Fine-Tuning the Pore Environment of the Microporous Cu-MOF for High Propylene Storage and Efficient Separation of Light Hydrocarbons

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ABSTRACT: Ethylene (C2H4) and propylene (C3H6) are important energy sources and raw materials in the chemical industry. Storage and separation of C2H4 and C3H6 are vital to their practical application. Metal–organic frameworks (MOFs) having adjustable structures and pore environments are promising candidates for C2H4/C3H6 separation. Herein, we obtained a Cu-based MOF synthesized by H2TTCA and pyrazine ligands. By adding different functional groups on the ligands within the MOFs, their pore environments are adjusted, and thus, the C3H6 storage capacity and C3H6/C2H4 separation efficiency are improved. Eventually, the fluoro- and methyl-functionalized iso-MOF-4 exhibits a better gas storage and C2H4/C3H6 separation performance compared with iso-MOF-1 (nonfunctionalized), iso-MOF-2 (fluoro-functionalized), and iso-MOF-3 (methyl-functionalized). A record-high C3H6 uptake of 293.6 ± 2.3 cm3 g−1 (273 K, 1 atm) is achieved using iso-MOF-4. Moreover, iso-MOF-4 shows excellent repeatability, and only 3.5% of C3H6 storage capacities decrease after nine cycles. Employing Grand Canonical Monte Carlo (GCMC) simulations, it is indicated that iso-MOF-4 preferentially adsorbs C2H4 rather than C3H6 at low pressure. Single-crystal X-ray diffraction on C3H6-adsorbed iso-MOF-4 crystals precisely demonstrates the adsorption positions and arrangement of C3H6 molecules in the framework, which is consistent with the theoretical simulations. Remarkably, gas sorption isotherms, molecular simulations, and breakthrough experiments comprehensively demonstrate that this unique MOF material exhibits highly efficient C3H6/C2H4 separation. Additionally, iso-MOF-4 also possesses efficient separation of C3H6/CH4 and C2H6/CH4, indicating its promising potential in storage/separation of light hydrocarbons in industry.

INTRODUCTION

Ethylene (C2H4) and propylene (C3H6) are important raw materials for the synthesis of polyethylene and polypropylene.1−4 The coal-to-olefins processes, include methanol-to-olefins (MTO) and methanol-to-propylene (MTP), are the most advanced strategies to produce C2H4 and C3H6: the products of the MTO process contain C2H4 of 51.1 wt % and C3H6 of 20.91 wt %, and the MTP process mainly produces C2H4 of 71 wt %.5,6 However, the high quality and purity of C2H4 and C3H6 are essential to their industrial applications.7−10 For example, producing ethylbenzene requires a high purity of C2H4 with a volume fraction of C2H4 less than 0.15%.11 The traditional separation process of the C2H4 and C3H6 mixture is cryogenic distillation based on different vapor pressures, which has a high energy consumption.11 The separation method of the MTO and MTP product is alkaline washing, which will produce a large amount of butter and affect the safety of the equipment. Compared with the cryogenic distillation and alkaline washing technologies, adsorptive separation is safer and more energy-efficient.13,14 Thus, preparing porous materials exhibiting highly selective adsorption of C3H6 is of significance to realize the safe and high-capacity storage of C3H6 and efficient separation of C2H4/C3H6.15−20

Metal–organic frameworks (MOFs), as a new type of promising adsorbents, have been widely investigated in storage and gas separation, such as H2, O2, CH4, CO2, etc.21−23 The prominent advantages of MOFs over the traditional porous materials, such as activated carbon and zeolites, are their high surface areas and adjustable pores.24−26 MOFs have been recently researched in light hydrocarbons storage and separation.27−29 For example, to effectively improve C3H6 and C2H6 storage capacity at room temperature, Cao et al. explored microporous anionic MOFs with different porosities and concluded that the narrow pore size, the charged skeleton, and cationic counterions are beneficial to enhance the storage capacity of C3H6 and C2H6.30 Chen et al. reported a series of MOFs with optimized pore/cage sizes and open metal sites for adsorption/separation of light hydrocarbons.31,32 To date,
most of the reported works are mainly focused on the separation of \( C_2 \) or \( C_3 \) hydrocarbons from methane (\( C_1 \)). However, functional MOFs that exhibit efficient separation of \( C_3/C_2 \) light hydrocarbons, especially \( C_3H_6/C_2H_4 \) separation, are seldom reported, although this type of MOF is practically favorable.

In this contribution, selecting iso-MOF-1 as the parent framework, we obtained a family of isostructural micro-porous copper MOFs through adding the functional organic ligands, and the pore environments were therefore optimized for higher \( C_3H_6 \) storage and \( C_3H_6/C_2H_4 \) separation. Due to the existence of multiple channels in the structure, the obtained frameworks have a strong affinity for hydrocarbons, which is beneficial to the hydrocarbons storage and separation. On the other hand, iso-MOFs possess high thermal stability, suitable pore spaces with rich benzene/ pyrazine rings, multipore environments, and moderately high porosities with open metal sites, which is ideal for light hydrocarbon storage and separation. Gas adsorption and breakthrough measurements reveal that the fluoro- and methyl-functionalized iso-MOF-4 exhibits ultrahigh propylene storage (293.6 ± 2.3 cm\(^3\) g\(^{-1}\) at 273 K and 1 atm) and excellent separation performances for \( C_3H_6/C_2H_4 \). Single-crystal X-ray diffraction reveals that there are three types of 1D channels in iso-MOF-1, as illustrated in Figure S1, which are the tetragonal shaped channel (I) with dimensions of 7.1 \( \times \) 6.4 Å\(^2\), the pentagonal channel (II) with dimensions of 14.8 \( \times \) 10.2 Å\(^2\), and the hexagonal channel (III) with dimensions of 17.2 \( \times \) 12.7 Å\(^2\) (Figure S1c,d), respectively, providing an ideal platform for light hydrocarbon storage and separation.

### RESULTS AND DISCUSSION

**Fine-Tuning of Pore Environment in the Crystal Structure.** Dark green crystals of iso-MOF-1 were obtained by the solvothermal reaction of \( H_3TTCA ([1,1'3',1"-terphenyl]-4,4',5-tricarboxylic acid) \), pyrazine, and Cu(NO\(_3\))\(_2\)\( \cdot \)3H\(_2\)O in DMF/H\(_2\)O (v/v, 3/1) at 75 °C for 12 h. Single-crystal X-ray diffraction reveals that there are three types of 1D channels in iso-MOF-1, as illustrated in Figure S1, which are the tetragonal shaped channel (I) with dimensions of 7.1 \( \times \) 6.4 Å\(^2\), the pentagonal channel (II) with dimensions of 14.8 \( \times \) 10.2 Å\(^2\), and the hexagonal channel (III) with dimensions of 17.2 \( \times \) 12.7 Å\(^2\) (Figure S1c,d), respectively, providing an ideal platform for light hydrocarbon storage and separation.

Functional groups (F, Cl, NH\(_2\), CH\(_3\), OCH\(_3\)) were introduced in the MOFs (Figure 1) to further improve the \( C_3H_6 \) and \( C_3H_4 \) storage. The above MOFs crystals were obtained by a one-pot reaction rather than postsynthesis modification. Taking the fluorinated ligand (\( H_3TTCA-F \)) and 2-methylpyrazine ligand as example, iso-MOF-2 can be isolated by substituting the \( H_3TTCA \) ligand with the \( H_3TTCA-F \) ligand, and iso-MOF-3 can be obtained by substituting 2-methylpyrazine for pyrazine. The \( H_3TTCA-F \) was also employed to further demonstrate the precise locations and arrangements of the adsorbed \( C_3H_6 \) molecules within the frameworks. These unique storage and separation performances make iso-MOF-4 a promising candidate for practical applications in industry for \( C_3H_6 \) storage and \( C_3H_6/C_2H_4 \) separation.

![Figure 1. Fine-tuning of pore environment through multifunctionalized ligand modification in an isoreticular MOF framework, coordination state of Cu$_2$O$_4$ SBU, and coordination modes of TTCA$^{3-}$-R.](image-url)
ligand and 2-methylpyrazine are simultaneously constructed into the same structure to obtain iso-MOF-4, realizing the multifunctional modification of the MOF pore environment.

Gas Sorption. iso-MOF-1, iso-MOF-2, iso-MOF-3, and iso-MOF-4 are stable up to 250 °C, as confirmed by variable-temperature powder X-ray diffraction (PXRD; Figure S3), which is consistent with TGA (Figure S8). The high thermal stability and porosity of the iso-MOFs prompt us to study their gas adsorption performances. The iso-MOF crystals were solvent-exchanged with dry acetone. The acetone-exchanged samples were degassed at 298 K for 12 h and then at 353 K for 10 h, until the outgas rate was 5 mmHg min⁻¹, to produce the activated iso-MOFs. The active phase is highly crystalline and remains almost the same as its as-synthesized phase (Figure S3). The N₂ gas sorption curves of the iso-MOFs at 77 K indicate their permanent porosities (Figure 2a). All iso-MOFs show a typical type I N₂ adsorption isotherm with Brunauer–Emmett–Teller (BET) surface area of 3211 m² g⁻¹ for iso-MOF-1, 3154 m² g⁻¹ for iso-MOF-2, 3067 m² g⁻¹ for iso-MOF-3, and 2925 m² g⁻¹ for iso-MOF-4, suggesting their permanent microporosities. Pore size distributions were determined applying the nonlocal DFT (NL DFT) calculations based on the N₂ adsorption isotherms. All iso-MOFs have the pore sizes of 12.0–13.0 and 20.5–21.5 Å, consistent with their crystallographic data.

Considering the permanent porosity and large cages with open metal sites in all iso-MOFs, low-pressure C₂H₂ and C₃H₆ uptakes were further measured under 1 atm (Figure 2b and Tables S4 and S5). As expected, the fluoro- and methyl-functionalized iso-MOF-4 exhibit the highest C₂H₂ and C₃H₆ adsorption amounts up to 293.6 and 268.6 cm³ g⁻¹ at 273 K, which are higher than 245.5 and 229.5 cm³ g⁻¹ for iso-MOF-1, 290.0 and 267.9 cm³ g⁻¹ for iso-MOF-2, and 269.1 and 250.4 cm³ g⁻¹ for iso-MOF-3. In addition, the adsorption amounts of C₂H₂ and C₃H₆ in iso-MOF-4 are record-high in the reported MOF materials (Tables S4 and S5). To examine the cycling stability, as well as the error bars, nine cycles of C₂H₂ adsorption–desorption at 273 K were recorded with the reactivation process for each cycle. The C₂H₂ adsorption capacity of iso-MOF-4 is 293.6 ± 2.3 cm³ g⁻¹ (Figure S12b). In practice, C₂H₂ and C₃H₆ gases are usually stored at ambient temperature, and the C₂H₂ and C₃H₆ adsorption experiments at room temperature (298 K) were carried out. Exhilaratingly, iso-MOF-4 exhibits adsorption amounts of 254.5 and 240.9 cm³ g⁻¹ for C₂H₂ and C₃H₆, respectively, which is dramatically higher than the previously reported UPC-21 (116.2 and 124.1 cm³ g⁻¹),²⁹ FJI-C1 (160.9 cm³ g⁻¹ for C₂H₂), and FJI-C4 (74.7 cm³ g⁻¹ for C₃H₆).³⁰ Remarkably, the C₂H₂ and C₃H₆ adsorption amounts of 231.7 and 219.0 cm³ g⁻¹ can still be achieved at a higher temperature of 305 K (Figure 2d). The C₂H₂ and C₃H₆ uptake capacity of iso-MOF-4 only decreased by a rate of 2.01 and 1.65 cm³ g⁻¹ K⁻¹, respectively, from 273 to 305 K. Therefore, iso-MOF-4 is more suitable for practical applications around room temperature. In consideration of its practical application, we also tested the repeatability of iso-MOF-4 for C₂H₂ and C₃H₆ storage. About 100 mg of desolvated sample was loaded onto an ASAP 2020 analyzer, and nine cycles of C₂H₂ and C₃H₆ adsorption–desorption at 298 K were recorded without the reactivation process for each cycle. There is only 3.5% and 2.8% loss in adsorption capacity of C₂H₂ and C₃H₆ after nine cycles, indicating that iso-MOF-4 is promising in refillable C₂H₂ and C₃H₆ storage (Figure 2ef).

To further check its adsorption capacity for other light hydrocarbons, single component gas sorption isotherms of iso-MOF-1, iso-MOF-2, iso-MOF-3, and iso-MOF-4 for CH₄, C₂H₂, C₂H₆, and C₃H₆ were performed. At both 273 and 298 K, iso-MOF-4 also exhibits a high adsorption capacity, which can take up moderate amounts of C₂H₂ (161.7 cm³ g⁻¹), C₃H₆
(131.8 cm$^3$ g$^{-1}$), C$_2$H$_6$ (185.6 cm$^3$ g$^{-1}$), and CH$_4$ (17.9 cm$^3$ g$^{-1}$) at 273 K; C$_2$H$_2$ (91.5 cm$^3$ g$^{-1}$), C$_2$H$_4$ (73.1 cm$^3$ g$^{-1}$), and C$_2$H$_6$ (114.0 cm$^3$ g$^{-1}$), but a relatively lower amount of CH$_4$ (13.4 cm$^3$ g$^{-1}$) at 298 K (Figure S9). It should be noted that the sorption capacity of iso-MOF-4 for C$_2$H$_4$ (73.1 cm$^3$ g$^{-1}$) at 298 K is higher than UTSA-30a (46 cm$^3$ g$^{-1}$) and UTSA-36a (45 cm$^3$ g$^{-1}$), and even comparable to UTSA-38a (70 cm$^3$ g$^{-1}$). It is well-known that the magnitude of the adsorption enthalpies of porous materials reveals the affinity of the pore surface toward adsorbents, determining the adsorptive selectivity. To evaluate the affinity of such light hydrocarbons in iso-MOFs, the adsorption enthalpy ($Q_{st}$) for different light hydrocarbons was calculated by the Clausius–Clapeyron equation. The $Q_{st}$ values of CH$_4$, C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$, and C$_3$H$_8$ in iso-MOF-4 are 14.0, 27.8, 25.4, 18.7, 30.9, and 28.0 kJ mol$^{-1}$ at zero coverage, respectively (Figure S10), which are higher than iso-MOF-1, iso-MOF-2, and iso-MOF-3 for the corresponding gas molecule, indicating that the framework of iso-MOF-4 possesses a higher affinity to C$_3$H$_6$ and C$_3$H$_8$ molecules.

**GCMC Simulations.** Theoretically, the determination of gas adsorption sites in the MOF framework is of great significance for the design of new gas storage and separation materials based on MOFs. Herein, the ultrahigh C$_3$H$_6$ storage capacity prompts us to explore the adsorption sites within the framework of iso-MOF-4. Theoretical simulation is a powerful tool enabling us to unveil the adsorption mechanisms and providing us the information on adsorption sites. Hence, GCMC simulations were performed for understanding the interactions and adsorption behaviors of C$_3$H$_6$ in iso-MOF-4 at the molecular level. The density distributions of C$_3$H$_6$ and C$_2$H$_4$ molecules mass center within the structure at 298 K under different pressures were analyzed (Figure 3a–f). As expected, the potential adsorption sites are located around the paddlewheel secondary building units (SBUs). At relatively low pressure, the C$_3$H$_6$ molecules in iso-MOF-4 are preferentially filled in the tetragon I, pentagon II, and hexagon III regions, surrounded by four benzene rings and one pyrazine ring, and pentagon regions, surrounded by six benzene rings and one pyrazine ring. It is noteworthy that the adsorption behaviors of C$_3$H$_6$ in I and II regions are due to the interactions between the guest molecules and the surrounding benzene and pyrazine rings. Therefore, the ultrahigh C$_3$H$_6$ uptake of iso-MOF-4 is related to the rich benzene and pyrazine rings, suitable pore space, and open metal sites. With the increases of pressure (from 0.5 to 1.5 kPa), I and II regions are saturated; hexagon III regions begin to fill. In contrast, although C$_2$H$_4$ molecules have the same filling tendency, the filling pressure (from 10 to 60 kPa) is significantly greater than that of C$_3$H$_6$. This is consistent with the experimental data that the C$_3$H$_6$ adsorption isotherm was much steeper at low pressure than those for C$_2$H$_4$ and...
other C1−C2 light hydrocarbons. Moreover, the filling tendency is attributed to the tetragon I and pentagon II being able to produce stronger van der Waals interactions due to their smaller diameters, and therefore, C3H6 prefers filling the tetragon I and pentagon II regions rather than the hexagon III.

**Crystal Structure of C3H6@iso-MOF-4.** The most intuitive way to determine the adsorption of the C3H6 molecule is single-crystal X-ray diffraction (SCXRD), which can provide precise information about the location and orientation of the adsorbed molecules. However, the accurate crystallographic location of gas molecules in an MOF is challenging, unless the gas molecules have a strong affinity to the framework of the MOF. Recently, Li et al. precisely described the locations and orientations of adsorbed molecules (carbon number (n): 2−4) in a microporous MOF by SCXRD and molecular simulations, providing useful information for the design and synthesis of MOFs with light hydrocarbon storage and separation functions. Considering that iso-MOF-4 exhibits ultrahigh C3H6 storage and high adsorption enthalpy (Qst) for C3H6 molecules, the accurate determination of the sorption sites in activated iso-MOF-4 through SCXRD was carried out. The C3H6-loaded single crystal of iso-MOF-4 was rapidly coated with Paratone oil. The resulting C3H6-loaded single-crystal sample can be determined with a conventional X-ray diffractometer at 100 K. The activated iso-MOF-4 with C3H6 has the same space group as as-synthesized iso-MOF-4 (I41/amd). However, the coordinated water molecules always remain on the paddlewheel SBUs because the operation was under the ambient atmosphere, and water molecules immediately coordinated to the open copper site. The single-crystal X-ray structures for iso-MOF-4·2.0C3H6 evidently reveal that the adsorbed C3H6 molecules can be accommodated in the channels along a and b axes. One refined C3H6 molecule (with 0.5 occupancy) forms C−H···F interactions (H···F distances of 3.30 Å) with the fluorine atom (F1) of the TTCA-F ligand (Figure 3g). The other C3H6 molecules are surrounded by benzene rings and a pyrazine ring with a strong C−H···π interaction (Figure 3g,h). From the packing of C3H6 molecules viewed along the crystallographic a axis, one C3H6 molecule filled in the tetragon I, five C3H6 molecules in the pentagon II regions, and four C3H6 molecules in the hexagon III (Figure 3i). As expected, the adsorption sites and arrangements of C3H6 adsorbed in iso-MOF-4 crystals revealed by single-crystal X-ray diffraction are in good agreement with the theoretical calculation.

**Ideal Absorbed Solution Theory (IAST) Selectivities.** The C3H6/C2H4 separation of iso-MOFs was investigated due to its great significance in industrial applications. On the basis of previous reports, the adsorption of C3H6 and C2H4 in adsorbents directly influences the separation efficiency. Obviously, the adsorption rates of C3H6 and C3H8 are much higher than those of C1 and C2 at low pressure in iso-MOFs, and the adsorption enthalpy of C3 light hydrocarbons is the highest, indicating that they may provide stronger affinity to the framework and preferentially adsorbed on the framework.
of all iso-MOFs. For example, the adsorption energies of one C\textsubscript{3}H\textsubscript{6} molecule on the pyrazine site, Cu site, F site, and benzene ring site in iso-MOF-4 are $-47.37$, $-35.1$, $-25.9$, and $-24.09$ kJ mol$^{-1}$, higher than the adsorption energies of the C\textsubscript{2}H\textsubscript{4} molecule ($-38.42$, $-29.1$, $-18.4$, and $-15.62$ kJ mol$^{-1}$ for corresponding sites) (Figure S21). Therefore, it may show the high selectivity of C\textsubscript{3} light hydrocarbons relative to C\textsubscript{2} and C\textsubscript{4}.

**Breakthrough Experiments.** To evaluate the C\textsubscript{3}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4} separation performances of iso-MOF-4 in practical adsorption processes, experimental breakthrough studies were conducted, in which equimolar C\textsubscript{3}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4} gas mixtures were flowed over a packed column of activated iso-MOF-4 with a total flow of 2.67 mL min$^{-1}$ at 298 K. As shown in Figure 4a, highly efficient separations of C\textsubscript{3}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4} are achieved: C\textsubscript{2}H\textsubscript{4} can be first detected from the outlet effluent gas during initial purges, exhibiting an acceptable purity of over 99.99%, while no detectable C\textsubscript{3}H\textsubscript{6} was found. When the dynamic mixture flow is 120 min g$^{-1}$, the adsorbent reached saturation. At this time, C\textsubscript{2}H\textsubscript{4} achieved its breakthrough point, and the corresponding C\textsubscript{2}H\textsubscript{4} productivity is 14.30 mol kg$^{-1}$ sorbent, which is significantly higher than other top-performing C\textsubscript{2}H\textsubscript{4}-selective MOFs, such as SIFSIX-1-Cu$^{44}$ (6.37 mol kg$^{-1}$), SIFSIX-2-Cu$^{44}$ (2.88 mol kg$^{-1}$), SIFSIX-3-Zn$^{44}$ (1.52 mol kg$^{-1}$), UTSA-280$^{46}$ (1.86 mol kg$^{-1}$), MAF-49$^{37}$ (1.68 mol kg$^{-1}$), and Fe$_2$(O$_2$(dobdc)$^3$ (0.79 mol kg$^{-1}$), but trails UTSA-2004$^{48}$ (87.5 mol kg$^{-1}$). Obviously, the desirable high-purity C\textsubscript{2}H\textsubscript{4} can be directly obtained in a single separating operation by using C\textsubscript{3}H\textsubscript{6}-selective adsorbents, which greatly simplifies the separation process of these important petrochemicals. In practical industrial applications, the recyclability of an ideal absorbent is a problem worth considering. Therefore, we conducted multiple C\textsubscript{3}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4} mixed-gas dynamic breakthrough experiments to evaluate the preservation of iso-MOF-4 separation performance. The recycling tests indicated that the C\textsubscript{2}H\textsubscript{4} productivity of the sorbent did not significantly reduce during five breakthrough experiments (Figure 4b), further exhibiting that iso-MOF-4 is a promising candidate for C\textsubscript{3}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4} mixture purification.

The C\textsubscript{3}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4} (v/v, 15/85) and C\textsubscript{3}H\textsubscript{8}/C\textsubscript{2}H\textsubscript{4} (v/v, 15/85) separations were also measured by breakthrough experiments, and C\textsubscript{3}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8} were efficiently removed from CH\textsubscript{4} in the fixed bed to yield a high-purity gas (Figure 4c,d). The purity of CH\textsubscript{4} monitored at the outlet is over 99.999%. Notably, the breakthrough time of C\textsubscript{3}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4} is 113 min g$^{-1}$, which is comparable to C\textsubscript{3}H\textsubscript{8}/C\textsubscript{2}H\textsubscript{4} and higher than C\textsubscript{2}H\textsubscript{4}/CH\textsubscript{4} (elution times is 25 min g$^{-1}$), suggesting the high C\textsubscript{3} capture capacities for iso-MOF-4 to these mixtures.

The separation of C\textsubscript{3}/C\textsubscript{2}/C\textsubscript{1} hydrocarbons is the most important but challenging process in industry, which is currently energy- and cost-intensive.$^{49-51}$ Although adsorption-based porous materials are expected to create cost-effective and energy-efficient separation technologies, there is a trade-off between adsorption capacity and selectivity of porous materials reported so far.$^{5,27,31,52}$ We have demonstrated that iso-MOF-4 affords the selective molecular exclusion of C\textsubscript{1} and C\textsubscript{2} hydrocarbons and a record-high amount of C\textsubscript{3} hydrocarbons adsorption; thus, iso-MOF-4 has the potential to overcome the trade-off effect for achieving a highly efficient separation of the mixture of C\textsubscript{1}/C\textsubscript{2} and C\textsubscript{3} hydrocarbons.

The high C\textsubscript{3}H\textsubscript{6} storage and efficient C\textsubscript{3}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4} separation, as well as moderate C\textsubscript{3}H\textsubscript{8}/CH\textsubscript{4} and C\textsubscript{3}H\textsubscript{8}/C\textsubscript{2}H\textsubscript{4} separations, make iso-MOF-4 extremely applicable to the emergent separation requirements in many industrial processes. For instance, methanol-to-olefins (MTO) products contain about 90% C\textsubscript{2}–C\textsubscript{3} light-olefins, and there is an urgent need for an effective method to extract the main product C\textsubscript{2}H\textsubscript{4}. The separation of Fischer–Tropsch-to-olefins (FTO) products or natural gas purification also have similar requirements with the high selectivity of C\textsubscript{3}/CH\textsubscript{4}. These issues are currently underway in our lab.

**Safety Statement.** No unexpected or unusually high safety hazards were encountered.

**CONCLUSIONS**

In conclusion, we describe a family of isostructural micro-porous copper MOFs based on iso-MOF-1 through adding functional organic ligands, and the pore environments are properly adjusted for high light hydrocarbon storage and separation. The fluoro- and methyl-functionalized iso-MOF-4 exhibits the best gas storage and separation performance. GCMC simulations show that iso-MOF-4 preferentially adsorbs C\textsubscript{3}H\textsubscript{6} rather than C\textsubscript{2}H\textsubscript{4} at low pressure. The C\textsubscript{3}H\textsubscript{6} adsorption sites in iso-MOF-4 are precisely determined by SCXRD and molecular simulations to demonstrate the remarkable adsorption capacity. Breakthrough experiments reveal that iso-MOF-4 exhibits excellent separation performances for C\textsubscript{3}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{8}/C\textsubscript{2}H\textsubscript{4}, and C\textsubscript{3}H\textsubscript{6}/CH\textsubscript{4} indicating that iso-MOF-4 is a promising candidate for these very important industrial applications. On the basis of the modified performance of MOFs directly designed, we are currently developing customizable adsorbents for specific gas separations such as C\textsubscript{3}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{8}/C\textsubscript{2}H\textsubscript{4}, etc.

**ASSOCIATED CONTENT**

* Supporting Information The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.9b00423.

Materials and methods, synthesis and characterization, crystallographic data, and adsorption and breakthrough experiment details (PDF).

Detailed characterization of iso-MOF-1 (CIF)

Detailed characterization of iso-MOF-2 (CIF)

Detailed characterization of iso-MOF-3-1 (CIF)

Detailed characterization of iso-MOF-3-2 (CIF)

Detailed characterization of iso-MOF-3-3 (CIF)

Detailed characterization of iso-MOF-3-4 (CIF)

Detailed characterization of iso-MOF-4 (CIF)

Detailed characterization of C\textsubscript{3}H\textsubscript{6}@iso-MOF-4 (CIF)

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Notes
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