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

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A new homochiral metal organic framework, $\{[Zn_4(\mu_3\text{-OH})_2(\text{D-2,4-cbs})_2(\text{H}_2\text{O})_4]\cdot 5\text{H}_2\text{O}\}_n$ (**Zn-CBS**), has been solvothermally synthesized using a new chiral amino acid based tricarboxylic acid ligand, (2-((4-carboxybenzyl)amino)succinic acid), H₃(D-2,4-cbs). **Zn-CBS** was characterized by various techniques like Fourier transform infrared spectroscopy (FTIR), UV-Vis solid-state diffuse reflectance spectroscopy, elemental microanalysis, thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), and energy dispersive X-ray analysis (EDX) and elemental mapping. The nanoflower arrangement in **Zn-CBS** is clearly seen from the FESEM and TEM images. Its microporous nature is established by the nitrogen adsorption measurements which exhibit a reversible type I isotherm with a BET surface area of 282 m² g⁻¹. Similarly, it shows a reversible type I isotherm for H₂ with an uptake of 0.5 wt% at 77 K. Based on its CO₂ sorption isotherm with an uptake of 85.9 cm³ g⁻¹ at 195 K, a high isosteric heat of adsorption (Q_{st}) of 35 kJ mol⁻¹ at zero coverage is obtained. This is illustrated by its high potential of selectivity towards CO₂ over N₂ and CH₄ under ambient conditions (298 K and 1 bar). With the help of configurational bias Monte Carlo molecular simulation, this selectivity is explained for an effective interaction between CO₂ and basic amine sites of the framework. The porous nature and functionality of **Zn-CBS** have also been utilized in encapsulating various small molecules, which is followed by FTIR, TGA and PXRD.

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Introduction

In the past couple of decades, there has been growing interest in the study of Metal–Organic Frameworks (MOFs), made from a combination of suitable organic ligands and metal ions, owing to their highly porous nature with structural diversity, tunable functionality and large surface area. These properties play vital roles in various applications, such as gas and vapour adsorption, catalysis, sensing, magnetism, *etc.*^{1–12} In particular, their promising roles in carbon capture have received significant attention for an urgent need to reduce the concentration of the major greenhouse gas CO₂ as it is a part of flue gases which has a toxic effect on the environment.¹³ Also, the composition of landfill gas has CO₂ along with CH₄ (CO₂/CH₄ = 50/50) that needs to be separated out, which is essential for natural gas

purification.^{14–16} As the landfill-gas is a combination of polar (CO₂) and non-polar (CH₄) gas, the criteria for the selectivity of CO₂ are: (a) an access to open metal sites and polar N-containing basic functional groups, which show adsorbate–adsorbent interaction due to quadrupole interaction of CO₂ molecules with the framework,^{14–32} and (b) an appropriate pore diameter of the framework for size/shape exclusion.^{31–36} It should be noted that initial efforts with zeolitic and zeolitic-like metal imidazolate frameworks (ZIFs) that have excellent affinity for CO₂ due to the presence of –N(H) donors on the imidazole moieties have suffered for less uptake capacity and selectivity for CO₂ for not having open metal sites.³⁷ On the other hand, flue gases also have water vapour apart from CO₂. Thus, the framework ought to eliminate water vapor alongside the greenhouse gas. To make an MOF potential for H₂O adsorption, it must be water stable and shows very good interaction with water. Among robust water and thermally stable MOF materials, those with the well-known Zn₄O core appeared to be desirable.³⁸ Interestingly, a limited number of MOFs with the Zn₄(μ₃-OH)₂ core has been reported; moreover, those with trianionic linkers such as benzene tricarboxylate (BTC) and 2-sulfoterephthalate (STP) are rare.^{25,39}

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† Electronic supplementary information (ESI) available: Scheme S1, Fig. S1–S21 and Tables S1–S4. Synthesis and characterization of H₃(D-2,4-cbs) and Zn-CBS; sorption isotherms; comparison of data with literature. See DOI: 10.1039/d0ma00481b



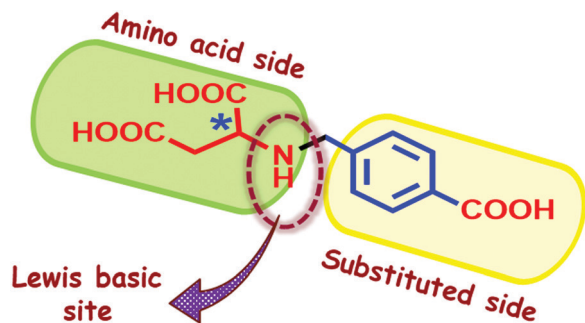


Fig. 1 Structure of $H_3(D-2,4-cbs)$ ligand.

With the above considerations, we chose to explore the use of amino acid functionalized tricarboxylates to synthesize MOFs with the $Zn_4(\mu_3-OH)_2$ core that will offer (a) to contain $-N(H)$ functional groups and open metal sites, and (b) to tailor pore sizes by varying the aldehyde used in making the tricarboxylate. We believe that our approach is simple and cost-effective to introduce multiple functionalities into the MOFs.^{40–43} Furthermore, the presence of amino acid in the system also provides an opportunity to add chirality in the MOFs.⁴⁴ Whereas, if the framework is found to be microporous in nature it will be suitable for hydrogen sorption.^{45,46} Thus, we targeted to make a microporous MOF using one of the two amino acids that have two carboxylic acid groups (aspartic acid and glutamic acid) and functionalize their amine part with 4-formyl benzoic acid through the reduced Schiff base chemistry to demonstrate our concept.

Herein, we have synthesized a new chiral ligand (2-((4-carboxybenzyl)amino)succinic acid) $H_3(D-2,4-cbs)$ with one secondary amine group and three carboxylic acid group (Fig. 1) from very cheap *D*-aspartic acid. Using this ligand, a microporous and versatile MOF, $\{[Zn_4(\mu_3-OH)_2(D-2,4-cbs)_2(H_2O)_4] \cdot 5H_2O\}_n$ (**Zn-CBS**), has been solvothermally synthesized and characterized by various analytical techniques. The basic functionality present on the pore wall is utilized for selective CO_2 capture and separation over N_2 (flue gas) and CH_4 (landfill gas). Along with CO_2 , **Zn-CBS** also shows smart adsorption behavior towards H_2 . Furthermore, its water vapour sorption isotherm illustrates steep uptake behavior at low relative pressure. **Zn-CBS** is also found to be efficient in encapsulating solvent molecules.

Experimental section

Materials and methods

All chemicals and solvents used for synthesis were obtained from Sigma-Aldrich and Merck and were used as received, without further purification. All reactions were carried out under aerobic conditions.

Physical measurements

Using samples prepared as KBr pellets, Fourier transform infrared (FTIR) spectra were measured in the $4000\text{--}400\text{ cm}^{-1}$ range on a PerkinElmer Spectrum I spectrometer. For melting

point determination, a Büchi M-565 instrument was used. Solid-state diffuse reflectance spectra were recorded using a Cary 5000 UV-vis-NIR instrument by Agilent Technology. The 1H NMR spectra were recorded on a Bruker ARX-400 spectrometer in D_2O at $25\text{ }^\circ C$. Thermogravimetric analysis (TGA) were carried out from 30 to $500\text{ }^\circ C$ (at a heating rate of $10\text{ }^\circ C\text{ min}^{-1}$) under a dinitrogen atmosphere using a Shimadzu DTG-60H instrument. High Resolution Mass Spectrometry (HRMS) data were measured by Thermo Scientific LTQ XL LC-MS instrument for the $50\text{--}2000$ amu range with ESI,⁺ ion source. Powder X-ray diffraction (PXRD) measurements were done on a Rigaku Ultima IV diffractometer equipped with a 3 kW sealed tube $Cu\ K\alpha$ X-ray radiation and a DTex Ultra detector using Bragg-Brentano beam geometry over a 2θ range from 5 to 40° with a scan speed of 2° per min and 0.02° step width. Wide angle X-ray (WAX) measurements were carried out using Xeuss Model C HP100 fm from Xenocs. Scattering vector ($q = 4\pi\sin\theta/\lambda$) and position of an incident X-ray beam on the detector were calibrated using several orders of layer reflections from silver behenate while scattering and diffraction images were recorded and integrated along the Debye-Scherrer ring using the FIT2D software. Field emission scanning electron microscopy (FESEM) experiments, including energy dispersive X-ray spectroscopy (EDX) for mapping of elements, were performed on a JEOL instrument; each sample was well dispersed in ethanol, drop casted on a silicon wafer, dried and coated with gold using a working distance of $4.5\text{--}15\text{ mm}$ and a voltage of $10\text{--}15\text{ kV}$. High-resolution transmission electron microscopy (HRTEM) was performed on a FEI Tecnai G2 F20 equipped with a field emission gun operated at 200 kV using a copper grid loaded with the dispersed sample (1 mg in 10 mL ethanol sonicated for 20 min) followed by drying with a lamp for 30 minutes . Gas sorption experiments were performed using a BELSORP MAX (BEL JAPAN) volumetric adsorption analyzer at different temperatures. Ultrapure (99.995%) N_2 , He , H_2 , CH_4 and CO_2 gases were used for the adsorption measurements. Prior to the adsorption measurement, the sample was ground into a fine powder, evacuated at 393 K for 24 h and purged with ultrapure nitrogen gas on cooling.

Synthesis of 2-((4-carboxybenzyl)amino)succinic acid [$H_3(D-2,4-cbs)$]

In a 50 mL round bottom flask, *D*-aspartic acid (106.4 mg , 0.8 mmol) and $NaOH$ (64 mg , 1.6 mmol) were dissolved in 20 mL dry methanol and stirred for half an hour at $25\text{ }^\circ C$. To the resulting mixture, 4-formyl benzoic acid (120 mg , 0.8 mmol) was added and stirred for 4 h to get a colorless solution that was cooled using an ice bath for the next step. Upon addition of solid $NaBH_4$ (60.48 mg , 0.62 mmol), the reaction mixture was stirred for another 8 h . After removal of methanol under reduced pressure, the obtained residue was dissolved in water and the pH was adjusted to $4\text{--}5$ by adding acetic acid, which resulted in the precipitation of a white solid. The solid was isolated by filtration, thoroughly washed with water, and dried under vacuum. Yield: 124 mg (60%). M.P. $243\text{ }^\circ C$. HRMS (ESI) m/z : cal. $[M + H]^+$: 268.058 , found: 268.057 . 1H NMR (D_2O , 400 MHz): δ 2.1 (m, $2H$), 3.2 (dd, $1H$), 3.5 (m, $2H$), 7.2 (d, $2H$),





Scheme 1 Solvothermal synthesis of Zn-CBS.

7.6 (d, 2H) ppm. Selected FTIR peaks (KBr pellet, cm^{-1}): 2969 (br), 1691 (s), 1618 (s), 1429 (m), 1299 (m), 1189 (m), 750 (m).

Synthesis of $\{[\text{Zn}_4(\mu_3\text{-OH})_2(\text{D-2,4-cbs})_2(\text{H}_2\text{O})_4] \cdot 5\text{H}_2\text{O}\}_n$ (Zn-CBS)

A mixture of $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$ (32 mg, 0.11 mmol), NaOH (8.88 mg, 0.22 mmol) and $\text{H}_3(\text{D-2,4-cbs})$ (20 mg, 0.074 mmol) in MeOH/H₂O (1 mL/1 mL) was heated in a 10 mL capacity Teflon lined stainless-steel reactor at 120 °C for 48 h and then cooled to room temperature in 24 h. A white precipitate that was formed was collected by filtration, washed with acetonitrile/toluene and dried in air. Yield: 19 mg (54%). Anal. Calc. (%) for $\text{C}_{24}\text{H}_{40}\text{N}_2\text{O}_{23}\text{Zn}_4$ (MW 986.09): C, 27.5; H, 3.79; N, 2.92. Found: C, 27.8; H, 3.40; N, 2.5. Selected FTIR peaks (KBr pellet, cm^{-1}): 3421 (br), 3239 (br), 1617 (s), 1398 (s), 1099 (w), 1010 (w), 882 (w).

Results and discussion

Synthesis and characterization

The chiral ligand $\text{H}_3(\text{D-2,4-cbs})$ used in this study was prepared from D-aspartic acid, which was first converted to its disodium salt, and 4-formylbenzaldehyde in a single pot using the standard Schiff base chemistry in dry methanol followed by reduction with sodium borohydride (Scheme S1, ESI[†]). Its isolation as a solid was aided by the addition of glacial acetic acid to the reduced Schiff base obtained in the second step. This ligand was characterized by FTIR, TGA, HRMS, and NMR spectroscopy (Fig. S1–S4, ESI[†]). For the synthesis of Zn-CBS, a solvothermal reaction of $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$, NaOH and $\text{H}_3(\text{D-2,4-cbs})$ was carried out in a mixture of methanol and water at 120 °C for 48 h followed by cooling to room temperature in 24 h with a yield of 54% (Scheme 1). Several attempts to obtain suitable single crystals of Zn-CBS for the X-ray study were not successful. However, in addition to the extensive characterization by elemental analysis, spectroscopic and microscopic analysis, the crystallinity and phase purity as well as thermal stability of Zn-CBS were studied by in-situ PXRD and TGA for its applications. These are discussed in detail below.

In the FTIR spectrum of Zn-CBS, the presence of water molecules and the OH groups within the core is substantiated by the observation of a strong peak at 3421 cm^{-1} . Similarly, a broad peak at 3239 cm^{-1} corresponds to the –NH group from the ligand (Fig. S5, ESI[†]).⁴⁷ The asymmetric and symmetric stretching frequencies for the carboxylate appears at 1622 cm^{-1} and 1397 cm^{-1} , respectively, with a difference of 225 cm^{-1} , which corresponds to the monodentate binding mode of the carboxylate groups.⁴⁷ The solid-state diffuse reflectance spectrum of Zn-CBS exhibited two peaks at 245 and 280 nm attributed to the ligand-based $\pi\text{-}\pi^*$ transitions (Fig. S6, ESI[†]).



Fig. 2 Variable temperature PXRD patterns of Zn-CBS.

Thermochemistry by TGA and VT-PXRD

To examine the thermal stability of Zn-CBS, the TG experiment was carried out from 30 °C to 500 °C under a nitrogen atmosphere. In the first step of its TG profile, a weight loss of 9.5% (calc. 9.3%) corresponding to five lattice water molecules is observed between 30 °C to 80 °C (Fig. S7, ESI[†]). Thereafter, it is stable up to 275 °C followed by decomposition.

The purity and crystallinity of Zn-CBS at room temperature was evaluated by PXRD (Fig. S8, ESI[†]) and further confirmed by the 2D WAX map (Fig. S9, ESI[†]). Based on the thermal stability of the framework shown by TGA, Zn-CBS was investigated by in-situ VTPXRD to provide insight into their crystalline properties at different temperatures (from –100 °C to 275 °C). As shown in Fig. 2, it maintains the structure and crystallinity throughout the cooling and heating cycles. The high crystallinity and stability of Zn-CBS up to 275 °C can be due to the formation of a stable $[\text{Zn}_4(\mu_3\text{-OH})_2]$ core in its 3D structure.³⁹

Surface analysis

To figure out the morphology of Zn-CBS, both FESEM and TEM were utilized. Its FESEM image (Fig. 3a) shows accumulation and assembling of leaves to form nanoflowers, which indicate the chiral nature of the framework.⁴⁸ The morphology is further confirmed by TEM showing aggregation of leaflets (Fig. 3b). Moreover, the TEM image shows that the size of the leaflet is in the range of 79–90 nm. The HRTEM image shows well-defined lattice fringes with spacing of 0.23 nm for the nanoflowers (Fig. 3c). Its compositional characterization was done by EDX and elemental mapping (Fig. 3d, e and Fig. S10, ESI[†]), where





Fig. 4 Gas sorption of Zn-CBS: (a) N₂ sorption isotherm and pore size distribution; (b) H₂ sorption isotherm at 77 K; (c) CO₂ sorption isotherms at 195 K, 263 K, 273 K, and 298 K; (d) CH₄ sorption isotherms at 263 K, 273 K and 298 K.



Fig. 5 Isosteric heat of adsorption (Q_{st}) for CO₂, CH₄ and N₂ using experimental isotherm data of Zn-CBS at 263 K, 273 K and 298 K.



Fig. 6 Water adsorption-desorption isotherm of Zn-CBS.



saturation plateau that are usually found for zeolites is remarkable. This type of materials which show more adsorption of the adsorbate at lower P/P_0 , can be good candidate as a desiccant.⁴⁹ At higher P/P_0 value (0.8–1.0), it shows an uptake of $\sim 221 \text{ cm}^3 \text{ (STP) g}^{-1}$ (Fig. 6), amounting to seven water molecules per formula unit. As indicated in the thermal analysis section and later utilized such property for solvent encapsulation, the framework is stable upon loss of lattice water molecules and has a permanent pore. This sorption study validates the hydrophilic interaction between the framework and the water molecules. The PXRD of the used **Zn-CBS**

was recorded after the gas and vapor adsorption experiments (Fig. S12, ESI[†]). It shows that the crystallinity and structural integrity of the framework are maintained. Interestingly, there are only few MOFs which show such permanent porosity.¹⁷ On the other hand, examples of amino acid-based MOFs demonstrating both CO_2 and water sorption are rare.

Selectivity of CO_2/N_2 and CO_2/CH_4 by IAST method

The potential for gas separation by **Zn-CBS** was investigated by using ideal adsorbed solution theory (IAST) method (see ESI[†] for details). The dual-site Langmuir–Freundlich (DSLFL)



Fig. 7 Separation selectivity of **Zn-CBS** at 263 K, 273 K, and 298 K predicted by IAST for (a) CO_2/N_2 (15/85); and (b) CO_2/CH_4 (50/50).



Fig. 8 CBMC simulation: (a) interaction and distance between CO_2 molecules and $\text{H}_3(\text{b-2,4-cbs})$ present as a trianion in **Zn-CBS** at 298 K; probability density of (b) CH_4 and (c) N_2 at 298 K; (d) binding energy of CO_2 , CH_4 , and N_2 .



isotherm model has been utilized for fitting the unary isotherm of three gases, *i.e.*, CO₂, N₂ and CH₄ at three different temperatures 263 K, 273 K and 298 K, respectively (Table S2 and Fig. S13–S21, ESI†). The selectivity values for CO₂/N₂ (15 : 85, flue gas composition) and CO₂/CH₄ (50 : 50, landfill gas composition) are measured using this equation. The calculated selectivity for CO₂/N₂ (15 : 85) mixture is 1832, 916 and 408 at 298 K, 273 K and 263 K, respectively (Fig. 7a). On the other hand, the selectivity of CO₂/CH₄ (50 : 50) mixture is 24.5, 17.2 and 12.2 at 298 K, 273 K and 263 K, respectively (Fig. 7b). The selectivity of CO₂/N₂ and CO₂/CH₄ is higher than the MOFs reported in Table S3 (ESI†).^{14–16,24,50–52} The high selectivity of CO₂ over CH₄ and N₂ may be accredited to the presence of an amine group in the framework.

To better understand the high selectivity of CO₂ over CH₄ and N₂, configurational bias Monte Carlo (CBMC) simulation using BIOVIA, Material studio 2007 was carried out.⁵³ The amine basic site in the H₃(D-2,4-cbs) ligand, which is present as a trianion in Zn-CBS, plays a crucial role in high selectivity. For this purpose H₃(D-2,4-cbs) was taken into account, optimized in Density Functional Theory (DFT) and put in a (1 × 1 × 1) cell. Using the sorption module, with respect to the ligand the position of different gases and their binding energy (BE) at

298 K with a fixed pressure of 1 bar have been determined. It is observed that only one CO₂ molecule was adsorbed and the intermolecular distance between CO₂ and the N–H moiety of the ligand was found to be 2.18 Å (N–H···O) and the bond angle of CO₂ is reduced to 174.9° (Fig. 8a). On the other hand, N₂ and CH₄ do not show any interaction but some electron density was observed near the N–H bond of the ligand (Fig. 8b and c). The probable electron density of CH₄ was almost triple compared to N₂. The BE of CO₂ (−7.45 kcal mol^{−1}) is higher than that of N₂ (−4.4 kcal mol^{−1}) and CH₄ (−5.5 kcal mol^{−1}), confirming the high sorption and selectivity (Fig. 8d).

Encapsulation of solvent molecules and chemical stability

Based on the porosity of Zn-CBS confirmed by nitrogen gas and water vapor sorption studies, the encapsulation of various organic solvents, like acetonitrile, ethanol, methanol, tetrahydrofuran, toluene, and *p*-xylene, inside the MOF was carried out by activating it at 100 °C for 3 h under high vacuum. Experiments were performed by soaking the activated Zn-CBS in different organic solvents for 3 days, where the respective fresh solvent was used after every 24 h, and dried in air. In order to understand the framework stability and get an estimate of



Fig. 9 Encapsulation of solvents by Zn-CBS: (a) comparison of FTIR spectra; (b) PXRD patterns; (c) TG profiles after encapsulation of various organic solvents; and (d) bar plot representing the total number of solvent molecules encapsulated per formula unit of the framework.



solvent absorbed by **Zn-CBS**, the solvated framework was examined by FTIR, PXRD, and TGA. The FTIR spectra (Fig. 9a) confirm the stability of the framework in the encapsulated solvents. Further, PXRD indicates that crystallinity and structural integrity of the framework are maintained after the encapsulation of different solvents (Fig. 9b). From the TG profiles of encapsulated **Zn-CBS** with various solvents compared to its activated form, the stability of the framework after the loss of solvent is intact (Fig. 9c). The number of solvent molecules encapsulated by the framework is calculated (Table S4, ESI[†]) and depicted in Fig. 9d. Based on this information, it is clear that the maximum absorbing capacity of **Zn-CBS** is for acetonitrile as it has the highest dipole moment and is linear in shape. The remarkable encapsulation of different solvents can be attributed to the interaction of the solvent with a framework depending on the size and polarity of the solvent.

Conclusion

A homochiral Zn(II)-organic nanoflower, **Zn-CBS**, was solvothermally synthesized using a new amino acid-based tricarboxylate ligand. Both FESEM and TEM images showed details of the nanoflower arrangement in **Zn-CBS**. Based on the N₂ adsorption measurements (reversible type I isotherm) the microporous nature of the framework was established. The amine functionality present in the micropore wall helped to capture more CO₂ over N₂ and CH₄ because of strong adsorbate-adsorbent interaction. However, the *Q*_{st} value for CH₄ (51.8 kJ mol⁻¹) is higher than that for CO₂ (35 kJ mol⁻¹) because of appropriate pore size of the framework. The high selectivity of CO₂ over CH₄ and N₂ shows its potential under relevant flue and landfill gas separation conditions. On the other hand, water sorption isotherm showed high water uptake (156 cm³ (STP) g⁻¹) at lower relative pressure, indicating a strong interaction between framework and polar molecules for a potential desiccant use. The porosity of the framework was further utilized for encapsulating small molecules such as various common solvents, which was monitored by FTIR, TGA and PXRD analysis. These gas and vapour sorption studies substantiate the permanent microporosity of **Zn-CBS**. Thus, with high thermal and water stability **Zn-CBS** is a versatile material that is suitable for selective CO₂ capture and separation, and encapsulating solvent molecules. Extension of this work with different ligand systems for generating new MOFs containing larger micropores with various applications is currently underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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