	47.5
N K	15.4	18.8
O K	25.5	27.1
Zn K	25.6	6.6
Total	100	

Fig. S10 EDX analysis of **Zn-CBS**.

Analysis of Sorption Isotherm

For this analysis, the BET equation is considered:

$$\nu = c\nu_m x / (1-x)[1 + (c-1)x]$$

where, $x = p/p_0$, ν is the volume of nitrogen adsorbed per gram of **Zn-CBS** at STP, ν_m is the monolayer capacity, and c is related to the heat of adsorption. It is noted that the line is fit to the low pressure isotherm data with range $0.05 < x < 0.3$.

The surface area is then calculated from: $A = \nu_m \sigma_0 N_{av}$

where, σ_0 is the cross-sectional area of nitrogen at liquid density (16.2 Å) and N_{av} is Avogadro's number.

These calculations are done through the "BET analysis" and "Langmuir analysis" function embedded in the Belsorp Adsorption/Desorption Data Analysis software version 6.3.1.0.

Pore size was calculated using microporous (MP) analysis method embedded in the Belsorp Adsorption/Desorption Data Analysis software.

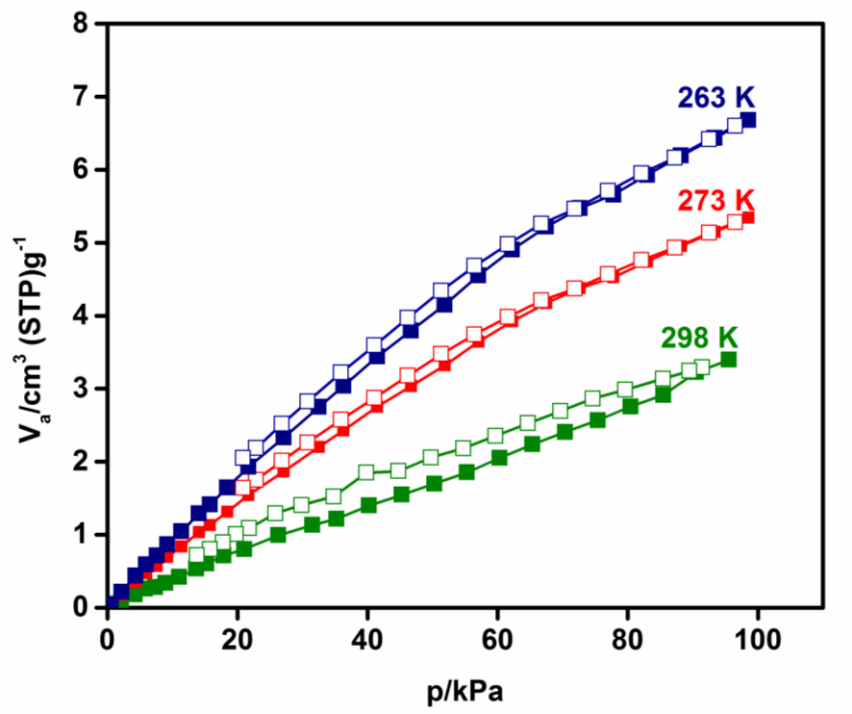


Fig. S11 N_2 sorption isotherms of **Zn-CBS** at 263 K, 273 K and 298 K.

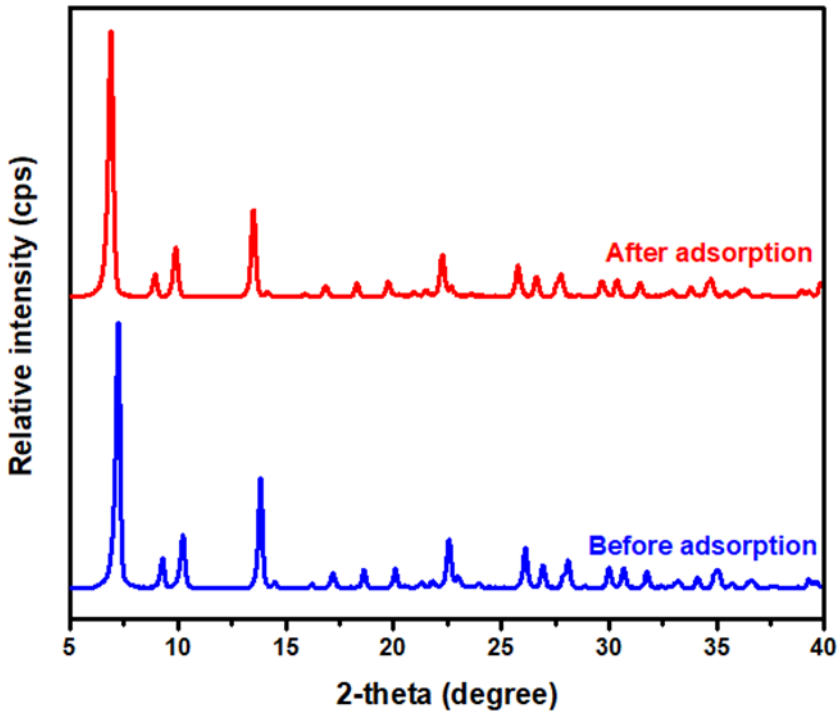


Fig. S12 PXRD pattern of before and after gas adsorption.

Calculation of Isosteric Heats of Adsorption:

Using the Clausius-Clapeyron equation

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 298 K. Q_{st} is defined as:

$$Q_{st} = -R(\partial lnx/\partial(1/T))y$$

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 Belsorp Adsorption/Desorption Data Analysis software version 6.3.1.0.

Table S1. Comparison of BET surface area, H_2, N_2, CO_2 and CH_4 uptake, isosteric heat of adsorption for N_2, CO_2 and CH_4 with literature reports.

Complex	BET surface area (m^2g^{-1})	*H_2 uptake at 77 K*	N_2 uptake			CO_2 uptake				CH_4 uptake			Qst N_2	Qst CO_2	Qst CH_4	Ref.
			298 K	273 K	263 K	298 K	273 K	263 K	195 K	298 K	273 K	263 K				
Zn-CBS	**282**	***64***	**4.1**	**6.6**	**8.3**	**38.7**	**47.5**	**49.3**	**85.9**	**15.1**	**21.2**	**24.8**	**0.7**	**35**	**51.8**	**This work**
$\{[Cd(ATAIA)]\cdot 4H_2O\}_n$	62	*20.12*				17.1	24.3							37.5		*ACS Apl. Mat. Int.,* 2018**, 10**, 25360-25371
TEA@bio-MOF-1 TMA@bio-MOF-1	1220 1460						4.16 mmol/g 4.446 mmol/g							26.5 23.9		*JACS*, 2010**, 132**, 5578
CPF-13		*223.9*				81	116							28.3		*Chem. Mater.*, 2012**, 24**, 2624-2626
JUC-141	1057		6.76	13.9		51.3	79.9			21.8	37.8		27.2	27.8	22.7	*Inorg. chem.*, 2017, **56**, 6938-6942
MAF-2						19	49							27		*JACS,* 2009, **131**, 5516-5521
$[Zn(atz)_2]$	1014		29.4	50.1		99	140							26	19.5	*Inorg. Chem.* 2012**, 51**, 9950-9955

$Zn_2(BDC)_2(DABCO)$	1725					13.7				5.3				20		*Microporous and mesoporous material,* 2010, **132**, 305
$((CH_3)_2NH_2)_{1.5}$ $[Zn_3L_2(HCOO)_{1.5}]\cdot xDMF$	153.4			8.93			57.5				2.48					*J. Mater. Chem. A*, 2014, **2**, 17771-17778
SNU-150, SNU-77S, SNU-151, and SNU-100	1563, 3670, 1852		0.546, 0.40, 0.519, and 0.624 (wt%)			6.09, 3.94, 14.1, and 14.1	12.0, 8.21, 22.2, and 19.9		78.6, 169, 67.8, and 45.2	0.859, 0.62, 1.24, and 1.41	1.29, 1.20, 2.00, and 2.56				12.8, 14.3, 18.2, and 26.5	*Chem. Eur. J.,* 2013, **19**, 17432-17438
IITKGP-5	366		4	5.5		49	56.4			13.6	17		4.6	22.6	14.8	Dalton Trans., 2017, **46**, 15280-15286
IITKGP-6	83.4		4.1	6.2		37.4	50.6			9.2	13.8		5.1	23	18.4	*Inorg. Chem.,* 2017, **56**, 13991-13997
IISERP-MOF20	945					3.5			9 mmol/g					26		*Inorg. Chem.,* 2018, **57**, 5267-5272

CO_2 selectivity over N_2 and CH4 - IAST selectivity calculation for CO_2/N_2 and CO_2/CH_4 mixture:

Gas selectivity for mixture of CO_2/N_2 (15:85) and CO_2/CH_4 (50:50) at different temperature were calculated based on the ideal absorbed solution theory (IAST) proposed by Myers and Prausnitz.[S1] In order to calculate the selective sorption ability of **Zn-CBS** towards the separation of binary mixed gases, the parameter fitted from the single component CO_2 and N_2 and CH_4 adsorption based on the Dual-Site Langmuir-Freundlich (DSLF) model and different parameter were used given below.

$$\mathbf{y} = \frac{q_{m1} b_1 p^{\frac{1}{n1}}}{1 + b_1 p^{\frac{1}{n1}}} + \frac{q_{m2} b_2 p^{\frac{1}{n2}}}{1 + b_2 p^{\frac{1}{n2}}}$$

where, p is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa); y is the adsorbed amount per mass of adsorbent (mmol/g), qm1 and qm2 are the saturation capacities of sites 1 and 2 (mmol/g); b1 and b2 are the affinity coefficients of sites 1 and 2, n1 and n2 represent the deviation from an ideal homogeneous surface.

The predicted adsorption selectivity is defined as

$$\mathbf{S} = \left(\frac{\frac{x1}{y1}}{\frac{x2}{y2}}\right)$$

where, xi and yi are the mole fractions of component 1 (i = 1, 2) in the adsorbed and bulk phases, respectively. The IAST calculation was carried out for a binary mixture containing 15% CO_2 (y1) and 85% N_2 (y2) and 50% CO_2 (y1) and 50% CH_4 (y2), which is typical for flue gases and landfill gases, respectively.

(S1) A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121-127.

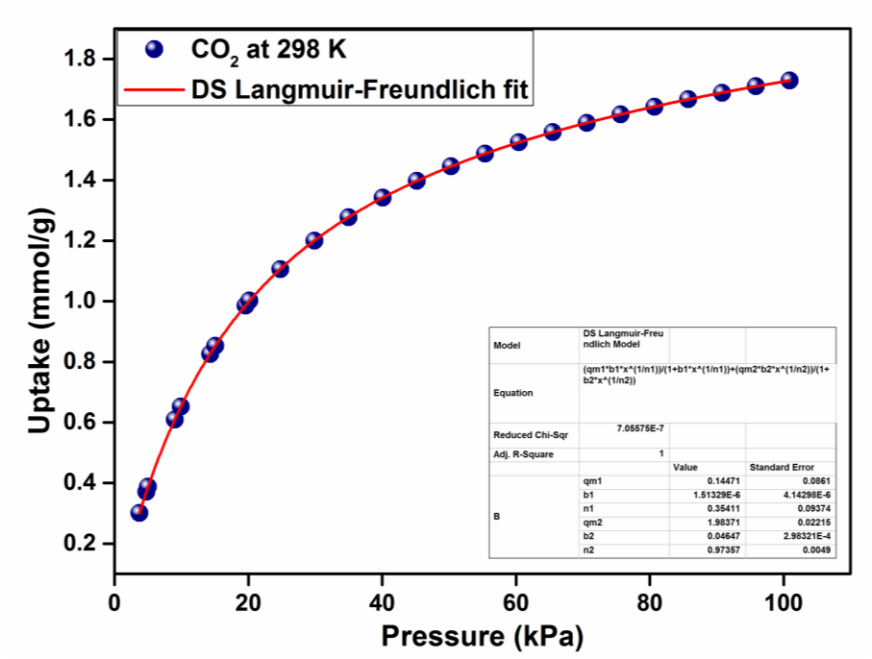


Fig. S13 Dual-site Langmuir-Freundlich fitted (red line) for CO_2 (blue circle) isotherm measure at 298 K.

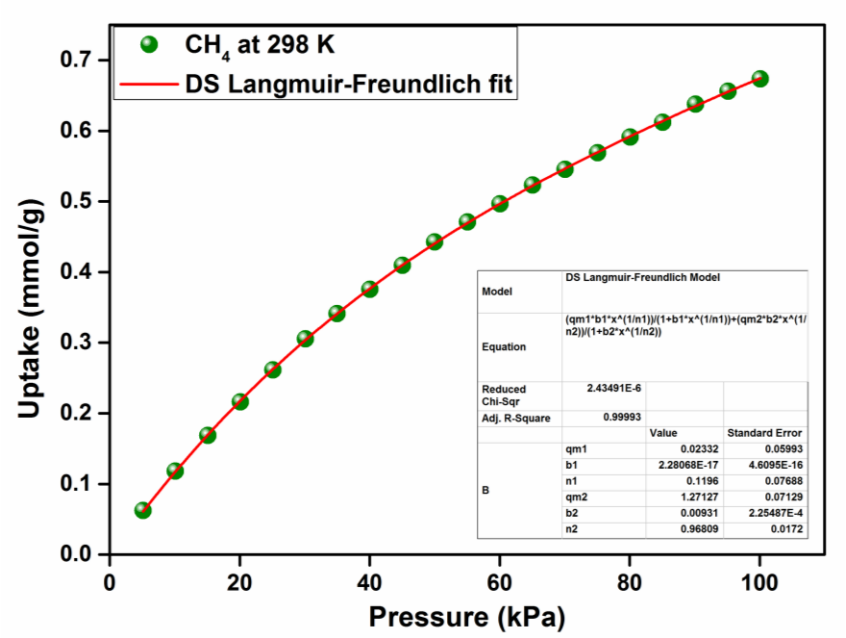


Fig. S14 Dual-site Langmuir-Freundlich fitted (red line) for CH_4 (green circle) isotherm measure at 298 K.

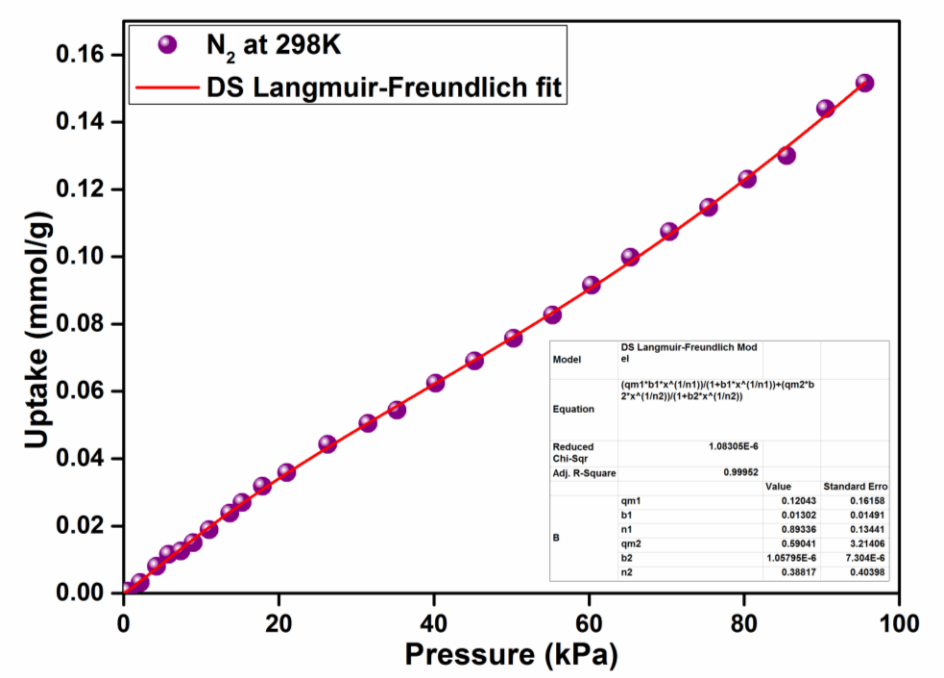


Fig. S15 Dual-site Langmuir-Freundlich fitted (red line) for N_2 (violet circle) isotherm measure at 298 K.

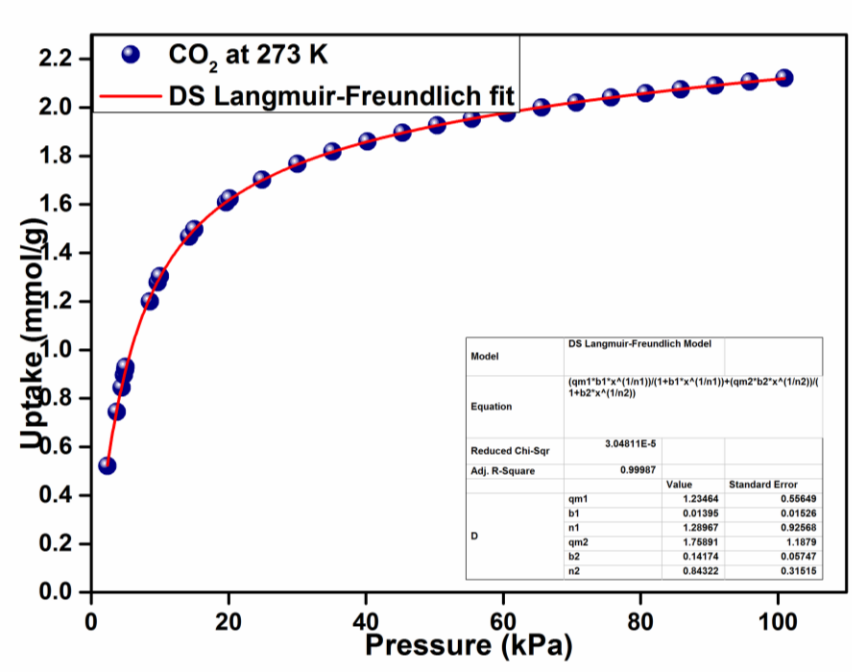


Fig. S16 Dual-site Langmuir-Freundlich fitted (red line) for CO_2 (blue circle) isotherm measure at 273 K.

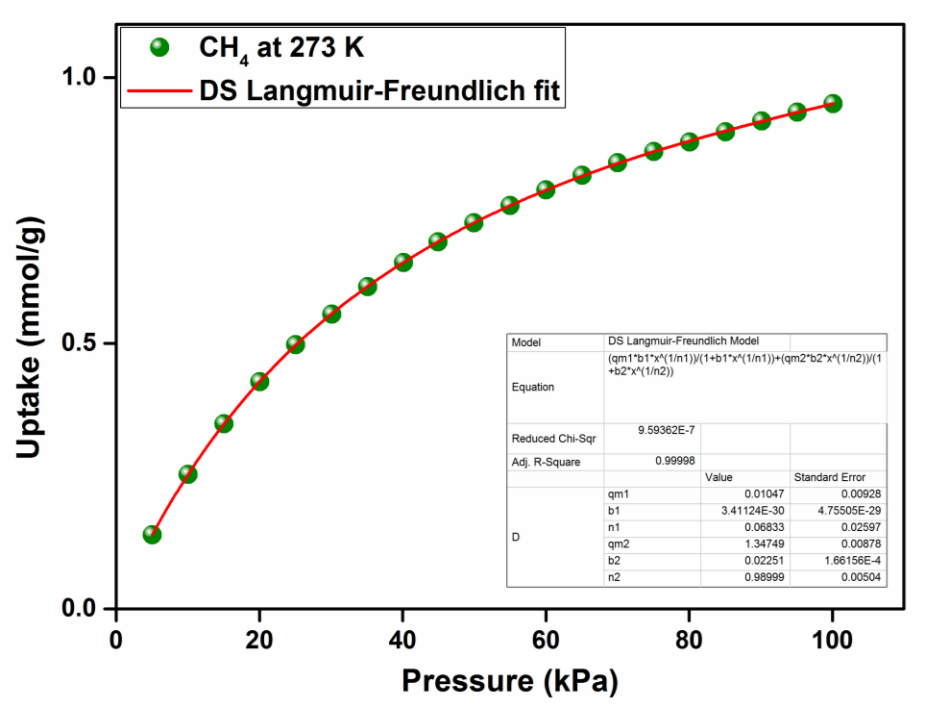


Fig. S17 Dual-site Langmuir-Freundlich fitted (red line) for CH_4 (green circle) isotherm measure at 273 K.

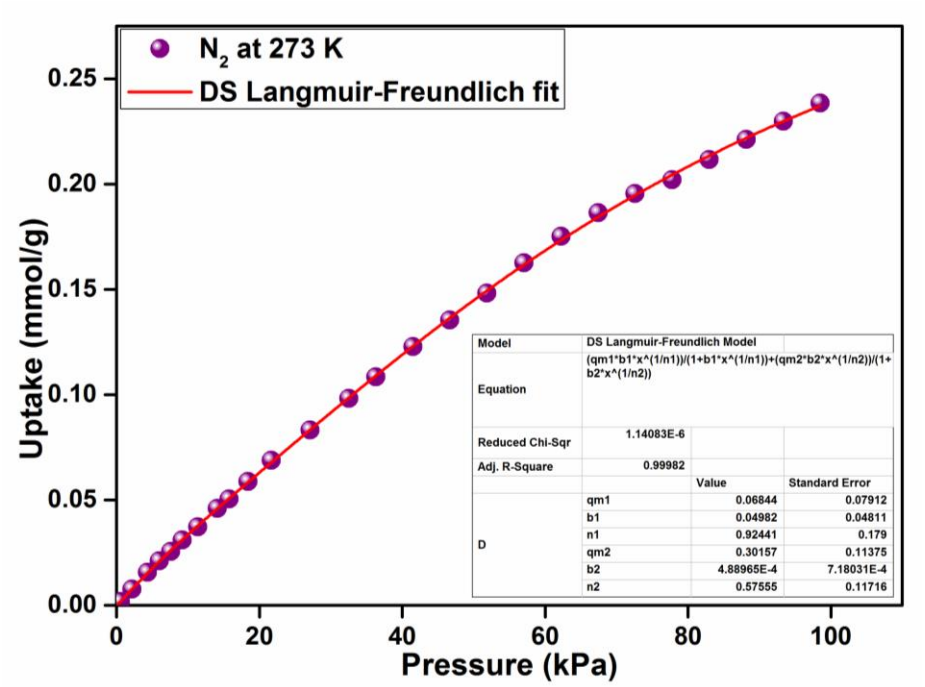


Fig. S18 Dual-site Langmuir-Freundlich fitted (red line) for N_2 (violet circle) isotherm measure at 273 K.

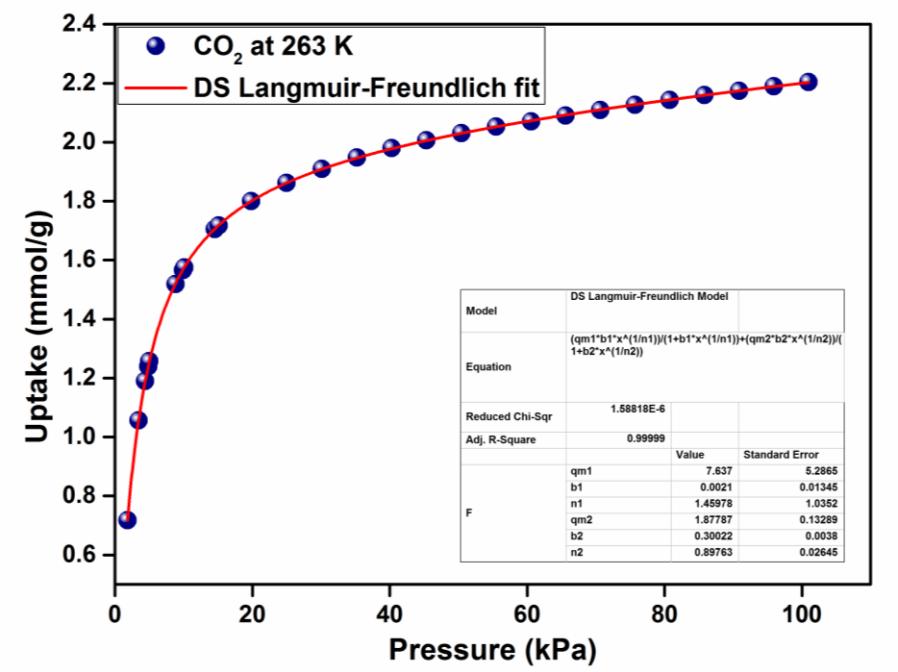


Fig. S19 Dual-site Langmuir-Freundlich fitted (red line) for CO_2 (blue circle) isotherm measure at 263 K.

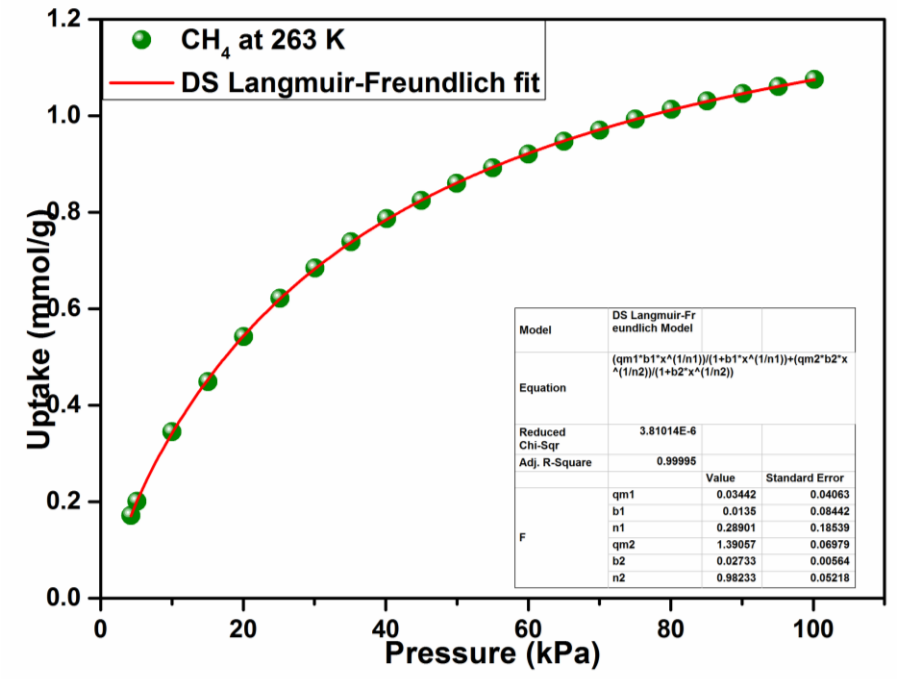


Fig. S20 Dual-site Langmuir-Freundlich fitted (red line) for CH_4 (green circle) isotherm measure at 263 K.

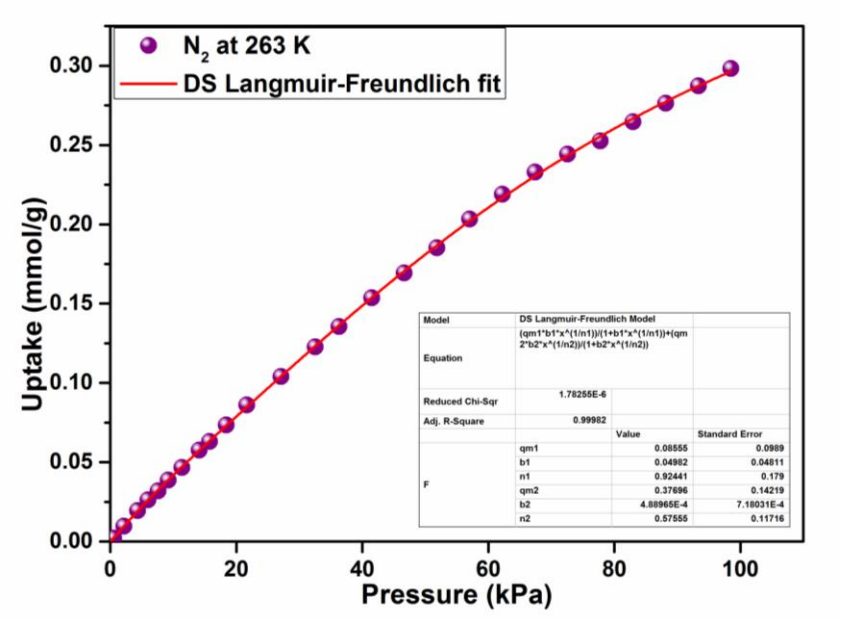


Fig. S21 Dual-site Langmuir-Freundlich fitted (red line) for N_2 (violet circle) isotherm measure at 263 K.

Table S2. Summary of parameters for the DSLF isotherm model.

Parameter → / Adsorbates ↓	q_{m1} (mmol/g)	b_1 (1/kPa)	n_1	q_{m2} (mmol/g)	b_2 (1/kPa)	n_2
CH_4 (298 K)	0.02332	2.2068E-17	0.1196	1.27127	0.00931	096809
CO_2 (298 K)	0.14471	1.51329E-6	0.35411	1.98371	0.04647	0.97357
N_2 (298 K)	0.12043	0.01302	0.89336	0.59041	1.05795E-6	0.38817
CH_4 (273 K)	0.01047	3.41124E-30	0.06833	1.34749	0.02251	0.98999
CO_2 (273 K)	1.23464	0.01395	1.28967	1.75891	0.14174	0.84322
N_2 (273 K)	0.06844	0.04982	092441	0.30157	4.88965E-4	0.57555
CH_4 (263 K)	0.03442	0.0135	0.28901	1.39057	0.02733	0.98233
CO_2 (263 K)	7.637	0.0021	1.45978	1.87787	0.30022	0.89763
N_2 (263 K)	0.08555	0.04982	0.92441	0.37696	4.88965E-4	0.57555

Table S3. Comparison for the selectivity of CO_2/N_2 and CO_2/CH_4 with literature reports.

Complex	Selectivity CO_2/N_2 uptake			Selectivity CO_2/CH_4 uptake			References
	298 K	273 K	263 K	298 K	273 K	263 K	
Zn-CBS	**408**	**916**	**1832**	**12.2**	**17.2**	**24.5**	**This work**
JUC-141	27.6	21.6		8.72	4.20		*Inorg. Chem.,* 2017**, 56***,* 6938-6942
SNU-150, SNU-77S, SNU-151, and SNU-100	5.4, 30, and 26.5			2.26, 7.20			*Chem. Eur. J,* 2013, **19***,* 17432–17438
$[Zn(atz)_2]$	225	403		5.8	7.5		*Inorg. Chem.,* 2012, **51***,* 9950-9955
IITKGP-5	147.8	435.5		23.8	151.6		*Dalton Trans*., 2017, **46**, 15280–15286
IITKGP-6	42.8	51.3		5.1	36		*Inorg. Chem.,* 2017, **56**, 13991-13997
IISERP-MOF20	250	220					*Inorg. Chem.,* 2018, **57***,* 5267-5272
MAF-66 UTSA-49a	225 93.5	403 193.7		5.8 33.7	7.5 34.8		*Chem. Commun*., 2014, **50**, 12101-12104
$(Me_2NH_2)_2[(In_2X)]\cdot 9DMF\cdot 5H_2O$		250		5.6	6.4		*Inorg. Chem*., 2013, **52**, 3127-3132
NOTT-202a	4.3	26.7		1.4	2.9		*Nat. Mater*., 2012, **11**, 710-716
UTSA-15a, UTSA-20a, UTSA-25a, UTSA-33a, and UTSA-34a				14.2, 8.3, 9.4, 7.0, and 5.1			*Nat. Commun*., 2012, **3**, 954-963

Density Functional Theory (DFT) and Configurational Bias Monte Carlo (CBMC) molecular simulation:

Ligand H_3(D-2,4-cbs) was optimized in DFT and put in a (1 x 1 x 1) cell for further calculation. The simulation boxes representing the ligand consist of (1 x 1 x 1) unit cells for CO_2, N_2 and CH_4 (optimized). All the calculations were perfomed at 298 K at fixed pressure 1 bar. Interatomic interactions were modeled with standard Lennard-Jones potential and Columbic potentials. Lorentz-Berthelot mixing rules were employed to compute the Lennard-Jones parameters between unlike atom types. The pairwise interactions between host and guest atoms of the particular force field were analysed by utilizing the non-bonding parameter. The long-range part of electrostatic interactions was handled using the Ewald summation technique with a relative precision of 10^{-6}. Periodic boundary conditions were applied in all three dimensions. For each state point, the CBMC simulation consists of 1 x 10^7 steps to guarantee equilibration, followed by 1 x 10^7 steps to sample the desired thermodynamic properties.

Table S4. Calculation of number of molecules absorbed per formula unit of Zn-CBS based on TGA.

Solvent	Found (wt%)	Calculated (wt%)	Number of guest molecules
Acetonitrile	15.0	14.6	3.75
Ethanol	15.0	15.2	3.5
Methanol	8.9	8.9	2.75
Tetrahydrofuran	12.5	12.3	1.75
Toluene	18.2	17.7	2.1
p-Xylene	14.7	15.0	1.5