A microporous, amino acid functionalized Zn(II)-organic framework nanoflower for selective CO₂ capture and solvent encapsulation†

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# Table of Contents

| Item(s)       | Description                                                                 | Page No. |
|---------------|-----------------------------------------------------------------------------|----------|
| Scheme S1     | Synthesis of H$_3$(D-2,4-cbs)                                               | S3       |
| Fig. S1-S4    | Characterization of H$_3$(D-2,4-cbs): FTIR spectrum, TGA, $^1$H NMR and Mass spectra | S4-S5    |
| Fig. S5-S10   | Characterization of **Zn-CBS**: FTIR spectrum, Solid-state reflectance spectrum, TGA, PXRD pattern, 2D WAX map and EDX analysis | S6-S8    |
| Fig. S11      | Analysis of sorption isotherms and N$_2$ sorption isotherm of **Zn-CBS**     | S9       |
| Fig. S12      | PXRD patterns of before and after gas adsorption of **Zn-CBS**              | S10      |
|               | Calculation of Isosteric heats of adsorption                               | S11      |
| Table S1      | Literature survey 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$_4$ | S12-S13  |
| Fig. S13-S21  | CO$_2$ selectivity over N$_2$ and CH$_4$: Dual-site Langmuir-Freundlich plots | S14-S19  |
| Table S2      | Summary of DSLF model fit                                                   | S20      |
| Table S3      | Literature survey for the selectivity of CO$_2$/N$_2$ and CO$_2$/CH$_4$     | S21      |
|               | DFT calculation and CBMC molecular simulation                               | S22      |
| Table S4      | Encapsulation of solvents by **Zn-CBS**                                     | S23      |
Scheme S1. Synthesis of $H_3(\text{D-2,4-cbs})$. 
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 $\text{H}_3$(D-2,4-cbs) in $\text{D}_2\text{O}$.

Fig. S4 HRMS of $\text{H}_3$(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.

Fig. S10 EDX analysis 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        |            |
Analysis of Sorption Isotherm

For this analysis, the BET equation is considered:

\[ \nu = \frac{c \nu_m x}{(1-x)[1 + (c-1)x]} \]

where, \( x = \frac{p}{p_0} \), \( \nu \) is the volume of nitrogen adsorbed per gram of Zn-CBS at STP, \( \nu_m \) 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, \( \sigma_0 \) 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 N₂ sorption isotherms of Zn-CBS at 263 K, 273 K and 298 K.](image)
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:

$$Q_{st} = -R \left( \frac{\partial \ln x}{\partial (1/T)} \right) y$$

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 Belsorp Adsorption/Desorption Data Analysis software version 6.3.1.0.
Table S1. Comparison of BET surface area, H₂, N₂, CO₂ and CH₄ uptake, isosteric heat of adsorption for N₂, CO₂ and CH₄ with literature reports.

| Complex                  | BET surface area (m²/g⁻¹) | H₂ uptake at 77 K | N₂ uptake | CO₂ uptake | CH₄ uptake | Qst N₂ | Qst CO₂ | Qst CH₄ | Ref.                          |
|--------------------------|---------------------------|-------------------|-----------|------------|------------|--------|---------|---------|--------------------------------|
|                          |                           |                   | 298 K     | 273 K      | 263 K      | 298 K  | 273 K  | 263 K  | 195 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)]₄H₂O)₆       | 62                        | 20.12             |           |            |            | 17.1   | 24.3   |        |       |      |      |      | 37.5 | |
| TEA@bio-MOF-1            | 1220                      |                   |           |            |            |        |        | 4.16 mmol/ g | 4.446 mmol/ g | 26.5 | |
| TMA@bio-MOF-1            | 1460                      |                   |           |            |            |        |        |        |       |      |      | 23.9 | |
| CPF-13                   |                           | 223.9             |           |            |            | 81     | 116    |        |       |      |      |      | 28.3 | |
| JUC-141                  | 1057                      |                   | 6.76      | 13.9       | 51.3       | 21.8   | 37.8   | 27.2   | 27.8  | 22.7 | |
| MAF-2                    |                           |                   |           |            |            | 19     | 49     |        |       |      |      |      | 27    | |
| [Zn(atz)₄]              | 1014                      |                   | 29.4      | 50.1       | 99         | 140    |        |        |       |      |      |      | 26    | 19.5 | Inorg. Chem. 2012, 51, 9950-9955 |
|                          |                           |                   |           |            |            |        |        |        |       |      |      |      |      | **ACS Appl. Mat. Int., 2018, 10, 25360-25371** |
| Material                        | T (°C) | t (h) | Microporous and mesoporous material, 2010, 132, 305 |
|--------------------------------|--------|-------|---------------------------------------------------|
| Zn_{2}(BDC)_{2}(DABCO)         | 1725   | 13.7  | 5.3                                               |
|                               |        | 20    |                                                   |
| (CH_{3})_{2}NH_{2}·[Zn_{3}L_{2}(HCOO)_{1.5}]xDMF | 153.4  | 8.93  | 57.5                                              |
|                               |        |       | 2.48                                              |
| SNU-150, SNU-775, SNU-151,    | 1563,  | 6.09, | 78.6, 169, 169, 67.8, and 45.2                   |
| and SNU-100                   | 3670,  | 3.94, | 12.0, 8.21, 22.2, and 19.9                       |
|                               | 1852   | 14.1, | 0.859, 0.62, 1.24, and 1.41                       |
|                               |        | 14.1  | 1.29, 1.20, 2.00, and 2.56                       |
|                               |        |       | 12.8, 14.3, 18.2, and 26.5                       |
| IITKGP-5                      | 366    | 4     | 13.6                                             |
|                               |        |       | 4.6                                              |
|                               |        |       | 22.6                                             |
|                               |        |       | 14.8                                             |
| IITKGP-6                      | 83.4   | 4.1   | 9.2                                              |
|                               |        | 6.2   | 13.8                                             |
|                               |        |       | 5.1                                              |
|                               |        |       | 23                                               |
|                               |        |       | 18.4                                             |
| IISERP-MOF20                  | 945    | 3.5   | 9 mmol/g                                          |
|                               |        |       | 26                                               |
|                               |        |       |                                                   |
**CO₂ selectivity over N₂ and CH₄ - IAST selectivity calculation for CO₂/N₂ and CO₂/CH₄ mixture:**

Gas selectivity for mixture of CO₂/N₂ (15:85) and CO₂/CH₄ (50:50) at different temperature were calculated based on the ideal absorbed solution theory (IAST) proposed by Myers and Prausnitz.¹ 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 CO₂ and N₂ and CH₄ adsorption based on the Dual-Site Langmuir-Freundlich (DSLF) model and different parameter were used given below.

\[
y = \frac{qm_1 b_1 p^{n_1}}{1 + b_1 p^{n_1}} + \frac{qm_2 b_2 p^{n_2}}{1 + b_2 p^{n_2}}
\]

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), \( qm_1 \) and \( qm_2 \) are the saturation capacities of sites 1 and 2 (mmol/g); \( b_1 \) and \( b_2 \) are the affinity coefficients of sites 1 and 2, \( n_1 \) and \( n_2 \) represent the deviation from an ideal homogeneous surface.

The predicted adsorption selectivity is defined as

\[
S = \left( \frac{x_1}{y_1} \right) \left( \frac{y_2}{x_2} \right)
\]

where, \( x_i \) and \( y_i \) 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% CO₂ (\( y_1 \)) and 85% N₂ (\( y_2 \)) and 50% CO₂ (\( y_1 \)) and 50% CH₄ (\( y_2 \)), 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\textsubscript{2} (violet circle) isotherm measure at 298 K.

**Fig. S16** Dual-site Langmuir-Freundlich fitted (red line) for CO\textsubscript{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.

| 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   |        |        |           |
| 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)$_2$]$_2$ | 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  | 225    | 403    | 5.8    | 7.5    |        |        | Chem. Commun., 2014, 50, 12101-12104 |
| UTSR-9a | 93.5   | 193.7  | 33.7   | 34.8   |        |        |           |
| (Me$_2$NH)$_2$[(In$_2$X)$_2$]$_2$DMF$\cdot$H$_2$O | 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 |
| UTSR-15a, UTSR-20a, UTSR-25a, UTSR-33a, and UTSR-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 performed at 298 K at fixed pressure 1 bar. Interatomic interactions were modeled with standard Lennard-Jones potential and Coulombic 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 $1 \times 10^7$ steps to guarantee equilibration, followed by $1 \times 10^7$ 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                      |