Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Metal–Organic Framework with Rich Accessible Nitrogen Sites for Highly Efficient CO₂ Capture and Separation

Yingxiang Ye,[®] Heng Zhang, Liangji Chen, Shimin Chen, Quanjie Lin, Fangfang Wei,* Zhangjing Zhang,*[®] and Shengchang Xiang[®]

Fujian Provincial Key Laboratory of Polymer Materials, College of Chemistry and Materials Science, Fujian Normal University, 32 Shangsan Road, Fuzhou 350007, P. R. China

S Supporting Information

ABSTRACT: A novel microporous metal-organic framework (FJU-44), with abundant accessible nitrogen sites on its internal surface, was constructed from the tetrapodal tetrazole ligand tetrakis(4-tetrazolylphenyl)ethylene (H₄TTPE) and copper chloride. Notably, the CO_2 uptake capacity (83.4 cm^3/g , at 273 K and 1 bar) in the activated FJU-44a is higher than most of tetrazolate-containing MOF materials. Particularly, FJU-44a exhibits superior adsorption selectivity of CO_2/N_2 (278–128) and CO_2/CH_4 (44–16), which is comparable to some well-known CO₂ capture materials. Furthermore, the fixed-bed breakthrough experiment indicates that the postcombustion flue gas flow over a packed column with FJU-44a adsorbents can be effectively separated.

INTRODUCTION

As a class of fascinating crystalline porous materials, metalorganic frameworks (MOFs),¹ also known as porous coordination polymers (PCPs),² have received considerable attention as potentially valuable gas storage, $^{3-6}$ separation, $^{7-18}$ sensing, $^{19-21}$ proton conducting, $^{22-24}$ and catalyst materials, $^{25-28}$ attributed to their rich structural tunability, high surface areas, and unique pore structures and surfaces. Over the past two decades, the scientists have designed and constructed a large number of novel MOF materials, mainly focused on the use of carboxyl and/or pyridine ligands. Nowadays, there is growing interest in fabricating MOFs by using azolates linkers, because the strong metal-nitrogen (M-N) bonds often endow excellent thermal and chemical stabilities to the host frameworks. $^{29-34}$ However, among the various azolates (e.g., imidazole, pyrazole, triazole and tetrazole) ligands, the tetrazolate ligands might be the most promising candidates in the construction of versatile MOFs, owing to their high number of donor N sites capable of adopting different bridging or chelating coordination modes.³⁵ For example, a series of polytetrazolate-based MOFs, $Mn_3[(Mn_4Cl)_3(BTT)_8]_2$, Cu(BDT)(DMF), and $Zn_3(BDT)_3(DMF)_4(H_2O)_2$, ^{36,37} were constructed by the Long group, in which the ligands display similar pyrazolate coordination modes. Furthermore, Bu and co-workers reported a chiral microporous MOF [Zn(dtp)]³⁸ in which the tetrazolate linker exhibits the similar imidazolate coordination modes. On the other hand, the decoration of the open N atoms into the pore surfaces of MOFs can significantly improve the gas uptake capacity, especially for CO_2 . For



instance, the polytetrazolate-based MOFs (FJU-56 and $[NC_2H_8]_4Cu_5(BTT)_3$ incorporated with rich uncoordinated nitrogen atoms show high stabilities and superior CO2 adsorption performances.³³

On the basis of the above considerations, we are particularly fascinated by ligands containing multiple tetrazole groups, because such ligands can realize high connectivity and a high proportion of accessible N atoms simultaneously. However, at present, only a few polytetrazole ligands possessing four tetrazole groups have been reported, and they are mainly focused on tetraphenylmethane, adamantane, and porphyrin as organic scaffolds. $^{40-42}$ In this study, we design and synthesize a new polytetrazole linker, tetrakis(4-tetrazolylphenyl)ethylene (H₄TTPE, Scheme S1, Figure 1a), on the basis of the following considerations: the partially twisted ethyl core and multiple rotational phenyl rings would result in a nonplanar configuration of the ligand, which facilitates the fabrication of highly connected porous structures. Then, a novel microporous MOF ([Cu₂Cl(HTTPE)(H₂O)]·xG, FJU-44) was successfully constructed from the H4TTPE ligand and a Cu(II) ion under solvothermal conditions. It is worth mentioning that the 1D rhombic channel of FJU-44 was decorated with abundant uncoordinated nitrogen atoms, which is beneficial to gas capture and separation. As expected, the activated FJU-44a shows a moderately high uptake value of CO₂ and excellent selective capture ability for CO₂/CH₄ and CO_2/N_2 , and more importantly, the CO_2/N_2 selectivity is

Received: January 18, 2019



Figure 1. Structure of **FJU-44** showing (a) the organic ligand H_4 TTPE and (b) the coordination mode of the copper(II) atoms. (c) 3D open framework with two types of 1D rhombic channel viewed along the crystallographic *c*-axis. (d) Illustration of the pore aperture sizes of **FJU-44** viewed along the crystallographic *c*-axis. Cross section of the two types of channel surfaces viewed along (e) the crystallographic *a*- and (f) *b*-axes. Color code: Cu, orange; C, dark gray or gray; Cl, green; O, red; N, blue. Hydrogen atoms and solvent molecules have been omitted for clarity.

comparable to some top-performing CO_2 capture materials.⁴³ Moreover, the dynamic breakthrough experiment shows that the simulated postcombustion flue gas (mainly containing CO_2 and N_2) can be effectively separated by a packed column containing **FJU-44a** solids.

RESULTS AND DISCUSSION

The solvothermal reaction of CuCl₂ and H₄TTPE in DMF solution at 85 °C for 3 days gave the blue rod-shaped crystals of FJU-44. Single-crystal X-ray structural analysis revealed that FJU-44 crystallizes in the monoclinic P_2/m space group. As shown in Figure 1b, there are three crystallographically independent Cu(II) ions all exhibiting six-connected octahedral coordination geometries. The Cu1 atom lying on an inversion center is surrounded by four nitrogen atoms from four TTPE ligands, and two axially positioned oxygen atoms from bridging water molecules. The Cu2 atom is surrounded by four N atoms from four TTPE ligands, one O atom and one Cl atom, forming a distorted octahedral geometry. The coordination mode of the Cu3 atom is like that of Cu1, except the two axially positioned O atoms changed to the Cl atoms. Notably, the Cu atoms were connected by the bridging of μ_2 -Cl and μ_2 -O atoms to form a 1D inorganic zigzag chain $[(Cu_2Cl(H_2O))_n]^{n+}$. Then, such 1D chains were further connected to four neighboring chains by the TTPE ligands to assemble a three-dimensional open framework (Figure 1c). The resulting structure contains two types of 1D rhombic channels with the pore aperture sizes of 10.2×6.0 Å² and 5.0 \times 4.9 Å², respectively, along the crystallographic *c*-axis (Figure 1d). It was worth noting that there are abundant uncoordinated nitrogen atoms toward the pore surfaces (Figure 1e,f), which will facilitate the gas selective adsorption and separation. Topologically, if the CuN_4X_2 (X = Cl or O) unit and TTPE ligand are both simplified as four-connected nodes, the host framework of FJU-44 displays a rare (4,4)-connected network with a point symbol of $(4.6^4.8)_2(4^2.6^2.8^2)$ (mog topology, Figure S1).⁴⁴ Without the free solvent molecules taken into consideration, the total accessible void volumes in FJU-44 are estimated to be 44.8%, as calculated by the PLATON/ SQUEEZE program.45

The phase purity of the bulk sample was verified by powder X-ray diffraction (PXRD), and further confirmed by elemental

analysis and thermogravimetric analysis (TGA) (Figures S3 and S4). The PXRD diffraction patterns of the as-synthesized sample matched well with the simulated one from the singlecrystal data. To explore the permanent porosity, the newly synthesized FJU-44 was solvent-exchanged with dry CH₂Cl₂ to remove the high boiling point guest molecules, and then degassed overnight at 80 °C to give a guest-free sample of FJU-44a. The PXRD profile of the activated FJU-44a exhibited no appreciable changes compared with the as-synthesized sample, confirming that the structural integrity was fully retained after activation (Figure S4).

Next, we collect the 77 K N_2 adsorption isotherm of FJU-44a (Figure 2), in which the isotherm shows a type-I



Figure 2. 77 K N_2 sorption isotherms of FJU-44a. Inset: pore size distribution (PSD) of FJU-44a.

adsorption behavior with the maximum N₂ uptake value of 217 cm³/g, and the pore volume is calculated to be 0.34 cm³/g. The Langmuir and Brunauer–Emmett–Teller (BET) surface areas of **FJU-44a** were up to 898.1 and 629.5 m²/g, respectively, which are comparable to that of $[(NC_2H_8)_4Cu_5-(BTT)_3]$ (701 m²/g)³⁹ and CPF-6 (599 m²/g)⁴⁶ but significantly larger than UTSA-57a (206.5 m²/g)⁴⁷ among the same type of MOF materials. With analysis based on the no-local density functional theory (NLDFT) model, **FJU-44a** displays a bimodal pore size distribution with the centers of 6.8 and 13.6 Å, respectively.



Figure 3. (a) 273 K and (b) 296 K CO₂, CH₄, and N₂ adsorption isotherms of FJU-44a.



Figure 4. (a–c) Mixture adsorption isotherms and adsorption selectivity of FJU-44a for CO_2/N_2 (15/85) and CO_2/CH_4 (50/50) at 296 K as predicted by IAST. (d) The CO_2 and CH_4 isosteric heat of adsorption (Q_{st}) in FJU-44a.

Establishment of permanent porosity, suitable pore space, and abundant accessible N atoms toward the pore surface makes us determine that **FJU-44a** might have good performances for carbon capture and separation. At 1 bar, the uptake amounts of CO₂ are 53.2 and 83.4 cm³/g at 296 and 273 K, respectively (Figures 3). At ambient conditions, the CO₂ uptake value in **FJU-44a** is lower than the those of the M-MOF-74 (179.5 cm³/g)⁴⁸ series with various open metal sites, but the adsorbed CO₂ is comparable to NENU-520a (60 cm³/g)⁴⁹ and $[(NC_2H_8)_4Cu_5(BTT)_3]$ (52 cm³/g),³⁹ and much higher than those of UTSA-57a (35 cm³/g)⁴⁷ and LIFM-WZ-3 (29.5 cm³/g)⁵⁰ in the same type of tetrazolate-based MOFs. For comparison, the uptakes amount of CH₄ and N₂ are very low at 296 K, with the values of 11.3 cm³/g and 2.7 cm³/g only.

To determine the CO₂ and CH₄ adsorption affinities in FJU-44a, the coverage-dependent isosteric heat of adsorption (Q_{st}) was calculated on the basis of the adsorption isotherms at 273 and 296 K. As shown in Figure 4d, the zero coverage enthalpies are 40.4 kJ/mol for CO₂ and 22.2 kJ/mol for CH₄. Notably, the adsorption enthalpy of CO₂ in FJU-44a is stronger than that of zeolite NaX (34 kJ/mol),⁴³ and some typical metal azolate framework materials such as ZTF-1 (25.4 kJ/mol), MAF-66 (26.0 kJ/mol), and UTSA-49 (27.0 kJ/mol).^{51–53} Moreover, the Q_{st} value for methane in FJU-44a is comparable to those of Cu-TDPAT (20.7 kJ mol⁻¹),⁵⁴ FJI-C4 (20.8–23.1 kJ mol⁻¹),⁵⁵ and UTSA-36a (24.4 kJ mol⁻¹).⁵⁶ The high uptake capacity and adsorption enthalpy of CO₂, accompanying the remarkable CO₂/CH₄ and CO₂/N₂ adsorption selectivity, may be reasonable evidence of the fact that CO₂ has stronger interactions with the uncoordinated N atoms, due to its larger polarizability and quadrupole moment.

The widespread approach based on the ideal adsorbed solution theory $(IAST)^{57}$ is adopted to calculate the adsorption selectivity of CO_2/N_2 (15%:85%) and CO_2/CH_4 (50%:50%) at different pressures (Figure 4a,b). At 296 K and



Figure 5. Experimental breakthrough curves for (a) CO_2/N_2 (15%:85%) gas mixtures and (b) the cycling test for CO_2/N_2 (15%:85%) gas mixtures in a packed column with FJU-44a adsorbent at 296 K and 1 bar.

100 kPa, the IAST selectivity for CO_2/N_2 in **FJU-44a** is up to 128 (Figure 4c), comparable to top-performing CO_2 capture materials MgMOF-74 (182) and NaX (146),⁴³ and significantly higher than those of other well-known MOFs, such as ZnMOF-74 (87.7), Bio-MOF-11 (80), and Cu-TDPAT (58).⁴³ The IAST selectivity (16) for CO_2/CH_4 is comparable to those of some famous MOFs, Fe₂(dobdc) (20.2), MOF-5 (15.5), and Cu-TDPAT (13.8).⁴³ Similarly, at 273 K, the IAST selectivity of **FJU-44a** lies in the ranges from 827 to 187 and 92 to 23 for CO_2/N_2 and CO_2/CH_4 (Figure S10). Thus, the high selectivity endows **FJU-44a** with the unfolding of the superior separation proficiency toward gas mixtures of CO_2/N_2 and CO_2/CH_4 .

It is well-known that carbon dioxide (CO_2) is one of the chief perpetrators of the greenhouse effect, mainly from the combustion of coal, oil, and natural gas. Meanwhile, carbon capture and separation (CCS) technology is one of the most effective strategies to reduce CO₂ in the atmosphere.^{58,59} To assess the feasibility of FJU-44a to capture CO₂ from the postcombustion flue gas (CO_2/N_2) in the actual processes, we implement dynamic breakthrough experiments, in which the CO₂/N₂ (15%:85%) mixed gases flow through a packed column containing solid adsorbent FJU-44a under ambient conditions. As shown in Figure 5a, the CO_2/N_2 mixed gases can be effectively separated by FJU-44a, in which N₂ was initial eluted and quickly reached pure grade, whereas CO₂ was not detected until after a period of time (~11 min g^{-1}). On the basis of the breakthrough curve, the dynamic CO₂ capture capacity and separation factor ($\alpha_{CO2/N2}$) in FJU-44a for CO₂/ N₂ gas mixtures were calculated to be 183 mmol/kg and 9.5, respectively. To ensure the recyclability and facile regeneration of FJU-44a, we thus performed multiple dynamic breakthrough experiments. Figure 5b shows that the dynamic uptake capacities of CO₂ and separation performances toward CO₂/ N₂ gas mixtures remain steady after three cycling tests, further demonstrating that FJU-44a is one of the promising candidates for carbon capture and separation.

CONCLUSIONS

In conclusion, we have successfully constructed a new polytetrazolate-based MOF (FJU-44), with abundantly accessible nitrogen atoms on its internal surface. Notably, FJU-44a displays a moderately high uptake value for CO_2 and outstanding CO_2/N_2 and CO_2/CH_4 adsorption selectivities, which are comparable to those of some top-performing CO_2 capture materials. Furthermore, the dynamic breakthrough

experiments indicate that postcombustion flue gas flow over a packed column with FJU-44a solid can be effectively separated. This work demonstrates that the strategy for constructing pore surfaces with rich accessible nitrogen atoms will promote the design and synthesis of novel MOF materials for other challenging gas separations in the future.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00182.

Experimental section, additional structural figures, FT-IR spectrum, TGA curve, PXRD patterns, and gas adsorption isotherms (PDF)

Accession Codes

CCDC 1890650 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: wfanfan@fjnu.edu.cn. *E-mail: zzhang@fjnu.edu.cn.

ORCID 🔍

Yingxiang Ye: 0000-0003-3962-8463 Zhangjing Zhang: 0000-0003-1264-7648 Shengchang Xiang: 0000-0001-6016-2587

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (21673039, 21573042, and 21273033), Fujian Science and Technology Department (2018J07001, 2016J01046, and 2014J06003). Y.Y. gratefully acknowledges the support of the China Scholarship Council.

REFERENCES

(1) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341*, 1230444.

(2) Kim, C. R.; Uemura, T.; Kitagawa, S. Inorganic nanoparticles in porous coordination polymers. *Chem. Soc. Rev.* **2016**, *45*, 3828–3845. (3) Li, B.; Wen, H. M.; Wang, H.; Wu, H.; Tyagi, M.; Yildirim, T.; Zhou, W.; Chen, B. A porous metal-organic framework with dynamic pyrimidine groups exhibiting record high methane storage working capacity. *J. Am. Chem. Soc.* **2014**, *136*, 6207–6210.

(4) Moreau, F.; da Silva, I.; Al Smail, N. H.; Easun, T. L.; Savage, M.; Godfrey, H. G.; Parker, S. F.; Manuel, P.; Yang, S.; Schroder, M. Unravelling exceptional acetylene and carbon dioxide adsorption within a tetra-amide functionalized metal-organic framework. *Nat. Commun.* **2017**, *8*, 14085.

(5) Liang, L.; Liu, C.; Jiang, F.; Chen, Q.; Zhang, L.; Xue, H.; Jiang, H.-L.; Qian, J.; Yuan, D.; Hong, M. Carbon dioxide capture and conversion by an acid-base resistant metal-organic framework. *Nat. Commun.* **2017**, *8*, 1233.

(6) Liu, B.; Zhang, R.; Pan, C.-Y.; Jiang, H.-L. Unprecedented Li⁺ Exchange in an Anionic Metal–Organic Framework: Significantly Enhanced Gas Uptake Capacity. *Inorg. Chem.* **2017**, *56*, 4263–4266. (7) Li, J. R.; Kuppler, R. J.; Zhou, H. C. Selective gas adsorption and separation in metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1477–1504.

(8) Liao, P.-Q.; Huang, N.-Y.; Zhang, W.-X.; Zhang, J.-P.; Chen, X.-M. Controlling guest conformation for efficient purification of butadiene. *Science* **2017**, *356*, 1193.

(9) Li, L.; Lin, R.-B.; Krishna, R.; Li, H.; Xiang, S.; Wu, H.; Li, J.; Zhou, W.; Chen, B. Ethane/ethylene separation in a metal-organic framework with iron-peroxo sites. *Science* **2018**, *362*, 443.

(10) Lin, R. B.; Li, L.; Zhou, H. L.; Wu, H.; He, C.; Li, S.; Krishna, R.; Li, J.; Zhou, W.; Chen, B. Molecular sieving of ethylene from ethane using a rigid metal-organic framework. *Nat. Mater.* **2018**, *17*, 1128–1133.

(11) Ye, Y.; Chen, S.; Chen, L.; Huang, J.; Ma, Z.; Li, Z.; Yao, Z.; Zhang, J.; Zhang, Z.; Xiang, S. Additive-Induced Supramolecular Isomerism and Enhancement of Robustness in Co(II)-Based MOFs for Efficiently Trapping Acetylene from Acetylene-Containing Mixtures. ACS Appl. Mater. Interfaces **2018**, 10, 30912–30918.

(12) Ye, Y.; Ma, Z.; Chen, L.; Lin, H.; Lin, Q.; Liu, L.; Li, Z.; Chen, S.; Zhang, Z.; Xiang, S. Microporous metal–organic frameworks with open metal sites and π -Lewis acidic pore surfaces for recovering ethylene from polyethylene off-gas. *J. Mater. Chem. A* **2018**, *6*, 20822–20828.

(13) Hu, T.-L.; Wang, H.; Li, B.; Krishna, R.; Wu, H.; Zhou, W.; Zhao, Y.; Han, Y.; Wang, X.; Zhu, W.; Yao, Z.; Xiang, S.; Chen, B. Microporous metal-organic framework with dual functionalities for highly efficient removal of acetylene from ethylene/acetylene mixtures. *Nat. Commun.* **2015**, *6*, 7328.

(14) Li, H.; Wang, K.; Sun, Y.; Lollar, C. T.; Li, J.; Zhou, H.-C. Recent advances in gas storage and separation using metal-organic frameworks. *Mater. Today* **2018**, *21*, 108–121.

(15) Wen, H.-M.; Liao, C.; Li, L.; Alsalme, A.; Alothman, Z.; Krishna, R.; Wu, H.; Zhou, W.; Hu, J.; Chen, B. A metal–organic framework with suitable pore size and dual functionalities for highly efficient post-combustion CO_2 capture. *J. Mater. Chem. A* **2019**, *7*, 3128–3134.

(16) Zhao, X.; Wang, Y.; Li, D.-S.; Bu, X.; Feng, P. Metal–Organic Frameworks for Separation. *Adv. Mater.* **2018**, *30*, 1705189.

(17) Lin, R.-B.; Wu, H.; Li, L.; Tang, X.-L.; Li, Z.; Gao, J.; Cui, H.; Zhou, W.; Chen, B. Boosting Ethane/Ethylene Separation within Isoreticular Ultramicroporous Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2018**, *140*, 12940–12946.

(18) Ye, Y.; Ma, Z.; Lin, R.-B.; Krishna, R.; Zhou, W.; Lin, Q.; Zhang, Z.; Xiang, S.; Chen, B. Pore Space Partition within a Metal–Organic Framework for Highly Efficient C_2H_2/CO_2 Separation. *J. Am. Chem. Soc.* **2019**, *141*, 4130–4136.

(19) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Van Duyne, R. P.; Hupp, J. T. Metal–Organic Framework Materials as Chemical Sensors. *Chem. Rev.* **2012**, *112*, 1105–1125.

(20) Liu, L.; Yao, Z.; Ye, Y.; Chen, L.; Lin, Q.; Yang, Y.; Zhang, Z.; Xiang, S. Robustness, Selective Gas Separation, and Nitrobenzene

Sensing on Two Isomers of Cadmium Metal-Organic Frameworks Containing Various Metal-O-Metal Chains. *Inorg. Chem.* **2018**, *57*, 12961–12968.

(21) Liu, L.; Yao, Z.; Ye, Y.; Liu, C.; Lin, Q.; Chen, S.; Xiang, S.; Zhang, Z. Enhancement of Intrinsic Proton Conductivity and Aniline Sensitivity by Introducing Dye Molecules into the MOF Channel. *ACS Appl. Mater. Interfaces* **2019**, *11*, 16490–16495.

(22) Ye, Y.; Wu, X.; Yao, Z.; Wu, L.; Cai, Z.; Wang, L.; Ma, X.; Chen, Q.-H.; Zhang, Z.; Xiang, S. Metal–organic frameworks with a large breathing effect to host hydroxyl compounds for high anhydrous proton conductivity over a wide temperature range from subzero to 125 °C. J. Mater. Chem. A **2016**, *4*, 4062–4070.

(23) Ye, Y.; Guo, W.; Wang, L.; Li, Z.; Song, Z.; Chen, J.; Zhang, Z.; Xiang, S.; Chen, B. Straightforward Loading of Imidazole Molecules into Metal-Organic Framework for High Proton Conduction. *J. Am. Chem. Soc.* **2017**, *139*, 15604–15607.

(24) Han, Y.-H.; Ye, Y.; Tian, C.; Zhang, Z.; Du, S.-W.; Xiang, S. High proton conductivity in an unprecedented anionic metalloring organic framework (MROF) containing novel metalloring clusters with the largest diameter. *J. Mater. Chem. A* **2016**, *4*, 18742–18746. (25) Xiao, J.-D.; Jiang, H.-L. Metal–Organic Frameworks for Photocatalysis and Photothermal Catalysis. *Acc. Chem. Res.* **2019**, *52*, 356–366.

(26) Wang, Y. R.; Huang, Q.; He, C. T.; Chen, Y.; Liu, J.; Shen, F. C.; Lan, Y. Q. Oriented electron transmission in polyoxometalatemetalloporphyrin organic framework for highly selective electroreduction of CO₂. *Nat. Commun.* **2018**, *9*, 4466.

(27) Qin, J.-S.; Yuan, S.; Zhang, L.; Li, B.; Du, D.-Y.; Huang, N.; Guan, W.; Drake, H. F.; Pang, J.; Lan, Y.-Q.; Alsalme, A.; Zhou, H.-C. Creating Well-Defined Hexabenzocoronene in Zirconium Metal– Organic Framework by Postsynthetic Annulation. *J. Am. Chem. Soc.* **2019**, *141*, 2054–2060.

(28) Zhang, X.; Zhang, X.; Johnson, J. A.; Chen, Y.-S.; Zhang, J. Highly Porous Zirconium Metal–Organic Frameworks with β -UH₃-like Topology Based on Elongated Tetrahedral Linkers. *J. Am. Chem. Soc.* **2016**, *138*, 8380–8383.

(29) Zhang, J. P.; Zhang, Y. B.; Lin, J. B.; Chen, X. M. Metal azolate frameworks: from crystal engineering to functional materials. *Chem. Rev.* **2012**, *112*, 1001–1033.

(30) Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 10186–10191.

(31) Wang, L.; Ye, Y.; Li, Z.; Lin, Q.; Ouyang, J.; Liu, L.; Zhang, Z.; Xiang, S. Highly Selective Adsorption of C_2/C_1 Mixtures and Solvent-Dependent Thermochromic Properties in Metal–Organic Frameworks Containing Infinite Copper-Halogen Chains. *Cryst. Growth Des.* **2017**, *17*, 2081–2089.

(32) Li, Z.; Zhang, Z.; Ye, Y.; Cai, K.; Du, F.; Zeng, H.; Tao, J.; Lin, Q.; Zheng, Y.; Xiang, S. Rationally tuning host–guest interactions to free hydroxide ions within intertrimerically cuprophilic metal–organic frameworks for high OH⁻ conductivity. *J. Mater. Chem. A* **2017**, *5*, 7816–7824.

(33) Zhang, J.; Ouyang, J.; Ye, Y.; Li, Z.; Lin, Q.; Chen, T.; Zhang, Z.; Xiang, S. Mixed-Valence Cobalt(II/III) Metal–Organic Framework for Ammonia Sensing with Naked-Eye Color Switching. *ACS Appl. Mater. Interfaces* **2018**, *10*, 27465–27471.

(34) Wang, Z.; Zhu, C.-Y.; Zhao, H.-S.; Yin, S.-Y.; Wang, S.-J.; Zhang, J.-H.; Jiang, J.-J.; Pan, M.; Su, C.-Y. Record high cationic dye separation performance for water sanitation using a neutral coordination framework. J. Mater. Chem. A 2019, 7, 4751–4758.

(35) Tăbăcaru, A.; Pettinari, C.; Galli, S. Coordination polymers and metal-organic frameworks built up with poly(tetrazolate) ligands. *Coord. Chem. Rev.* **2018**, *372*, 1–30.

(36) Dincǎ, M.; Dailly, A.; Liu, Y.; Brown, C. M.; Neumann, D. A.; Long, J. R. Hydrogen Storage in a Microporous Metal–Organic Framework with Exposed Mn^{2+} Coordination Sites. *J. Am. Chem. Soc.* **2006**, *128*, 16876–16883.

Ε

(37) Dincă, M.; Yu, A. F.; Long, J. R. Microporous Metal–Organic Frameworks Incorporating 1,4-Benzeneditetrazolate: Syntheses, Structures, and Hydrogen Storage Properties. *J. Am. Chem. Soc.* **2006**, *128*, 8904–8913.

(38) Li, J.-R.; Tao, Y.; Yu, Q.; Bu, X.-H.; Sakamoto, H.; Kitagawa, S. Selective Gas Adsorption and Unique Structural Topology of a Highly Stable Guest-Free Zeolite-Type MOF Material with N-rich Chiral Open Channels. *Chem. - Eur. J.* **2008**, *14*, 2771–2776.

(39) Dong, B. X.; Zhang, S. Y.; Liu, W. L.; Wu, Y. C.; Ge, J.; Song, L.; Teng, Y. L. Gas storage and separation in a water-stable $[Cu(I)_{5}BTT_{3}]^{4}$ anion framework comprising a giant multi-prismatic nanoscale cage. *Chem. Commun.* **2015**, *51*, 5691–5694.

(40) Dincă, M.; Dailly, A.; Long, J. R. Structure and charge control in metal-organic frameworks based on the tetrahedral ligand tetrakis(4-tetrazolylphenyl)methane. *Chem. - Eur. J.* **2008**, *14*, 10280–10285.

(41) Boldog, I.; Domasevitch, K. V.; Baburin, I. A.; Ott, H.; Gil-Hernández, B.; Sanchiz, J.; Janiak, C. A rare alb-4,8-Cmce metalcoordination network based on tetrazolate and phosphonate functionalized 1,3,5,7-tetraphenyladamantane. *CrystEngComm* **2013**, *15*, 1235–1243.

(42) Liu, D.; Liu, T. F.; Chen, Y. P.; Zou, L.; Feng, D.; Wang, K.; Zhang, Q.; Yuan, S.; Zhong, C.; Zhou, H. C. A Reversible Crystallinity-Preserving Phase Transition in Metal-Organic Frameworks: Discovery, Mechanistic Studies, and Potential Applications. J. Am. Chem. Soc. **2015**, 137, 7740–7746.

(43) Xiang, S.; He, Y.; Zhang, Z.; Wu, H.; Zhou, W.; Krishna, R.; Chen, B. Microporous metal-organic framework with potential for carbon dioxide capture at ambient conditions. *Nat. Commun.* **2012**, *3*, 954.

(44) Wei, F.; Ye, Y.; Huang, W.; Lin, Q.; Li, Z.; Liu, L.; Chen, S.; Zhang, Z.; Xiang, S. A naphthalene diimide-based MOF with mog net featuring photochromic behaviors and high stability. *Inorg. Chem. Commun.* **2018**, *93*, 105–109.

(45) Spek, A. Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. 2003, 36, 7–13.

(46) Lin, Q.; Wu, T.; Zheng, S. T.; Bu, X.; Feng, P. Single-walled polytetrazolate metal-organic channels with high density of open nitrogen-donor sites and gas uptake. *J. Am. Chem. Soc.* **2012**, *134*, 784–787.

(47) Guo, Z.; Yan, D.; Wang, H.; Tesfagaber, D.; Li, X.; Chen, Y.; Huang, W.; Chen, B. A three-dimensional microporous metalmetalloporphyrin framework. *Inorg. Chem.* **2015**, *54*, 200–204.

(48) Caskey, S. R.; Wong-Foy, A. G.; Matzger, A. J. Dramatic Tuning of Carbon Dioxide Uptake via Metal Substitution in a Coordination Polymer with Cylindrical Pores. *J. Am. Chem. Soc.* **2008**, *130*, 10870–10871.

(49) Bao, S.-J.; Krishna, R.; He, Y.-B.; Qin, J.-S.; Su, Z.-M.; Li, S.-L.; Xie, W.; Du, D.-Y.; He, W.-W.; Zhang, S.-R.; Lan, Y.-Q. A stable metal-organic framework with suitable pore sizes and rich uncoordinated nitrogen atoms on the internal surface of micropores for highly efficient CO_2 capture. *J. Mater. Chem. A* **2015**, *3*, 7361–7367.

(50) Wang, Z.; Zhang, J.-H.; Jiang, J.-J.; Wang, H.-P.; Wei, Z.-W.; Zhu, X.; Pan, M.; Su, C.-Y. A stable metal cluster-metalloporphyrin MOF with high capacity for cationic dye removal. *J. Mater. Chem. A* **2018**, *6*, 17698–17705.

(51) Panda, T.; Pachfule, P.; Chen, Y.; Jiang, J.; Banerjee, R. Amino functionalized zeolitic tetrazolate framework (ZTF) with high capacity for storage of carbon dioxide. *Chem. Commun.* **2011**, 47, 2011–2013.

(52) Lin, R.-B.; Chen, D.; Lin, Y.-Y.; Zhang, J.-P.; Chen, X.-M. A Zeolite-Like Zinc Triazolate Framework with High Gas Adsorption and Separation Performance. *Inorg. Chem.* **2012**, *51*, 9950–9955.

(53) Xiong, S.; Gong, Y.; Wang, H.; Wang, H.; Liu, Q.; Gu, M.; Wang, X.; Chen, B.; Wang, Z. A new tetrazolate zeolite-like framework for highly selective CO_2/CH_4 and CO_2/N_2 separation. *Chem. Commun.* **2014**, *50*, 12101–12104.

(54) Liu, K.; Ma, D.; Li, B.; Li, Y.; Yao, K.; Zhang, Z.; Han, Y.; Shi, Z. High storage capacity and separation selectivity for C_2 hydrocarbons over methane in the metal–organic framework Cu–TDPAT. *J. Mater. Chem. A* **2014**, *2*, 15823–15828.

(55) Li, L.; Wang, X.; Liang, J.; Huang, Y.; Li, H.; Lin, Z.; Cao, R. Water-Stable Anionic Metal-Organic Framework for Highly Selective Separation of Methane from Natural Gas and Pyrolysis Gas. *ACS Appl. Mater. Interfaces* **2016**, *8*, 9777–9781.

(56) Das, M. C.; Xu, H.; Xiang, S.; Zhang, Z.; Arman, H. D.; Qian, G.; Chen, B. A New Approach to Construct a Doubly Interpenetrated Microporous Metal–Organic Framework of Primitive Cubic Net for Highly Selective Sorption of Small Hydrocarbon Molecules. *Chem.* - *Eur. J.* **2011**, *17*, 7817–7822.

(57) Myers, A. L.; Prausnitz, J. M. Thermodynamics of mixed-gas adsorption. *AIChE J.* **1965**, *11*, 121–127.

(58) Zhang, Z.; Yao, Z.-Z.; Xiang, S.; Chen, B. Perspective of microporous metal-organic frameworks for CO_2 capture and separation. *Energy Environ. Sci.* **2014**, *7*, 2868–2899.

(59) Ye, Y.; Xiong, S.; Wu, X.; Zhang, L.; Li, Z.; Wang, L.; Ma, X.; Chen, Q. H.; Zhang, Z.; Xiang, S. Microporous Metal-Organic Framework Stabilized by Balanced Multiple Host-Couteranion Hydrogen-Bonding Interactions for High-Density CO_2 Capture at Ambient Conditions. *Inorg. Chem.* **2016**, 55, 292–299.