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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 CO$_2$ capture†

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An air-stable tetrazolate-containing framework, [Zn$_2$L$_2$]·2DMF (NENU-520, H$_2$L = 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 CO$_2$ uptake of 79.9 cm$^3$ cm$^{-3}$ at 298 K and 100 kPa, as well as excellent adsorption selectivity for CO$_2$ over CH$_4$ and N$_2$. Particularly, its exceptionally high selectivity of CO$_2$ over N$_2$ at 298 K has ranked NENU-520 among the highest MOFs for selective CO$_2$ separation. Furthermore, the potential application of NENU-520 for the fixed bed pressure swing adsorption (PSA) separation of CO$_2$ from CH$_4$ and N$_2$ has been validated via simulated breakthrough experiments. The small channel with the size of 3.6 Å, combined with CO$_2$-accessible free nitrogen atoms directed toward the inner surface, is believed to contribute to its high CO$_2$ uptake capacity and selectivity. Thus, this work represents a unique way to target MOF materials for highly selective CO$_2$ separation by incorporating CO$_2$-philic functional sites on pore surfaces, and at the same time optimizing pore sizes.

Introduction

Carbon dioxide (CO$_2$) 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.$^{1-5}$ With the growing increase in the amount of CO$_2$ in the atmosphere, the undesirable global warming and climate change have attracted increasing attention.$^{5-10}$ Moreover, in addition to its involvement in the greenhouse effect, CO$_2$ is also highly associated with many issues such as the separation of CO$_2$ from industrial gas for bioremediation, demand of selectively captured CO$_2$ from methane in biogas streams and post-combustion flue gases generated from coal-fired power stations.$^{11-13}$ Consequently, there is still an urgent need to selectively capture and sequester CO$_2$ 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 able to maintain their stability over multiple cycles for practical applications as functional materials.$^{14,15}$ Secondly, as a promising adsorbent for practical applications, they should possess not only good adsorption capacity but also high selectivity.$^{16-18}$ 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 CO$_2$ 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.$^{19-22}$ 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 H₂L (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, [Zn₂L₂]·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 H₂L 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(n) 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 (4·6²)(6²·8) 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 (4²·6⁶·8), 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. S6f) and PXRD patterns (Fig. S5f), 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.\textsuperscript{37,38} Using the Horvath–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. S7af. 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.\textsuperscript{39} NENU-520a shows a near-zero coverage $Q_m$ value of 10.7 kJ mol$^{-1}$ (Fig. S7bf), 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$^{-1}$).\textsuperscript{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.\textsuperscript{42,43} In addition, the uncoordinated N-heteroatom sites also aid in the low-pressure uptake by this material.\textsuperscript{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 S3f) 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)$_2$]$_x$ (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).\textsuperscript{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. S8f) 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 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](image-url) The N$_2$ sorption isotherms at 77 K. Inset: the pore size distribution of NENU-520a using the Horvath–Kawazoe (HK) method.

![Fig. 3](image-url) 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,$^{37}$ 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]$^{35,36}$ exhibiting high CO$_2$/N$_2$ separation selectivity are also included. Fig. 4 presents the IAST calculations for CO$_2$/N$_2$ adsorption selectivity. Remarkably, NENU-520 has the highest selectivity (about 400) towards CO$_2$ for the mixture compositions. To the best of our knowledge, only two MOFs were reported to display higher CO$_2$/N$_2$ selectivity than NENU-520. One example is SIFSIX-3–Zn, which exhibits the highest CO$_2$/N$_2$ selectivity (with selectivity of 1539 ± 307).$^{24}$ During the course of this work, SIFSIX-3–Zn had more-regular square-shaped channels with a dimension of 3.84 Å and was lined with Lewis basic groups on the SiF$_6$ anions which notably enhance the uptake of CO$_2$ into the material, whereas neither charged units nor favourable groups exist in the channels of NENU-520. The other MOF is [Cu(bcppm)$_2$H$_2$O]. Although [Cu(bcppm)$_2$H$_2$O] has slightly higher selectivity, its uptake capacity (1.70 and 1.85 mmol g$^{-1}$ at 293 and 273 K, respectively) is apparently lower than NENU-520 (2.71 and 3.59 mmol g$^{-1}$ at 298 and 273 K, respectively).$^{26}$ Its selectivity is evidently superior to most MOFs and this ranks NENU-520 among the highest selectivity values (Table S5†) with the absence of unsaturated metal centres, charged units and amine groups.$^{46,48–57}$ 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.$^{58–61}$ 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, $\tau$, which is defined by dividing the actual time, $t$, by the characteristic times, $L/\nu$. 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 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. 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
the high productivity is a combination of higher selectivity and higher CO$_2$ uptake capacity. NENU-520a was demonstrated to be a promising candidate for CO$_2$ capture and separation from fuel gas.

5/95 CO$_2$/CH$_4$ 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 CH$_4$ with a specified purity level, which is typically 500 ppm CO$_2$, i.e. 0.05 mole percent CO$_2$. Fig. S11b† shows the gas composition, expressed as mole percent of CH$_4$, in outlet gas as a function of dimensionless time for a selection of porous adsorbent materials. During the time interval $\Delta \tau$, 99.95% + pure CH$_4$ 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 CO$_2$ and CH$_4$ 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 $\Delta \tau$. The results from all these studies confirm that NENU-520 has the ability to separate N$_2$ and CH$_4$ in the pure form from gas mixtures. Based on the presented evidence, NENU-520 is a superior adsorbent for CO$_2$/N$_2$ and CO$_2$/CH$_4$ separation at ambient conditions than reported for most of the MOFs.

The CO$_2$ 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 CH$_4$ adsorption enthalpy is 29 kJ mol$^{-1}$. The high uptake and enthalpy of CO$_2$ as well as the remarkable selectivity over CH$_4$ and N$_2$ may be reasonable considering the fact that: (i) with its greater polarizability and larger quadrupole moment, CO$_2$ has stronger interactions with the accessible N-sites of NENU-520 than CH$_4$ and N$_2$; (ii) the abundant uncoordinated N-heteroatom sites directed toward the inner surface in the narrow cavities are beneficial to interact with CO$_2$ molecules; (iii) as mentioned above, the kinetic diameters of the cylinders are 3.3 Å, 3.64 Å and 3.80 Å for CO$_2$, N$_2$ and CH$_4$, respectively. The limiting pore size (about 3.6 Å) of NENU-520 is just right for CO$_2$. Thus, CO$_2$ molecules are more prone to be injected than CH$_4$ and N$_2$.

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.\cite{70-71} The intensity of NENU-520 was nearly completely quenched at a concentration of 100 ppm with a high quenching efficiency of 96.6%, which is higher than other MOF sensors toward nitrobenzene.\cite{72} In addition, NENU-520 can be regenerated for recycling by centrifuging the solution after use and then washing several times with DMF. The quenching efficiencies of cycle 1–4 did not decrease (100 ppm), displaying its high recyclability and stability in detection applications (Fig. S14, S15 and S16†), which is favourable for its potential application in detecting explosives containing nitrobenzene molecules. Referring to the reported works of Sun\cite{71} and Zhang,\cite{72} NENU-520 is presumably attributed to not only the good dispersible nature of its MOF particles but also to the electron deficient nature of nitrobenzene and the high electron rich conjugated framework structure.\cite{76,77}

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 H$_2$ and CO$_2$ with the high adsorption enthalpy of 10.7 kJ mol$^{-1}$ and 33 kJ mol$^{-1}$, respectively. Moreover, NENU-520a shows high CO$_2$/CH$_4$ and CO$_2$/N$_2$ 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 CO$_2$ over N$_2$ at 298 K of NENU-520a is amongst the highest values for CO$_2$ selective separation. Consequently, NENU-520a has significant potential for use as an adsorbent in CO$_2$-capture for natural gas sweetening and post-combustion power plants, by combining the higher uptake and higher selectivity toward CO$_2$. Its narrow but suitable channel as well as...
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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Notes and references