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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<sub>2</sub> capture†

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An air-stable tetrazolate-containing framework, [Zn<sub>2</sub>L<sub>2</sub>]·2DMF (NENU-520, H<sub>2</sub>L = 4-(1*H*-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<sub>2</sub> uptake of 79.9 cm<sup>3</sup> cm<sup>-3</sup> at 298 K and 100 kPa, as well as excellent adsorption selectivity for CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub>. Particularly, its exceptionally high selectivity of CO<sub>2</sub> over N<sub>2</sub> at 298 K has ranked NENU-520 among the highest MOFs for selective CO<sub>2</sub> separation. Furthermore, the potential application of NENU-520 for the fixed bed pressure swing adsorption (PSA) separation of CO<sub>2</sub> from CH<sub>4</sub> and N<sub>2</sub> has been validated via simulated breakthrough experiments. The small channel with the size of 3.6 Å, combined with CO<sub>2</sub>-accessible free nitrogen atoms directed toward the inner surface, is believed to contribute to its high CO<sub>2</sub> uptake capacity and selectivity. Thus, this work represents a unique way to target MOF materials for highly selective CO<sub>2</sub> separation by incorporating CO<sub>2</sub>-philic functional sites on pore surfaces, and at the same time optimizing pore sizes.

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## Introduction

Carbon dioxide (CO<sub>2</sub>) 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.<sup>1–5</sup> With the growing increase in the amount of CO<sub>2</sub> in the atmosphere, the undesirable global warming and climate change have attracted increasing attention.<sup>6–10</sup> Moreover, in addition to its involvement in the greenhouse effect, CO<sub>2</sub> is also highly associated with many issues such as the separation of CO<sub>2</sub> from industrial gas for bioremediation, demand of selectively captured CO<sub>2</sub>

from methane in biogas streams and post-combustion flue gases generated from coal-fired power stations.<sup>11–13</sup> Consequently, there is still an urgent need to selectively capture and sequester CO<sub>2</sub> 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.<sup>14,15</sup> Secondly, as a promising adsorbent for practical applications, they should possess not only good adsorption capacity but also high selectivity.<sup>16–18</sup> 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<sub>2</sub> 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.<sup>19–22</sup> 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

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† Electronic supplementary information (ESI) available: Experimental details, PXRD patterns, TGA, IR curves, crystallographic data, additional figures, IAST and breakthrough calculations for NENU-520. CCDC 990058. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ta00256g

(for instance,  $-\text{COOH}$ ,  $-\text{NH}_2$ ,  $-\text{OH}$ ), have been explored to enforce their interactions and thus enhance the adsorption capacity and selectivity of MOFs toward  $\text{CO}_2$ .<sup>23–27</sup> Moreover, given the fact that the kinetic diameters of the cylinders are 3.3 Å, 3.64 Å and 3.80 Å for  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{CH}_4$ , respectively, size selectivity is an attractive characteristic for  $\text{CO}_2$  separation and capture.<sup>28,29</sup> To effectively realize  $\text{CO}_2$  separation on the basis of size, precise control of the limiting pore diameter is of significant importance. The study of  $\text{CO}_2$  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.<sup>30–33</sup> The introduction of abundant uncoordinated nitrogen atoms may produce a stronger interaction with  $\text{CO}_2$ . Typically, the interaction between the localized dipoles of a N-containing group and the quadrupole moment of  $\text{CO}_2$  could induce dispersion and electrostatic forces to enhance the  $\text{CO}_2$  adsorption and separation abilities of MOFs. Nevertheless, a high percentage of N-donor sites is not always beneficial to further enhance the interaction with  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{H}_2\text{L}$  (4-(1*H*-tetrazole-5-yl)biphenyl-4-carboxylic acid) as an organic linker to construct a new MOF. Fortunately, an air-stable zinc-based MOF,  $[\text{Zn}_2\text{L}_2] \cdot 2\text{DMF}$  (**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  $\text{CO}_2$ ), which is favourable for its potential application in gas capture and separation. As anticipated, an activated sample **NENU-520a** exhibits a high uptake of  $\text{CO}_2$  and  $\text{H}_2$  with high isosteric heat. Its selectivities for  $\text{CO}_2/\text{CH}_4$  and  $\text{CO}_2/\text{N}_2$  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  $\text{CO}_2/\text{N}_2$  has featured **NENU-520** among the highest porous MOFs for  $\text{CO}_2$  selective separation under ambient conditions. **NENU-520** is one of the best materials to facilitate effective  $\text{CO}_2$  separation and capture.

## Results and discussion

**NENU-520** was synthesized by the solvothermal reaction of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{H}_2\text{L}$  in a solvent mixture of DMF–EtOH with the addition of a small amount of  $\text{HNO}_3$  at 90 °C for 3 days. The highly crystallized **NENU-520** was formulated as  $[\text{Zn}_2\text{L}_2] \cdot 2\text{DMF}$  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

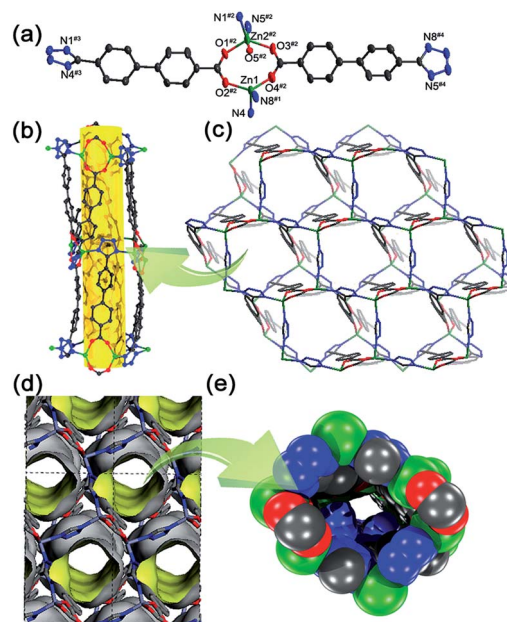


Fig. 1 The structure of **NENU-520**: (a) the coordination environments of Zn(II) atoms, symmetry codes: #1  $0.5 + x, 0.5 + y, z$ ; #2  $1 + x, y, z$ ; #3  $0.5 + x, 1.5 - y, 0.5 + z$ ; #4  $x, 1 - y, -0.5 + z$ ; (b) the 1D channel along the *b* axis; (c) 3D framework of **NENU-520** along the *c* axis; (d) the Connolly surface diagram displays the three dimensional irregular tunnels of **NENU-520**, and (e) the 1D channel in spacefilling mode along the *c* axis. All the hydrogen atoms are omitted for clarity.

$\text{L}^{2-}$  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  $\sim 3.6$  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  $(4 \cdot 6^2)_2(4^2 \cdot 6^7 \cdot 8^6)$  analyzed by the TOPOS program, if the  $\text{L}^{2-}$  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  $(4^2 \cdot 6^6 \cdot 8)$ , when each Zn atom and  $\text{L}^{2-}$  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.<sup>34</sup> 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.<sup>35,36</sup>

The permanent porosity of **NENU-520** was unambiguously established by its  $\text{N}_2$  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  $387 \text{ m}^2 \text{ g}^{-1}$  and a pore volume of  $0.27 \text{ cm}^3 \text{ g}^{-1}$  based on its  $\text{N}_2$  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.<sup>37,38</sup> Using the Horvath–Kawazoe (HK) method on the  $\text{N}_2$  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  $\text{H}_2$  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  $\text{H}_2$  ( $152.4 \text{ cm}^3 \text{ g}^{-1}$  or 19.6  $\text{H}_2$  molecules per formula unit) at 77 K, and 1.09 wt% ( $121.6 \text{ cm}^3 \text{ g}^{-1}$  or 15.5  $\text{H}_2$  molecules per formula unit) at 87 K. It is indicative of the presence of strongly polarizing binding sites with a high affinity for  $\text{H}_2$  from the steep initial portion of each isotherm. To gain further insight into  $\text{H}_2$  adsorption, the behaviour of the isosteric heat was calculated using the Clausius–Clapeyron equation.<sup>39</sup> **NENU-520a** shows a near-zero coverage  $Q_{\text{st}}$  value of  $10.7 \text{ kJ mol}^{-1}$  (Fig. S7b†), which is comparable with many famous porous materials such as MOF-5 ( $7.6 \text{ kJ mol}^{-1}$ ), Zn–MOF-74 ( $8.3 \text{ kJ mol}^{-1}$ ), NOTT-101 ( $5.3 \text{ kJ mol}^{-1}$ ) and UCMC-150 ( $7.3 \text{ kJ mol}^{-1}$ ).<sup>40,41</sup> 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  $\text{H}_2$  molecule.<sup>42,43</sup> In addition, the uncoordinated N-heteroatom sites also aid in the low-pressure uptake by this material.<sup>31</sup>

Because accessible N-donor sites are expected to enhance interactions between frameworks and  $\text{CO}_2$ , the  $\text{CO}_2$  sorption isotherms were measured at different temperatures, which shows a fully reversible type I behaviour with no hysteresis

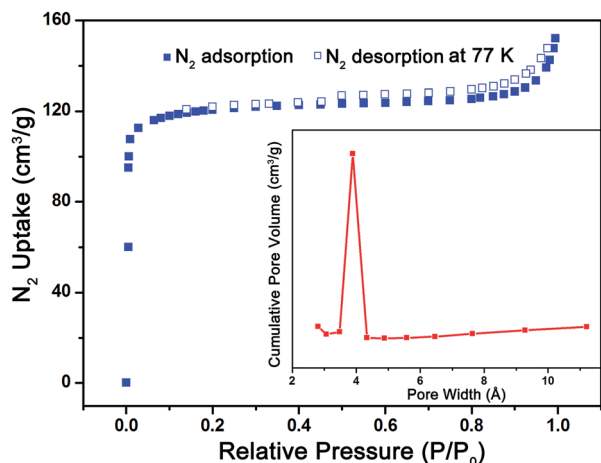


Fig. 2 The  $\text{N}_2$  sorption isotherms at 77 K. Inset: the pore size distribution of **NENU-520a** using the Horvath–Kawazoe (HK) method.

(Fig. 3). The  $\text{CO}_2$  uptake of **NENU-520a** at saturation was  $106.0 \text{ cm}^3 \text{ cm}^{-3}$  (corresponding to 15.7 wt% or 10.3  $\text{CO}_2$  per formula unit, Table S3†) at 273 K and  $79.9 \text{ cm}^3 \text{ cm}^{-3}$  (corresponding to 11.9 wt% or 7.8  $\text{CO}_2$  per formula unit) at 298 K. Albeit these values are lower than the M–MOF-74 series ( $162 \text{ cm}^3 \text{ cm}^{-3}$ ) with different open metal sites, they are considerably higher than lots of well-known MOFs such as MAF-23 (or  $\text{Zn}_2(\text{btm})_2$ ,  $74.2 \text{ cm}^3 \text{ g}^{-1}$  and  $56.1 \text{ cm}^3 \text{ g}^{-1}$  at 273 K and 298 K) with multiple strong adsorption sites and  $[\text{Cu}(\text{tba})_2]_n$  ( $51.8 \text{ cm}^3 \text{ g}^{-1}$  or 10.2 wt% at 273 K), the currently best performing ZIF-69 ( $70 \text{ cm}^3 \text{ g}^{-1}$  at 273 K and 1 atm).<sup>44–46</sup> 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  $\text{CH}_4$  and  $\text{N}_2$  were also studied at 273 and 298 K (Fig. 3). The desolvated **NENU-520a** only has a maximum  $\text{CH}_4$  uptake of  $31.3 \text{ cm}^3 \text{ g}^{-1}$  ( $1.4 \text{ mmol g}^{-1}$ , 2.24 wt%) and  $21.41 \text{ cm}^3 \text{ g}^{-1}$  ( $0.96 \text{ mmol g}^{-1}$ , 1.53 wt%) at 273 and 298 K, respectively, which is substantially lower than  $\text{CO}_2$ . In sharp contrast to  $\text{CO}_2$  and  $\text{CH}_4$ , the uptake of  $\text{N}_2$  reaches a maximum of only  $6.6 \text{ cm}^3 \text{ g}^{-1}$  ( $0.29 \text{ mmol g}^{-1}$ ) at

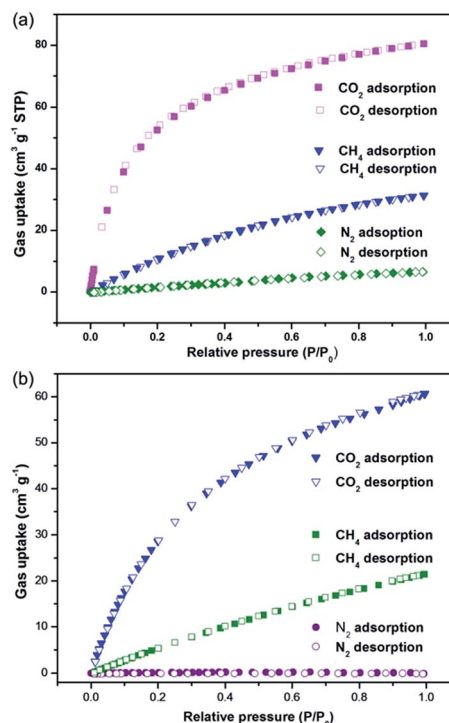


Fig. 3 The  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2$  sorption isotherms for **NENU-520a** at 273 K (a) and 298 K (b), respectively.



273 K and  $0.23 \text{ cm}^3 \text{ g}^{-1}$  ( $0.01 \text{ mmol g}^{-1}$ ) at 298 K, respectively. It is clearly shown that the pore structure of **NENU-520a** is readily accessible to  $\text{CO}_2$ . The relatively high  $\text{CO}_2$  and marginal  $\text{N}_2$  uptake at ambient temperature prompted us to investigate the capacity of **NENU-520a** to selectively adsorb  $\text{CO}_2$  over  $\text{CH}_4$  and  $\text{N}_2$ .

The ideal adsorbed solution theory (IAST) calculation, which originated from Myers and Prausnitz,<sup>47</sup> was employed to predict the adsorption selectivity and  $\text{CO}_2$  uptake of **NENU-520a** for the following binary gas mixtures: 15/85  $\text{CO}_2/\text{N}_2$ , 50/50  $\text{CO}_2/\text{CH}_4$  and 5/95  $\text{CO}_2/\text{CH}_4$ . 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  $\text{CO}_2$ – $\text{N}_2$  mixture was essential for a realistic post-combustion capture of  $\text{CO}_2$ . In these calculations, the partial pressures of  $\text{CO}_2$  and  $\text{N}_2$  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)<sup>35,36</sup> exhibiting high  $\text{CO}_2/\text{N}_2$  separation selectivity are also included. Fig. 4 presents the IAST calculations for  $\text{CO}_2/\text{N}_2$  adsorption selectivity. Remarkably, **NENU-520** has the highest selectivity (about 400) towards  $\text{CO}_2$  for the mixture compositions. To the best of our knowledge, only two MOFs were reported to display higher  $\text{CO}_2/\text{N}_2$  selectivity than **NENU-520**. One example is SIFSIX-3–Zn, which exhibits the highest  $\text{CO}_2/\text{N}_2$  selectivity (with selectivity of  $1539 \pm 307$ ).<sup>28</sup> 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  $\text{SiF}_6$  anions which notably enhance the uptake of  $\text{CO}_2$  into the material, whereas neither charged units nor favourable groups exist in the channels of **NENU-520**. The other MOF is  $[\text{Cu}(\text{bcppm})\text{H}_2\text{O}]$ . Although  $[\text{Cu}(\text{bcppm})\text{H}_2\text{O}]$  has slightly higher selectivity, its uptake capacity (1.70 and 1.85  $\text{mmol g}^{-1}$  at 293 and 273 K, respectively) is apparently lower than **NENU-520** (2.71 and 3.59  $\text{mmol g}^{-1}$  at 298 and 273 K, respectively).<sup>36</sup> 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,

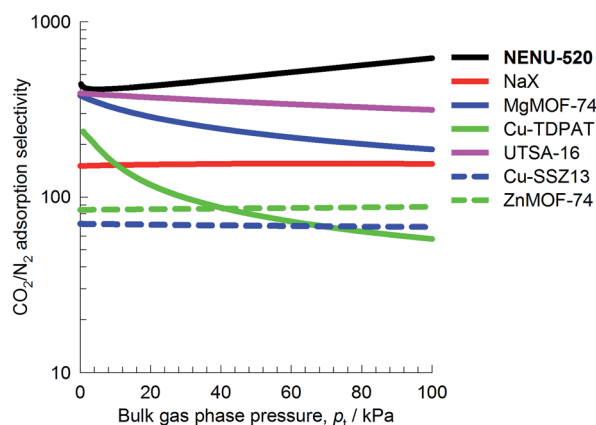


Fig. 4 Calculated selectivity of  $\text{CO}_2/\text{N}_2$  predicted by IAST calculations 298 K for the variety of MOFs considered in this work. In these calculations, the partial pressures of  $\text{CO}_2$  and  $\text{CH}_4$  are taken to be  $p_1/p_2 = 15/85$ .

charged units and amine groups.<sup>46,48–57</sup> Thus, **NENU-520** is one of the best materials to facilitate effective  $\text{CO}_2$  capture and separation from the perspective of comprehensive properties.

The selectivities for  $\text{CO}_2/\text{CH}_4$  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.<sup>58–64</sup> The performance of industrial fixed bed adsorbents 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,  $L\varepsilon/u$ . 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 a 15/85  $\text{CO}_2/\text{N}_2$  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  $\text{CO}_2$  elutes last in the sequence. Fig. 5c presents the mole percent of  $\text{N}_2$  in outlet gas as a function of dimensionless time with **NENU-520a. It is possible to recover pure  $\text{N}_2$  from the gas mixture in a certain interval of time. We arbitrarily set the purity requirement to be 99.95%  $\text{N}_2$ . This amount can be determined from a material balance. The productivity of  $\text{N}_2$  with a purity of 99.95%+ was determined to be 4.84  $\text{mol kg}^{-1}$  of **NENU-520**. The reason for**

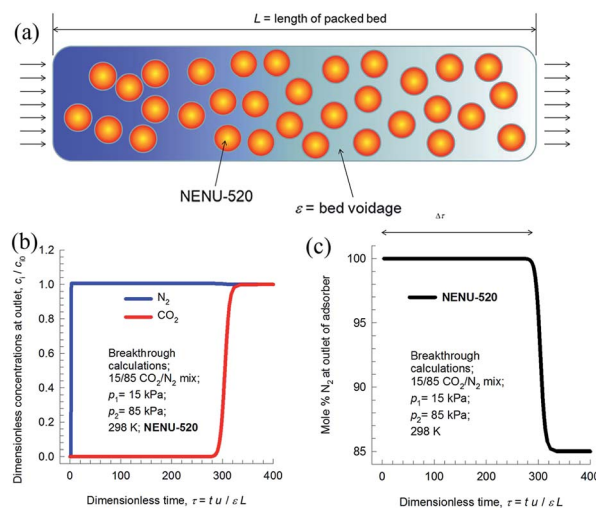


Fig. 5 (a) Schematic view of a packed bed adsorber. The tube length  $L = 0.3 \text{ m}$ . The apparatus was operated at 298 K. The bed porosity,  $\varepsilon = 0.4$ . The interstitial gas velocity,  $u = 0.04 \text{ m s}^{-1}$ ; (b) breakthrough characteristics of an adsorber packed with **NENU-520** and maintained at isothermal conditions at 298 K, and (c) mole percent  $\text{N}_2$  in outlet gas as a function of dimensionless time for operation at a total pressure of 100 kPa for 15/85  $\text{CO}_2/\text{N}_2$  mixture.

the high productivity is a combination of higher selectivity and higher CO<sub>2</sub> uptake capacity. **NENU-520a** was demonstrated to be a promising candidate for CO<sub>2</sub> capture and separation from fuel gas.

5/95 CO<sub>2</sub>/CH<sub>4</sub> 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.<sup>28</sup> In natural gas purification processes, the primary objective is to produce CH<sub>4</sub> with a specified purity level, which is typically 500 ppm CO<sub>2</sub>, *i.e.* 0.05 mole percent CO<sub>2</sub>. Fig. S11b† shows the gas composition, expressed as mole percent of CH<sub>4</sub>, in outlet gas as a function of dimensionless time for a selection of porous adsorbent materials. During the time interval Δτ, 99.95% + pure CH<sub>4</sub> can be produced. The productivity of methane with a purity of 99.95%+ is calculated to be 6.7 mol kg<sup>-1</sup> 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<sub>2</sub> and CH<sub>4</sub> 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 N<sub>2</sub> and CH<sub>4</sub> in the pure form from gas mixtures. Based on the presented evidence, **NENU-520** is a superior adsorbent for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separation at ambient conditions than reported for most of the MOFs.

The CO<sub>2</sub> adsorption enthalpy of **NENU-520a** is 33 kJ mol<sup>-1</sup> (Fig. 6), which is stronger than siliceous zeolite (27 kJ mol<sup>-1</sup>), and the series of MAF materials (MAF-4, 25.1 kJ mol<sup>-1</sup>; MAF-7, 17.2 kJ mol<sup>-1</sup>; MAF-25, 26.3 kJ mol<sup>-1</sup> and MAF-26, 23.3 kJ mol<sup>-1</sup>; MAF stands for metal azolate framework).<sup>30,65,66</sup> Its CH<sub>4</sub> adsorption enthalpy is 29 kJ mol<sup>-1</sup>. The high uptake and enthalpy of CO<sub>2</sub> as well as the remarkable selectivity over CH<sub>4</sub> and N<sub>2</sub> may be reasonable considering the fact that: (i) with its greater polarizability and larger quadrupole moment, CO<sub>2</sub> has

stronger interactions with the accessible N-sites of **NENU-520** than CH<sub>4</sub> and N<sub>2</sub>;<sup>67–69</sup> (ii) the abundant uncoordinated N-heteroatom sites directed toward the inner surface in the narrow cavities are beneficial to interact with CO<sub>2</sub> molecules; (iii) as mentioned above, the kinetic diameters of the cylinders are 3.3 Å, 3.64 Å and 3.80 Å for CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>, respectively. The limiting pore size (about 3.6 Å) of **NENU-520** is just right for CO<sub>2</sub>. Thus, CO<sub>2</sub> molecules are more prone to be injected than CH<sub>4</sub> and N<sub>2</sub>.

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.<sup>70,71</sup> 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.<sup>72</sup> 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<sup>71</sup> and Zhang<sup>72</sup>, **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.<sup>70,71</sup>

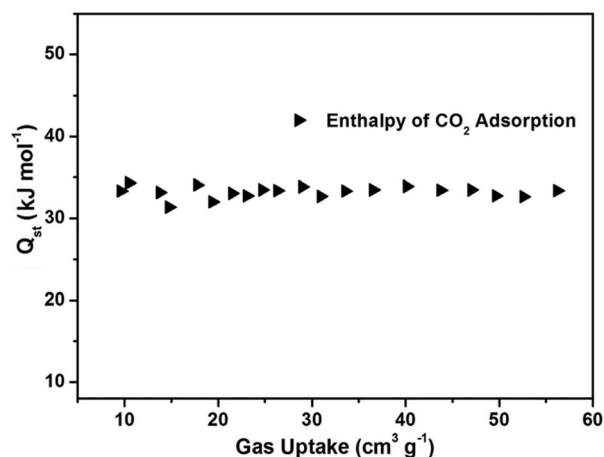


Fig. 6 Heats of CO<sub>2</sub> adsorption as a function of CO<sub>2</sub> uptake for **NENU-520**.

## 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 H<sub>2</sub> and CO<sub>2</sub> with the high adsorption enthalpy of 10.7 kJ mol<sup>-1</sup> and 33 kJ mol<sup>-1</sup>, respectively. Moreover, **NENU-520a** shows high CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> 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<sub>2</sub> over N<sub>2</sub> at 298 K of **NENU-520a** is amongst the highest values for CO<sub>2</sub> selective separation. Consequently, **NENU-520a** has significant potential for use as an adsorbent in CO<sub>2</sub>-capture for natural gas sweetening and post-combustion power plants, by combining the higher uptake and higher selectivity toward CO<sub>2</sub>. 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

- J. R. Li, J. Sculley and H. C. Zhou, *Chem. Rev.*, 2012, **112**, 869.
- D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem., Int. Ed.*, 2010, **49**, 6058.
- M. Z. Jacobson, *Energy Environ. Sci.*, 2009, **2**, 148.
- K. M. K. Yu, I. Curcic, J. Gabriel and S. C. E. Tsang, *ChemSusChem*, 2008, **1**, 893.
- G. Petron, P. Tans, G. Frost, D. Chao and M. Trainer, *J. Geophys. Res.*, 2008, **113**, 1.
- S. Solomon, G. K. Plattner, R. Knutti and P. Friedlingstein, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 1704.
- N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C. S. Adjiman, C. K. Williams, N. Shah and P. Fennell, *Energy Environ. Sci.*, 2010, **3**, 1645.
- E. D. Bloch, L. J. Murray, W. L. Queen, S. Chavan, S. N. Maximoff, J. P. Bigi, R. Krishna, V. K. Peterson, F. Grandjean, G. J. Long, B. Smit, S. Bordiga, C. M. Brown and J. R. Long, *J. Am. Chem. Soc.*, 2011, **133**, 14814.
- S. Chaemchuen, N. A. Kabir, K. Zhou and F. Verpoort, *Chem. Soc. Rev.*, 2013, **42**, 9304.
- J. Wang, L. Huang, R. Yang, Z. Zhang, J. Wu, Y. Gao, Q. Wang, D. O'Hare and Z. Zhong, *Energy Environ. Sci.*, 2014, **7**, 3478.
- R. Service, *Science*, 2004, **305**, 962.
- B. A. Peppley, *Int. J. Green Energy*, 2006, **3**, 195.
- N. Muradov, *Int. J. Hydrogen Energy*, 2001, **26**, 1165.
- H.-L. Jiang, D. Feng, K. Wang, Z.-Y. Gu, Z. Wei, Y.-P. Chen and H.-C. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 13934.
- Z. Yin, Q. X. Wang and M. H. Zeng, *J. Am. Chem. Soc.*, 2012, **134**, 4857.
- Y. He, W. Zhou, R. Krishna and B. Chen, *Chem. Commun.*, 2012, **48**, 11813.
- Y. Q. Lan, H. L. Jiang, S. L. Li and Q. Xu, *Adv. Mater.*, 2011, **23**, 5015.
- F. Akhtar, Q. Liu, N. Hedin and L. Bergström, *Energy Environ. Sci.*, 2012, **5**, 7664.
- J. B. DeCoste and G. W. Peterson, *Chem. Rev.*, 2014, **114**, 5727.
- Y. He, B. Li, M. O'Keeffe and B. Chen, *Chem. Soc. Rev.*, 2014, **43**, 5618.
- Z. Zhang, Y. Zhao, Q. Gong, Z. Li and J. Li, *Chem. Commun.*, 2013, **49**, 653.
- J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477.
- S. Couck, J. F. M. Denayer, G. V. Baron, T. Remy, J. Gascon and F. Kapteijn, *J. Am. Chem. Soc.*, 2009, **131**, 6326.
- R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Angew. Chem., Int. Ed.*, 2012, **51**, 1826.
- J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4670.
- B. Zheng, Z. Yang, J. Bai, Y. Li and S. Li, *Chem. Commun.*, 2012, **48**, 7025.
- Y. Wang, C. Tan, Z. Sun, Z. Xue, Q. Zhu, C. Shen, Y. Wen, S. Hu, Y. Wang, T. Sheng and X. Wu, *Chem.-Eur. J.*, 2014, **20**, 1341.
- P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80.
- J. M. Taylor, K. W. Dawson and G. K. H. Shimizu, *J. Am. Chem. Soc.*, 2013, **135**, 1193.
- J. B. Lin, J. P. Zhang and X. M. Chen, *J. Am. Chem. Soc.*, 2010, **132**, 6654.
- J. S. Qin, D. Y. Du, W. L. Li, J. P. Zhang, S. L. Li, Z. M. Su, X. L. Wang, Q. Xu, K. Z. Shao and Y. Q. Lan, *Chem. Sci.*, 2012, **3**, 2114.
- P. Cui, Y. G. Ma, H. H. Li, B. Zhao, J. R. Li, P. Cheng, P. B. Balbuena and H. C. Zhou, *J. Am. Chem. Soc.*, 2012, **134**, 18892.
- Q. Lin, T. Wu, S. T. Zheng, X. Bu and P. Feng, *J. Am. Chem. Soc.*, 2012, **134**, 784.
- A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
- S. Xiang, Y. He, Z. Zhang, H. Wu, W. Zhou, R. Krishna and B. Chen, *Nat. Commun.*, 2012, **3**, 954.
- W. M. Bloch, R. Babarao, M. R. Hill, C. J. Doonan and C. J. Sumby, *J. Am. Chem. Soc.*, 2013, **135**, 10441.
- S. Xiang, J. Huang, L. Li, J. Zhang, L. Jiang, X. J. Kuang and C.-Y. Su, *Inorg. Chem.*, 2011, **50**, 1743.
- L. Hou, L. N. Jia, W. J. Shi, Y. Y. Wang, B. Liu and Q. Z. Shi, *Dalton Trans.*, 2013, **42**, 3653.
- S. S. Kaye and J. R. Long, *J. Am. Chem. Soc.*, 2005, **127**, 6506.
- M. P. Suh, H. J. Park, T. K. Prasad and D. W. Lim, *Chem. Rev.*, 2012, **112**, 782.
- R. B. Lin, D. Chen, Y. Y. Lin, J. P. Zhang and X. M. Chen, *Inorg. Chem.*, 2012, **51**, 9950.
- M. Dincă, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 16876.

- 43 S. L. Li and Q. Xu, *Energy Environ. Sci.*, 2013, **6**, 1656.
- 44 J. Duan, M. Higuchi, R. Krishna, T. Kiyonaga, Y. Tsutsumi, Y. Sato, Y. Kubota, M. Takata and S. Kitagawa, *Chem. Sci.*, 2014, **5**, 660.
- 45 P. Q. Liao, D. D. Zhou, A. X. Zhu, L. Jiang, R. B. Lin, J. P. Zhang and X. M. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 17380.
- 46 M. Du, C. P. Li, M. Chen, Z. W. Ge, X. Wang, L. Wang and C. S. Liu, *J. Am. Chem. Soc.*, 2014, **136**, 10906.
- 47 A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121.
- 48 B. Zheng, J. Bai, J. Duan, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2011, **133**, 748.
- 49 M. Zhang, Q. Wang, Z. Lu, H. Liu, W. Liu and J. Bai, *CrystEngComm*, 2014, **16**, 6287.
- 50 A. K. Sekizkardes, T. İslamoğlu, Z. Kahveci and H. M. El-Kaderi, *J. Mater. Chem. A*, 2014, **2**, 12492.
- 51 T. M. McDonald, W. R. Lee, J. A. Mason, B. M. Wiers, C. S. Hong and J. R. Long, *J. Am. Chem. Soc.*, 2012, **134**, 7056.
- 52 X. Lv, L. Li, S. Tang, C. Wang and X. Zhao, *Chem. Commun.*, 2014, **50**, 6886.
- 53 Y. Liu, S. Wu, G. Wang, G. Yu, J. Guan, C. Pan and Z. Wang, *J. Mater. Chem. A*, 2014, **2**, 7795.
- 54 R.-J. Li, M. Li, X.-P. Zhou, S. W. Ng, M. O'Keeffe and D. Li, *CrystEngComm*, 2014, **16**, 6291.
- 55 L. Du, Z. Lu, K. Zheng, J. Wang, X. Zheng, Y. Pan, X. You and J. Bai, *J. Am. Chem. Soc.*, 2013, **135**, 562.
- 56 J. B. Lin and G. K. H. Shimizu, *Inorg. Chem. Front.*, 2014, **1**, 302.
- 57 T. M. McDonald, D. M. D'Alessandro, R. Krishna and J. R. Long, *Chem. Sci.*, 2011, **2**, 2022.
- 58 R. Krishna and J. R. Long, *J. Phys. Chem. C*, 2011, **115**, 12941.
- 59 R. Krishna, *Microporous Mesoporous Mater.*, 2014, **185**, 30.
- 60 D. L. Chen, H. Shang, W. Zhu and R. Krishna, *Chem. Eng. Sci.*, 2014, **117**, 407.
- 61 D. L. Chen, N. Wang, F. F. Wang, J. Xie, Y. Zhong, W. Zhu, J. K. Johnson and R. Krishna, *J. Phys. Chem. C*, 2014, **118**, 17831.
- 62 H. H. Wu, K. X. Yao, Y. H. Zhu, B. Y. Li, Z. Shi, R. Krishna and J. Li, *J. Phys. Chem. C*, 2012, **116**, 16609.
- 63 C. Song, Y. He, B. Li, Y. Ling, H. Wang, Y. Feng, R. Krishna and B. Chen, *Chem. Commun.*, 2014, **50**, 12105.
- 64 J. J. Perry, S. L. TeichMcGoldrick, S. T. Meek, J. A. Greathouse, M. Haranczyk and M. D. Allendorf, *J. Phys. Chem. C*, 2014, **118**, 11685.
- 65 Z. Zhang, Z. Z. Yao, S. Xiang and B. Chen, *Energy Environ. Sci.*, 2014, **7**, 2868.
- 66 R. Dawson, E. Stockel, J. R. Holst, D. J. Adams and A. I. Cooper, *Energy Environ. Sci.*, 2011, **4**, 4239.
- 67 K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724.
- 68 Y.-S. Bae and C. H. Lee, *Carbon*, 2005, **43**, 95.
- 69 S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870.
- 70 H. Xu, F. Liu, Y. Cui, B. Chen and G. Qian, *Chem. Commun.*, 2011, **47**, 3153.
- 71 M. Guo and Z.-M. Sun, *J. Mater. Chem.*, 2012, **22**, 15939.
- 72 D. Tian, Y. Li, R.-Y. Chen, Z. Chang, G. Wang and X. H. Bu, *J. Mater. Chem. A*, 2014, **2**, 1465.