Supporting information

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

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1. Structural characterizations

1.1. Crystal structure analysis and isotherms adsorption

Powder X-ray diffraction (PXRD) experiment was conducted on the Bruker D8 Advance X-ray diffractometer with Cu Ka emission at room temperature. In situ PXRD patterns were collected at 298 K using a capillary tube packed with the sample, which was firstly evacuated, and then filled with C\textsubscript{3}H\textsubscript{6} gas. Then, the Reflex refinements process on C\textsubscript{3}H\textsubscript{6}-loaded PXRD were carefully conducted through the Reflex Module in Materials Studio 2019 program. Given the fact that a larger number of atoms in one unit cell, the ligand molecule and the gas molecule were both treated as rigid motifs during the refinements process, with the molecule orientation and center of mass freely refined. Finally, the satisfactory $R$-factor and $R_{wp}$ values can be yielded through refining the parameters step by step, including lattice parameters, background, thermal factors, occupancies, profiles, etc.

N\textsubscript{2} adsorption–desorption isotherms were measured through the analyzer (ASAP2460, Micromeritics) at 77 K. The samples were initially degassed under reduced pressure for 12 h at 423 K. Single-gas adsorption experiments of various guests were conducted on the Micromeritic ASAP2020 analyzer. During each experiment, about 150 mg of activated 1 powder was placed in the sample cell and dried for 12 h at 373 K.

1.2. Temperature programmed desorption (TPD) experiments

The TPD experiments were carried out on a gas chromatography workstation at different heating rates from 4 to 8 K min\textsuperscript{-1}. For each operation, 0.02 g of activated 1 sample which had adsorbed guest molecules was packed in a stainless-steel column with an inner diameter of 0.35 cm and a packed length of ca. 0.56 cm. Then the stainless tube was placed in a reaction furnace and heated in the high purity N\textsubscript{2} flow at an initial flow rate of 4 sccm. The desorbed molecule was recorded by using the chromatograph with a TCD detector.

1.3. Calculation of desorption activation energy

Desorption activation energy was an important indicator to assess the binding strength between guest molecule and framework. The TPD curves obtained from chromatograph can be well described by the Polanyi-Wigner equation, which is expressed as Equation 1:\textsuperscript{1}

$$r_d = -\frac{d\theta_A}{dt} = k_0\theta_A^m\exp(-E_dRT)$$

where $r_d$ is the desorption rate (mol s\textsuperscript{-1}); $\theta_A$ is the fractional surface coverage; $k_0$ is a constant that depends on the desorption kinetics (s\textsuperscript{-1}); $m$ is the order of the desorption process; $E_d$ is the desorption activation energy of adsorbate (kJ mol\textsuperscript{-1}); $R$ is the gas constant [8.314 J (Kmol)\textsuperscript{-1}]. Providing that the desorption process follows first-order kinetics ($n = 1$), the desorption activation energy can be obtained from Equation 2:
\[
\ln \left( \frac{\beta_H}{RT_p} \right) = - \frac{E_d}{RT_p} - \ln \left( \frac{E_d}{k_0} \right)
\]  

(2)

where \( \beta_H \) is the heating rate (K min\(^{-1}\)) and \( T_p \) is the peak desorption temperature (K).
2. Spectroscopy tests

2.1. In situ Fourier transform infrared spectroscopy

The in situ Fourier transform infrared (FTIR) tests were recorded using a Tensor II FTIR spectrometer (Bruker) equipped with an in situ diffuse reflectance cell. Adsorbent was pretreated at 373 K for 6 h (flow rate: 20 sccm) to remove the adsorbed gas impurities and then cooled it to room temperature. After the background signal was collected with the flowing He and then was subtracted. Subsequently, 1 was exposed to propylene with a pressure of 1 atm for 36 h to ensure that the adsorption process has reached equilibrium state. All the spectra were recorded over accumulative 256 scans with a resolution of 4 cm\(^{-1}\) in the range of 4000~400 cm\(^{-1}\) range.

2.2. In situ Raman spectroscopy test

In-situ Raman spectrum was recorded with a RENISHAW-inVia Raman microscope system (USA). Sample was excited with a focused laser beam (\(\lambda = 405\) nm), 0.5 mW of output power and 75s of acquisition time were used. First, 0.1 g of 1 sample was placed in heating accessories pure argon gas was bubbled over 20 min to ensure an inert atmosphere. As-synthesized 1 was tested at 298 K and C\(_3\)H\(_6\)-loaded 1 was activated prior to measurement; activation was implemented in a quartz tube at 373 K for 60 min. Finally, 1 was cooled down to 298 K to get the data. The Raman spectra were recorded in the range of 100~4000 cm\(^{-1}\). Data acquisition were carried out by a computer with Renishaw WiRE Raman software version 2.0.
3. Modeling details

3.1. Crystal modeling and optimization analysis

For isostructural 1, the Crystallographic data in CIF format have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers: 2084733, which can be obtained free of charge via the link https://www.ccdc.cam.ac.uk/structures/ (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.). The initial structure was first optimized in the Dmol³ module, adopting the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional. The energy, force and displacement convergence criterions were set as $1 \times 10^{-5}$ Ha, $2 \times 10^{-3}$ Ha and $3 \times 10^{-4}$ Å, respectively. To obtain the gas binding energy, an isolated gas molecule placed in a cell unit (with the same cell dimensions as the MOF crystal). The static binding energy (at $T = 0$ K) could be expressed: $E_B = E(MOF) + E(gas) - E(MOF + gas)$.

3.2. Grand Canonical Monte Carlo (GCMC) calculation

The preferential binding conformation between guests and MOF structure were initially searched through GCMC simulations. Note that host framework and the gas molecule were both rigid in GCMC simulations through using Metropolis method, so that the produced the host-guest binding energies were equal to adsorption enthalpies. For all the GCMC simulations, the frameworks and the gas molecules were described by the universal forcefield (UFF). The Mulliken charges and ESP charges, calculated by PDFT, were employed to the framework atoms and guest atoms, respectively. The loading steps, equilibration steps and the production steps were all set to $2.0 \times 10^5$ and the temperature was set at 298 K. The cut-off radius was chosen as 15.0 Å for the Lennard-Jones (LJ) potential and the long-range electrostatic interactions were handled by the Ewald & Group summation method.

3.3. Molecular dynamics (MD) simulations

MD simulations were carried out in the Forcite module in Materials studio program. The output is a collection of snapshots in time of the trajectories of the atoms, which can be used in subsequent analysis. The initial host-guest configurations for the MD simulations were produced by GCMC simulations. The host framework and the gas molecule were both regarded as rigid. The constant-volume and temperature (NVT) ensemble were adopted to simulate the dynamic processes. The charges and force field were the same with that for GCMC simulations. The Nose-Hoover thermostat and Berendsen barostat were employed for temperature and pressure control, respectively. The Verlet method with a time step of 5 fs was used to integrate the particle equations of motion, and atomic trajectories were recorded every 5 ps. Besides, the velocity verlet algorithm was used for integration in the MD simulations, which were used to constrain rigid bonds and to integrate the equations of motion. MD simulations were then run for 30 ns (i.e., $1 \times 10^6$ steps with a time step of 2 fs)
after 5 ns of equilibration. The configurations were further stored every 2000 timesteps. The electrostatic interactions and the van der Waals interactions were evaluated by the Ewald summation method.

4. Calculation of separation potential

4.1. Dual Langmuir-Freundlich parameter fits

Dual-Langmuir-Freundlich isotherm model was adopted to fit the single-component loadings at 298 K, as shown in Equation 3 and 4.

\[
q = N_1 \frac{ap^b}{1 + ap^b} + N_2 \frac{cp^d}{1 + cp^d}
\]  (3)

With T-dependent parameters \(a\) and \(c\),

\[
a = a_0 \exp \left( \frac{E_A}{RT} \right); \quad c = c_0 \exp \left( \frac{E_B}{RT} \right)
\]  (4)

Here, \(p\) is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), \(q\) is the adsorbed amount per mass of adsorbent (mol kg\(^{-1}\)), \(N_1\) and \(N_2\) is the saturation capacities of site (mol kg\(^{-1}\)) of two different binding sites, \(a\) and \(c\) (1 kPa\(^{-1}\)) is the corresponding adsorption equilibrium constants reflecting the affinity coefficients of sites 1 and 2, and \(b\) and \(d\) represent the deviations from an ideal homogeneous surface for site 1 and 2.

4.2. Calculations of ideal adsorbed solution theory

The gas adsorption selectivity at 298 K and 1 bar was calculated using ideal adsorbed solution theory (IAST) on the basis of the single-component adsorption data. The adsorption selectivity for \(\text{C}_3\text{H}_6/\text{C}_3\text{H}_8\) separation is defined by Equation 5:

\[
S_{ads} = \frac{q_1}{p_1} \frac{q_2}{p_2}
\]  (5)

In above equation, the fitting parameters \(q_1\) and \(q_2\) reflected the molar adsorption in the adsorbed phase in equilibrium with the bulk gas phase with partial \(p_1\) and \(p_2\). In this work, dual-site Langmuir-Freundlich (DSLF) model was applied to fit \(\text{C}_3\text{H}_6\) and \(\text{C}_3\text{H}_8\) isotherms.

4.3. Calculations of isosteric heat

The isosteric heat (\(Q_{st}\)), being the crucial thermodynamic variable in adsorption process, affording serviceable information about the binding affinity between the adsorbate molecules and the adsorbent surfaces at different coverage. For this sake, the coverage-dependent adsorption enthalpy was evaluated from sorption data profiles measured at 273 and 298 K by adopting virial fitting method. In detail, a Virial-type equation mainly contained parameters \(a_i\) and \(b_i\), which were independent of temperature. In the equation, \(a_i\) and \(b_i\) represent the fitting Virial coefficients, \(m\) and \(n\) stands for the numbers of coefficients needed to precisely the
Isotherms, as shown in Equation 6:

\[ \ln P = \ln n + \sum_{i=0}^\infty a_i n^i + \sum_{j=0}^\infty b_j n^j \]  

(6)

The value of isosteric heat \( Q_{st} \) could be achieved by virtue of following Clausius-Clapeyron equation, as defined in Equation 7:

\[ Q_{st} = -R \left[ \frac{\partial \ln p}{\partial (1/T)} \right]_n \quad \text{and} \quad -R \sum_{i=0}^\infty a_i n^i \]  

(7)

5. Transient breakthrough simulations

The performance of industrial fixed bed adsorbers is dictated by a combination of adsorption selectivity and uptake capacity. Transient breakthrough simulations were carried out for \( \text{C}_3\text{H}_6/\text{C}_3\text{H}_8 \) (30/30/40, v/v/v) and \( \text{CH}_4/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_6/\text{C}_3\text{H}_8 \) (3/5/6/42/44, v/v/v/v/v) mixtures operating at a total pressure of 100 kPa and \( T = 298 \text{ K} \), using the methodology described in earlier publications. For the adsorber of length, \( L \), cross-sectional area, \( A \), voidage of the packed bed, \( \varepsilon \), the volume of MOF is:

\[ V_{ads} = L A (1 - \varepsilon) \text{ m}^3 \]

If \( \rho \) is the crystal framework density, the mass of adsorbent in the bed is:

\[ m_{ads} = (1 - \varepsilon) \times (L \text{ m}) \times (A \text{ m}^2) \times (\rho \text{ kg m}^{-3}) \text{ kg} \]

The breakthrough simulations are presented in terms of the following parameter, as shown in Equation 8:

\[ \left( Q_0 = \frac{\text{flow rate at inlet mL min}^{-1}}{\text{g MOF packed in tube}} \right) \times (\text{time in minutes}) = \frac{Q_0 t}{m_{ads}} = \text{mL g}^{-1} \]  

(8)

The breakthrough simulations demonstrate the potential of producing product gas \( \text{C}_3\text{H}_6 \) of required purity during the interval \( \Delta \tau \).
Notation

- $a$: Langmuir-Freundlich constant for species i at adsorption site A, $P_a^{-\nu a}$
- $c$: Langmuir-Freundlich constant for species i at adsorption site A, $P_a^{-\nu b}$
- $E$: Energy parameter, J mol$^{-1}$
- $Q_{st}$: Isosteric heat of adsorption, J mol$^{-1}$
- $c_i$: Molar concentration of species i in gas mixture, mol m$^{-3}$
- $c_{i0}$: Molar concentration of species i in gas mixture at inlet to adsorber, mol m$^{-3}$
- $t$: Time, s
- $T$: Absolute temperature, K

Greek letters

- $\varepsilon$: Voidage of packed bed, dimensionless
- $\nu$: Freundlich exponent, dimensionless
- $\rho$: Crystal framework density, kg m$^{-3}$
**Supporting figures**

**Figure S1.** Powder x-ray patterns of 1 simulated from single-crystal topology and obtained experimentally.
Figure S2. Rietveld structural refinements of 1 recorded at (a) 298 K and (b) 373 K; (c-d) refers to the conformational comparisons of 1 between pristine model structure (orange) and refined structure (turquoise) after heating tests at 298 and 373 K, respectively.
Figure S3. TGA of 1 under air atmosphere.
Figure S4. Isotherm fitting of (a) C$_3$H$_6$ and (b) C$_3$H$_8$ over 1 at 298 K and 1 bar.
Figure S5. (a) TPD of C$_3$H$_6$ on 1 at different heating rates from 4 ~ 8 K min$^{-1}$; (b) Linear dependence between $-\ln\left(\frac{\beta \cdot H}{R \cdot T^2 \cdot p}\right)$ and $1000/T_p$ for TPD of C$_3$H$_6$ on 1.
Figure S6. Experimental (dots) and simulated (line) adsorption isotherms of various guests on activated 1 at 298 K and 1 bar.
Figure S7. Visualized planes of guest molecule yielded from Figure 3b (3 and 4, marking with red color in Figure 3b) and created by three C atoms on a molecule (The atoms in guest molecules are highlighted with orange and other atoms in MOF structure are highlighted with light turquoise for clarity)
Figure S8. Visualized guest molecule planes created by the three C atoms on a molecule.
Figure S9. (a) DFT calculated adsorption conformation of C$_3$H$_8$-loaded 1 in Site I and (b) DFT calculated adsorption conformation of C$_3$H$_8$-loaded 1 in Site II. (Note that the binding types are colored with gray and red, corresponding to van der Waals interaction and hydrogen-bonding; Color modes: H in ligands, white; H in guest molecule, light blue; Zn, bright green; O, pink; N, blue; C, sea green)
Figure S10. (a) Experimental in situ PXRD pattern (black dots) and refined XRD spectra (red line) of C₃H₆-loaded 1; Refined geometry conformation of (b) C₃H₆-loaded 1 in Site I and (c) C₃H₆-loaded 1 in Site II; (d) Visualized guest molecule planes yielded from (b) created by the three C atoms on a molecule.
Figure S11. (a) In situ FTIR spectra of activated 1 (black) and C\textsubscript{3}H\textsubscript{6}-loaded 1 (red) in the wavelength number of 500~4000 cm\textsuperscript{-1}; (b) In situ Raman spectra of activated 1 (black) and C\textsubscript{3}H\textsubscript{6}-loaded 1 (red), collected with a 405 nm laser.
Figure S12. Hirshfeld surface (de) displaying host-guest interactions in Site II of C$_3$H$_6$-loaded 1 topology.
Figure S13. MD-derived self-diffusion rates of various guests in 1.
Figure S14. Selected snapshots for MD simulated C₃H₆ adsorption process in 1: (a) entering aperture of the host framework and (b) staying in the cavity of the host framework with a stable geometry configuration.
Figure S15. Comparisons of experimental selectivity and C₃H₆ uptake obtained from breakthrough curves over 1 and other benchmark materials.
Figure S16. PXRD pattern of 1 after 8th cycle and further immersed in water for one week.
**Figure S17.** (a) N\textsubscript{2} uptake of 1 after cycling breakthrough tests; (b) Comparison of static C\textsubscript{3}H\textsubscript{6} uptake at 0.01/0.1 atm at 298 K after ten cycles; (c) Variable-temperature PXRD of 1 at the temperature of 298 ~ 343 K; (d) Top contour plots of variable-temperature PXRD patterns on 1 collected from 298 ~ 343 K in a top view.
Figure S18. Comparisons of costs of raw materials for 1 and other advanced MOFs.

(For unified comparison, the referenced packages for raw materials and reagents were 100 g and 25 L, respectively)
Figure S19. Schematic illustration of the apparatus for the breakthrough tests.
## Supporting tables

### Table S1. Physical properties of gas molecules used in this work.

| Molecule | Kinetic diameter $^a$ (Å) | Three-dimensional molecule size $^b$ (Å³) | Polarizability $(\times 10^{-25}\,\text{cm}^3)$ | Dipole moment $(\times 10^{-18}\,\text{esu.} cm)$ | Boiling point $^c$ (K) |
|----------|----------------------------|------------------------------------------|---------------------------------------------|-------------------------------------------------|-----------------------|
| CH$_4$   | 3.80                       | $3.9 \times 4.0 \times 4.2$             | 25.93                                       | 0                                              | 111.5                 |
| C$_2$H$_4$ | 4.16                      | $3.4 \times 4.2 \times 4.9$             | 42.7                                        | 0                                              | 169.3                 |
| C$_2$H$_6$ | 4.44                      | $3.9 \times 4.2 \times 5.1$             | 44.3-44.7                                   | 0                                              | 184.4                 |
| C$_3$H$_6$ | 4.7                       | $4.16 \times 4.65 \times 6.45$         | 62.6                                        | 0.366                                          | 225.5                 |
| C$_3$H$_8$ | 5.1                       | $4.20 \times 4.80 \times 6.80$         | 63.7                                        | 0.084                                          | 231.0                 |

$^a$ Kinetic diameter refers to the shortest distance of two colliding identical molecules whose kinetic energies are equal to zero, in which the molecular shape is simplified as a sphere. The value is calculated from the experimental virial coefficients of the gas by assuming that the intermolecular interactions follow the Lenard-Jones potential, but the accurate virial coefficients are very difficult to measure. Therefore, the kinetic diameter of complicated molecules like C$_2$ differ a lot.

$^b$ Calculated from the atomic positions from the molecular geometries derived by DFT optimization and corresponding van der Waals radii (C/H/O: 1.7/1.2/1.5 Å).

$^c$ refers to the value at 298 K.
Table S2. List of atomic positions for Zn-MOF (denoted as 1) model obtained from crystallography files.

| NO. | Element | Symbol | x/a     | x/b     | x/c     |
|-----|---------|--------|---------|---------|---------|
| 1   | Zn      | Zn1    | 0.17588 | 0.05771 | 0.43679 |
| 2   | N       | N1     | 0.0308  | -0.1108 | 0.3683  |
| 3   | N       | N2     | -0.0922 | -0.1475 | 0.4100  |
| 4   | N       | N3     | -0.0992 | -0.2914 | 0.2259  |
| 5   | O       | O1     | 0.4098  | 0.0761  | 0.6102  |
| 6   | O       | O2     | 0.6753  | 0.0307  | 0.6732  |
| 7   | C       | C1     | 0.0215  | -0.1983 | 0.2588  |
| 8   | H       | H1     | 0.0932  | -0.1955 | 0.2086  |
| 9   | C       | C2     | -0.1655 | -0.2554 | 0.3232  |
| 10  | H       | H2     | -0.2559 | -0.3029 | 0.3289  |
| 11  | C       | C3     | 0.5248  | 0.0308  | 0.5815  |
Table S3. Crystallographic parameters and refinement details of experimental and theoretical models.

| Crystals      | 1\#     | 1       | 1@298 K | 1@373 K  |
|---------------|---------|---------|---------|----------|
| Formula weight| 195.72  | 195.76  | 195.72  | 196.75   |
| Crystal system| monoclinic | monoclinic | monoclinic | monoclinic |
| Space group   | P21/c   | P21/c   | P21/c   | P21/c    |
| a (Å)         | 8.9138  | 8.9139  | 8.9136  | 8.9151   |
| b (Å)         | 9.6934  | 9.6932  | 9.6935  | 9.6934   |
| c (Å)         | 9.4839  | 9.4836  | 9.4831  | 9.4836   |
| Cell volume (Å\(^3\)) | 819.46  | 819.42  | 819.38  | 819.55   |
| Calc. density (g cm\(^-3\)) | 1.762   | 1.760   | 1.762   | 1.763    |
| \(R_p\) (%)  | 4.17    | 9.48    | 10.17   | 11.27    |
| \(R_{wp}\) (%) | 10.24   | 16.11   | 20.81   | 17.21    |

\# represent the values derived from optimized crystal model.
**Table S4.** Summary of the adsorption capacity, uptake ratio, selectivities and heat of adsorption data for C$_3$H$_6$ and C$_3$H$_8$ in various propylene-based MOF adsorbents.

| Adsorbents   | C$_3$H$_6$ uptake a (cm$^3$ cm$^{-3}$) | IAST b (50/50, v/v) | $Q_{st}$(C$_3$H$_6$) c (kJ mol$^{-1}$) | Ref. |
|--------------|--------------------------------------|---------------------|---------------------------------------|------|
|              | C$_3$H$_6$ | C$_3$H$_8$ | 0.1 bar | 1 bar |                                      |      |
| 1 | 92.4 | 59.7 | 63.0 | 107.0 | 38.2 d | This Work |
| UiO-66-CF$_3$ | 35.2 | 22.2 | 82.1 | 103.0 | 38.1 d | 9 |
| MAF-23-O | 35.0 | 18.5 | 8.9 | 8.9 | 54.0 d | 10 |
| SIFSIX-2-Cu-i | 30.5 | 9.5 | 4.2 | 5.1 | 35.8 d | 11 |
| Zn$_2$(5-aip)$_2$(bpy) | 36.2 | 4.0 | 14.0 | 20 | 46.0 d | 12 |
| CPL-1 | 5.4 | 3.8 | N.R. g | N.R. g | N.R. g | 13 |
| MIL-100(Fe) | 40.9 | 25.8 | 3.8 | 2.0 | N.R. | 14 |
| ZU-36-Co | 41.4 | 8.3 | 9.5 | 15 | 38.0 d | 15 |
| GeFSIX-2-Cu-i | 32.2 | 13.7 | 3.8 | 4.1 | 36.2 d | 16 |
| HOF-16a | 52.3 | 33.0 | 2.0 | 5.4 | 30.2 e | 17 |
| JNU-3a | 14.4 | 7.5 | 2.7 | 513 | 29.3 f | 18 |

a refers to adsorption uptake at 298 K and 0.1 bar.
b IAST selectivity. These values are only for the qualitative comparison purpose.
c $Q_{st}$ values at low surface coverage.
d refers to $Q_{st}$ was obtained through the virial method.
e refers to $Q_{st}$ was obtained through the Clausius-Clapeyron equation.
f refers to $Q_{st}$ was obtained through differential scanning calorimetry.
g N.R. represent not reported.
Table S5. Dual-site Langmuir-Freundlich parameters fits for C$_3$H$_6$ and C$_3$H$_8$ of 1.

|          | Site A |           | Site B |           |
|----------|--------|-----------|--------|-----------|
|          | $N_1$  | $a$       | $b$    | $N_2$     | $c$       | $d$    |
|          | mol kg$^{-1}$ | Pa$^{-v_A}$ | dimensionless | mol kg$^{-1}$ | Pa$^{-v_A}$ | dimensionless |
| C$_3$H$_6$ | 2.6802 | 1.4501    | 0.5902 | 2.6817    | 1.4511    | 0.6011 |
| C$_3$H$_8$ | 1.0025 | 0.5615    | 0.6602 | 0.7112    | 1.5115    | 4.0125 |
Table S6. The parameters of virial equation for various gas adsorption isotherms on 1.

| Gas   | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $a_5$ | $a_6$ | $a_7$ | $b_0$ | $b_1$ | $b_2$ | $R^2$  |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| C$_3$H$_8$ | -3478 | 401   | -882  | 2001  | -1197 | 2808  | -3297 | 206   | 18.4  | 0.017 | -0.273 | 0.9945 |
| C$_3$H$_6$ | -4608 | 1468  | 406   | -2808 | 349   | 916   | -1995 | 3078  | 5.78  | 0.210 | -1.27  | 0.9987 |
| C$_2$H$_6$ | -2708 | 822   | -1080 | 2104  | 204   | 2747  | -3107 | 76    | 10.2  | -0.004 | 1.28   | 0.9889 |
| C$_2$H$_4$ | -2508 | 302   | -907  | 1576  | 198   | 2574  | -2479 | 128   | 8.00  | 0.297 | -5.37  | 0.9967 |
| CH$_4$   | -1008 | 22    | -1026 | 1508  | 174   | 2875  | -2439 | 1022  | 26.4  | 0.087 | -1.87  | 0.9937 |
Table S7. List of atomic positions for C$_3$H$_6$-loaded 1 obtained from DFT calculations.

| Atom | x/a  | x/b  | x/c  | Atom | x/a  | x/b  | x/c  |
|------|------|------|------|------|------|------|------|
| O1   | 0.53007 | 0.52537 | 0.2966 | O28  | 0.55843 | 0.34357 | 0.55773 |
| O2   | 0.44157 | 0.51023 | 0.2756 | C29  | 0.3405 | 0.60057 | 0.4196 |
| C3   | 0.49173 | 0.51027 | 0.30617 | H30  | 0.3644 | 0.6015 | 0.40287 |
| Zn4  | 0.39196 | 0.48076 | 0.31226 | C31  | 0.6115 | 0.58153 | 0.44107 |
| Zn5  | 0.60804 | 0.3141 | 0.52107 | C32  | 0.50827 | 0.3436 | 0.52717 |
| O6   | 0.53007 | 0.30797 | 0.46327 | Zn33 | 0.60804 | 0.51924 | 0.3544 |
| O7   | 0.44157 | 0.3231 | 0.44227 | N34  | 0.6564 | 0.46307 | 0.37723 |
| C8   | 0.49173 | 0.32307 | 0.47283 | N35  | 0.36407 | 0.45083 | 0.36333 |
| N9   | 0.3026 | 0.6175 | 0.47 | N36  | 0.3664 | 0.40287 | 0.4247 |
| N10  | 0.30027 | 0.56953 | 0.40863 | O37  | 0.53007 | 0.52537 | 0.62993 |
| C11  | 0.27817 | 0.58153 | 0.44107 | O38  | 0.44157 | 0.51023 | 0.60893 |
| Zn12 | 0.27471 | 0.51924 | 0.3544 | C39  | 0.6595 | 0.4339 | 0.41373 |
| N13  | 0.32307 | 0.46307 | 0.37723 | H40  | 0.6356 | 0.43483 | 0.43047 |
| C14  | 0.32617 | 0.4339 | 0.41373 | C41  | 0.3885 | 0.41487 | 0.39227 |
| H15  | 0.30227 | 0.43483 | 0.43047 | C42  | 0.49173 | 0.51027 | 0.6395 |
| Zn16 | 0.27471 | 0.64743 | 0.52107 | Zn43 | 0.60804 | 0.64743 | 0.52107 |
| N17  | 0.32307 | 0.37027 | 0.5439 | N44  | 0.6564 | 0.37027 | 0.5439 |
| C18  | 0.32617 | 0.39943 | 0.5804 | N45  | 0.36407 | 0.3825 | 0.53 |
| H19  | 0.30227 | 0.3985 | 0.59713 | N46  | 0.3664 | 0.43047 | 0.59137 |
| N20  | 0.3026 | 0.54917 | 0.63667 | O47  | 0.53007 | 0.6413 | 0.46327 |
| N21  | 0.30027 | 0.59713 | 0.5753 | O48  | 0.44157 | 0.65643 | 0.44227 |
| C22  | 0.27817 | 0.58513 | 0.60773 | C49  | 0.6595 | 0.39943 | 0.5804 |
| Zn23 | 0.39196 | 0.35257 | 0.47893 | H50  | 0.6356 | 0.3985 | 0.59713 |
| N24  | 0.3436 | 0.62973 | 0.4561 | C51  | 0.3885 | 0.41847 | 0.55893 |
| N25  | 0.63593 | 0.6175 | 0.47 | C52  | 0.49173 | 0.6564 | 0.47283 |
| N26  | 0.6336 | 0.56953 | 0.40863 | Zn53 | 0.39196 | 0.48076 | 0.6456 |
| O27  | 0.46993 | 0.3587 | 0.53673 | N54  | 0.3436 | 0.53693 | 0.62277 |
| N55  | 0.63593 | 0.54917 | 0.63667 | O83  | 0.55843 | 0.48977 | 0.7244 |
| N56  | 0.6336 | 0.59713 | 0.5753 | C84  | 0.50827 | 0.48973 | 0.69383 |
| O57  | 0.46993 | 0.47463 | 0.37007 | C85  | 0.38046 | 0.49996 | 0.51523 |
| O58  | 0.55843 | 0.48977 | 0.39107 | C86  | 0.4212 | 0.46972 | 0.5039 |
| C59  | 0.3405 | 0.5661 | 0.58627 | C87  | 0.4732 | 0.49803 | 0.51263 |
| H60  | 0.3644 | 0.56517 | 0.56953 | H88  | 0.3669 | 0.48094 | 0.54277 |
| C61  | 0.6115 | 0.58513 | 0.60773 | H89  | 0.34247 | 0.50784 | 0.47708 |
|     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C62 | 0.50827 | 0.48973 | 0.3605 |     | H90 | 0.40184 | 0.53348 | 0.53423 |     |
| Zn63 | 0.72529 | 0.35257 | 0.47893 |     | H91 | 0.41015 | 0.43244 | 0.49121 |     |
| N64 | 0.67693 | 0.62973 | 0.4561 |     | H92 | 0.5013 | 0.48656 | 0.49411 |     |
| C65 | 0.67383 | 0.60057 | 0.4196 |     | H93 | 0.48358 | 0.53047 | 0.5376 |     |
| H66 | 0.69773 | 0.6015 | 0.40287 |     | C94 | 0.56762 | 0.50957 | 0.46511 |     |
| N67 | 0.6974 | 0.45083 | 0.36333 |     | C95 | 0.58889 | 0.46427 | 0.49534 |     |
| N68 | 0.69973 | 0.40287 | 0.4247 |     | C96 | 0.58856 | 0.4681 | 0.54919 |     |
| C69 | 0.72183 | 0.41487 | 0.39227 |     | H97 | 0.53398 | 0.50175 | 0.42424 |     |
| N70 | 0.6974 | 0.3825 | 0.53 |     | H98 | 0.60353 | 0.5283 | 0.46206 |     |
| N71 | 0.69973 | 0.43047 | 0.59137 |     | H99 | 0.5496 | 0.53221 | 0.48667 |     |
| C72 | 0.72183 | 0.41847 | 0.55893 |     | H100 | 0.60179 | 0.43466 | 0.47675 |     |
| Zn73 | 0.72529 | 0.48076 | 0.6456 |     | H101 | 0.61524 | 0.44389 | 0.58214 |     |
| N74 | 0.67693 | 0.53693 | 0.62277 |     | H102 | 0.56162 | 0.49515 | 0.55609 |     |
| C75 | 0.67383 | 0.5661 | 0.58627 |     |     |     |     |     |     |
| H76 | 0.69773 | 0.56517 | 0.56953 |     |     |     |     |     |     |
| Zn77 | 0.39196 | 0.6859 | 0.47893 |     |     |     |     |     |     |
| O78 | 0.46993 | 0.69203 | 0.53673 |     |     |     |     |     |     |
| O79 | 0.55843 | 0.6769 | 0.55773 |     |     |     |     |     |     |
| C80 | 0.50827 | 0.67693 | 0.52717 |     |     |     |     |     |     |
| Zn81 | 0.60804 | 0.51924 | 0.68774 |     |     |     |     |     |     |
| O82 | 0.46993 | 0.47463 | 0.7034 |     |     |     |     |     |     |
Table S8. Comparisons of binding distances obtained from DFT calculations and in situ PXRD tests.

| Binding types            | Binding Sites | Distance $^a$ (Å) | Distance $^b$ (Å) | Relative error $^c$ (%) |
|--------------------------|---------------|-------------------|-------------------|------------------------|
| van der Waals interaction| Site I, D1    | 2.46              | 2.41              | 2.0                    |
| van der Waals interaction| Site I, D2    | 2.86              | 2.79              | 2.4                    |
| hydrogen-bonding         | Site I, D3    | 2.50              | 2.54              | 1.6                    |
| hydrogen-bonding         | Site I, D4    | 2.37              | 2.36              | 0.4                    |
| intramolecular interaction| Site I, D5    | 2.56              | 2.52              | 1.6                    |
| intramolecular interaction| Site I, D6    | 2.42              | 2.48              | 2.5                    |
| van der Waals interaction| Site II, D1   | 2.59              | 2.64              | 1.9                    |
| van der Waals interaction| Site II, D2   | 2.48              | 2.43              | 2.0                    |
| hydrogen-bonding         | Site II, D3   | 2.72              | 2.72              | 0.0                    |
| hydrogen-bonding         | Site II, D4   | 2.48              | 2.46              | 0.8                    |
| intramolecular interaction| Site II, D5   | 2.56              | 2.48              | 3.1                    |
| intramolecular interaction| Site II, D6   | 2.42              | 2.42              | 0.0                    |

$^a$ represent the binding distance was obtained from DFT calculations

$^b$ represent the binding distance was obtained from in situ PXRD tests

$^c$ relative error (absolute value) was calculated based on the equation: $\frac{\text{Distance}^b - \text{Distance}^a}{\text{Distance}^a} \times 100\%$
Table S9. Comparison of simulated diffusion parameters for diffusivity.

| Adsorbates | Fitting $K$ value ($\times10^{-3}$) | $D_M$ ($\times10^{-12}$ m² s⁻¹) |
|------------|----------------------------------|---------------------------------|
| C₃H₈       | 80                               | 133                             |
| C₃H₆       | 1550                             | 2580                            |
| C₂H₆       | 4.3                              | 7.17                            |
| C₂H₄       | 3.1                              | 5.17                            |
| CH₄        | 1.3                              | 2.17                            |
Table S10. Estimated raw material cost for the preparation of C₃H₆-selective adsorbents.

| Material                  | Main raw chemicals                                | Amount of raw (g) per g product | Label* | Price ($) | TCPG ($/kg) | Ref.  |
|---------------------------|----------------------------------------------------|---------------------------------|--------|-----------|-------------|-------|
| 1                         | zinc oxalate dihydrate                             | 0.9041 g                        | Z303988-100 g | 8.49      | 167         | This work |
|                           | 1,2,4-triazole                                    | 0.6849 g                        | T100645-100 g | 7.15      |             |        |
|                           | methanol                                           | 9.041 mL                        | M116115-25 L  | 102.96     |             |        |
|                           | ethanol                                            | 1.018 mL                        | E118433-25 L  | 104.15     |             |        |
| ZU-36-Ni*                 | nickel tetrafluoroborate hexahydrate               | 1.199 g                         | N189039-100 g | 65.71     | 17,399      | 15     |
|                           | ammonium hexafluorogermanate                       | 0.7846 g                        | A167837-5 g   | 99.68      |             |        |
|                           | pyrazine                                           | 3.523 g                         | P109613-100 g | 26.37     |             |        |
|                           | water                                              | 7.046 mL                        | W119424-25 L  | 42.17      |             |        |
| MAF-23-O                  | zinc hydroxide                                     | 0.3247 g                        | Z274616-100 g | 19.22     | 205         | 19     |
|                           | bis(5-methyl-1H - 1,2,4-triazol-3-yl)methane       | 0.5779 g                        | A107218-100 g | 10.13     |             |        |
|                           | aqueous ammonia (25%)                              | 12.99 mL                        | A359072-4 L   | 19.22      |             |        |
|                           | water                                              | 12.99 mL                        | W119424-25 L  | 42.17      |             |        |
| Zn₂(5-aip)₂(bpy)          | zinc nitrate hexahydrate                           | 1.716 g                         | Z111703-100 g | 25.18     | 1,880       | 20     |
|                           | 5-aminoisophthalic acid                            | 0.5228 g                        | A107450-100 g | 16.99     |             |        |
|                           | 4,4'-bipyridine                                    | 0.4526 g                        | B105217-100 g | 47.83     |             |        |
|                           | DMF                                                | 117.1 mL                        | D111999-25 L  | 208.45     |             |        |
|                           | water                                              | 39.02 mL                        | W119424-25 L  | 42.17      |             |        |
| UiO-66*                   | zirconium(IV) chloride                             | 1.207 g                         | Z109460-100 g | 65.41     | 5,859       | 9      |
|                           | terephthalic acid                                  | 0.7742 g                        | P108506-100 g | 7.60      |             |        |
|                           | m-(trifluoromethyl) benzoic acid                   | 0.1055 g                        | T107270-100 g | 22.80     |             |        |
|                           | DMF                                                | 598.1 mL                        | D111999-25 L  | 208.45     |             |        |
| JNU-3a                    | cobalt nitrate hexahydrate                         | 0.7275 g                        | C112729-100 g | 8.34      | 1,055       | 18     |
|                           | 5-(3-methyl-5-|                                | 0.8100 g                        |          |             |        |
| System | Components | Amount | Reference Code | Solvent | Volume |
|--------|------------|--------|----------------|---------|---------|
| Ni(AIP)(BP Y)$_{0.5^*}$ | (pyridin-4-yl)-4H-1,2,4-triazol-4-yl)-1,3-benzenedicarboxylic acid | 75.00 mL | M116115-25 L | methanol | 102.96 |
| | DMA | 75.00 mL | D108098-10 L | DMA | 91.34 |
| | nickel acetate tetrahydrate | 1.118 g | N112914-100 g | methanol | 657 |
| | 5-aminoisophthalic acid | 0.8142 g | A107450-100 g | DMA | 21 |
| | 4,4'-bipyridine | 0.3505 g | B105217-100 g | DMA | 47.83 |
| | water | 44.93 mL | W119424-25 L | water | 42.17 |
| | methanol | 58.41 mL | M116115-25 L | methanol | 102.96 |
| MIP-202 | Zirconium(IV) chloride | 1.334 g | Z109460-100 g | MeOH | 65.41 |
| | L-aspartic acid | 1.624 g | A108860-100 g | MeOH | 996 |
| | water | 11.60 mL | W119424-25 L | water | 42.17 |
| MCF-57 | Cobalt nitrate hexahydrate | 0.8595 g | C112729-100 g | DMA | 10,073 |
| | 3-(3-methylpyridin-4-yl)benzoic acid | 1.254 g | B176426-100 g | DMA | 692.55 |
| | DMA | 117.7 mL | D108098-10 L | DMA | 91.34 |
| | methanol | 58.87 mL | M116115-25 L | methanol | 102.96 |
| Cu(0.6)/MIL-100(Fe)* | iron powder | 0.2069 g | I116359-100 g | H_{2}O | 545 |
| | copper(II) chloride | 0.3750 g | C106774-100 g | H_{2}O | 14 |
| | trimethyl 1,3,5-benzenetricarboxylate | 0.6259 g | T137552-100 g | H_{2}O | 73.76 |
| | nitric acid | 0.1490 mL | N116240-500 mL | H_{2}O | 23.39 |
| | hydrofluoric acid | 0.3222 mL | H278731-2.5 L | H_{2}O | 12.22 |
| | water | 18.47 mL | W119424-25 L | H_{2}O | 42.17 |
| Fe$_2$(dobdc) | anhydrous ferrous chloride | 0.5500 g | I106504-100 g | MeOH | 4,527 |
| | 2,5-dioxido-1,4-benzodicarboxylate | 0.3050 g | D134233-100 g | MeOH | 136.93 |
| | DMF | 150.0 mL | D111999-25 L | MeOH | 208.45 |
| | methanol | 18.00 mL | M116115-25 L | MeOH | 102.96 |
a. The prices are based on Aladdin (https://www.aladdin-e.com/) with the unified package. For unified comparison, the referenced packages for raw materials and reagents were 100 g and 25 L, respectively.

b. Based on average exchange rates as of June 2022, 1 CNY was equal to 0.149 USD.

c. TCPG represent the total costs per gram of adsorbent.

* represent the supposed productivity (80%) of the samples.
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