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Quasi-Orthogonal Configuration of Propylene within a Scalable Metal–Organic Framework Enables Its Purification from Quinary Propane Dehydrogenation Byproducts

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1. INTRODUCTION

Propylene (C₃H₆), as one of the most important chemical products, is widely used in the production of various chemicals, including polymers (e.g., polypropylene) and oxygenates (e.g., acetone and propylene oxide) etc.,¹,² and is expected to grow above 130 million metric tons by 2023.³ In the petrochemical industry, nonoxidative propane dehydrogenation (PDH) is becoming popular and is regarded as a promising way to meet the ever-increasing demand for propylene across the globe.⁴ The resultant byproducts in PDH reactions including methane (CH₄), ethylene (C₂H₄), ethane (C₂H₆), and propane (C₃H₈) impurities doubtlessly reduce the purity and productivity of C₃H₆. Effective C₃H₆ separation from binary C₂H₆/C₃H₈ mixtures (only 0.04 nm in kinetic diameter, Table S1) and even quinary mixtures in PDH byproducts (typically consisting of ca. 1–3% CH₄, 0.5–6% C₂H₆, 0.2–5% C₂H₄, 40–45% C₃H₈, and 42–50% C₃H₄) is a prerequisite for improving the quality of propylene. The separation technologies currently used are based on energy- and capital-intensive distillation operation, certainly contributing to larger energy loss and economic costs. Adsorbent-based separation strategies could theoretically alleviate the above-mentioned energy consumption without a phase change, namely, distinguishing the gas molecules only through molecule size, shape, polarity, and other characteristics.⁵

Metal–organic frameworks (MOFs), as well-known porous adsorbents, have been extensively explored for gas separation due to their adjustable pore chemistry and structural diversity etc.⁶–⁹ In terms of separation mechanisms, it can be roughly divided into thermodynamic separation and nonequilibrium separation. Compared with unilateral thermodynamic equilibrium dominated by binding affinities, the strategies that rely on nonequilibrium separation (including sieving separation and kinetic-driven separation) can be more energy-efficient and realistic given the fact that industrial pressure swing adsorption (PSA), vacuum swing adsorption (VSA), and temperature swing adsorption (TSA) processes are actually operating under nonequilibrium operating conditions. For example, Chen et al.¹⁰ covered the Co-gallate for sieving

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separation of C₆H₆/C₃H₈, which suggested a notable adsorption capacity of 66.6 cm³ g⁻¹ at 1 bar and 298 K. Breakthrough tests revealed the high purity of propylene (97.7%) with a high dynamic separation productivity of 36.4 cm³ cm⁻² under ambient conditions. Another praiseworthy sieving stage, JNU-3α, designed by Li et al., featured one-dimensional channels with embedded molecular pockets and realized the sieving separation of binary C₆H₆/C₃H₈, yielding high-purity C₆H₆ (>99.5%) and a C₆H₆ productivity of 53.5 L kg⁻¹. Unfortunately, strong sieving restriction in the pore channels might cause some unavoidable issues associated with the diffusion behavior and regeneration process. From the perspective of structural flexibility, most linkers are flexible in nature; accurately controlling pore size within a critical range to fully sieve C₆H₆ from C₃H₈/C₆H₆ mixtures is still in its infancy. Conversely, the kinetic effects, a significative diffusion-driven mechanism in the nonequilibrium process, could be dexterously designed to effectively accomplish the nonequilibrium separation. Li et al. prepared a MOF (termed as ELM-12), showing an enhanced C₆H₆ uptake of 62.0 mg g⁻¹ at 298 K and 1 bar and higher kinetic C₆H₆/C₃H₈ selectivity (204 at 298 K and 971 at 308 K). Breakthrough tests also confirmed the separation performance for binary mixtures, yielding a C₆H₆ productivity of 457 mmol per liter. Also, the Li and Eddaoudi groups developed several MOFs containing CH₄/C₂H₆/C₃H₈/C₄H₁₀/C₃H₆ mixtures, suggesting that 1 possesses the record-high C₆H₆ uptake of 92.4 cm³ cm⁻³ at 298 K and 0.1 atm, indicating a great potential for C₆H₆ capture at lower partial pressure. Further, comprehensive analysis including in situ spectroscopies, crystallographic experiments, and modeling analysis have cooperatively demonstrated that the decent pore microenvironment and multiple task-specific groups enabled synergetic equilibrium effects and “sweet spots” of kinetics for trapping C₆H₆ evidently boosting C₆H₆ separation. In particular, two C₆H₆ molecules adsorbed in one unit cell exhibit an unusual quasi-orthorhombic configuration, which favors the intramolecular interaction and multiple binding modes with pore pockets. Breakthrough tests demonstrate that 1 is capable of separating high-purity C₆H₆ (95.0–99.4%) from an equimolar C₂H₆/C₆H₆ mixture under ambient conditions, giving a maximum C₆H₆ productivity of 30.8 L for 1 kg of activated 1 under ambient conditions. The excellent separation property of C₆H₆ on 1 is also validated by the experimental and simulated breakthrough tests of quinary PDH byproducts containing CH₄/C₂H₆/C₃H₈/C₄H₁₀/C₃H₆ (3/5/6/42/44, v/v/v/v/v) mixtures, suggesting that 1 could inherit the preferable separation performance for trapping C₆H₆ from PDH byproducts. Notably, 1 possesses good structural stability and can be easily synthesized on the kilogram scale using cheap raw materials (only $167 for per kilogram of 1), awarding 1 the potential benchmark stage to purify C₆H₆ from multiple components.

2. EXPERIMENTAL SECTION

2.1. Materials. All reagents and solvents were purchased commercially and used without further processing. Zinc oxalate and 1,2,4-triazole were purchased from Macklin, Shanghai, China. Ethanol (C₂H₅OH, 99.5%) and methanol (CH₃OH, 99.5%) were purchased from Aladdin Industrial Co., Ltd., Shanghai, China.

2.2. Scalable Synthesis of Robust Zn-MOF (1). 1 was prepared according to the following method with some modifications. In detail, zinc oxalate and 1,2,4-triazole were mixed at the molar ratio of 1:2.3, then added into aqueous solution containing methanol/ethanol and ultrasonic stirring.
Subsequently, the solutions were transferred to a Teflon autoclave and heated at 453 K for 72 h. The yielded products were then washed with methanol and ethanol and then heated in a vacuum oven at 373 K for 12 h to afford desolvated 1.

2.3. Dynamic Column Breakthrough Experiments. Dynamic breakthrough experiments were tested in a homemade breakthrough setup and monitored on a gas chromatograph (GC). Prior to the breakthrough experiments, 0.3 g of activated 1 adsorbent was filled into the customized adsorption column (7.0 mm I.D. and 250 mm in length); glass wool was used to plug the two ends of the column. Then, the column was in situ heated at a temperature of 373 K for 12 h with a helium flow (5 sccm) to remove the adsorbed gas impurities. After the system was stabilized, the device was cooled to 298 K, and the gas mixtures of C$_2$H$_6$/C$_3$H$_8$/He (30/30/40, v/v/v) were introduced into the pipeline. The gas mixtures were passed through the column at a flow rate of 2 sccm and detected through GC. In the regeneration procedure, the adsorbent was in situ heated at 373 K for 12 h through using sweeping He gas at a rate of 5 sccm. For quinary CH$_4$/C$_2$H$_6$/C$_3$H$_8$/C$_4$H$_6$ (3/5/6/42/44, v/v/v/v/v), 0.01 kg of 1 was filled into the customized adsorption column (21.0 mm I.D. and 250 mm in length); note that the adsorbents were extruded, ground, and sieved into 40–60 mesh particles to minimize the impacts of diffusion and pressure drop). Other procedures were kept the same. The captured capacity of gas on I could be estimated using eq 1:

$$Q = \frac{CV}{22.4 \times m} \times \int_{t_0}^{t} \left(1 - \frac{F}{F_0}\right) \, dt$$

where $Q$ is the equilibrium adsorption capacity of gas $i$ (mmol g$^{-1}$), $C_i$ is the feed gas concentration, $V$ is the volumetric feed flow rate (sccm), $t$ is the adsorption time (min), $F_0$ and $F$ are the inlet and outlet gas molar flow rates, respectively, and $m$ is the mass of the adsorbent (g).

3. RESULTS AND DISCUSSION

3.1. Structural Analysis of Robust 1. In the case of single unit structure, the Zn center was five-coordinated with a distorted trigonal bipyramidal geometry (Figure 1a). In detail, the nitrogen atoms located in the 1,2-positions of the triazolate coordinated with Zn dimers and further connected to the next dimer via the nitrogen atom in the 4-position of the triazolate, as a result, forming into two-dimensional (2D) lattice planes. Interestingly, the layers of 1,2,4-triazolate-bridged zinc(II) were further pillared by oxalate species to construct the three-dimensional (3D) lattice and 3D pore geometry (Figure 1b,c; a detailed list of atomic positions for the Zn-MOF model are available in Table S2). The crystalline phase and purity of as-prepared bulk I was verified by combing the comparisons of theoretical and experimental PXRD diffractions. As clearly shown in Figure S1, all of the experimentally measured characteristic peaks agreed well with the simulated data and crystallized in the $P2_1/ c$ space group, indicating the isostructural topological structure of 1. Further, the cell volumes derived from refinement analysis between experimental and the theoretical model gave a ΔV/V of 0.005% (Table S3), being much lower than that of reported rigid MOF-5 (0.8%). The quasis-unchanged cell volume shrinkage revealed the excellent skeleton rigidity of 1, although indirectly. In order to confirm the structural rigidity under variable-temperature conditions, we conducted PXRD tests at 298 and 373 K to investigate the evolution of the unit cell. As shown in Figure S2a,b, it is suggested that there are no apparent shifts in the positions of all peaks for 1, revealing a higher framework lattice rigidity and structure stability without phase changes observed. In addition, the cell volumes of 1 at 298 (Figure S2a) and 373 K (Figure S2b) afforded a ΔV/V of 0.02% (Table S3). Intuitively, the cell structures of 1 underwent quasi-unchanged conformation deformations (Figure S2c,d) compared with that of theoretical topology, suggesting a credible structure stability. The excellent structure stability was
also demonstrated by TGA analysis (Figure S3), yielding a higher decomposition temperature exceeding 600 K.

Intuitive visualization of pore conformation, the simulated Connolly pore surface exhibited a zigzag shaped one-dimensional pore geometry along the crystallographic a axis, with a cross-sectional size of ca. 4.27 Å (Figure 1d,e; excluding the distances of the van der Waals radii), which would be favorable for distinguishing the gas diffusion behaviors. Especially for C₆H₆ and C₇H₈ guests with highly similar molecular attributes, the decent pore window seemed to be unfulfillable for both C₆H₆ (with the kinetic diameter of 5.1 Å) and C₇H₈ (4.7 Å) to diffusion into the pore channels from the kinetic diameter point of view. Nevertheless, the suitable pore space and the van der Waals molecular dimension differentiation could be expected to realize the separation of C₆H₆ (4.20 × 4.80 × 6.80 Å³) and C₇H₈ (4.16 × 4.65 × 6.45 Å³; Table S1). Thus, the propylene molecule with a minimum cross-section size of 4.16 × 4.65 Å² or 19.34 Å² could theoretically diffuse into the channel of 1 with a contented cross-section size (4.27 × 4.60 Å² or 19.64 Å²), while propane with a minimum cross-section size of 4.20 × 4.80 Å² or 20.16 Å² would be excluded from the pore channels due to the limited cross-section size of 1. Note that this slight shape sieving may not achieve an ideal sieving effect, but it is important to influence the diffusion behavior of molecules. A deep insight into the Hirshfeld surface (Figure 1f) is that it can be observed that a highly attractive negative electrostatic potential mapped with −0.05 au (red) was clearly distributed in the pore channel, suggesting the enriched pore polarity, which favored the binding interaction with the molecule that had a larger dipole moment.¹⁸,¹⁹ In brief, due to decent molecule dimensions and the large dipole moment of C₃H₆, it is expected to form strong interactions with the polar pore surface and will effortlessly diffuse into the adaptive pore channel.

### 3.2. Isothermal Adsorption and Selectivity Analysis.

The eternal pore attributes of 1 were determined at 77 K through using N₂ as the probe molecule. As clearly seen in Figure 2a, 1 exhibited a representative I-type profile, yielding a N₂ capacity of 127.4 cm³ g⁻¹ at 1 atm. The Brunauer–Emmett–Teller (BET) surface area and pore volume were evaluated to be 526.1 m² g⁻¹ and 0.35 cm³ g⁻¹ by adopting the ASAP 2020 physisorption analyzer, being nearly identical to the theoretical values of 510.8 m² g⁻¹ and 0.29 cm³ g⁻¹ (calculated from the optimized crystal structure). The pore size distribution (PSD) according to the Horvath–Kawazoe model revealed the ultramicropore with a peak centered at ca. 4.62 Å (inset in Figure 2a). The permanent ultraporosity and the decent pore dimensions motivated us to explore the potential adsorption performance of propane dehydrogenation byproducts including CH₄, C₂H₂, C₂H₂, C₂H₆, and C₃H₈ on activated 1. We collected the single-component adsorption isotherms of various guests on 1 at 298 K up to 1 atm. Here, volumetric uptake is adopted to evaluate the adsorption performance of the adsorbents in industry as that would determine the footprint of the gas separation units.²⁰ As clearly depicted in Figure 2b, 1 exhibited a distinguished C₃H₈ adsorption steepness at lower concentrations of 0.01–0.1 bar, giving the ultrahigh volumetric C₃H₈ uptake of 56.8 cm³ g⁻¹ (0.01/0.1 bar) at 298 K, as revealed by the steepness of the C₃H₈ adsorption isotherms. Conversely, it indicated eclipsed adsorption capacity for other guest molecules under identical conditions (Figure 2b). Further increasing pressure to 1 bar, 1 suggested quasi-saturated capacity of 97.4 cm³ g⁻¹, corresponding to 9.4 wt % or 1.94 C₃H₈ molecule per cell unit. In addition, the differences of statical adsorption capacity (denoted as ΔQ) for C₃H₈ and C₃H₈ at a lower pressure of 0.01/0.1 bar afforded ΔQ₁ and ΔQ₂ values of 20.2 and 32.0 cm³ g⁻¹ at 298 K (Figure 2b), confirming the preference for trapping trace C₃H₈ under lower partial pressure. Such differences could be visually observed at 273 K (Figure 2c).
remained the record-high volumetric capacity of C$_3$H$_8$ (DSLF) model (Figure S4a,b and Table S5). The adsorption heats ($Q_{st}$) were evaluated using the double site Langmuir isotherm model at 298 K and 0.1 bar. Results evidenced that the saturated C$_3$H$_8$ capacity, the density of gaseous C$_3$H$_8$ in I was determined to be 281.3 g L$^{-1}$ at 298 K and 0.1 bar. To our knowledge, the storage density of confined C$_3$H$_8$ in the channel far surpassed that of other benchmark materials including Zn$_2$-(5-ap)$_2$-(bpy) (135.9 g L$^{-1}$), SIFSIX-2-Cu-i (135.5 g L$^{-1}$), and CPL-1 (43.7 g L$^{-1}$) etc. Such a higher storage density of C$_3$H$_8$ at 0.1 atm was more than 164-fold higher than that of gaseous C$_3$H$_8$ (1.707 g L$^{-1}$) under similar conditions, suggesting that cooperative stacking models or intramolecular binding affinities may be responsible for C$_3$H$_8$ capture under lower pressure. Such an unusual adsorption configuration for trace C$_3$H$_8$ capture on 1 was mainly attributed to the larger polarization/dipole moment of C$_3$H$_8$ (Table S1), which exerted a crucial effect on the purification of propylene at lower concentrations, especially for propane cracking-gas mixtures containing multiple components.

In order to further highlight the advantages of 1 at low pressure, detailed comparisons with other advanced materials were integrated at 298 K and 0.1 bar. Results evidenced that 1 remained the record-high volumetric capacity of C$_3$H$_8$ (92.4 cm$^3$ cm$^{-3}$), surpassing that of most state-of-the-art competitors, including the newly reported MOF platforms ZU-36-Co (41.4 cm$^3$ cm$^{-3}$), Zn$_2$-(5-ap)$_2$-(bpy) (36.2 cm$^3$ cm$^{-3}$) and JNU-3a (14.4 cm$^3$ cm$^{-3}$) etc. (Figure 2d). To quantitatively evaluate the separation potential of 1 for binary C$_3$H$_8$/C$_4$H$_8$ mixtures, the ideal adsorbed solution theory (IAST) selectivity was evaluated using the double site Langmuir–Freundlich (DSLF) model (Figure S4a,b and Table S5). Obviously, 1 indicated a remarkable C$_3$H$_8$/C$_4$H$_8$ IAST selectivity, with a value of 63 at 0.1 bar (Table S4), far ascendant to many C$_3$H$_8$ selective prototypes covered, including MAF-23-O (8.9), Zn$_2$-(5-ap)$_2$-(bpy) (14.2) and MIL-100(Fe) (3.8). In addition, the comprehensive comparisons between C$_3$H$_8$ uptakes and the selectivity of C$_3$H$_8$/C$_4$H$_8$ at 0.1 bar suggested that 1 ranked in the “ceiling” level (Figure 2e), uncovering that 1 can effectively overcome the obstacles in balancing insurmountable “trade-off” effects. The unwonted breakthrough in trapping trace C$_3$H$_8$ is of the utmost importance, especially from multiple components with lower partial pressures of propylene. Note that IAST methods are often subject to uncertainties and limited requirements, and large errors can arise from narrow pores (nonideal gas solution), framework flexibility, a large binding difference, etc. So, the IAST selectivities were calculated here just for qualitative comparison. The coverage-dependent isosteric adsorption heats ($Q_m$) were calculated using the virial method (Figure 2f and Table S6) to explore the interaction energies between various molecules and the host framework. Apparently, the $Q_m$ of 1 at zero coverage followed the hierarchy of C$_3$H$_8$ (38.3 kJ mol$^{-1}$) > C$_4$H$_8$ (28.9 kJ mol$^{-1}$) > C$_3$H$_4$ (22.4 kJ mol$^{-1}$) > C$_3$H$_6$ (20.7 kJ mol$^{-1}$) > CH$_4$ (8.2 kJ mol$^{-1}$) etc. (Figure 2f), confirming 1 with the obvious potential stage to capture C$_3$H$_8$ from propane dehydrogenation byproducts. To be noted, the $Q_m$ of C$_3$H$_8$ at zero coverage was much lower than that of known Zn$_2$-(5-ap)$_2$-(bpy) (46 kJ mol$^{-1}$) and MAF-23-O (54 kJ mol$^{-1}$) etc. (Figure 2f) being comparable to SIFSIX-2-Cu-I (35.8 kJ mol$^{-1}$) and ZU-36-Co (38.0 kJ mol$^{-1}$). The desorption activation energy of C$_3$H$_8$ obtained from the TPD profiles was calculated to be 41.5 kJ mol$^{-1}$ (Figure S5a,b), also evidently confirming the strong binding affinity between C$_3$H$_8$ and the framework. Such a low adsorption enthalpy not only awarded the 1 platform a lower regeneration energy to yield higher C$_3$H$_8$ productivity but also avoided C$_3$H$_8$ oligomerization/polymerization that may damage the binding sites.

### 3.3. Adsorption Conformation and Binding Mechanism

To deeply elucidate the binding sites, we adopted Grand Canonical Monte Carlo (GCMC) simulations to investigate the binding models and adsorption mechanism between guest molecules and 1. As obviously observed, the simulated adsorption isotherms on 1 agreed well with the experimental...
results on the overall trend at 298 K, although some points at ultralow pressure and higher pressure were not particularly intimate (Figure S6). The inconsistent paces may derive from the strong binding affinity between guest molecules and the framework, which were intractable to construct the topology models using simple force fields. Additionally, the visualized density distribution contours of C\textsubscript{3}H\textsubscript{6}-loaded I (Figure 3a) suggested that the adsorbed C\textsubscript{3}H\textsubscript{6} was concentrated and arranged in the pore space one by one in a straight line along the zigzag shaped open channels. The optimized C\textsubscript{3}H\textsubscript{6} configurations obtained from GCMC-simulated saturated capacity also indicated 2-fold disordering over two binding configurations with partial occupancy, which oriented linearly with its C==C axis along the channels and tilted with its minimum cross-section along the pore wall (Figure 3b). The saturated adsorption orientation in the pore pocket would minimize any possible steric hindrance and electrostatic repulsion from the polar framework. Further, the spatial stacking conformation of two C\textsubscript{3}H\textsubscript{6} molecules located at labels 1 and 2 (Figure 3b, highlighted with red color) were amplified and shown in geometrical-plane perspectives (Figure 3c). Note that in order to intuitively mirror the stacking models of the two molecules, the C==C==C bond in a single molecule was selected as the reference point to construct the conformational plane. Interestingly, two C\textsubscript{3}H\textsubscript{6} molecules located in one unit cell adopted a quasi-orthogonal arrangement from a static view, giving the dihedral angles of 93.5° for label 1 and 88.3° for label 2 (Figure 3c), respectively. Likewise, for the C\textsubscript{3}H\textsubscript{6} molecules located at labels 3 and 4, the geometrical planes also displayed quasi-orthogonal packing models, with dihedral angles of 96.4° for label 3 and 90.5° for label 4 (Figure S7). Such an orthogonal array of C\textsubscript{3}H\textsubscript{6} molecules would maximize its binding interactions with a polar pore surface and favor its preferential capture.

Subsequently, density functional theory (DFT) optimizations of GCMC derived host-guest structures showed that there were mainly two adsorption sites (termed as site I and site II) for C\textsubscript{3}H\textsubscript{6}-loaded I (Figure 3d,e and Table S7), being well located at the unit cell through multiple binding interactions. In detail, for C\textsubscript{3}H\textsubscript{6}-adsorbed I in site I, two hydrogen atoms in the methyl group were grasped through forming chummy van der Waals interactions (C==H···π) with adjacent triazole ligands, giving binding distances of 2.46 Å (D1) and 2.86 Å (D2), respectively (Figure 3d). Meanwhile, another hydrogen atom in the propenyl group and the one in the methyl group were confined through forming additional hydrogen bonds with the oxygen atom in the oxalate ion, resulting in shorter distances of 2.50 Å (D3) and 2.37 Å (D4). It should be noted that the latent intramolecular interaction between two C\textsubscript{3}H\textsubscript{6} molecules also favored the C\textsubscript{3}H\textsubscript{6} adsorption. As visually observed in Figure S8, the static conformation of C\textsubscript{3}H\textsubscript{6} adsorbed in site I after geometry optimization oriented linearly with its C==C axis along the vertical direction of the propylene plane in site II for yielding intramolecular affinities through forming Lewis acid/base interactions, yielding a binding distance (C==H···C==H) of 2.56 Å for D5 and 2.42 Å for D6 (Figure 3d and Figure S8). Similar with that in site I, other C\textsubscript{3}H\textsubscript{6} molecule in site II were also confined through strong binding affinities. As seen in Figure 3e, in addition to the mentioned intramolecular interaction (namely D5 and D6, inset in Figure 3d), the hydrogen atoms in the methyl group and methylene group were spatially captured with a combination of the van der Waals effects (distance: 2.59 Å for D1 and 2.48 Å for D2). In addition, other H atoms in the propenyl and methyl groups were well immobilized through hydrogen-bond interactions with oxygen atoms (distance: 2.72 Å for D3 and 2.48 Å for D4; Figure 3e). On the contrary, for C\textsubscript{3}H\textsubscript{6}-loaded I, it suggested a weaker binding interaction, although having two adsorption sites (detailed adsorption configurations are available in Figure S9a,b). The theoretical binding energies between the host and guest showed an expected Q\textsubscript{st} order of C\textsubscript{3}H\textsubscript{6} (1 (38.9 kJ mol\textsuperscript{−1}) > C\textsubscript{3}H\textsubscript{6} (1 (26.4 kJ mol\textsuperscript{−1}), which was consistent with that obtained from experimental results (38.3 kJ mol\textsuperscript{−1} for C\textsubscript{3}H\textsubscript{6} and 28.9 kJ mol\textsuperscript{−1} for C\textsubscript{3}H\textsubscript{6} Figure 2f). Notably, the binding interactions between the gas molecules and framework were modest (van der Waals interaction, hydrogen bonding, and electrostatic interaction in nature), indicating that enriched C\textsubscript{3}H\textsubscript{6} can then be recovered with high purity during the regeneration step.

To further elucidate the unwanted geometrical conformational adsorption and adsorption mechanism of C\textsubscript{3}H\textsubscript{6} in the I skeleton, an in situ PXRD test and Rietveld structural refinements of C\textsubscript{3}H\textsubscript{6}-loaded I were carefully analyzed. As shown in Figure S10a, the refined lattice parameters (a = 8.9427 Å, b = 9.7210 Å, c = 9.5827 Å) of C\textsubscript{3}H\textsubscript{6}-loaded I seemed to be somewhat larger than that of pristine I (a = 8.9139 Å, b = 9.6932 Å, c = 9.4836 Å; Table S3), attributed to C\textsubscript{3}H\textsubscript{6} occupation in the unit cell of I. An intuitional binding scenario (Figure S10b,c) yielded from structural refinements demonstrated that the geometry configurations derived from in situ crystallographic experiments were quasi-consistent with those calculated by theoretical DFT calculations (Figure 3d,e). By comparing the binding distances of the same binding types obtained from experimental and theoretical results, the low relative errors are between 0.0 and 3.1% (Table S8). Such lower relative errors further reveal that the adsorption conformation yielded from crystallographic tests were convincing. In addition, the geometrical planes of two C\textsubscript{3}H\textsubscript{6} molecules also exhibited an approximate orthogonal adsorption configuration from a static view, with a dihedral angle of ca. 93.1° (Figure S10d), being consistent with that obtained from theoretical values.

Further, in situ Fourier transform infrared (FT-IR) tests were recorded to reveal the potential host-guest interaction between C\textsubscript{3}H\textsubscript{6} and I. As clearly shown in Figure S11a, the peaks located in 1630, 1320, and 1171 cm\textsuperscript{−1} in both activated I and C\textsubscript{3}H\textsubscript{6}-loaded I were assigned to the C==N adsorption band, symmetric carbonyl stretching, and C==O stretching vibrations in I structure.\textsuperscript{32-34} While for C\textsubscript{3}H\textsubscript{6}-loaded I, some characteristic peaks associated with the propylene molecule were clearly observed. For example, the emerging peaks located at about 2924 and 1436 cm\textsuperscript{−1} could be attributed to symmetric C==H bending of terminal methyl and methylene motifs in propylene.\textsuperscript{35,36} Also, the peak at around 996 cm\textsuperscript{−1} was the C==C stretching mode in propylene.\textsuperscript{37} Such spectral changes evidently confirmed the fact that propylene molecules could be adsorbed in the I structure. We investigated in situ Raman spectra of C\textsubscript{3}H\textsubscript{6}-loaded I to carefully analyze the host-guest interaction. As explicated in Figure S11b, the peak centered at 3147 cm\textsuperscript{−1} was the stretching mode of the C==H bond in the triazole ring of the I structure,\textsuperscript{38,39} and the other Raman vibration of the triazole ring (i.e., heterocyclic methyl C==H bending) could be observed at 1477 cm\textsuperscript{−1}.\textsuperscript{38} In addition, it was also found that there was an emerging peak that appeared at 1624 cm\textsuperscript{−1}, corresponding to the C==C stretching vibrations in the propylene molecule. This value was downshifted in...
comparison with that for gaseous propylene, which was 1640 cm$^{-1}$, mainly ascribed to the formed binding interaction between propylene and the framework, as demonstrated by Yaghi. The negative shift to lower frequency could also be visualized for the Zn–N peak (Figure S11b). Obviously, the Zn–N peak of I also experienced a downshift behavior upon propylene adsorption on I, suggestive of potential adsorption sites between propylene and I.

In addition, Hirshfeld surface analysis was used for probing the host–guest interactions and quantifying the binding interaction types. Hirshfeld surface was a novel partitioning of crystal space, affording a unique 3D $d_{norm}$ surface which could further be resolved into a 2D fingerprint plot. As shown in Figure 3f, it revealed the Hirshfeld surfaces of adsorbed C$_3$H$_8$ in site I mapped over $d_{norm}$, where the larger red spots in the map indicated strong short-range interactions with close contact effects (i.e., hydrogen-bonding) and a negative $d_{norm}$ value. White spots corresponded to contacts around the van der Waals separation and with a $d_{norm}$ value of zero, and blue spots reflected the long-range binding contact with a positive $d_{norm}$ value. Clearly, for C$_3$H$_8$-loaded I at site I, hydrogen-bonding interactions (red spots) and van der Waals effects (white spots) reflected in the map (Figure 3f) were basically consistent with the results obtained by DFT calculations (Figure 3d). Further, the binding types could be quantified by plotting two-dimensional (2D) fingerprint plots. Results showed that van der Waals interaction occupied 48.6% of the total Hirshfeld surface, while hydrogen bonding and intramolecular interaction occupied 33.0 and 18.4%, albeit not being particularly precise. Such consistence also could be found for the C$_3$H$_8$ molecule adsorbed at site II (Figure S12).

3.4. Molecular Dynamics and Diffusion Analysis. Diffusion-driven adsorption behavior, a realistic and signifcative separation metric in industrial PSA, VSA, and TSA-based nonequilibrium working conditions, needed to be given enough attention. We hereby adopted a molecular dynamics (MD) method to probe the diffusion behavior of guest molecules in channels. During the simulations, the initial configurations for the MD simulations were produced by GCMC simulation; the host framework and the gas molecule were both regarded as rigid. As shown in Figure S13 and Table S9, MD-derived diffusion coefficients of C$_3$H$_8$/C$_3$H$_4$/He, C$_3$H$_8$/C$_6$H$_6$/C$_3$H$_4$/He for I were calculated as 0.217/0.717/0.517/13.3/258 × 10$^{-11}$ m$^2$ s$^{-1}$. Therefore, the obtained diffusion coefficient of C$_3$H$_8$ (258 × 10$^{-11}$ m$^2$ s$^{-1}$) on I was much higher than that of the covered UiO-66 analogue (97.8 × 10$^{-12}$ m$^2$ s$^{-1}$) and MAF-23-O (0.82 × 10$^{-16}$ m$^2$ s$^{-1}$) confirming the fast diffusion rate. The obtained diffusion selectivity of C$_3$H$_8$/C$_3$H$_4$ was calculated to be 19.4, which was eclipsed compared with that of MAF-23-O (112.3). Intuitional snapshots of the MD results with both the host and guests as rigid suggested that two C$_3$H$_8$ molecules can be adaptively located in the confined channel of I after being steadily confined in the pore pocket (Figure S14b), yet that in I seemed to be escaping from the host when entering the aperture of the host framework (Figure S14a). Such transient diffusion trajectories further confirmed the favorable diffusion intensity for trapping C$_3$H$_8$ molecule.

3.5. Dynamic Column Breakthrough Experiments. To further explore separation natures of propylene on I from imitated propane dehydrogenation byproducts, transient breakthrough simulations were first probed for C$_3$H$_8$/C$_3$H$_4$/He (30/30/40, v/v/v) mixtures in a column adsorption–desorption cycle. Simulation results suggested that C$_3$H$_8$/C$_3$H$_4$/He mixtures with distinct breakthrough time could be effectively separated (Figure 4a), yielding a higher C$_3$H$_8$ capture capacity of 51.5 L kg$^{-1}$. These excellent breakthrough results from simulation motivated us to evaluate the separation performance of I in the actual separation process. As shown in Figure 4b, C$_3$H$_8$ first broke through the adsorption bed, while targeted C$_3$H$_4$ was still captured over a flow gas volume of 100 mL. To be noted, the simulated breakthroughs are sharper than those observed experimentally, mainly attributed to the fact that, in the simulations, intracrystalline diffusional influences

Figure 4. (a) Simulated breakthrough curves of I for C$_3$H$_8$/C$_3$H$_4$/He (30/30/40, v/v/v) at 298 K. (b) Experimental breakthrough curves of I for C$_3$H$_8$/C$_3$H$_4$/He (30/30/40, v/v/v) at 298 K and 1 bar, with a flow rate of 2 sccm. (c) Desorption curves of adsorbed C$_3$H$_8$ and C$_3$H$_4$ through helium purge, with a flow rate of 5 sccm. (d) Cycling breakthrough experiments of I for C$_3$H$_8$/C$_3$H$_4$/He (30/30/40, v/v/v) over eight cycles (inset represents the scaled-up production on the kilogram level). (e) Simulated breakthrough curves and (f) experimental breakthrough curves of I for quinary CH$_4$/C$_2$H$_6$/C$_3$H$_6$/C$_6$H$_6$/C$_3$H$_4$ (3/5/6/42/44, v/v/v/v/v) mixtures at 298 K and 1 bar.
are ignored. The captured C\textsubscript{6}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8} uptakes were also calculated to be ca. 52.0 and 2.0 L kg\textsuperscript{-1}, giving the outstanding experimental selectivity (or separation factor) of 26. Such a value was much higher than that of other benchmark materials including ZU-36-Ni (19.1), MAF-23-O (15), and Co-(AIP)/(BPY)\textsubscript{0.5} (2.92)\textsuperscript{16} etc. We also evaluated the captured amount and experimental selectivity with other well-known materials to demonstrate the “trade-off” effects (namely incompatible adsorption capacity and selectivity). As obviously seen in Figure S15, I was compatible with adsorption capacity and selectivity, anticipated to be a late-model paradigm for trace C\textsubscript{6}H\textsubscript{6} purification.

In addition to the capacity and adsorption selectivity mentioned above, the productivity and purity of C\textsubscript{3}H\textsubscript{8} yielded from desorption operation were also two important metrics to assess the separation performance of adsorbents. Apparently, the outlet concentration of the C\textsubscript{3}H\textsubscript{8} product was much higher than that of the C\textsubscript{6}H\textsubscript{6} competitor, and the whole desorption process can be fully desorbed within 35 min (Figure 4c). The obtained C\textsubscript{3}H\textsubscript{8} purities at different time periods were somewhat different, among which the obtained propylene purity between 5.4 and 24.3 min was up to 99.4%, albeit being somewhat overshadowed with actual requirements (≥99.5%) required by the polymer-grade purity of propylene.\textsuperscript{16} In addition, it could be estimated that about 30.8 L of the C\textsubscript{3}H\textsubscript{8} product with a serviceable purity of 95.0–99.4% could be accomplished from the equimolar C\textsubscript{6}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} mixtures for 1 kg of activated I in a single breakthrough operation. Such higher productivity and purity far exceeded that of KAUST-7 (16.3 L kg\textsuperscript{-1} with 90.0% purity) and Y-abtc (1.3 L kg\textsuperscript{-1} with 90.0% purity), yet was inferior in comparison to the laudable precedent, i.e., JNU-3a (34.2 L kg\textsuperscript{-1} with 99.5% purity) reported so far.\textsuperscript{11} In actual industrial separation units, there is a huge gap between laboratory pilot studies and commercial applications, making mass production of MOFs on a large scale a strong necessity. Here, kilogram scale breakthrough tests were conducted through filling 0.1 ± 0.5%ee kg of activated I into the customized column. As revealed in Figure 4d, I could still retain the quasi-unchanged separation performance for eight cycles, even in the presence of flow moisture having a certain temperature. The PXRD spectra after eight cycles still kept its intact crystalline structure when immersed in water for 1 week (Figure S16), echoing well with its excellent structural rigidity and stability.

Although I suggested efficient C\textsubscript{3}H\textsubscript{8} separation from C\textsubscript{6}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} binary mixtures, there are tremendous current impediments and challenges in the recovery of valuable propylene from propane dehydrogenation byproducts (typically consisting of ca. 1–3% CH\textsubscript{4}, 0.5–6% C\textsubscript{2}H\textsubscript{6}, 0.2–5% C\textsubscript{3}H\textsubscript{8}, 40–45% C\textsubscript{4}H\textsubscript{10}, and 42–50% C\textsubscript{6}H\textsubscript{6}). Targeting the C\textsubscript{3}H\textsubscript{8} purification from quinary mixtures could be expected to earn substantial economic benefits. Transient breakthrough simulations were first predicted with the various feed compositions of CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8}/C\textsubscript{4}H\textsubscript{10}/C\textsubscript{6}H\textsubscript{6} (3/5/6/42/44, v/v/v/v/v) to assess the universality of I for separation of quinary components. As shown in Figure 4e, efficient separation can be accomplished by I for quinary mixtures, wherein CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, and C\textsubscript{6}H\textsubscript{6} occurred first, and then C\textsubscript{4}H\textsubscript{10} passed through the column after a certain time (t\textsubscript{break}). Further, the experimental breakthrough tests were tested in the packed column of I under the same gas feed ratios under ambient conditions. The breakthrough profiles described in Figure 4f evidently confirmed that I could effectively purify C\textsubscript{3}H\textsubscript{8} from imperative propane dehydrogenation byproducts.

3.6. Structural Stability Tests and Costs Evaluation. It is well perceived that structural stability is the first and necessary prerequisite for MOFs to develop from laboratory research to the pilot scale and industry applications. We herein carried out multifaceted investigations on I, which had experienced cycling breakthrough experiments, including N\textsubscript{2} adsorption, single-gas adsorption, and crystallographic tests under variable-temperature conditions etc., to systematically analyze the structural stability of I. We first probed the pore geometry changes through N\textsubscript{2} adsorption at 77 K. As shown in Figure S17a, the N\textsubscript{2} uptake of I still inherited the quasi-unchanged adsorption capacity after cycling breakthrough tests, and the aperture distribution was concentrated at 4.67 Å (inset in Figure S17a), suggesting the unfading ultramicropore nature. In addition, single-gas adsorption isotherms of C\textsubscript{6}H\textsubscript{6} on I yielded a higher capacity of 31.1–35.0/88.5–94.1 cm\textsuperscript{3} g\textsuperscript{-1} at 0.01/0.1 atm and 298 K after 10 cycles (Figure S17b). Further, the variable-temperature PXRDs of I after cycling tests were recorded. As observed in Figure S17c, all of the diffractions all exhibited extremely consistent patterns compared with the theoretical diffractions, indicative of intact structural integrity. The derived top contour plots of variable-temperature PXRD (Figure S17d) evidenced that a main peak shift could hardly be observed, confirming a higher structural rigidity and thermal stability.

Of particular note was the costs of raw materials should also be taken into account for laboratory-scale synthesis. As visualized in Figure S18 and Table S10, the total costs of raw materials were just $167 for per kilogram of I adsorbent, which were much cheaper than other materials, including ZU-36-Ni ($17 399), Fe\textsubscript{4}(dobdc) ($45 277), and MCF-57 ($10 073) etc. (Table S10), further reinforcing its potential application for C\textsubscript{3}H\textsubscript{8} purification. Therefore, the excellent separation performance, steam stability, scalability of production, and cheap costs etc. awarded I the prominent potential to purify C\textsubscript{3}H\textsubscript{8} from PDH byproducts.

4. CONCLUSIONS

To sum up, an ultramicroporous Zn-MOF with scaled-up production could be easily synthesized using the cost-effective raw materials. An optimized geometry model revealed the ultramicroporous pore conformation for I, with a cross-sectional size of 4.27 × 4.60 Å\textsuperscript{2} (19.64 Å\textsuperscript{2}). The decent pore aperture was slightly larger than that of the propylene molecule with a minimum cross-section size of 4.16 × 4.65 Å\textsuperscript{2} (19.34 Å\textsuperscript{2}) but less than that of propane molecule with minimum cross-section size of 4.20 × 4.80 Å\textsuperscript{2} (20.16 Å\textsuperscript{2}), anticipating a diffusion barrier for the highly similar molecules. Static isotherm adsorption suggested that I possessed a record-high C\textsubscript{3}H\textsubscript{8} uptake of 92.4 cm\textsuperscript{3} g\textsuperscript{-1} at 298 and 0.1 bar, yielding an IAST selectivity of up to 63 among the reported benchmark MOFs. In situ spectroscopies, crystallographic experiments, and modeling demonstrated that two C\textsubscript{3}H\textsubscript{8} molecules confined in one unit cell were grasped through multiple binding interaction including van der Waals effects, hydrogen bonding, and intramolecular interaction. Molecular dynamics showed that I possessed a higher diffusion selectivity of 19.4 for C\textsubscript{3}H\textsubscript{8}/C\textsubscript{6}H\textsubscript{6}. Column breakthrough tests demonstrated that about 30.8 L of C\textsubscript{3}H\textsubscript{8} product with a purity of 95.0–99.4% could be accomplished from the equimolar C\textsubscript{3}H\textsubscript{8}/C\textsubscript{6}H\textsubscript{6} mixtures for 1 kg of activated I in a single breakthrough.
operation. Such an excellent separation property of propylene on 1 is also validated by the experimental and simulated breakthrough tests of quinary PDH byproducts containing CH₄/C₂H₆/C₂H₄/C₃H₆/C₃H₈ (3/5/6/42/44, v/v/v/v/v). Particularly, structurally stable 1 can be easily synthesized on the kilogram scale using cheap raw materials (only $167 for per kilogram of 1). The excellent separation performance, steam stability, scalability of production, and cheap costs etc. awarded 1 the prominent potential to purify C₃H₆ from PDH byproducts.

# ASSOCIATED CONTENT

+ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.2c00554.

Structural characterizations, spectroscopy tests, modeling details, calculation of separation potential, transient breakthrough simulations, supporting figures and tables (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


(33) Başaran, E.; Demircioğlu, Z.; Tarti, G. Ö.; Ceylan, Ü.; Karakıçlı-İliyioğan, A.; Oruç-Emre, E. E.; Aygün, M. Experimental, spectroscopic and theoretical investigation of (+)-(R)-5′-[1-(Benzenesulfonamido)-2-phenylthyl]-4-phenethyl-2,4-dihydro-3H-1,2,4-triazole-3-thione. *J. Mol. Struct.* 2022, 1251, 131996.


