

RESEARCH ARTICLE

View Article Online
View Journal | View IssueCite this: *Inorg. Chem. Front.*, 2023,
10, 2438

A dense 3d–4f metal–organic framework with “gas pockets” for highly efficient CH₄/N₂ separation†

 Li-Min Zhu,^a Wen-Liang Li,^a Tian-Ran Li,^a Lin-Ping Shi,^a Li-Ting Li,^a
Zhao-Quan Yao,^{*a} Hong-Liang Huang,^{id *b} Jiong-Peng Zhao^{id *a} and
Fu-Chen Liu^{id *a}

In this work, we report a multi-component MOF [CuCe L(Cl₄-bdc)_{0.5}(H₂O)₂·(H₂O)₆]_n (L = 1*H*-pyrazole-3,4,5-tricarboxylic acid, Cl₄-bdc = 2,3,5,6-tetrachloroterephthalate) with a pillar-layered structure. In the structure, the polydentate ligand (L) linked Cu^{II} and Ce^{III} atoms constitute 3d–4f layers that serve as the pedestal base and the chlorinated Cl₄-bdc ligands acting as bolsters are installed between the layers through Ce^{III}. The moderate pore size and the unique chloride decorated surface of channels endow this MOF with excellent separation ability for methane (CH₄) and nitrogen (N₂). According to the adsorption tests, this MOF exhibits a high adsorption capacity for CH₄ (28.41 cm³/cm³) at 298 K and 1 bar, while the N₂ adsorption capacity is only 3.43 cm³/cm³. The DFT calculations demonstrate that the adjacent Cl₄-bdc in the network can act as “gas pockets” or nano traps to immobilize the CH₄ molecules effectively through multiple interactions between Cl atoms and CH₄. The high performance of this MOF in CH₄/N₂ separation has been verified by the outstanding IAST selectivity of 13.32 and breakthrough experiments. This work provides a new perspective for capturing CH₄ from coal-mine gas to recover fuel and reduce greenhouse gas emissions.

Received 7th February 2023,
Accepted 15th March 2023

DOI: 10.1039/d3qi00235g

rsc.li/frontiers-inorganic

Due to the rapid consumption of fossil fuels, energy and environmental problems have to be solved urgently in this century. Conventional natural gas (mainly composed of methane) is considered to be an ideal alternative to petroleum fuels because of its abundance and cleanliness.¹ Unconventional natural gas (such as coal bed methane (CBM), landfill gas, and shale gas) also produces a large amount of methane, which is an excellent complement to conventional natural gas.² Currently, due to the lack of suitable purification methods, a large amount of methane is introduced into air, which not only brings about a serious greenhouse effect (21 times that from CO₂) but also causes a waste of energy.³ Therefore, utilization of this low-quality natural gas is extremely important. Generally, in unconventional natural gas, the concentration of nitrogen (N₂) is much higher than that of

methane (*e.g.* the methane concentration in CBM is less than 30%), which limits its direct utilization.^{2,3} So, the separation of CH₄/N₂ mixtures to obtain high purity methane has important industrial value. Currently, the prevalent industrial approach to separate methane from CH₄/N₂ mixtures is cryogenic distillation (boiling point: 112 K for CH₄ and 77 K for N₂) which is not only an energy-intensive process but also a burden to the environment.⁴ Thus, a cost- and energy-efficient CH₄/N₂ separation process is urgently desired.

Compared with traditional cryogenic distillation methods, adsorbent-based gas adsorption using porous materials is an economical and energy-efficient method.⁵ Many traditional porous materials, such as zeolites and porous carbons, have been extensively studied for CH₄ purification.^{6–12} Although these kinds of porous material adsorbents have been widely reported and have exhibited prominent adsorption separation performance toward CH₄/N₂ mixtures, their selectivity and yields are still low. The main reason is the similar physical properties of CH₄ and N₂, including polarizability and kinetic diameters (3.8 Å for CH₄ and 3.64 Å for N₂).^{13–23} As a new class of crystalline porous materials, metal–organic frameworks (MOFs) featuring diverse structures, programmable topology, and tailorable and modifiable porosity offer an ideal platform for gas adsorption and separation.^{3,24–26} Besides, the crystal-

^aSchool of Chemistry and Chemical Engineering, TKL of Organic Solar Cells and Photochemical Conversion, Tianjin University of Technology, Tianjin 300384, China. E-mail: yaozq@email.tjut.edu.cn, zhaojp@tjut.edu.cn, fcliu@tjut.edu.cn

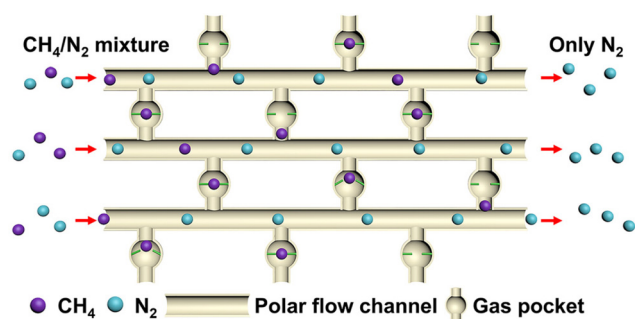
^bSchool of Chemistry and Chemical Engineering, Tiangong University, Tianjin 300387, China. E-mail: huanghongliang@tiangong.edu.cn

† Electronic supplementary information (ESI) available: Additional crystallographic data. CCDC 2223795. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3qi00235g>

line nature of MOFs also provides an opportunity to investigate the gas adsorption mechanisms. Up to now, various methods have been used to improve the separation performance of CH₄/N₂ in MOF systems including the design and synthesis of new structures, decorating with functional groups, compositing with other materials *etc.* By using these methods, although the interaction between CH₄ and frameworks has been improved, the adsorption and separation performances are still unsatisfactory.^{18,20,27,28} Inspired by the vital effect of R-H...X (X = heteroatoms in MOFs) interaction in hydrocarbon (alkene and alkane, alkene and alkyne) separation,^{29–34} decorating heteroatoms in the inner wall of channels or frameworks might endow the frameworks with a stronger binding effect for CH₄. Besides, considering the non-polar nature of CH₄ molecules, anchoring heteroatoms to specific sites (*e.g.* cages or nanopores) using the inherent confinement effect to enhance the host framework–guest CH₄ molecule interaction might be a promising protocol (Scheme 1).

In this work, a novel pillar-layered MOF [CuCeL(Cl₄-bdc)_{0.5}(H₂O)₂(H₂O)₆]_n (**1**) (L: 3,4,5-pyrazoletricarboxylate; Cl₄-bdc: 2,3,5,6-tetrachloroterephthalate) has been constructed successfully. In this structure, L connected Ce^{III} and Cu^{II} atoms form 3d–4f layers, while the Cl₄-bdc ligands which act as pillars are installed between layers through Ce^{III} to form the 3D-pillar-layered framework with obvious 1D channels (9.0 Å × 9.5 Å) along the *a*-axis. On the sides of the channels, a large number of small hallways constructed by the adjacent Cl₄-bdc ligands were formed (5.0 Å × 7.0 Å × 9.5 Å). According to the result of DFT calculation, due to the synergistic effect between the confinement effect and abundant C–H...Cl interactions in these small hallways, the methane molecules can be trapped in these confined spaces effectively. As a result, **1** presents a high adsorption capacity for CH₄ (28.41 cm³/cm³ at 298 K) and a high IAST selectivity of 13.32 for CH₄/N₂ separation.

Single-crystal X-ray diffraction study on a suitable single crystal of [CuCeL(Cl₄-bdc)_{0.5}(H₂O)₂(H₂O)₆]_n at 298 K revealed that **1** crystallizes in the triclinic space group *P* $\bar{1}$ (Table S1†) with high densities of 2.145 g cm⁻³ and 1.700 g cm⁻³ for the complex and the activated framework, respectively. The asymmetric unit cell has one Ce^{III}, one Cu^{II}, one L ligand, half Cl₄-bdc ligand, two coordinated water molecules and six free water molecules (Fig. S1†). As shown in Fig. 1a, each Cu ion presents



Scheme 1 Schematic representation of the 1D channels and gas pockets in this pillar-layered MOF.

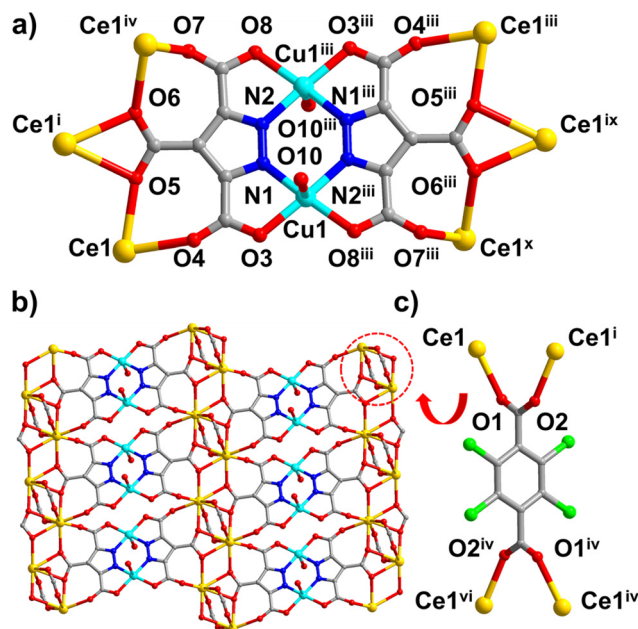


Fig. 1 (a) Coordination modes and linkage of the Cu ions and L ligands. (b) The 3d–4f Cu–Ce layer bridged by L ligands. (c) Coordination modes of bridging Cl₄-bdc ligands. Symmetry codes: ⁱ 2 – X, 1 – Y, 1 – Z; ⁱⁱ 1 + X, +Y, +Z; ⁱⁱⁱ 1 – X, 1 – Y, –Z; ^{iv} –1 + X, +Y, +Z; ^v 2 – X, 2 – Y, 1 – Z; ^{vi} +X, 1 + Y, +Z; ^{vii} 3 – X, 1 – Y, 1 – Z; ^{viii} 2 + X, +Y, +Z; ^{ix} –1 + X, +Y, –1 + Z; ^x 2 – X, 1 – Y, –Z.

a pyramidal coordination geometry: two Cu1 are chelated by two L ligands to form a Cu₂N₄O₄ coordination plane, in which N1, O3, and N2ⁱⁱⁱ, O8ⁱⁱⁱ are assigned to two L ligands, respectively. The axial positions of each Cu ion are occupied by one water molecule (O10). In this manner, two Cu ions (Cu1 and Cu1ⁱⁱⁱ) are bridged by two L ligands forming a Cu₂L₂ plane (Fig. 1a, Table S2†). The residual carboxyl oxygen atoms in L are coordinated to six Ce ions in the chelating mode to form the 3d–4f Cu–Ce layer (Fig. 1b). In this layer structure, each Ce^{III} ion is coordinated with five oxygen atoms which can be assigned to three L ligands (O4, O5, O6, O7) and a water molecule (O9), respectively. However in the perpendicular direction of the layer, each Ce^{III} ion is coordinated with four oxygen atoms which come from two Cl₄-bdc ligands (O1 and O2) (Fig. 1c and S2†). Consequently, the Cl₄-bdc ligands serve as pillars to sustain the neighbouring 3d–4f layers into a 3D framework with 1D open channels along the *a* and *c* axes (Fig. 2a–c).

As shown in Fig. 2a, the framework of **1** has moderate 1D channels with a rectangular cross-section in dimensions of 9.0 × 9.5 Å along the *a*-axis. The chlorinated Cl₄-bdc ligands which serve as pillars are located on either side of the channels and provide a large number of chloride atoms on the inner wall of channels. Besides, between the two neighbouring Cu^{II}–Ce^{III} layers, the adjacent Cl₄-bdc ligands also form small cavities or confined spaces in dimensions of 9.5 × 7.0 × 5.8 Å which are vertically distributed on both sides of the one-dimensional channel (Fig. 2c). Due to the narrow size of these cavities and abundant chlorine binding sites, various gas molecules with a

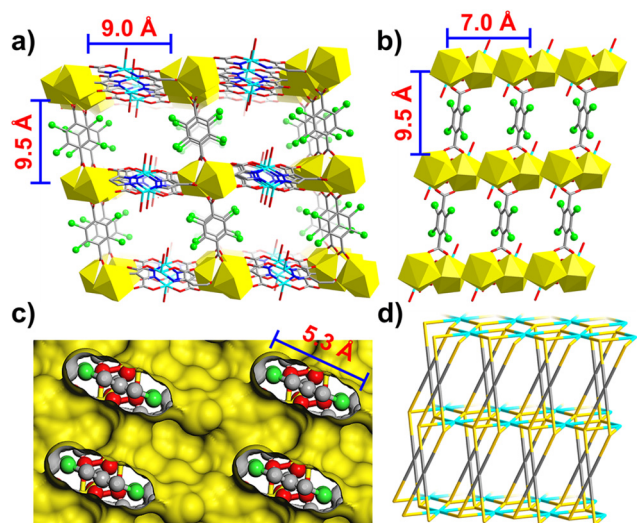


Fig. 2 (a and b) Three-dimensional structural diagram of **1** along the *a* and *c*-axes. Note: in order to clearly express the pore structure, all free solvent (water) molecules are deleted. (c) Internal structure of pores in **1** illustrated using the Connolly surface in yellow along the *b*-axis. (d) The topological map of **1** along the *c*-axis.

small size could access the cavity and be trapped within these “gas pockets”. In addition, PLATON analysis shows that the effective free volume of **1** can reach up to 43.3% of the crystal volume after squeezing out free water molecules.³⁵ To further investigate the structure, the topological simplification of the structure was carried out. As shown in Fig. 2d, the Cu_2L_2 units which connected to six Ce^{III} ions can be viewed as six connected nodes, while the $\text{Cl}_4\text{-bdc}$ ligands which coordinated with four Ce^{III} ions can be viewed as four-connected nodes. The Ce^{III} ions could be viewed as five-connected nodes. Finally, the whole framework can be simplified as a 4,5,6-connected topological network using the Schläfli notation $\{4^2; 8^4\}^{20}\{4^8; 6^2\}_2\{4^6; 6^6; 8^3\}$.^{36–38}

Due to the moderate pore size, large porosity, and exposed halogen atoms in specific cavities, this MOF may have a special interaction with some gas molecules and is beneficial in the field of adsorption and separation. Before the adsorption investigation, the purity of **1** and the rigidity of the framework were verified by PXRD and IR under different conditions (Fig. 3a and Fig. S3†). The PXRD data reveal that all diffraction

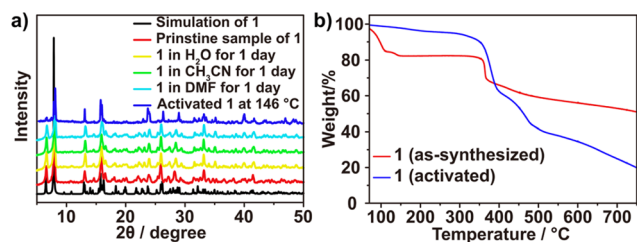


Fig. 3 (a) Powder X-ray diffraction patterns of **1** under different conditions. (b) TGA curves of **1** before and after activation.

peaks in the experimental patterns match well with the simulation, suggesting the high purity of the synthesized sample. Furthermore, the PXRD patterns of the samples which were immersed in H_2O , acetonitrile, and DMF solutions for 24 hours are also consistent with those obtained by simulation. Even for the sample activated at 146 °C for 8 h, both the PXRD pattern and FT-IR spectra matched well with those of the pristine sample which indicates that **1** could keep the framework intact under these conditions (Fig. 3a and S3†). The thermogravimetric analysis (TGA) of this MOF reveals an obvious weight loss of 20% when the temperature was increased to 152 °C , corresponding to the loss of coordinated and free water molecules in channels (calculated to be 20.7%) and the framework did not collapse until 320 °C , which suggested the good thermal stability of the MOF. The TGA curve of the activated sample showed that almost all water molecules had been removed under the activation process. And the slight mass loss at a low temperature indicated there were still some residues in the channel, which may be attributed to the adsorption of water or VOCs in the air of the activated sample during the sample transfer process.³⁹ Besides, the framework remained intact until 320 °C , which further proves the excellent stability and rigidity of the framework.

Due to the smaller molecular radius and the better packing ability on the inner surface of Ar than those of diatomic N_2 molecules, the 87 K Ar adsorption measurement was carried out for investigating the permanent porosity of **1**. As shown in Fig. 4a, **1** exhibits a reversible type-I isotherm with the characteristic of microporosity, and the Brunauer–Emmett–Teller (BET) surface area was estimated to be $536.63\text{ m}^2\text{ g}^{-1}$. The experimental total pore volume was determined to be $0.214\text{ cm}^3\text{ g}^{-1}$ (calculated by the single point method at $P/P_0 = 0.98$). Using nonlocal density functional theory, the pore size distribution was calculated to be 5.4 Å , which is consistent with the value from SCXRD data. Owing to the microporous nature and the unique chlorinated “gas pocket” structure, the

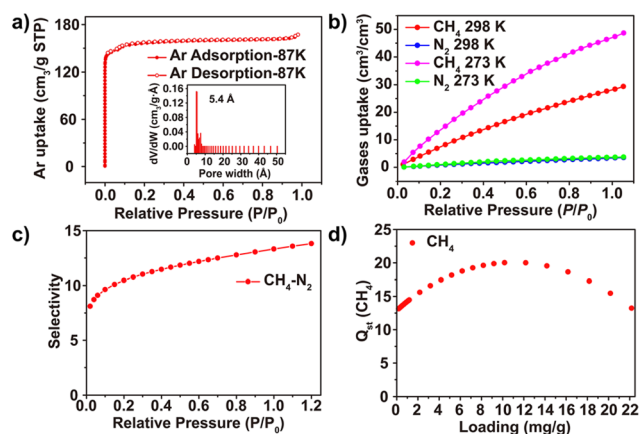


Fig. 4 (a) Ar adsorption/desorption isotherms of **1** at 87 K, inset figure: the pore size distribution of **1**. (b) The CH_4 and N_2 volume adsorption isotherms of **1** at 273 K and 298 K, respectively. (c) IAST selectivity for CH_4/N_2 of the MOF. (d) Q_{st} curves of **1** for CH_4 and N_2 .

adsorption capacity for CH₄ gas of **1** was tested at 273 and 298 K, respectively. As shown in Fig. 4b and Fig. S4,† the CH₄ adsorption at 273 K and 298 K can reach up to 47.36 cm³/cm³ and 28.41 cm³/cm³, respectively. However under the same conditions, the adsorption capacities for N₂ are only 3.67 cm³/cm³ (273 K) and 3.43 cm³/cm³ (298 K). The isosteric enthalpies of adsorption (Q_{st}) of this MOF for CH₄ were calculated from the virial equation based on the isotherms collected at 273 and 298 K. As shown in Fig. 4d, the initial Q_{st} value for CH₄ of **1** is 13.2 kJ mol⁻¹. Besides, with the increase of adsorption capacity, the Q_{st} values for CH₄ exhibit a turnover behaviour.

For an industrial process the volume adsorption capacity is more important than the mass adsorption capacity, and the volume adsorption capacity for CH₄ is a key metric for evaluating the separation effect. As shown in Fig. 5, the adsorption capacity of **1** (28.41 cm³/cm³) exceeds that of Co₃(C₄O₄)₂(OH)₂ (19.81 cm³/cm³), ROD-8 (21.89 cm³/cm³), and Ni(OAc)₂L (20.92 cm³/cm³) and is comparable to that of Cu(NIA)₂, MOF-890 and MOF-889 (Table S3†) but is smaller than that of MOF-891, Al-CDC and ACT-Cu.^{14,40,41} In order to verify the separation ability of **1** for CH₄/N₂ separation, the ideal adsorption solution theory (IAST) was used to investigate its CH₄/N₂ selectivity. After calculation and fitting, the IAST selectivity of **1** is shown in Fig. 4c, which indicates a gradually increasing trend in the whole pressure range, and the maximum selectivity at normal pressure is 13.32, which is rare in published MOFs and higher than that of Co₃(C₄O₄)₂(OH)₂ (12.5), STAM-1 (11.1) and Al-CDC (13.1) in the first echelon (detailed information can be found in the ESI (Table S3†)).

In addition, DFT calculations were used to investigate the interactions between the MOF and CH₄ molecules. As shown in Fig. 6, multiple interactions occurred between CH₄ and adjacent Cl₄-bdc with a binding energy of CH₄ of -13.95 kJ mol⁻¹, and the distances between the hydrogen atoms of CH₄ and the Cl atoms in Cl₄-bdc ranged from 3.154 to 4.359 Å,

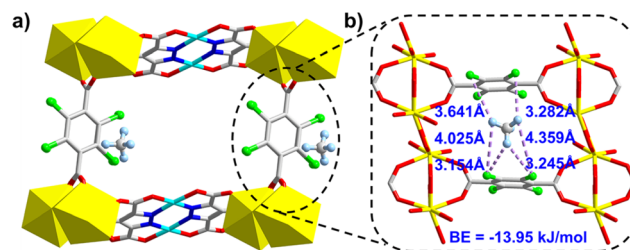


Fig. 6 (a and b) Preferential adsorption sites and binding energies of CH₄ in the MOF obtained from the DFT-optimized structural model; BE stands for binding energy in (b).

which is in the range of the van der Waals' (vdW) interaction. Besides, the adjacent Cl₄-bdc ligands can form confined spaces which not only exhibit multipoint vdW interactions between CH₄ and the host framework but also enhance the interaction by the confinement effect. DFT calculations show that the surface C-Cl plays an important role in the enhancement of the adsorption selectivity of the MOF toward CH₄/N₂ mixtures.

Static adsorption and selectivity calculation indicated that **1** has great advantages in the separation of CH₄/N₂. To further confirm the separation performance of **1** for mixed gases in practical applications, two consecutive cycles of breakthrough experiments of **1** for a CH₄/N₂ (50/50, v/v) mixture were carried out. As shown in Fig. 7, the adsorption time of CH₄ was longer than that of N₂ during the process. N₂ first broke through the packed column, whereas CH₄ was preferentially adsorbed by **1** and broke through the column after a longer time delay which means that a clear separation between CH₄ and N₂ was achieved. Besides, during these two consecutive cycles of breakthrough experiments, the separation ability of **1** remains almost unchanged which demonstrates the good circulation stability of **1** in actual application. The above results indicate that **1** possesses good thermal/chemical stability, high separ-

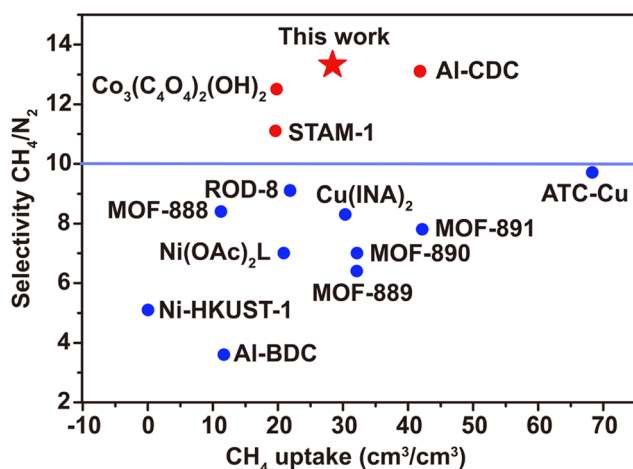


Fig. 5 Comparison of the IAST selectivity for a CH₄/N₂ mixture and CH₄ adsorption of **1** with those of previously reported CH₄-selective MOFs at 298 K and 1 bar. Red represents selectivity higher than 10, and blue represents selectivity lower than 10.

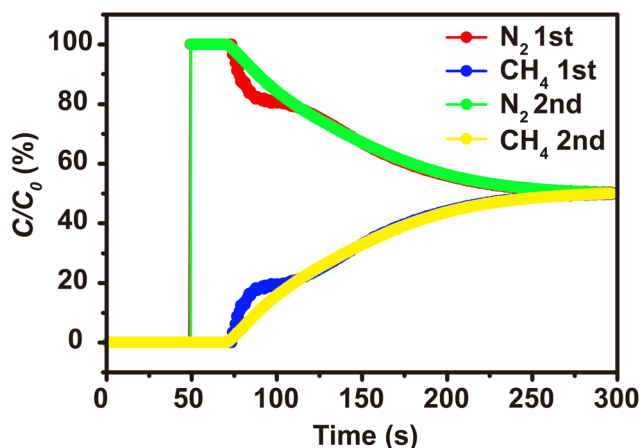


Fig. 7 Experimental breakthrough curves of N₂/CH₄ (v/v = 1:1) at 298 K during two consecutive cycles (red and blue for the 1st cycle; green and yellow for the 2nd cycle).

ation selectivity for CH₄/N₂ and good recyclability which make this MOF have potential application in CH₄ purification.

In conclusion, a pillar-layered multi-component metal-organic framework [CuCeL(Cl₄-bdc)_{0.5}(H₂O)₂·(H₂O)₆]_n was constructed. Through the coordination bonds between Cl₄-bdc ligands and adjacent 3d–4f layers, 1D open channels along the *a*-axis and small confined cavities along the sides of channels were constructed precisely. Due to the synergistic effect between the abundant Cl atoms in Cl₄-bdc which can form multiple C–H...Cl interactions and the confinement effect which enhances the interaction between guest molecules and host framework, this MOF exhibits a strong binding effect for CH₄. More strikingly, this synergistic effect can enhance the CH₄ affinity and endow **1** with great separation ability for CH₄/N₂. As a result, **1** presents a high CH₄ adsorption capacity of 28.41 cm³/cm³ at 298 K and high IAST selectivity of 13.32 for CH₄/N₂ separation. DFT calculations show that the confined cavity which is decorated by chlorine atoms is crucial to binding CH₄ molecules and can be used as a molecular trap for CH₄. The breakthrough experiments revealed that the MOF-based CH₄ nano-trap is a new benchmark for CH₄/N₂ separation and this MOF can be a potential material for capturing CH₄ from coal-mine methane to recover fuel and reduce greenhouse gas emissions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21571139, 22035003, 22001132, 22271217).

References

- 1 Y. He, W. Zhou, G. Qian and B. Chen, Methane storage in metal-organic frameworks, *Chem. Soc. Rev.*, 2014, **43**, 5657–5678.
- 2 D. Saha, H. A. Grappe, A. Chakraborty and G. Orkoulas, Postextraction separation, on-board storage, and catalytic conversion of methane in natural gas: a review, *Chem. Rev.*, 2016, **116**, 11436–11499.
- 3 M. Chang, Y. Zhao, D. Liu, J. Yang, J. Li and C. Zhong, Methane-trapping metal-organic frameworks with an aliphatic ligand for efficient CH₄/N₂ separation, *Sustainable Energy Fuels*, 2020, **4**, 138–142.
- 4 S. M. Wang, M. Shivanna and Q. Y. Yang, Nickel-based metal-organic frameworks for coal-bed methane purification with record CH₄/N₂ selectivity, *Angew. Chem., Int. Ed.*, 2022, **61**, e202201017.
- 5 H. Wang, Y. Liu and J. Li, Designer metal-organic frameworks for size-exclusion-based hydrocarbon separations: progress and challenges, *Adv. Mater.*, 2020, **32**, 2002603.
- 6 J. Liu, H. Shang, J. Yang, J. Wang, J. Li and S. Deng, Novel zeolite/carbon monolith adsorbents for efficient CH₄/N₂ separation, *Chem. Eng. J.*, 2021, **426**, 130163.
- 7 R. Tang, Q. Dai, W. Liang, Y. Wu, X. Zhou, H. Pan and Z. Li, Synthesis of novel particle rice-based carbon materials and its excellent CH₄/N₂ adsorption selectivity for methane enrichment from Low-rank natural gas, *Chem. Eng. J.*, 2020, **384**, 123388.
- 8 Z. Yang, D. Wang, Z. Meng and Y. Li, Adsorption separation of CH₄/N₂ on modified coal-based carbon molecular sieve, *Sep. Purif. Technol.*, 2019, **218**, 130–137.
- 9 Y. Wu, D. Yuan, D. He, J. Xing, S. Zeng, S. Xu, Y. Xu and Z. Liu, Decorated traditional zeolites with subunits of metal-organic frameworks for CH₄/N₂ separation, *Angew. Chem., Int. Ed.*, 2019, **58**, 10241–10244.
- 10 S. Xu, W. C. Li, C. T. Wang, L. Tang, G. P. Hao and A. H. Lu, Self-pillared ultramicroporous carbon nanoplates for selective separation of CH₄/N₂, *Angew. Chem., Int. Ed.*, 2021, **60**, 6339–6343.
- 11 Q. Shi, J. Wang, H. Shang, H. Bai, Y. Zhao, J. Yang, J. Dong and J. Li, Effective CH₄ enrichment from N₂ by SIM-1 via a strong adsorption potential SOD cage, *Sep. Purif. Technol.*, 2020, **230**, 115850.
- 12 M. Chang, T. Yan, Y. Wei, J.-X. Wang, D. Liu and J.-F. Chen, Enhancing CH₄ capture from coalbed methane through tuning van der Waals affinity within isoreticular Al-based metal-organic frameworks, *ACS Appl. Mater. Interfaces*, 2022, **14**, 25374–25384.
- 13 Z. Niu, X. Cui, T. Pham, P. C. Lan, H. Xing, K. A. Forrest, L. Wojtas, B. Space and S. Ma, A metal-organic framework based methane nano-trap for the capture of coal-mine methane, *Angew. Chem., Int. Ed.*, 2019, **58**, 10138–10141.
- 14 C. E. Kivi, B. S. Gelfand, H. Dureckova, H. T. K. Ho, C. Ma, G. K. H. Shimizu, T. K. Woo and D. Song, 3D porous metal-organic framework for selective adsorption of methane over dinitrogen under ambient pressure, *Chem. Commun.*, 2018, **54**, 14104–14107.
- 15 D. Saha, G. Orkoulas, S. Yohannan, H. C. Ho, E. Cakmak, J. Chen and S. Ozcan, Nanoporous boron nitride as exceptionally thermally stable adsorbent: role in efficient separation of light hydrocarbons, *ACS Appl. Mater. Interfaces*, 2017, **9**, 14506–14517.
- 16 K. X. Yao, Y. Chen, Y. Lu, Y. Zhao and Y. Ding, Ultramicroporous carbon with extremely narrow pore distribution and very high nitrogen doping for efficient methane mixture gases upgrading, *Carbon*, 2017, **122**, 258–265.
- 17 X. Ren, T. Sun, J. Hu and S. Wang, Highly enhanced selectivity for the separation of CH₄ over N₂ on two ultra-microporous frameworks with multiple coordination modes, *Microporous Mesoporous Mater.*, 2014, **186**, 137–145.
- 18 P. T. K. Nguyen, H. T. D. Nguyen, H. Q. Pham, J. Kim, K. E. Cordova and H. Furukawa, Synthesis and selective CO₂ capture properties of a series of hexatopic linker-based

- metal-organic frameworks, *Inorg. Chem.*, 2015, **54**, 10065–10072.
- 19 X. W. Liu, Y. Guo, A. Tao, M. Fischer, T. J. Sun, P. Z. Moghadam, D. Fairen-Jimenez and S. D. Wang, “Explosive” synthesis of metal-formate frameworks for methane capture: an experimental and computational study, *Chem. Commun.*, 2017, **53**, 11437–11440.
- 20 J. Hu, T. Sun, X. Liu, Y. Guo and S. Wang, Separation of CH₄/N₂ mixtures in metal-organic frameworks with 1D micro-channels, *RSC Adv.*, 2016, **6**, 64039–64046.
- 21 Y. Guo, J. Hu, X. Liu, T. Sun, S. Zhao and S. Wang, Scalable solvent-free preparation of [Ni₃(HCOO)₆] frameworks for highly efficient separation of CH₄ from N₂, *Chem. Eng. J.*, 2017, **327**, 564–572.
- 22 A. Jayaraman, A. J. Hernandez-Maldonado, R. T. Yang, D. Chinn, C. L. Munson and D. H. Mohr, Clinoptilolites for nitrogen/methane separation, *Chem. Eng. Sci.*, 2004, **59**, 2407–2417.
- 23 D. Saha, Z. Bao, F. Jia and S. Deng, Adsorption of CO₂, CH₄, N₂O, and N₂ on MOF-5, MOF-177, and Zeolite 5A, *Environ. Sci. Technol.*, 2010, **44**, 1820–1826.
- 24 H. Noh, C.-W. Kung, T. Islamoglu, A. W. Peters, Y. Liao, P. Li, S. J. Garibay, X. Zhang, M. R. DeStefano, J. T. Hupp and O. K. Farha, Room temperature synthesis of an 8-connected Zr-based metal-organic framework for top-down nanoparticle encapsulation, *Chem. Mater.*, 2018, **30**, 2193–2197.
- 25 R.-B. Lin, S. Xiang, W. Zhou and B. Chen, Microporous metal-organic framework materials for gas separation, *Chem*, 2020, **6**, 337–363.
- 26 S. Wang, H. Reinsch, N. Heymans, M. Wahiduzzaman, C. Martineau-Corcoss, G. De Weireld, G. Maurin and C. Serre, Toward a rational design of titanium metal-organic frameworks, *Matter*, 2020, **2**, 440–450.
- 27 M. Chang, J. Ren, Q. Yang and D. Liu, A robust calcium-based microporous metal-organic framework for efficient CH₄/N₂ separation, *Chem. Eng. J.*, 2021, **408**, 127294.
- 28 X. Jia, N. Yuan, L. Wang, J. Yang and J. Li, (CH₃)₂NH-assisted synthesis of high-purity Ni-HKUST-1 for the adsorption of CO₂, CH₄, and N₂, *Eur. J. Inorg. Chem.*, 2018, **8**, 1047–1052.
- 29 R. B. Lin, L. Li, H. L. Zhou, H. Wu, C. He, S. Li, R. Krishna, J. Li, W. Zhou and B. Chen, Molecular sieving of ethylene from ethane using a rigid metal-organic framework, *Nat. Mater.*, 2018, **17**, 1128–1133.
- 30 A. Cadiou, K. Adil, P. M. Bhatt, Y. Belmabkhout and M. Eddaoudi, A metal-organic framework-based splitter for separating propylene from propane, *Science*, 2016, **353**, 137–140.
- 31 H. Wang, X. Dong, V. Colombo, Q. Wang, Y. Liu, W. Liu, X. L. Wang, X. Y. Huang, D. M. Proserpio, A. Sironi, Y. Han and J. Li, Tailor-made microporous metal-organic frameworks for the full separation of propane from propylene through selective size exclusion, *Adv. Mater.*, 2018, **30**, 1805088.
- 32 B. Liang, X. Zhang, Y. Xie, R. B. Lin, R. Krishna, H. Cui, Z. Li, Y. Shi, H. Wu, W. Zhou and B. Chen, An ultramicroporous metal-organic framework for high sieving separation of propylene from propane, *J. Am. Chem. Soc.*, 2020, **142**, 17795–17801.
- 33 J. Wang, Y. Zhang, P. Zhang, J. Hu, R. Lin, Q. Deng, Z. Zeng, H. Xing, S. Deng and B. Chen, Optimizing pore space for flexible-robust metal-organic framework to boost trace acetylene removal, *J. Am. Chem. Soc.*, 2020, **142**, 9744–9751.
- 34 T. Ke, Q. Wang, J. Shen, J. Zhou, Z. Bao, Q. Yang and Q. Ren, Molecular sieving of C₂-C₃ alkene from alkyne with tuned threshold pressure in robust layered metal-organic frameworks, *Angew. Chem., Int. Ed.*, 2020, **59**, 12725–12730.
- 35 Y. T. Zhang, X. L. Wang, E. L. Zhou, X. S. Wu, B. Q. Song, K. Z. Shao and Z. M. Su, Polyoxovanadate-based organic-inorganic hybrids: from {V₅O₉Cl} clusters to nanosized octahedral cages, *Dalton Trans.*, 2016, **45**, 3698–3701.
- 36 M. O’Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, The reticular chemistry structure resource (RCSR) database of, and symbols for, crystal nets, *Acc. Chem. Res.*, 2009, **41**, 1782–1789.
- 37 V. Robins, S. J. Ramsden and S. T. Hyde, 2D hyperbolic groups induce three-periodic euclidean reticulations, *Eur. Phys. J. B*, 2004, **39**, 365–375.
- 38 A. P. Shevchenko, I. A. Blatov, E. V. Kitaeva and V. A. Blatov, Local coordination versus overall topology in crystal structures: deriving knowledge from crystallographic databases, *Cryst. Growth Des.*, 2016, **17**, 774–785.
- 39 L.-H. Xie, X.-M. Liu, T. He and J.-R. Li, Metal-Organic Frameworks for the Capture of Trace Aromatic Volatile Organic Compounds, *Chem*, 2018, **4**, 1911–1927.
- 40 L. Li, L. Yang, J. Wang, Z. Zhang, Q. Yang, Y. Yang, Q. Ren and Z. Bao, Highly efficient separation of methane from nitrogen on a squarate-based metal-organic framework, *AIChE J.*, 2018, **64**, 3681–3689.
- 41 R.-J. Li, M. Li, X.-P. Zhou, S. W. Ng, M. O’Keeffe and D. Li, ROD-8, a rod MOF with a pyrene-cored tetracarboxylate linker: framework disorder, derived nets and selective gas adsorption, *CrystEngComm*, 2014, **16**, 6291–6295.