

Check fo updates

WILEY-VCH

A microporous MOF with inorganic nitrate ions immobilized in pore surface displaying efficient C_2H_2 separation and purification

Xiaoxia Gao,^[a] Haoyan Zhong,^[a] Yingying Zhang,^[a] Yongna Yao,^[a] De-li Chen,^{*[b]} and Yabing He^{*[a]}

Abstract: A microporous MOF based on a heterotopic ligand was successfully synthesized under solvothermal conditions and fully characterized using single-crystal and powder X-ray diffraction, TGA, FTIR, and microanalyses. Single-crystal X-ray diffraction analyses showed that the title MOF contains rich inorganic nitrate ions decorating the channel surface that can serve as C₂H₂ recognition sites. Its selective gas adsorption properties towards C₂H₂ over CO₂ and CH₄ were evaluated by single-component equilibrium adsorption measurements and IAST calculations, establishing its promising potential for C₂H₂ separation and purification. At ambient conditions, the C_2H_2 uptake capacity reaches 92.2 cm³ (STP) g⁻¹, while the IAST-predicted adsorption selectivities are up to 30.6 and 4.5 for the equimolar C_2H_2 -CH₄ and C_2H_2 -CO₂ binary gas mixtures, respectively. Furthermore, DFT computation studies revealed that the inorganic nitrate ion plays a very important role for preferential adsorption of C₂H₂ over CO₂ and CH₄.

Introduction

Acetylene (C_2H_2) is not only widely used as a fuel gas for metal cutting and welding, but is also an important raw material for the synthesis of some platform chemicals. Despite very important role C₂H₂ plays in daily life as well as industrial chemistry, it is still highly demanded to address the challenging issue associated with its separation and purification. Typically, C₂H₂ is industrially produced by oxidative coupling of natural gas or methane (CH₄) in which carbon dioxide (CO₂) is unavoidably generated as a spin-off. To meet the requirement of high-purity C₂H₂ for its more efficient utilization, it is highly desired and imperative to remove CO_2 as well as unreacted CH_4 from C_2H_2 . Compared to C₂H₂/CH₄ separation, C₂H₂/CO₂ separation is more difficult due to their identical or similar properties in terms of kinetic diameters (C₂H₂: 3.3 Å and CO₂: 3.3 Å), molecular dimensions (C₂H₂: $3.3 \times 3.3 \times 5.7$ Å³ and CO₂: $3.3 \times 3.3 \times 5.7$ Å³), critical temperatures (C₂H₂: 308.3 K and CO₂: 304.12 K), and boiling points (C₂H₂: 188.4 K and CO₂: 194.5 K).^[1] Among various separation schemes for such a task, adsorption-based separation utilizing porous solid

[a] X. Gao, H. Zhong, Y. Zhang, Y. Yao, Prof. Dr. Y. He Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Life Sciences, Zhejiang Normal University Jinhua 321004 (China) E-mail: heyabing@zjnu.cn
[b] Dr. D.-I. Chen Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University Jinhua 321004 (China) E-mail: chendl@zjnu.cn

Supporting information for this article is given via a link at the end of the document.

materials as adsorbents has received increasing attention due to its energy-saving, cost-economic, and environmentally friendly nature, thus galvanizing extensive research efforts to develop efficient adsorbents for removing CO_2 and CH_4 from C_2H_2 .

As a new generation of porous materials, metal-organic frameworks (MOFs, also named porous coordination polymers) are composed of metal-containing nodes, either a metal ion or metal cluster, bridged by organic ligands through dative bonds to form multi-dimensional networks with regular pore structure and interesting pore chemistry. The organic-inorganic hybrid characteristics, namely, the great abundance of metal ions and functional ligands, endows MOF materials with a variety of physical and chemical properties. Uniquely, distinguished from the traditional porous materials such as zeolites and carbonbased materials, the pore size of MOFs can be tailored by ingenious selection of appropriate inorganic and organic building units and/or by controlling the framework interpenetration to achieve the sieving effect. Furthermore, the pore surface can be controllably immobilized by diversified functionalities (such as hydrophilic/hydrophobic, polar/nonpolar, and chiral/achiral groups) and/or open metal sites to strengthen host-guest recognition ability towards a specific species. Most significantly, the well-ordered structure can be characterized by X-ray diffraction technologies, thus conducive to in-depth understanding of structure-property relationship and further structure design and performance optimization. These superior characteristics, which are apparently unattainable for the traditional porous materials, qualify MOFs as promising candidates applied in the field of gas separation and purification that is industrially important among others.

Over the last decades, only a few dozens of MOFs have been synthesized and examined for the above-mentioned challenging C_2H_2 separation and purification,^[2] despite thousands of research publications on MOFs-based gas separation. $^{\left[3\right] }$ For example, at the year of 2005, Kitagawa etal. reported the first microporous MOF with a potential for selective sorption of C_2H_2 over CO_2 , which is ascribed to non-coordinated oxygen atoms in the pore wall surface being capable of forming hydrogen bonds with two hydrogen atoms of the incoming C_2H_2 molecules.^[4] An isomer of the well-known ZnMOF-74, named UTSA-74, was synthesized by Chen and coworkers, displaying a remarkable capacity for selective C₂H₂/CO₂ separation, which is attributable to high density of open zinc sites immobilized in the channel surface that each bind two C₂H₂ molecules while are bridged by CO_2 molecules.^[5] Two hybrid ultramicroporous materials exhibited reversed adsorption preference for the separation of a C_2H_2 -CO₂ binary gas mixture due to the distinct adsorbate binding sites in the two materials.^[6] Lee et al. designed and fabricated an imidazolium-functionalized MOF that can selectively capture C₂H₂ species from a C₂H₂-CO₂ mixture, which was explained by the stronger interactions between

imidazolium functional groups and counterion nitrate ions with C₂H₂ compared to CO₂.^[7] Zhang *et al.* constructed an ultramicroporous MOF featuring ultrahigh C₂H₂/CO₂ adsorption selectivity up to 25 at ambient conditions for an equimolar C₂H₂-CO₂ gaseous mixture, which results from C₂H₂ molecule strongly interacting with the surface-immobilized sulphur atoms through hydrogen bonding.^[8] Among the high-performance MOFs above mentioned, almost all of them except UTSA-74 incorporate hydrogen-bond accepting atoms including inorganic anions, oxygen and sulphur atoms, and imidazolium groups to recognize C₂H₂ molecule. In views of these observations, introduction of some hydrogen-bond accepting atoms to the framework surface is expected to be a very effective protocol to improve C₂H₂/CO₂ separation performance.

In this work, we developed a microporous MOF featuring inorganic nitrate ions on the pore surface, which was solvothermally assembled from $Cu(NO_3)_2 3H_2O$ and a heterotopic ligand 3.5-di(pyridin-4-yl) benzoic acid (HL, Scheme 1) consisting of two peripheral pyridine units nonlinearly connected to the central benzoate moieties. Given that nitrate ion can serve as potential C_2H_2 recognition site, its adsorption performance with respect to C_2H_2 separation and purification was systematically evaluated by single-component gas isotherms as well as IAST (ideal adsorbed solution theory) calculations, and the underlying separation mechanism was also investigated by comprehensive DFT computations. Herein, we reported the syntheses, characterizations and gas adsorption properties of the title compound.



Scheme 1. The molecular structure of the organic ligand HL used in this work.

Results and Discussion

The synthesis of the heterotopic ligand could be readily achieved via Suzuki-Miyaura cross-coupling reaction between 4-pyridine boric acid and methyl 3.5dibromobenzoate followed by hydrolysis and acidification. The molecular structure of the ligand was unambiguously confirmed by ¹H and ¹³C NMR (Figure S8 in the Supporting Information) as well as FTIR spectroscopy (Figure S4). Subsequently, blue block-shaped single crystals (which we termed ZJNU-8 for the sake of description convenience, Figure S1) were obtained by a solvothermal reaction of the heterotopic ligand and copper nitrate trihydrate in N,Ndimethylformamide (DMF) at 343 K at the presence of a small amount of HNO3. The as-synthesized ZJNU-8 is insoluble and stable in tested organic solvents including DMF, methanol, tetrahydrofuran (THF), acetone, and chloroform. A good agreement between experimental and simulated PXRD profiles verified the phase purity of the asprepared bulk material (Figure S2). TGA carried out under

WILEY-VCH

N₂ atmosphere displayed a mass decrease of 26.4% below 556 K (Figure S3), which is attributable to the departure of non-coordinated two DMF molecules *per* formula unit (calcd. 26.7%). FTIR revealed full deprotonation of the organic ligand (Figure S4), which is consistent with the single-crystal structural analyses below.

Single-crystal X-ray diffraction studies revealed that the title compound is a three-dimensional (3D) charge-neutral coordination network crystallizing in the orthogonal space group Pccn with the lattice parameter a = 16.2205 Å, b = 20.7353 Å and c = 14.9655 Å. Besides the disordered lattice molecules, the fundamental building unit includes one crystallographically independent copper(II) ion, one fully deprotonated ligand anion, and one nitrate ion. The presence of nitrate ion in the framework was also confirmed by FTIR spectra that exhibit stretching vibration band at 1389 cm⁻¹. The copper ion is surrounded by two carboxylate oxygen atoms coming from two different ligands, one oxygen atom of one nitrate ion, and two nitrogen atoms belonging to two distinct ligands, displaying a distorted square pyramidal coordination geometry. The Cu-Ocarboxylate and Cu- N_{pyridine} bond lengths are within the ranges of 1.954-2.208 Å and 2.001-2.004 Å, respectively, which are consistent with other literature data.^[9] Two neighboring copper ions are bridged by two *cis-trans* $\mu_2 \eta^1: \eta^1$ carboxylate groups to generate a dicopper $Cu_2(COO)_2(Py)_4(NO_3)_2$ secondary building unit (SBU, Figure 1a) with the Cu-Cu separation of 4.520 Å, which can be considered as a 6-connected node (Figure 1b). The heterotopic ligand is not coplanar with distortion angles of 40.8° and 24.3° between the terminal pyridine segments and the central benzene ring, and adopts a μ_4 -bridging mode to coordinate with four copper(II) ions through its two pyridine-nitrogen atoms and one carboxylate group. Each organic ligand links to three dicopper-based SBUs, and thus can be simplified as a 3-connected node (Figure 1c). In this way, the interconnection of 3-connected ligands and 6connected dicopper-based SBUs leads to the formation of an infinitely extended (3,6)-connected network of fit-3 topology with the Schläfli symbol of $\{4 6^2\}_2 \{4^2 6^4 8^7 \cdot 10^2\}$ with a stoichiometry of (3-c)₂(6-c) as determined by TOPOS program (Figure S5).^[10] Notably, one-dimensional channels with the diameters of ca. 4.1 and 2.2 Å running along the crystallographic a and c axis can be



Figure 1. Single-crystal X-ray structure of ZJNU-8. View of (a) dicopper SBU, connectivities of (b) dicopper SBU and (c) heterotopic ligand, and 3D network structures along the crystallographic (d) *a* and (e) *c* directions. The carbon atoms are displayed in grey, oxygen in red, nitrogen in blue, hydrogen in white, and copper in brown.

WILEY-VCH

observed, respectively, with the inorganic nitrate ions pointing toward the channel center (Figures 1d and 1e). PLATON computations revealed that the potential solvent-accessible pore volume is 45.6% of the unit cell, highlighting its moderate porosity. The desolvated framework density is 1.058 g cm⁻³.

To establish permanent porosity and evaluate pore textural parameters, we measured nitrogen (N₂) adsorption-desorption isotherm at 77 K. Prior to sorption analysis, sample activation was performed by degassing the acetone-exchanged ZJNU-8 at room temperature for 24 h followed by at 363 K until the degassed rate of 2 µmHg min⁻¹ was reached. ZJNU-8 retained its crystallinity and structural integrity after activation as confirmed by PXRD experiments (Figure S2). As illustrated in Figure 2, ZJNU-8 exhibited a pseudo Type-I isotherm according to the IUPAC classification with a rapid increase of N2 uptake in low relative pressure region and the saturated N₂ uptake amount of 277.8 cm³ (STP) g⁻¹, indicative of its microporous nature. Analysis of N2 adsorption data by employing the BET (Brunauer-Emmett-Teller)^[11] and Langmuir theories gave the corresponding specific surface areas of 1015 and 1186 m² g⁻¹, respectively (Figure S6). The total pore volume determined from the maximal amount of N₂ adsorbed at $p/p_0 = 0.95$, considering the pores to be filled with condensed N₂ at its normal liquid state, is 0.4297 cm³ g⁻¹, which is very close to the theoretical value of 0.4316 cm³ g⁻¹ derived from single-crystal X-ray data, indicating high phase purity and full desolvation of bulk materials. As shown in the inset in Figure 2, the pore size distribution based on DFT (density functional theory) model is mainly centered at 5.36 Å, which is coincident with the single-crystal X-ray structure.



Figure 2. 77 K N₂ adsorption (solid symbols) and desorption (open symbols) isotherm of **ZJNU-8**. The pore size distribution is displayed in the inset. STP stands for standard temperature and pressure.

Intrigued by the establishment of inherent permanent porosity, together with built-in inorganic nitrate ions in pore surface as C_2H_2 recognition sites, we examined its application potential as an adsorbent for the separation of CO_2 and CH_4 from C_2H_2 . Accordingly, the single-component adsorption-desorption isotherms for C_2H_2 , CO_2 , and CH_4 were collected at three different temperatures of 278 K, 288 K, and 298 K and pressures up to 1 atm (Figure 3). The adsorption branches were overlapped with the desorption ones for all isotherms, indicating the adsorption and desorption process are fully reversible. At the

pressure of 1 atm, C₂H₂, CO₂, and CH₄ uptake capacities of **ZJNU-8** are 92.2, 83.2 and 30.1 cm³ (STP) g⁻¹ at 298 K, which increase to 97.8, 94.6, and 36.3 cm3 (STP) g-1 at 288 K, and 102.5, 106.3 and 43.4 $\rm cm^3$ (STP) g^{-1} at 278 K due to the exothermic physisorption process. The C2H2 uptake of ZJNU-8 at 298 K and 1 atm was found to surpass those of most majority of reported porous MOFs without open metal sites such as ZIF-8 $(25 \text{ cm}^3 \text{ (STP) } g^{-1})^{[12]}$, MOF-5 (26 cm³ (STP) $g^{-1})^{[12]}$, BSF-1 (52.6 cm^{3} (STP) g^{-1} ^[13], [Zn₁₂(tdc)₆(glycerol)₆(dabco)₃] (55.1 cm³ (STP) g^{-1} ^[14], UTSA-36 (56.8 cm³ (STP) g^{-1} ^[15], Cu₂(bdc)₂(dabco) (60 cm³ (STP) g⁻¹)^[16], Mg(HCOO)₂ (66 cm³ (STP) g⁻¹),^[17] (Me₂NH₂)₂[Zn₆(TBAPy)₂(Ade-NH₂)₄(µ₄-O)] (69.4 cm³ (STP) g⁻¹)^[18] CPL-2 (70 cm³ (STP) g^{-1})^[19], SIFSIX-3-Ni (74 cm³ (STP) g^{-1})^[6], UTSA-220 (76 cm³ (STP) g^{-1})^[20], Ni-gallate (80.4 cm³ (STP) g^{-1}) $^{1})^{[21]}$, and TIFSIX-2-Cu-i (91.8 cm³ (STP g⁻¹)^[6]. To our delight, ZJNU-8 adsorbed much more amount of C₂H₂ than CO₂ and CH₄ especially at low pressure. For example, at 0.5 bar, a typical partial pressure of C_2H_2 encountered at the practical mixed gas,



Figure 3. $C_2H_2,\,CO_2,\,and\,CH_4$ isotherms of ZJNU-8 at (a) 298 K, (b) 288 K, and (c) 278 K.

the molar ratio of C₂H₂/CH₄ and C₂H₂/CO₂ adsorbed is 3.6 and 1.2 at 278 K, which increase to 4.4 and 1.3 at 288 K, and 5.2 and 1.5 at 298 K. Besides the discrepancies of adsorption amounts, ZJNU-8 exhibited distinctly different affinity towards C₂H₂, CO₂, and CH₄ as reflected by isotherm profile slopes at the low pressure region. The slope of C₂H₂ isotherm is much steeper than the corresponding CO₂ and CH₄ ones, indicating a stronger interaction between the framework and C₂H₂ compared to CO₂ and CH₄. To quantify the adsorbate-adsorbent affinity, the loading-dependent isosteric heat (Qst) of C2H2, CO2, and CH4 adsorption were extracted from the isosteric plots of the temperature-dependent gas isotherms according to a Clausius-Clapeyron equation, which was depicted in in Figure 4a as a function of gas loadings. Across the entire adsorption process, the Q_{st} value for C_2H_2 is noticeably higher than those for CO_2 and CH₄. Specifically, at near zero surface loadings, the Q_{st} values are 32.4±0.2, 26.2±0.1 and 22.2±2.2 kJ mol⁻¹ for C₂H₂, CO₂, and CH₄, respectively. In addition, the Henry constant was also calculated, which is 0.474, 0.0830, and 0.0157 mmol kPa⁻¹ at 298 K for C₂H₂, CO₂, and CH₄, respectively. The Henry constant of C_2H_2 is obviously higher than those of CO_2 and CH_4 , furthermore corroborating the view that the framework has stronger interactions with C₂H₂ compared to CO₂ and CH₄.

As discussed above, the adsorption amount and strength of **ZJNU-8** follow the order of $C_2H_2 > CO_2 > CH_4$, indicating that ZJNU-8 can be used as an adsorbent for C2H2/CO2 and C₂H₂/CH₄ separations. To illustrate this point, we employed a well-known IAST model proposed by Myers and Prausnitz^[22] to forecast the adsorption selectivity from the experimentally measured single-component isotherms, since the adsorption selectivity is a very important criterion for the evaluation of gas separation performance of a given adsorbent. The isotherm data can be correlated with a single-site Langmuir-Freundlium equation with the fitting correlation coefficients all above 0.99 (Figure S7). The fitting parameters obtained, provided in Table S2 in the supporting information, were then used to calculate IAST selectivity. Figure 4b and 4c presented the adsorption selectivity for the equimolar binary gas mixtures of C2H2/CH4 and C₂H₂/CO₂ at three different temperatures. It can be observed that the adsorption selectivity is dependent on the total gas pressure as well as temperature. Both C2H2/CO2 and C2H2/CH4 adsorption selectivities decreased with increasing total gas pressures. The reason for this can be explained as following. The primary adsorption sites are easily occupied by C2H2 molecules at the low pressure. With the increase of pressure, there are fewer and fewer such locations for adsorbing C₂H₂. As a result, the selectivity decreases accordingly. When the temperatures are lowered, the C₂H₂/CH₄ adsorption selectivity increases, while the C2H2/CO2 adsorption selectivity remains almost unchanged. At the atmospheric pressure, the C₂H₂/CH₄ and C₂H₂/CO₂ adsorption selectivity reach 30.6 and 4.5 at 298 K, 35.2 and 4.4 at 288 K, and 41.2 and 4.3 at 278 K. Although the C_2H_2/CH_4 and C_2H_2/CO_2 adsorption selectivities are not the highest reported thus far, these values are still comparable to and even higher than those of some MOFs reported for such a separation such as [Zn₁₂(tdc)₆(ethylene glycol)₆(dabco)₃] $(C_2H_2/CO_2: 3.3)^{[14]}, UTSA-68 (C_2H_2/CO_2 = 3.4)^{[23]}, BSF-1$ $(C_2H_2/CO_2 = 3.3)^{[13]}$, ZJNU-100 $(C_2H_2/CO_2 = 3.81)^{[24]}$, ZJU-10 $(C_2H_2/CO_2 = 4.2)^{[25]}$, FJU-90 $(4.3)^{[2c]}$, UTSA-220 $(C_2H_2/CO_2 = 4.2)^{[25]}$ $(4.4)^{[20]}$, and SNNU-45 (C₂H₂/CO₂ = 4.5)^[2h]. Taken together, the impressive adsorption selectivity of C2H2 over CO2 and CH4

WILEY-VCH

combined with high C_2H_2 adsorptivity endows **ZJNU-8** with the promising application potential as a solid sorbent for the separation of CO_2 and CH_4 from C_2H_2 at ambient conditions.



Figure 4. (a) The loading-dependent isosteric heats of C_2H_2 , CO_2 , and CH_4 adsorption, and (b) C_2H_2/CH_4 and (c) C_2H_2/CO_2 adsorption selectivities calculated using IAST model as a function of the total gas pressures at three different temperatures of 278 K, 288 K, and 298 K for the equimolar binary gas

To figure out the underlying mechanism on preferential adsorption of C_2H_2 over CO_2 , we performed comprehensive DFT computations. Figure 5a displays the primary C_2H_2 adsorption site that is located between two adjacent nitrate ions coming from two dicopper SBUs connected by the same heterotopic ligand. At this binding site, the acetylene molecule hydrogenbonds with the two nitrate oxygen atoms with the $O(NO_3^-)^{...}H(C_2H_2)$ distances of 2.32 Å and 2.27 Å, leading to a high binding energy of -40.5 kJ mol⁻¹. As for CO_2 adsorption, two principal binding sites were found, with the similar binding energy of -31.7 and -28.9 kJ mol⁻¹, respectively (Figure 5b and

WILEY-VCH

FULL PAPER

5c). The CO₂ binding energy is significantly smaller than that of C₂H₂, which is also consistent with the aforementioned experimental results. In CO₂-I site, CO₂ interacts with the four hydrogen atoms of four aromatic rings belonging to two neighbouring dicopper SBUs with the corresponding H^{...}O(CO₂) distances of 2.92 Å, 2.81 Å, 3.10 Å and 3.00 Å, while in CO₂-II site, CO₂ binds with the four hydrogen atoms of four aromatic rings belonging to the same SBU with four H^{...}O(CO₂) distances of 2.77 Å, 3.00 Å, 3.12 Å, and 3.16 Å. Apparently, the inorganic nitrate ion does not take participation in CO₂ binding but is involved in C₂H₂ adsorption, suggesting that as expected, nitrate ion plays a very important role for preferential adsorption of C₂H₂ over CO₂.



Figure 5. The energetically favourable adsorption sites and binding energies of C_2H_2 and CO_2 in **ZJNU-8**. The units of distance and binding energy are Å and kJ mol⁻¹, respectively

Conclusions

In conclusion, we used a heterotopic ligand to successfully fabricate a microporous copper-based MOF that incorporates inorganic nitrate ions immobilized in the pore surface. By integrating the C_2H_2 recognition ability of nitrate ions and the suitable pore size of the framework, the obtained MOF exhibited the promising potential for C_2H_2 separation and purification. DFT computations revealed that the preferential adsorption of C_2H_2 over CO_2 and CH_4 can be mainly ascribed to the inorganic nitrate ions functioning as C_2H_2 recognition sites. The design and synthesis of other inorganic anion-incorporated MOFs with interesting features and promising applications are undergoing in our lab.

Experimental Section

Materials and Methods: All the chemicals purchased from commercial sources were directly used as received without any further purification, and all organic solvents were analytical grade. Unless mentioned, all materials characterizations were performed at room temperature. ¹H and ¹³C NMR spectra measurements were carried out on a Bruker AVANCE 400 or 600 NMR spectrometer. FTIR (Fourier-transform infrared) spectra were recorded in a transmission mode on a Nicolet 5DX FTIR instrument using pressed KBr pellets technique in the 4000-400 cm⁻¹ wavenumber range. Elemental analyses for C, H, and N were taken on a PerkinElmer 240 CHN elemental analyser. TGA (thermogravimetric analyses) were conducted with a Netzsch STA 449C thermal analyser over the temperature range from room temperature to 1073 K in a N2 stream at a heating rate of 5 K min⁻¹. The powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer with Cu-Kn1 radiation at a 2θ range of 5–45° at room temperature. The simulated PXRD pattern was calculated from single-crystal X-ray diffraction data using the Mercury 1.4.1 program. Gas adsorption isotherm data were collected by a volumetric method using an ASAP 2020HD88 gas adsorption instrument (Micromeritics, USA). The cryogenic temperature of 77 K required for N₂ sorption test was controlled using a liquid N₂ bath, and the other temperatures required for C₂H₂, CO₂, and CH₄ tests were maintained using a cycling water bath (Julabo F12). The C₂H₂, CO₂, CH₄, and N₂ gases used throughout adsorption experiments have the following purities of 99.9%, 99.99%, 99.999% and 99.9999%, respectively. BET surface areas were determined by BET model and based on three criteria,^[26] and the pore size distribution was calculated from the adsorption branch by DFT.

Single-crystal X-ray Crystallography: The single-crystal X-ray measurements were carried out using a Bruker D8 Venture diffractometer with a graphite-monochromated Cu- K_{α} radiation ($\lambda = 1.54178$ Å) at 120 K. The structure was solved by direct methods and refined on F^2 by a full-matrix least-squares method using the SHELXTL-2014 program package.^[27] All the non-H atoms were refined with anisotropic parameters, whereas the H atoms fixed to their geometrically ideal positions were refined isotropically. Because the guest molecules occupying in the channels are highly disordered and could not be modelled, the SQUEEZE routine of PLATON program was used to remove the electron densities of these disordered species.^[28] The relevant crystallographic data were summarized in Table S1 in the supporting information. CCDC 1973607 contains the supplementary crystallographic data for this paper.

Synthesis and Characterization of the Organic Linkers

3,5-dibromobenzoate (1.50 g, 5.10 mmol), pyridin-4-ylboronic acid (3.78 g, 15.30 mmol), K₃PO₄ (11.25 g, 42.3 mmol), Pd(PPh₃)₄ (0.38 g, 0.30 mmol) and 1,4-dioxane (120 mL) were taken in a 500-mL round-bottom flask which was equipped with a Teflon-coated magnetic stirring bar and a refluxing condenser. The flask was evacuated under vacuum and refilled with N2 for three times. The resulting mixture was firmly stirred under N₂ atmosphere in a 393-K oil bath with reflux for 3 days. After that, the reaction mixture was filtered while hot through a plug of celite, and the filter cake was washed with chloroform and THF for several times. The combined organic solvent was removed under reduced pressure, and the residue was crystallized from toluene, affording the off-white ester intermediate in a good isolation yield of 74% (1.10 g, 3.79 mmol). ¹H NMR (CDCl₃, 400.1 MHz) δ (ppm): 8.764 (d, J = 6.4 Hz, 4H), 8.403 (d, *J* = 1.6 Hz, 2H), 8.073 (t, *J* = 1.6 Hz, 1H), 7.619 (d, *J* = 6.4 Hz, 4H), 4.031 (s, 3H). The ester intermediate (1.10 g, 3.79 mmol) was suspended in 60 mL of a mixed solution containing THF and MeOH of equal volumes, and then a solution of 2 mol L⁻¹ NaOH was added. The mixture was stirred under reflux overnight until a transparent solution was formed. After the resulting solution was allowed to cool to ambient temperature, the organic solvent was removed by rotary evaporation, and then 2 mol L⁻¹ HCI was added to the remaining aqueous solution until pH value equals to 5. Brown precipitation formed was filtered, washed with water (H₂O) for three times, and subsequently dried in vacuum at 343 K. The ligand HL was obtained as an off-white solid in 47% yield (0.70 g, 2.50 mmol). ¹H NMR (DMSO- d_6 , 600.1 MHz) δ (ppm): 8.706 (d, J = 5.4 Hz, 4H), 8.406 (s, 1H), 8.356 (s, 2H), 7.897 (d, J = 5.4 Hz, 4H); ¹³C NMR (DMSO- d_6 , 150.9 MHz) δ (ppm): 167.145, 150.802, 146.287, 139.238, 133.307, 130.196, 128.484, 122.156; selected FTIR (KBr, cm⁻¹): 1716, 1633, 1597, 1508, 1444, 1396, 1346, 1259, 1217, 1068, 904, 818, 779, 739, 714, 688, 619, 580, 542, 474.

Synthesis and Characterization of ZJNU-8: A mixture of the organic linker HL (5.0 mg, 18.1 μ mol) and Cu(NO₃)₂·3H₂O (10 mg, 41.39 mmol) was ultrasonically dissolved into DMF (1.5 mL) in a 20-mL screw-capped scintillation vial, and then 50 μ L of 6 M HNO₃ were added. The vial was tightly capped and heated in an oven at 343 K under autogenous pressure for 48 h. Blue block-shaped crystals suitable for X-ray diffraction analysis were isolated by suction filtration and washed with DMF several times. The yield is about 30% based on the organic ligand. The chemical composition of the framework was determined by single-crystal X-ray diffraction, while the guest molecules were assayed by TGA in conjunction with microanalyses. Based on these results, the final

WILEY-VCH

FULL PAPER

chemical formula of **ZJNU-8** was best determined to be $[CuL(NO_3)]$ 2DMF. Anal. Calcd. for $C_{23}H_{25}CuN_5O_7$, Calcd. (%): C, 50.50, H, 4.61, N, 12.80; found (%): C, 50.68; H, 4.77, N, 12.76; selected FTIR (KBr, cm⁻¹): 1655, 1616, 1572, 1504, 1444, 1389, 1315, 1225, 1070, 1030, 831, 789, 671, 636, 550.

Theoretical details: The periodic density functional theory (DFT) based method was employed to compute the potential adsorption sites for both gases. The dispersion energy was corrected by Grimme's method, DFT-D3.^[29] The Perdew-Burke-Ernzerhof^[30] functional was used to describe the exchange-correlation functional. A kinetic energy cutoff of 500 eV in the plane wave basis set was used for the structural optimizations. The lattice parameters of the **ZJNU-8** crystal were fixed during the calculations, while all of the atoms were allowed to relax, until the force on each ion was less than 0.01 eV Å⁻¹. All of the calculations were carried out by using the Vienna ab initio Simulation Package.^[31]

Acknowledgements ((optional))

This research work was funded by the National Natural Science Foundation of China (No. 21771162) and the Natural Science Foundation of Zhejiang Province, China (LR16B010001, LY17B060001).

Keywords: Metal-Organic Frameworks • Gas Separation • C_2H_2 Separation and Purification • C_2H_2/CO_2 Separation • C_2H_2/CH_4 Separation

- [1] J.-R. Li, R. J. Kuppler, H.-C. Zhou, Chem. Soc. Rev. 2009, 38, 1477-1504.
- a) L. Zhang, K. Jiang, J. Zhang, J. Pei, K. Shao, Y. Cui, Y. Yang, B. Li, [2] B. Chen, G. Qian, ACS Sustainable Chem. Eng. 2019, 7, 1667-1672; b) H. Zeng, M. Xie, Y.-L. Huang, Y. Zhao, X.-J. Xie, J.-P. Bai, M.-Y. Wan, R. Krishna, W. Lu, D. Li, Angew. Chem. Int. Ed. 2019, 58, 8515-8519; c) Y. Ye, Z. Ma, R.-B. Lin, R. Krishna, W. Zhou, Q. Lin, Z. Zhang, S. Xiang, B. Chen, J. Am. Chem. Soc. 2019, 141, 4130-4136; d) H.-M. Wen, C. Liao, L. Li, L. Yang, J. Wang, L. Huang, B. Li, B. Chen, J. Hu, Chem. Commun. 2019, 55, 11354-11357; e) O. T. Qazvini, R. Babarao, S. G. Telfer, Chem. Mater. 2019, 31, 4919-4926; f) A. Luna-Triguero, J. M. Vicent-Luna, R. M. Madero-Castro, P. Gómez-Álvarez, S. Calero, ACS Appl. Mater. Interfaces 2019, 11, 31499-31507; g) R. Liu, Q.-Y. Liu, R. Krishna, W. Wang, C.-T. He, Y.-L. Wang, Inorg. Chem. 2019, 58, 5089-5095; h) Y.-P. Li, Y. Wang, Y.-Y. Xue, H.-P. Li, Q.-G. Zhai, S.-N. Li, Y.-C. Jiang, M.-C. Hu, X. Bu, Angew. Chem. Int. Ed. 2019, 58, 13590-13595; i) L. Li, J. Wang, Z. Zhang, Q. Yang, Y. Yang, B. Su, Z. Bao, Q. Ren, ACS Appl. Mater. Interfaces 2019, 11, 2543-2550; j) R.-B. Lin, L. Li, H. Wu, H. Arman, B. Li, R.-G. Lin, W. Zhou, B. Chen, J. Am. Chem. Soc. 2017, 139, 8022-8028; k) D.-M. Chen, X.-H. Liu, J.-Y. Tian, J.-H. Zhang, C.-S. Liu, M. Du, Inorg. Chem. 2017, 56, 14767-14770.
- [3] a) Y.-Z. Li, G.-D. Wang, H.-Y. Yang, L. Hou, Y.-Y. Wang, Z. Zhu, Inorg. Chem. Front. 2020, 7, 746-755; b) O. T. Qazvini, R. Babarao, Z.-L. Shi, Y.-B. Zhang, S. G. Telfer, J. Am. Chem. Soc. 2019, 141, 5014-5020; c) B. R. Barnett, S. T. Parker, M. V. Paley, M. I. Gonzalez, N. Biggins, J. Oktawiec, J. R. Long, J. Am. Chem. Soc. 2019, 141, 18325-18333; d) M. H. Mohamed, Y. Yang, L. Li, S. Zhang, J. P. Ruffley, A. G. Jarvi, S. Saxena, G. Veser, J. K. Johnson, N. L. Rosi, J. Am. Chem. Soc. 2019. 141, 13003-13007; e) L. Li, R.-B. Lin, R. Krishna, H. Li, S. Xiang, H. Wu, J. Li, W. Zhou, B. Chen, Science 2018, 362, 443-446; f) L. Li, H.-M. Wen, C. He, R.-B. Lin, R. Krishna, H. Wu, W. Zhou, J. Li, B. Li, B. Chen, Angew. Chem. Int. Ed. 2018, 57, 15183-15188; g) P.-Q. Liao, N.-Y. Huang, W.-X. Zhang, J.-P. Zhang, X.-M. Chen, Science 2017, 356, 1193-1196; h) A. Cadiau, K. Adil, P. M. Bhatt, Y. Belmabkhout, M. Eddaoudi, Science 2016, 353, 137-140; i) L.-Y. Du, W.-J. Shi, L. Hou, Y.-Y. Wang, Q.-Z. Shi, Z. Zhu, Inorg. Chem. 2013, 52, 14018-14027; j) S. Horike, K. Kishida, Y. Watanabe, Y. Inubushi, D. Umeyama, M.

Sugimoto, T. Fukushima, M. Inukai, S. Kitagawa, J. Am. Chem. Soc. 2012, 134, 9852-9855.

- [4] R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, *Nature* **2005**, *436*, 238-241.
- [5] F. Luo, C. Yan, L. Dang, R. Krishna, W. Zhou, H. Wu, X. Dong, Y. Han, T.-L. Hu, M. O'Keeffe, L. Wang, M. Luo, R.-B. Lin, B. Chen, *J. Am. Chem. Soc.* 2016, *138*, 5678-5684.
- [6] K.-J. Chen, H. S. Scott, D. G. Madden, T. Pham, A. Kumar, A. Bajpai, M. Lusi, K. A. Forrest, B. Space, J. J. P. IV, M. J. Zaworotko, *Chem* 2016, *1*, 753-765.
- [7] J. Lee, C. Y. Chuah, J. Kim, Y. Kim, N. Ko, Y. Seo, K. Kim, T. H. Bae, E. Lee, Angew. Chem. Int. Ed. 2018, 57, 7869-7873.
- [8] Y.-L. Peng, T. Pham, P. Li, T. Wang, Y. Chen, K.-J. Chen, K. A. Forrest, B. Space, P. Cheng, M. J. Zaworotko, Z. Zhang, *Angew. Chem. Int. Ed.* 2018, 57, 10971-10975.
- [9] H. Liu, Q. Wang, M. Zhang, J. Jiang, *CrystEngComm* 2015, 17, 4793-4798.
- [10] V. A. Blatov, Struct. Chem. 2012, 23, 955-963.
- [11] J. Rouquerol, P. Llewellyn, F. Rouquerol, Stud. Surf. Sci. Catal. 2007, 160, 49-56.
- [12] S. Xiang, W. Zhou, J. M. Gallegos, Y. Liu, B. Chen, J. Am. Chem. Soc. 2009, 131, 12415-12419.
- [13] Y. Zhang, L. Yang, L. Wang, S. Duttwyler, H. Xing, Angew. Chem. Int. Ed. 2019, 58, 8145-8150.
- [14] A. A. Lysova, D. G. Samsonenko, P. V. Dorovatovskii, V. A. Lazarenko,
 V. N. Khrustalev, K. A. Kovalenko, D. N. Dybtsev, V. P. Fedin, *J. Am. Chem. Soc.* 2019, *141*, 17260-17269.
- [15] M. C. Das, H. Xu, S. Xiang, Z. Zhang, H. D. Arman, G. Qian, B. Chen, *Chem. Eur. J.* 2011, *17*, 7817-7822.
- [16] D. Tanaka, M. Higuchi, S. Horike, R. Matsuda, Y. Kinoshita, N. Yanai, S. Kitagawa, Chem. Asian J. 2008, 3, 1343-1349.
- [17] D. G. Samsonenko, H. Kim, Y. Sun, G.-H. Kim, H.-S. Lee, K. Kim, *Chem. Asian J.* 2007, 2, 484-488.
- [18] Y.-L. Huang, P.-L. Qiu, H. Zeng, H. Liu, D. Luo, Y. Y. Li, W. Lu, D. Li, *Eur. J. Inorg. Chem.* **2019**, 4205-4210.
- F. Zheng, L. Guo, B. Gao, L. Li, Z. Zhang, Q. Yang, Y. Yang, B. Su, Q.
 Ren, Z. Bao, ACS Appl. Mater. Interfaces 2019, 11, 28197-28204.
- [20] H. Li, L. Li, R.-B. Lin, G. Ramirez, W. Zhou, R. Krishna, Z. Zhang, S. Xiang, B. Chen, ACS Sustainable Chem. Eng. 2019, 7, 4897-4902.
- [21] J. Wang, L. Li, L. Guo, Y. Zhao, D. Xie, Z. Zhang, Q. Yang, Y. Yang, Z. Bao, Q. Ren, *Chem. Eur. J.* 2019, 25, 15516-15524.
- [22] A. L. Myers, J. M. Prausnitz, A.I.Ch.E.J. 1965, 11, 121-127.
- [23] G. Chang, B. Li, H. Wang, T. Hu, Z. Bao, B. Chen, *Chem. Commun.* 2016, *52*, 3494–3496.
- [24] Y. Wang, M. He, X. Gao, X. Wang, G. Xu, Z. Zhang, Y. He, *Inorg. Chem. Front.* 2019, 6, 263-270.
- [25] X. Duan, H. Wang, Z. Ji, Y. Cui, Y. Yang, G. Qian, J. Solid State Chem. 2016, 241, 152-156.
- [26] a) T. Xu, Z. Jiang, M. He, X. Gao, Y. He, *CrystEngComm* **2019**, *21*, 4820-4827; b) X. Gao, T. Xu, Z. Jiang, H. Yu, Y. Wang, Y. He, *Dalton Trans.* **2019**, *48*, 16793-16799.
- [27] G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122...
- [28] a) A. L. Spek, Acta Crystallogr., Sect. D: Biol. Crystallogr., 2009, 65, 148–155; b) A. L. Spek, Acta Crystallogr., Sect. C: Struct. Chem., 2015, 71, 9–18.
- [29] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.
- [30] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, 77, 3865.
- [31] a) G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* **1996**, *6*, 15-50; b) G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169-11186; cG. Kresse, *J. Non-Cryst. Solid* **1995**, *192-193*, 222-229; dG. Kresse, J. Hafner, *Phys. Rev. B* **1994**, *49*, 14251-14264.

WILEY-VCH

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

A microporous MOF featuring inorganic nitrate ions immobilized on pore surface as C_2H_2 recognition sites was constructed, exhibiting the promising potential for the separation of CO₂ and CH₄ from C_2H_2 at ambient conditions.



X. Gao, H. Zhong, Y. Zhang, Y. Yao, D.-I. Chen,* and Y. He*

Page No. – Page No.

A microporous MOF with inorganic nitrate ions immobilized in pore surface displaying efficient C₂H₂ separation and purification

Key Topic for the Table of Contents: Gas separation