A water-stable fcu-MOF material with exposed amino groups for the multi-functional separation of small molecules

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ABSTRACT The energy-efficient purification of methane from C₂-hydrocarbons is of great significance for the upgrading of natural gas. So does the capture of carbon dioxide for remission of greenhouse effect. It is well established that some functional sites, such as open metals sites, Lewis basic nitrogen sites and fluorine groups, have shown significantly enhanced affinity toward more polarizable molecules. Thus, a water-stable Eu³⁺-based fcu-metal-organic framework (MOF) (compound 1) with amino functional groups has been successfully constructed through a reticular chemistry approach. As a result, the activated compound 1 exhibits moderately high uptakes of C₂-hydrocarbons, but a less obvious adsorption of CH₄ at the same conditions. Among them, the adsorption capacity of C₂H₂ is up to 143.6 cm³ cm⁻³ and a relatively high selectivity of C₂H₂/CH₄ (107.7) is obtained at near room temperature. Moreover, compound 1 is also validated as an exceptional adsorbent for CO₂ capture, with the fairly high capacity of CO₂ (92.6 cm³ cm⁻³) and CO₂/N₂ selectivity (151.7) at ambient conditions. The excellent performance of compound 1 is mainly driven by the exposed amino functional groups within the contracted pores. Such effect thus leads to the achievement of dual-functional platform for methane purification and carbon dioxide capture. Furthermore, compound 1 features a satisfactory water stability, which is confirmed by the powder X-ray diffraction (PXRD) analysis and the retest of porosity after being soaked in water.

Keywords: porous material, metal-organic frameworks, small molecule gas, functional groups, gas selectivity

INTRODUCTION

Methane (CH₄) is the main valuable component of natural gas and perceptibly considered as an alternative to conventional fossil fuels due to its abundance and en-

vironment-friendly features [1–4]. Hence, to obtain high-purity methane from C₂-hydrocarbon impurities is of great importance for the upgrading of natural gas. Nevertheless, this purification has been mainly accomplished by energy-intensive cryogenic fractionation at present. Besides, the excessive release of CO₂ from the typical power plants results in the worrisome greenhouse effect [5–7]. However, the conventional alkylamine-containing liquids applied for CO₂ capture are faced with high regeneration cost. Thus, the construction of efficient gas capture and purification system is necessary, especially in energy-efficient ways.

Adsorptive separation based on porous materials is considered as a non-thermal separation. Thus, it is regarded as a suitable alternative to save the tremendous energy of distillation-based separation. Metal-organic frameworks (MOFs) [8–23], a class of promising porous materials, offer promise for gas storage and separation due to their highly versatile nature in pore structure and functionalization [24–37]. Some accomplished pore tuning strategies were used to directly increase the pore sizes within MOFs aiming at gas storage at high pressure. Nevertheless, the contracted pore apertures, relative to the enlarged pores, possibly show better performance at gas separation due in part to their potential size sieve effect. Moreover, many studies have been realized that MOFs with functional sites, including open metal sites (OMS) [38], Lewis basic nitrogen sites [39] and fluorine groups [40], show enhanced affinity toward more polarizable molecules *via* thermodynamic selectivity. In fact, many copper- and zinc-based MOFs have indeed shown the benchmark performance at gas separation and purification. However, most of them are hardly deployed under real-world conditions since they undergo hydro-

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lysis in the presence of moisture [41,42].

Herein, we opted to use a 2-connected bridging ligand equipped with amino group, to successfully construct a rare-earth (RE) fcu-MOF material (compound **1**) [43,44]. As a result, the highly-connected fcu topology guarantees the rigidity of framework to a great extent. It is depressing that few RE based MOFs were explored for gas separation and purification, plausibly due to that most of MOFs lack OMS and/or robustly available porosity. Thus, we incorporated amino functional groups on the pore walls of this material, which would selectively enhance the affinity toward polarizable molecules (i.e. C₂-hydrocarbon and CO₂) (Table 1), thus further improve the gas selectivity. As a result, this activated material exhibits moderately high uptakes of C₂-hydrocarbon (86.6–143.6 cm³ cm⁻³), but a less obvious adsorption for CH₄ (22.6 cm³ cm⁻³) at near room temperature. Thus, the relatively high C₂/CH₄ selectivities (35.9–138.8) have been obtained which are even comparable to other top-performing materials reported so far. Moreover, most MOF adsorbents show moderate uptake of CO₂ (generally below 2.0 mmol g⁻¹) and the selectivities of CO₂/N₂ in these MOFs are generally below 100. Conversely, compound **1** features a potential block-off of N₂ gas, thus resulting in a very high selectivity of CO₂/N₂ separation up to 151.7 at ambient conditions. Thus, compound **1** is also validated as an exceptional adsorbent for CO₂ capture among the reported MOFs, with the moderately high capacity of CO₂ (92.6 cm³ cm⁻³) and very high CO₂/N₂ selectivity (151.7). Herein, this resultant fine-tuned MOF material permits the achievement of a dual-functional platform for effective CH₄ purification and carbon dioxide capture. Such excellent performance of this MOF adsorbent is mostly driven by the incorporation of amino functional groups within the restricted apertures. It is noteworthy that this material features an exceptional chemical stability, further confirmed by powder X-ray diffraction (PXRD) analysis and the retest of porosity after being soaked in deionized water for two days.

EXPERIMENTAL SECTION

Materials and methods

All reagents and solvents were commercially available and used without further purification. Infrared spectrum (IR) was performed on a Thermo Fisher Nicolet iS10 spectrometer using KBr pellets. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209F3 with a heating rate of 10°C min⁻¹ in N₂ atmosphere. PXRD patterns were collected in the 2 θ = 5°–60° range on an

Table 1 Important physical parameters of the selected gas adsorbates

Adsorbate	Kinetic diameter (Å)	Polarizability (10 ²⁵ cm ⁻³)
N ₂	3.64–3.80	17.403
CO ₂	3.3	29.11
CH ₄	3.758	25.93
C ₂ H ₂	3.3	33.3–39.3
C ₂ H ₄	4.163	42.52
C ₂ H ₆	4.443	44.3–44.7

X'Pert PRO diffractometer with Cu K α (λ = 1.542 Å) radiation at room temperature. The morphology was investigated using a field-emission scanning electron microscopy (FE-SEM, Hitachi S4800). Crystallographic measurements were taken on an Oxford Xcalibur Gemini Ultra diffractometer equipped with an Atlas detector using graphite-monochromatic Mo K α radiation (λ = 0.71073 Å) at 293 K.

Synthesis of Eu³⁺-based fcu-MOF (compound **1**)

A mixture of the organic linker 2-aminoterephthalic acid (H₂BDC-NH₂, 131.3 mg, 0.725 mmol), Eu(NO₃)₃·6H₂O (323.4 mg, 0.725 mmol) and 2-fluorobenzoic acid (2-FBA, 812.6 mg, 5.8 mmol) was dissolved into 41.5 mL mixed solvent (*N,N*-dimethylformamide (DMF)/H₂O/HNO₃, 36.5 mL/3 mL/2 mL, HNO₃ (3.5 mol L⁻¹ in DMF)) in a 100-mL Teflon cup. The Teflon cup was capped and heated in an oven at 110°C for 60 h. The transparent polyhedral crystals were obtained by filtration and washed with DMF several times to afford Eu³⁺-based fcu-MOF.

Gas sorption measurements

The gas sorption isotherms were measured by the Micromeritics ASAP 2020 surface area analyzer. In order to remove all the guest solvents from compound **1**, the fresh sample was guest-exchanged with dry acetone at least 10 times, filtered and degassed at 298 K for 1 day and 373 K for 10 h successively under high vacuum until the outgas rate was 5 μ mHg min⁻¹ to yield the activated material for further gas sorption studies. The sorption measurement was maintained at 77 K with liquid nitrogen. An ice-water bath and water bath were used for adsorption isotherms at 273 and 298 K, respectively.

RESULTS AND DISCUSSION

Reactions of Eu(NO₃)₃·6H₂O with the organic linker, H₂BDC-NH₂ (Fig. S1), in the solvothermal condition successfully yielded transparent polyhedral crystals Eu-

BDC-NH₂ (compound **1**). The morphology of the synthesized material was characterized comprehensively by optical microscopy and FE-SEM. As illustrated in Fig. 1, it displays a homogeneous polyhedral morphology with a particle size of around 50 μm . The phase purity of the bulk material was further confirmed by PXRD analyses (Fig. S2).

The crystal structure reveals that compound **1** crystallizes in *Fm*3*m* space group as depicted in Fig. 2. The adjacent Eu³⁺ ions are bridged with deprotonated BDC-NH₂²⁻ and μ_3 -OH to give 12-connected MBBs [Eu₆(μ_3 -OH)₈(O₂C-)₁₂] (Fig. 2a). Accordingly, the carbon atoms of the coordinated carboxylates act as points of extension, which further coordinate the carboxylate ligands and MBBs to form a 3D framework (Fig. 2b). The resultant compound **1** features a rigid fcu topology that is isostructural to the net in the NDC-fcu-MOF [43]. The structure in compound **1** encloses two distinct cages of octahedral and tetrahedral cages. Correspondingly, the average sizes are estimated to be 4.0 and 7.8 Å for octahedral and tetrahedral cages, respectively. Most importantly, extensive amino groups expose on the pore wall within the framework, rendering it bright potential for small molecule separation and purification.

We further characterized its permanent porosity. After the sufficient acetone-exchange, the crystal sample was

Figure 1 The optical microscopy image (a) and FE-SEM image of compound **1** (b), displaying the homogeneous polyhedral morphology with a particle size of around 50 μm .

evacuated at 298 K for 1 day and 373 K for 10 h successively to yield the activated material. It is noteworthy that the structure of compound **1** after activation still holds the pristine topology, as determined by PXRD analysis (Fig. S2). Permanent porosity studies of activated **1** were performed by nitrogen sorption studies at 77 K. The corresponding isotherms (Fig. 3) show a classical Type-I sorption behavior with a saturation uptake of 9.13 mmol g⁻¹ and a pore volume of 0.32 cm³ g⁻¹. Thus, the corresponding Brunauer-Emmett-Teller (BET) surface area was estimated to be 605.8 m² g⁻¹. Moreover, the distribution of pore aperture was dominantly focused on 4.1 and 7.3 Å, basically consistent with the theoretical results from the crystal structure. Particularly, an exceptional water stability of compound **1** was determined *via*

Figure 2 X-ray single crystal structure of compound **1** indicating that, (a) the 12-connected Eu₆O₄(OH)₄(CO₂)₁₂ molecular building block (MBB) and the 2-connected linker (2-aminoterephthalic acid); (b) the bigger octahedral cage constructed from 6 MBBs and 12 ligands with a diameter of around 7.8 Å, while the smaller tetrahedral cage constructed from 4 MBBs and 6 ligands with a diameter of around 4.0 Å, and the 3D framework is viewed from a, b or c axes (C, white; O, red; Eu, cambridge blue; N, purple; H, green).

Figure 3 N_2 sorption isotherms and pore size distribution of compound **1** at 77 K. Closed symbols, adsorption; open symbols, desorption.

the PXRD analysis and the retest of porosity after soaking it in deionized water for 2 days (Figs S2 and S3). In other words, compound **1** is stable enough to maintain its structural integrity from water/moisture attack under real-world conditions. Further, the thermogravimetric

analysis of compound **1** indicates that its framework could be thermally stable up to 350°C, featuring its highly thermal stability (Fig. S4).

Inspired by the extensive amino groups within the contracted pores and water stability of compound **1**, we further investigated it for gas adsorption and separation at low pressure. Thus, the adsorption tests of C_2 hydrocarbons (i.e., C_2H_2 , C_2H_4 , and C_2H_6) and CH_4 were carried out at 298 and 273 K, respectively (Fig. 4). The C_2 hydrocarbon adsorption isotherms especially for C_2H_2 isothermal, are much steeper than the corresponding isothermal of CH_4 , indicating relatively stronger affinity of the framework toward C_2 over CH_4 . Moreover, the gas uptake capacities at atmospheric pressure (Table 2), finally follow the sequence of $C_2H_2 > C_2H_4 > C_2H_6 > CH_4$. Thus, it is a desired feature for compound **1** on separating C_2 from CH_4 . Among them, the adsorption capacity of C_2H_2 is highest up to $113.1 \text{ cm}^3 \text{ cm}^{-3}$ ($75.4 \text{ cm}^3 \text{ g}^{-1}$), significantly higher than that of CH_4 ($17.9 \text{ cm}^3 \text{ cm}^{-3}$) at ambient conditions (Fig. 4b). The C_2H_2 uptake of compound **1** is lower than some copper-based MOF materials with ultra-high porosity and open metal sites, such as

Figure 4 Single-component adsorption isotherms of compound **1** for C_2 -hydrocarbons and CH_4 at 273 (a) and 298 K (b); single-component adsorption isotherms of compound **1** for CO_2 and N_2 at 273 (c) and 298 K (d).

Table 2 The gas sorption, selectivity and Q_{st} of compound **1**

Adsorbate	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	CH ₄	CO ₂	N ₂
Uptake capacity at 273 K and 1.0 bar (cm ³ cm ⁻³)	143.6	94.9	86.6	22.6	126.4	4.5
Uptake capacity at 298 K and 1.0 bar (cm ³ cm ⁻³)	113.1	76.8	71.9	17.9	92.6	3.7
S_{i/CH_4} or S_{i/N_2} at 273 K	107.7	47.3	39.7	/	474.1	/
S_{i/CH_4} or S_{i/N_2} at 298 K	33.4	30.5	22.3	/	151.7	/
Q_{st} (kJ mmol ⁻¹)	34.5	32.8	34.0	16.1	18.3	13.0

ZJNU-71 (200.4 cm³ g⁻¹) [45], ZJU-195 (214 cm³ g⁻¹) [46] and FJI-H8 (224 cm³ g⁻¹) [47]. However, it is significantly higher than other promising materials, such as M'MOF-20a (21 cm³ g⁻¹) [48], UTSA-72a (27.8 cm³ g⁻¹) [49], UTSA-15a (34 cm³ g⁻¹) [50] and ZJU-30 (52.6 cm³ g⁻¹) [51]. Especially, the adsorption capacity of C₂H₂ can be further improved to 143.6 cm³ cm⁻³ when the temperature reduces to 273 K (Fig. 4a). Such distinctive adsorption performance of compound **1** is mainly attributed to the enhanced affinity between the extensive amino groups on the pore wall and the C₂ hydrocarbons.

In light of the aforementioned results, we envisioned that such feature of compound **1** should be available for other separation. Thus, we further explored the separation of other small molecules, including the capture of

CO₂ over N₂. As expected, almost no uptake for N₂ gas was observed at both 273 and 298 K. Conversely, it selectively captured CO₂ molecule up to 126.4 cm³ cm⁻³ and 92.6 cm³ cm⁻³ at 273 and 298 K, respectively (Fig. 4c, d). Such exceptional features of compound **1** lead to the achievement of dual-functional platform in methane purification and CO₂ capture.

We further utilized the recognized ideal adsorbed solution theory (IAST) to calculate the equilibrium selectivity for C₂/CH₄ (50/50, v/v) and CO₂/N₂ (20/80, v/v) mixtures. The results of IAST calculations for C₂/CH₄ and CO₂/N₂ at 273 and 298 K are expressed in Fig. 5 and Table 2. Compound **1** exhibits a relatively high selectivity for C₂/CH₄ both at 273 and 298 K (Fig. 5a, b). Especially, the selectivity value of C₂H₂ over CH₄ is high up to 33.4 at

Figure 5 IAST calculations of compound **1** for C₂/CH₄ selectivity at 273 (a) and 298 K (b); IAST calculations of compound **1** for CO₂/N₂ selectivity (c); the isosteric heats of gases in compound **1** (d); comparison of reported MOF materials for C₂H₂/CH₄ selectivity (e); comparison of reported MOF materials for CO₂ uptake and CO₂/N₂ selectivity (f).

ambient conditions, among the promising MOF materials ever reported for C_2 -hydrocarbons/methane separation (Fig. 5e). The value of C_2H_2/CH_4 selectivity for compound **1** is just lower than those of ZJU-195 (43.4) [46] and FJI-C1 (39.3) [52], but higher than other porous materials like ZJU-30 (9.59) [51], UTSA-222a (16) [53] and BUT-70B (23.3) [54]. Moreover, the selectivity of C_2H_2 versus CH_4 can be further improved to 107.7 when the operation temperature is decreased to 273 K. Apparently, compound **1** is a promising adsorbent for the upgrading of fairly.

Moreover, fairly high selectivities of CO_2/N_2 have been obtained up to 474.1 and 151.7 for 273 and 298 K, respectively, owing to the almost block-off for N_2 adsorption. Thus, we further compared the CO_2 uptake and the CO_2/N_2 selectivity among the reported MOF materials (Fig. 5f). We can read that most MOF adsorbents show moderate uptake of CO_2 (generally below 2.0 mmol g^{-1}) [55–59] except few MOFs materials like Mg-MOF-74 [60–62] with ultra-high open metal sites. Furthermore, the selectivity values of CO_2/N_2 are generally below 100 for most of MOF materials. Thus, compound **1** is recognized as an exceptional adsorbent for CO_2 capture among the reported MOF materials, overall considering the moderately high capacity of CO_2 and very high CO_2/N_2 selectivity.

Such excellent performance reveals the bright promise of compound **1** for small molecule separation and purification. The aforementioned results were further confirmed by the isosteric heat of adsorption (Q_{st}) which was calculated via the experimental adsorption data, as illustrated in Fig. 5d. As anticipated, all the Q_{st} values of C_2 gases were found to be over 30.0 kJ mol^{-1} while only 16.1 kJ mol^{-1} was observed for CH_4 . Interestingly, the isosteric heat of C_2 adsorption does not decrease as gas loading increases. Thus, it indicates the homogenous binding affinity toward C_2 hydrocarbons within the whole range of gas loading. Meanwhile, the isosteric heat value of CO_2 (18.3 kJ mol^{-1}) is higher than the corresponding value of N_2 (12.9 kJ mol^{-1}), further confirming its much stronger affinity of framework toward more polarizable molecules.

CONCLUSIONS

In summary, we herein reported a water-stable Eu^{3+} -based fcu-MOF material (compound **1**) with exposed amino groups for multi-functional separation of small molecules. The foregoing results of compound **1** permit the achievement of dual-functional platform for methane purification and CO_2 capture. The adsorbent affords not

only the effective separation of C_2 hydrocarbon from CH_4 , but the excellent capture of CO_2 over N_2 . Among them, the adsorption capacity of C_2H_2 is up to $143.6 \text{ cm}^3 \text{ cm}^{-3}$ and a high selectivity of C_2H_2/CH_4 (107.7) are obtained at near room temperature. Moreover, compound **1** is also validated as an exceptional adsorbent for CO_2 capture, overall considering the fairly high capacity of CO_2 ($92.6 \text{ cm}^3 \text{ cm}^{-3}$) and CO_2/N_2 selectivity (151.7) at ambient conditions. The excellent water stability further makes this fcu-MOF material as a particularly potential candidate for natural gas upgrading and CO_2 capture.

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Author contributions Jiang K designed and performed the experiments, analyzed the data, and wrote the paper; Zhang L conceived the experiments and contributed to gas sorption measurements; Xia T synthesized the MOF Eu-BDC- NH_2 ; Yang Y and Li B analyzed the data; Cui Y and Qian G conceived the framework of this paper and revised the paper. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Chemical stability data, thermo stability data and the performance comparison data with other MOF materials are available in the online version of the paper.

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具有水稳性且携带氨基官能团的多功能fcu-MOF用于小分子分离

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摘要 甲烷的高效净化对天然气的升级改造具有重要意义。有效捕获二氧化碳对缓解温室效应同样具有重要的科研价值。众所周知, 在材料内部引入一些功能位点, 如开放金属位点、路易斯碱氮位点、氟基团, 可以显著提高材料对易极化分子的亲和力。本文中, 我们成功地构建了一种具有水稳性且携带氨基功能基团的铜基金属有机框架材料。活化后的样品表现出较强的 C_2 气体吸附, 但对甲烷的吸附不明显。其中, 在近室温条件下, 样品对乙炔的吸附量可达 $143.6\text{ cm}^3\text{ cm}^{-3}$, 并且可获得较高的乙炔/甲烷选择性分离系数(107.7)。此外, 该材料还被证实是一种优异的二氧化碳捕获吸附剂。在环境条件下, 具有较高的二氧化碳吸附量($92.6\text{ cm}^3\text{ cm}^{-3}$)和二氧化碳/氮气选择性分离系数(151.7)。上述优异的小分子吸附分离性能主要由收缩孔笼内大量裸露的氨基官能团驱动所致。这种独特的效应使该材料呈现优异的甲烷净化和二氧化碳捕获等多功能属性。此外, 进一步PXRD分析与水中浸泡后孔隙率的重新测试证实, 该材料具有令人满意的水稳性。