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A stable metal–organic framework with suitable pore sizes and rich uncoordinated nitrogen atoms on the internal surface of micropores for highly efficient CO₂ capture†

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An air-stable tetr唑olate-containing framework, [Zn₂L₂]·2DMF (NENU-520, H₂L = 4-(1H-tetrazole-5-yl)biphenyl-4-carboxylic acid), with uncoordinated N atoms on its internal surface was solvothermally synthesized and structurally characterized. This metal–organic framework (MOF) exhibited high CO₂ uptake of 79.9 cm³ cm⁻³ at 298 K and 100 kPa, as well as excellent adsorption selectivity for CO₂ over CH₄ and N₂. Particularly, its exceptionally high selectivity of CO₂ over N₂ at 298 K has ranked NENU-520 among the highest MOFs for selective CO₂ separation. Furthermore, the potential application of NENU-520 for the fixed bed pressure swing adsorption (PSA) separation of CO₂ from CH₄ and N₂ has been validated via simulated breakthrough experiments. The small channel with the size of 3.6 Å, combined with CO₂-accessible free nitrogen atoms directed toward the inner surface, is believed to contribute to its high CO₂ uptake capacity and selectivity. Thus, this work represents a unique way to target MOF materials for highly selective CO₂ separation by incorporating CO₂-phlic functional sites on pore surfaces, and at the same time optimizing pore sizes.

Introduction

Carbon dioxide (CO₂) emissions, which are inevitable, are mainly generated from the anthropogenic combustion of coal, oil and natural gas, the main energy resources for our daily life, economic growth and industrial development. With the growing increase in the amount of CO₂ in the atmosphere, the undesirable global warming and climate change have attracted increasing attention. Moreover, in addition to its involvement in the greenhouse effect, CO₂ is also highly associated with many issues such as the separation of CO₂ from industrial gas for bioremediation, demand of selectively captured CO₂ from methane in biogas streams and post-combustion flue gases generated from coal-fired power stations. Consequently, there is still an urgent need to selectively capture and sequester CO₂ to reduce its negative effect in the atmosphere. Two points must first be made with regards to captured materials and their long-term usage. Firstly, they should be highly air-stable and be able to maintain their stability over multiple cycles for practical applications as functional materials. Secondly, as a promising adsorbent for practical applications, they should possess not only good adsorption capacity but also high selectivity. Adsorption capacity depends on the equilibrium pressure and temperature, the nature of the adsorbate, and the nature of the micropores in the adsorbent. To a great extent, the selective capture of CO₂ is related to the nature of the adsorbent in addition to the operational temperature and pressure.

Due to their high surface areas, high void volumes and controlled pore sizes, metal–organic frameworks (MOFs) represent a rapidly expanding, probable new class of porous adsorbents with a large range of possibilities for the design of functional materials. The focus on exploiting their high surface areas and large pore size conventionally are far from enough. To date, various feasibility strategies, such as the introduction of a high density of open metal sites, charged skeleton of MOFs, and decoration with polar substituent groups...
(for instance, –COOH, –NH2, –OH), have been explored to enforce their interactions and thus enhance the adsorption capacity and selectivity of MOFs toward CO2.\textsuperscript{21–27} Moreover, given the fact that the kinetic diameters of the cylinders are 3.3 Å, 3.64 Å and 3.80 Å for CO2, N2 and CH4, respectively, size selectivity is an attractive characteristic for CO2 separation and capture.\textsuperscript{28,29} To effectively realize CO2 separation on the basis of size, precise control of the limiting pore diameter is of significant importance. The study of CO2 selectivity based on small pore size is numbered, albeit more and more MOFs have been reported.

A straightforward approach was put forward and tested by the groups of Chen, Bu, Zhao and Su.\textsuperscript{30–33} The introduction of abundant uncoordinated nitrogen atoms may produce a stronger interaction with CO2. Typically, the interaction between the localized dipoles of a N-containing group and the quadrupole moment of CO2 could induce dispersion and electrostatic forces to enhance the CO2 adsorption and separation abilities of MOFs. Nevertheless, a high percentage of N-donor sites is not always beneficial to further enhance the interaction with CO2 molecules. For example, when the lone electron pairs of partially exposed nitrogen atoms do not point into the channels of the frameworks or the uncoordinated N-donor sites are blocked by functionalized groups, they have a lower effect on the improvement of the CO2 capacity. It is of crucial importance to construct MOFs that effectively utilize the accessible nitrogen atoms from organic linkers.

Herein, we selected a tetrazolate-containing H4L (4-(1H-tetrazole-5-yl)biphenyl-4-carboxylic acid) as an organic linker to construct a new MOF. Fortunately, an air-stable zinc-based MOF, [Zn2(L2)2]·2DMF (NENU-520, NENU = Northeast Normal University) was successfully synthesized and the inner surface is polarized with uncoordinated nitrogen atoms. It features a small channel (3.6 Å, which is slightly larger than the kinetic diameter of CO2), which is favourable for its potential application in gas capture and separation. As anticipated, an activated sample NENU-520a exhibits a high uptake of CO2 and H2 with high isosteric heat. Its selectivities for CO2/CH4 and CO2/N2 were evaluated using the ideal adsorbed solution theory (IAST) and simulated breakthrough experiments. Remarkably, the results from these studies all confirm that the selectivity of CO2/N2 has featured NENU-520 among the highest porous MOFs for CO2 selective separation under ambient conditions. NENU-520 is one of the best materials to facilitate effective CO2 separation and capture.

**Results and discussion**

**NENU-520** was synthesized by the solvothermal reaction of Zn(NO3)2·6H2O and H4L in a solvent mixture of DMF–EtOH with the addition of a small amount of HNO3 at 90 °C for 3 days. The highly crystallized NENU-520 was formulated as [Zn2L2]·2DMF on the basis of the single-crystal X-ray diffraction study. The X-ray crystallographic analysis reveals that NENU-520 crystallizes in the monoclinic space group Cc (Table S1†). The asymmetric unit consists of two independent Zn(ii) atoms, one coordinated DMF molecule, one DMF solvent and two distinct L2− moieties (Fig. 1a). In NENU-520, Zn1 and Zn2 atoms are linked by carboxyl groups to form a binuclear zinc cluster, in addition, each tetrazolyl group bonds two independent Zn atoms from two zinc clusters. In NENU-520, each ligand uses just two N atoms for the framework formation, leaving two other open N-donor sites. Such interlinkage generates a 1D smaller-size curving channel running along the b axis with a size of ~3.6 Å (Fig. 1b and c). The Connolly surface diagram (Fig. 1d) displays the irregular channels of the framework structures. It is evident that the left two N atoms point to the inner surface (Fig. 1e). The overall framework can be designated as a (3, 3, 6)-connected network (Fig. S4a†) with the point symbol of (4 64)4(42 6−86) analyzed by the TOPOS program, if the L2− and binuclear zinc cluster are regarded as 3- and 6-connected nodes, respectively. Further close observation of the structure shows that NENU-520 can be simplified as a (4, 4)-connected topology with the point symbol of (42 6−8), when each Zn atom and L2− fragment is considered as a discrete 4-connected node (Fig. S3†). In addition, the phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD, Fig. S4b†). Upon removing DMF solvent molecules, NENU-520 forms a microporous framework containing 27.4% solvent void accessible.\textsuperscript{34} It is noteworthy that NENU-520 shows good air-stability even when exposed to air for more than two weeks (Fig. S5†), which is of utmost importance for practical applications.\textsuperscript{35,36}

The permanent porosity of NENU-520 was unambiguously established by its N2 sorption isotherm at 77 K. The activated sample NENU-520a was prepared by exchanging the solvent and
it was characterized by thermal gravimetric analysis (TGA, Fig. S6†) and PXRD patterns (Fig. S5†), indicating that the framework was maintained because the broadened peaks positions remained. NENU-520a shows a characteristic type I behaviour with a BET surface area of 387 m$^2$ g$^{-1}$ and a pore volume of 0.27 cm$^3$ g$^{-1}$ based on its N$_2$ sorption isotherm (Fig. 2). The slight hysteresis between the adsorption and desorption profile can perhaps be explained by the 1D narrow channel system, which hints the escape of adsorbed gas molecules, as well as probably involving the structural breathing of the framework during the adsorption–desorption process.$^{37,38}$ Using the Horváth–Kawazoe (HK) method on the N$_2$ desorption isotherms, pore size distribution (Fig. 2) was estimated, which is basically identical to the results from the single-crystal X-ray diffraction study.

Low-pressure H$_2$ adsorption isotherms for NENU-520a were collected at 77 and 87 K, which are completely reversible, as shown in Fig. S7a.$^†$ NENU-520a adsorbs 1.36 wt% of H$_2$ (152.4 cm$^3$ g$^{-1}$ or 19.6 H$_2$ molecules per formula unit) at 77 K, and 1.09 wt% (121.6 cm$^3$ g$^{-1}$ or 15.5 H$_2$ molecules per formula unit) at 87 K. It is indicative of the presence of strongly polarizing binding sites with a high affinity for H$_2$ from the steep initial portion of each isotherm. To gain further insight into H$_2$ adsorption, the behaviour of the isosteric heat was calculated using the Clausius–Clapeyron equation.$^{39}$ NENU-520a shows a near-zero coverage $Q_m$ value of 10.7 kJ mol$^{-1}$ (Fig. S7b$^†$), which is comparable with many famous porous materials such as MOF-5 (7.6 kJ mol$^{-1}$), Zn–MOF-74 (8.3 kJ mol$^{-1}$), NOTT-101 (5.3 kJ mol$^{-1}$) and UCMC-150 (7.3 kJ mol$^{-1}$)$^{40,41}$ This result was attributed to the small pore diameter in NENU-520a, wherein overlapping potentials from two or more pore walls interact with a single H$_2$ molecule.$^{42,43}$ In addition, the uncoordinated N-heteroatom sites also aid in the low-pressure uptake by this material.$^{31}$

Because accessible N-donor sites are expected to enhance interactions between frameworks and CO$_2$, the CO$_2$ sorption isotherms were measured at different temperatures, which shows a fully reversible type I behaviour with no hysteresis (Fig. 3). The CO$_2$ uptake of NENU-520a at saturation was 106.0 cm$^3$ cm$^{-3}$ (corresponding to 15.7 wt% or 10.3 CO$_2$ per formula unit, Table S3†) at 273 K and 79.9 cm$^3$ cm$^{-3}$ (corresponding to 11.9 wt% or 7.8 CO$_2$ per formula unit) at 298 K. Albeit these values are lower than the M–MOF-74 series (162 cm$^3$ cm$^{-3}$) with different open metal sites, they are considerably higher than lots of well-known MOFs such as MAF-23 (or Zn$_2$(btm)$_2$, 74.2 cm$^3$ g$^{-1}$ and 56.1 cm$^3$ g$^{-1}$ at 273 K and 298 K) with multiple strong adsorption sites and [Cu(tba)$_2$]$_n$ (51.8 cm$^3$ g$^{-1}$ or 10.2 wt% at 273 K), the currently best performing ZIP-69 (70 cm$^3$ g$^{-1}$ at 273 K and 1 atm)$^{44,46}$ For the practical use of an adsorptive material, its regeneration and recycling properties are crucial and are also important standards to evaluate an adsorption material. Keeping this in mind, the regenerative feature of NENU-520a was investigated. The powder X-ray diffraction pattern (Fig. S8†) of NENU-520a after three cycles is in good agreement with that of its original structural characteristics, revealing its good stability. Moreover, NENU-520a basically maintains high adsorption capacity after three cycles of the regeneration experiment. This excellent behavior is significant for all of the MOFs analyzed, and the reproducibility demonstrates that uptake and release is nondestructive.

The sorption behaviours of NENU-520a toward CH$_4$ and N$_2$ were also studied at 273 and 298 K (Fig. 3). The desolvated NENU-520a only has a maximum CH$_4$ uptake of 31.3 cm$^3$ g$^{-1}$ (1.4 mmol g$^{-1}$, 2.24 wt%) and 21.41 cm$^3$ g$^{-1}$ (0.96 mmol g$^{-1}$, 1.53 wt%) at 273 K and 298 K, respectively, which is substantially lower than CO$_2$. In sharp contrast to CO$_2$ and CH$_4$, the uptake of N$_2$ reaches a maximum of only 6.6 cm$^3$ g$^{-1}$ (0.29 mmol g$^{-1}$) at

![Fig. 2](https://example.com/f2.png)  
**Fig. 2** The N$_2$ sorption isotherms at 77 K. Inset: the pore size distribution of NENU-520a using the Horváth–Kawazoe (HK) method.

![Fig. 3](https://example.com/f3.png)  
**Fig. 3** The CO$_2$, CH$_4$ and N$_2$ sorption isotherms for NENU-520a at 273 K (a) and 298 K (b), respectively.
273 K and 0.23 cm$^3$ g$^{-1}$ (0.01 mmol g$^{-1}$) at 298 K, respectively. It is clearly shown that the pore structure of NENU-520a is readily accessible to CO$_2$. The relatively high CO$_2$ and marginal N$_2$ uptake at ambient temperature prompted us to investigate the capacity of NENU-520a to selectively adsorb CO$_2$ over CH$_4$ and N$_2$.

The ideal adsorbed solution theory (IAST) calculation, which originated from Myers and Prausnitz, was employed to predict the adsorption selectivity and CO$_2$ uptake of NENU-520a for the following binary gas mixtures: 15/85 CO$_2$/N$_2$, 50/50 CO$_2$/CH$_4$ and 5/95 CO$_2$/CH$_4$. The Langmuir–Freundlich equation fits extremely well with the single-component isotherms at 273 and 298 K (Fig. S9†), and the fitting parameters are listed in Table S4.† The evaluation of the selectivity of adsorbents at atmospheric pressure for the CO$_2$–N$_2$ mixture was essential for a realistic post-combustion capture of CO$_2$. In these calculations, the partial pressures of CO$_2$ and N$_2$ are taken to be 15 kPa and 85 kPa, respectively. For comparison, six representative MOFs or zeolites [NaX, MgMOF-74, Cu–TDPAT, UTSA-16, Cu–SSZ13 and ZnMOF-74] exhibiting high CO$_2$/N$_2$ separation selectivity are also included. Fig. 4 presents the IAST calculations for the adsorption selectivity and CO$_2$ uptake of NENU-520a as a function of dimensionless time for operation at a total pressure of 100 kPa for a 15/85 CO$_2$/N$_2$ mixture, which represents the conditions relevant for flue gas processing. For NENU-520a, the sequence of breakthroughs is dictated by its adsorption strength and the more strongly adsorbing CO$_2$ elutes last in the sequence. Fig. 5 presents the mole percent of N$_2$ in outlet gas as a function of dimensionless time with the selective retention of CO$_2$ (NENU-520a). It is possible to recover pure N$_2$ from the gas mixture in a certain interval of time. We arbitrarily set the purity requirement to be 99.95% N$_2$. This amount can be determined from a material balance. The productivity of N$_2$ with a purity of 99.95% was determined to be 4.84 mol kg$^{-1}$ of NENU-520. The reason for

charged units and amine groups. Thus, NENU-520 is one of the best materials to facilitate effective CO$_2$ capture and separation from the perspective of comprehensive properties.

The selectivities for CO$_2$/CH$_4$ were also evaluated when the gas phase compositions were 5/95 and 50/50 (Fig. S10†), and the corresponding values are comparable to most MOFs reported in the literature, although it has a lower selectivity than Mg–MOF-74.

In view of the feasibility of the separation performance of NENU-520, transient breakthrough simulations using the methodology described in the literature was performed.† The performance of industrial fixed bed adsorbers is dictated by a combination of adsorption selectivity and uptake capacity. The proper combination of both of these factors is obtained by the use of breakthrough calculations. Fig. 5a shows a schematic of a packed bed adsorber. The x axis in Fig. 5b and c is dimensionless time, $t$, which is defined by dividing the actual time, $t$, by the characteristic times, $L/u$. A longer breakthrough time is desirable from a practical point of view because this indicates a less frequent requirement for regeneration. Fig. 5b presents the breakthrough characteristic as a function of the dimensionless time in an adsorber packed with NENU-520a at a total pressure of 100 kPa for 15/85 CO$_2$/N$_2$ mixture, which represents the conditions relevant for flue gas processing. For NENU-520a, the sequence of breakthroughs is dictated by its adsorption strength and the more strongly adsorbing CO$_2$ elutes last in the sequence. Fig. 5c presents the mole percent of N$_2$ in outlet gas as a function of dimensionless time with NENU-520a. It is possible to recover pure N$_2$ from the gas mixture in a certain interval of time. We arbitrarily set the purity requirement to be 99.95% N$_2$. This amount can be determined from a material balance. The productivity of N$_2$ with a purity of 99.95% was determined to be 4.84 mol kg$^{-1}$ of NENU-520. The reason for

![Fig. 4](image-url) Calculated selectivity of CO$_2$/N$_2$ predicted by IAST calculations 298 K for the variety of MOFs considered in this work. In these calculations, the partial pressures of CO$_2$ and CH$_4$ are taken to be $p_1/p_2 = 15/85$.

![Fig. 5](image-url) (a) Schematic view of a packed bed adsorber. The tube length $L = 0.3$ m. The apparatus was operated at 298 K. The bed porosity, $\varepsilon = 0.4$. The interstitial gas velocity, $u = 0.04$ m s$^{-1}$. (b) breakthrough characteristics of an adsorber packed with NENU-520 and maintained at isothermal conditions at 298 K, and (c) mole percent N$_2$ in outlet gas as a function of dimensionless time for operation at a total pressure of 100 kPa for 15/85 CO$_2$/N$_2$ mixture.
the high productivity is a combination of higher selectivity and higher CO₂ uptake capacity. **NENU-520a** was demonstrated to be a promising candidate for CO₂ capture and separation from fuel gas.

5/95 CO₂/CH₄ mixture breakthrough characteristics as a function of dimensionless time were measured in an adsorber packed with **NENU-520** (as shown in Fig. S11†). **NENU-520** outperforms ZIF-78 (81), UTSA-20a (86), MIL-101 (32) and many others by having a longer breakthrough time. In natural gas purification processes, the primary objective is to produce CH₄ with a specified purity level, which is typically 500 ppm CO₂, i.e. 0.05 mole percent CO₂. Fig. S11b† shows the gas composition, expressed as mole percent of CH₄, in outlet gas as a function of dimensionless time for a selection of porous adsorbent materials. During the time interval Δτ, 99.95% + pure CH₄ can be produced. The productivity of methane with a purity of 99.95%+ is calculated to be 6.7 mol kg⁻¹ of **NENU-520**, which was determined from the material balance on the fixed bed adsorber. In addition, the composition of natural gas changes frequently. The breakthrough characteristics for a binary 50/50 mixture of CO₂ and CH₄ are also presented (Fig. S12†). The breakthrough occurs at a shorter dimensionless time than for the 5/95 binary mixture. And the productivity is 1.79 mol per kg of **NENU-520** during the time interval Δτ. The results from all these studies confirm that **NENU-520** has the ability to separate N₂ and CH₄ in the pure form from gas mixtures. Based on the presented evidence, **NENU-520** is a superior adsorbent for CO₂/N₂ and CO₂/CH₄ separation at ambient conditions than reported for most of the MOFs.

The CO₂ adsorption enthalpy of **NENU-520a** is 33 kJ mol⁻¹ (Fig. 6), which is stronger than siliceous zeolite (27 kJ mol⁻¹), and the series of MAF materials (MAF-4, 25.1 kJ mol⁻¹; MAF-7, 17.2 kJ mol⁻¹; MAF-25, 26.3 kJ mol⁻¹ and MAF-26, 23.3 kJ mol⁻¹; MAF stands for metal azolate framework). Its CH₄ adsorption enthalpy is 29 kJ mol⁻¹. The high uptake and enthalpy of CO₂ as well as the remarkable selectivity over CH₄ and N₂ may be reasonable considering the fact that: (i) with its greater polarizability and larger quadrupole moment, CO₂ has stronger interactions with the accessible N-sites of **NENU-520** than CH₄ and N₂; (ii) the abundant uncoordinated N-heteroatom sites directed toward the inner surface in the narrow cavities are beneficial to interact with CO₂ molecules; (iii) as mentioned above, the kinetic diameters of the cylinders are 3.3 Å, 3.64 Å and 3.80 Å for CO₂, N₂ and CH₄, respectively. The limiting pore size (about 3.6 Å) of **NENU-520** is just right for CO₂. Thus, CO₂ molecules are more prone to be injected than CH₄ and N₂.

Inspired by the reported charge transfer electron transitions between microporous MOFs and guest molecules, the potential luminescent sensitivity and selectivity of **NENU-520** were also investigated in different organic solvents such as cyclohexane, toluene, acetonitrile, benzene, chloroform, p-xylene, n-hexane, m-xylene, THF and nitrobenzene. The results suggest that the emission intensities are largely dependent on different solvent molecules (Fig. S13a and b†). Moreover, the evident quenching phenomenon for nitrobenzene was examined in detail (see ESI†). As shown in Fig. S13c and d† **NENU-520** can sensitively detect a very small amount of nitrobenzene (30 ppm in DMF) through noticeable fluorescence decay, demonstrating extremely high sensitivity towards nitrobenzene. To date, several MOF-based fluorescent sensors have been developed for the detection of nitroaromatic explosives. Its CH₄ luminescent sensitivity and selectivity of **NENU-520** is amongst the highest values for CO₂ selective separation. Consequently, **NENU-520a** has significant potential for use as an adsorbent in CO₂-capture for natural gas sweetening and post-combustion power plants, by combining the higher uptake and higher selectivity toward CO₂. Its narrow but suitable channel as well as

![Fig. 6](Image)

**Fig. 6** Heats of CO₂ adsorption as a function of CO₂ uptake for **NENU-520**.

**Conclusions**

In conclusion, a new N-rich MOF has been successfully synthesized by means of a solvothermal reaction. **NENU-520** has good air-stability even in the presence of moisture. Activated **NENU-520a** exhibits a strong adsorption capacity towards H₂ and CO₂ with the high adsorption enthalpy of 10.7 kJ mol⁻¹ and 33 kJ mol⁻¹, respectively. Moreover, **NENU-520a** shows high CO₂/CH₄ and CO₂/N₂ selectivities, which were calculated via a combination of the ideal adsorbed solution theory and breakthrough simulations for a realistic consideration. In particular, the selectivity of CO₂ over N₂ at 298 K of **NENU-520a** is amongst the highest values for CO₂ selective separation. Consequently, **NENU-520a** has significant potential for use as an adsorbent in CO₂-capture for natural gas sweetening and post-combustion power plants, by combining the higher uptake and higher selectivity toward CO₂.
effective accessible nitrogen donors directed toward the inner surface is demonstrated to be the predominant factors for its high uptake capacity and unprecedented selectivity. In addition, NENU-520a displays highly selective, sensitive and recyclable properties in the detection of nitrobenzene as a fluorescent sensor because of its quenching effect on nitrobenzene.

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