

Flexible–Robust Metal–Organic Framework for Efficient Removal of Propyne from Propylene

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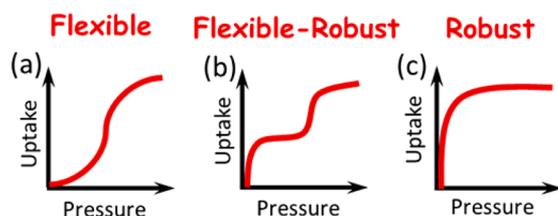
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Supporting Information

ABSTRACT: The removal of trace amounts of propyne from propylene is critical for the production of polymer-grade propylene. We herein report the first example of metal–organic frameworks of flexible–robust nature for the efficient separation of propyne/propylene mixtures. The strong binding affinity and suitable pore confinement for propyne account for its high uptake capacity and selectivity, as evidenced by neutron powder diffraction studies and density functional theory calculations. The purity of the obtained propylene is over 99.9998%, as demonstrated by experimental breakthrough curves for a 1/99 propyne/propylene mixture.

As novel porous materials, metal–organic frameworks (MOFs) have found various applications in gas storage, separation, sensing, catalysis, and so on because of their unique pore structures and designable frameworks.¹ Research on porous MOFs for gas separation and purification has been mainly focused on those robust MOFs (Scheme 1c).² Although

Scheme 1. Schematic Illustration of the Representative Adsorption Isotherms of (a) Flexible, (b) Flexible–Robust, and (c) Robust MOFs



flexible or dynamic MOFs (Scheme 1a) can be theoretically useful as well for gas separation and purification, as indicated by their single gas sorption isotherms, they have rarely been explored for separation of gas mixtures,³ mainly because the separation performance of flexible MOFs for gas mixtures can be hardly predicted from their single gas sorption isotherms. Once gas molecules of one type open the pore windows/spaces

of the flexible MOFs, the opened spaces will simultaneously take up other gas molecules as well.⁴ Furthermore, flexible MOFs typically take up negligible amounts of gas at low pressure, making them unsuitable for gas purification, in which trace impurities from gas mixtures need to be efficiently removed.⁵

During our exploration of porous MOFs for gas separation, we realized that one unique class of porous MOFs, so-called flexible–robust ones (Scheme 1b), has basically been overlooked.⁶ This class of porous MOFs is different from traditional flexible (Scheme 1a) and robust ones (Scheme 1c) in that their guest-free phases or intermediate phases possess robust pore structures. These phases can preserve their overall structures within a substantial low-pressure range (before the structures become fully flexible and transform into large-pore phases at higher gas pressures) and correspondingly exhibit well-defined plateaus in their multistep adsorption isotherms. Exploration of such flexible–robust MOFs can not only significantly broaden our choices of suitable porous MOFs for gas separation but also provide us the possibility to make use of different robust phases for gas separation (such flexible–robust MOFs will exhibit adsorbate-dependent gas sorption isotherms and thus can be theoretically applied to separations of different types of gas mixtures). In this regard, a previously reported flexible–robust MOF, [Cu(bpy)₂(OTf)₂] (ELM-12) (bpy = 4,4'-bipyridine, OTf[−] = trifluoromethanesulfonate),⁷ is of special interest. Its flexible–robust nature has been exclusively established through N₂ gas sorption isotherms and the inclusions of different solvent molecules (e.g., methanol and tetrahydrofuran). Herein we report its application for propyne (C₃H₄)/propylene (C₃H₆) separation, in which trace amounts of C₃H₄ can be readily removed from a C₃H₄/C₃H₆ (1/99) mixture to produce high-purity propylene (over 99.9998%) under ambient conditions. As one of most important chemical products (over 120 million tons produced in 2016), propylene is currently produced by steam cracking in petroleum refining. The raw C₃H₆ product contains a trace impurity of C₃H₄, which is highly undesirable.⁸ The C₃H₄ concentration in

Received: April 26, 2017

Published: June 5, 2017

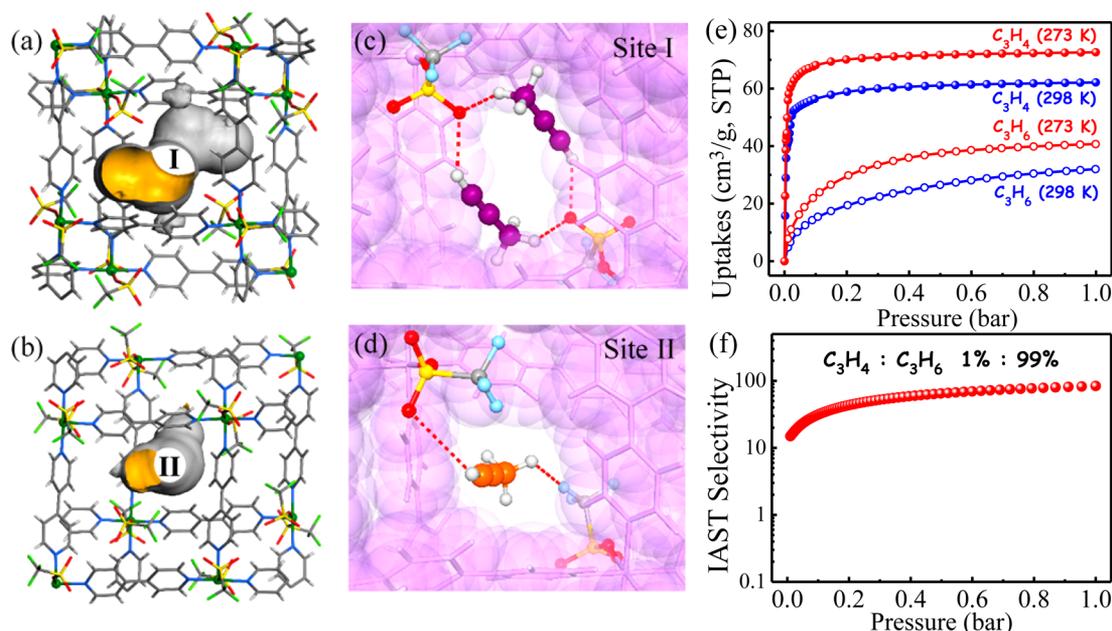


Figure 1. (a, b) Schematic diagrams of the two types of cavities (I and II) in ELM-12 (Cu, green; C, gray; O, red; S, yellow; F, light green). (c, d) Neutron diffraction crystal structure of ELM-12@C₃D₄ showing the preferential binding sites for C₃D₄ molecules (sites I and II) and their close contacts with the framework. (e) C₃H₄ and C₃H₆ adsorption isotherms of ELM-12. (f) Predicted selectivity of ELM-12 for C₃H₄/C₃H₆ (1/99) at 298 K.

polymer-grade propylene is required to be lower than 5 ppm.^{8c} Compared with cryogenic distillation and catalytic hydrogenation, adsorptive separation using porous materials is more environmentally friendly and energy-efficient. However, their similar molecular sizes (kinetic diameters: C₃H₄, ~4.76 Å; C₃H₆, ~4.68 Å)⁹ make C₃H₆ purification a great challenge.

ELM-12 consists of a rigid square-grid copper bipyridine scaffold with dynamic dangling OTf⁻ groups. After guest removal, ELM-12 still shows porosity (void fraction = 20.5%, pore volume = 0.141 cm³/g; see Table S2)^{7a} with two kinds of cavities (I and II; see Figure 1a,b). Type I cavities are dumbbell-shaped with small pockets (6.1 Å × 4.3 Å × 4.3 Å) at each end that are connected to each other through a small aperture (3.2 Å × 4.3 Å). Type II cavities are ellipsoid-shaped with a size of 6.8 Å × 4.0 Å × 4.2 Å and are separated from type I cavities by dynamic OTf⁻ groups. These cavities match well with the size and shape of C₃H₄ (6.2 Å × 3.8 Å × 3.8 Å, compared with 6.5 Å × 4.0 Å × 3.8 Å for C₃H₆), suggesting a potential application for C₃H₄ separation.

Single-component adsorption isotherms of guest-free ELM-12 for C₃H₄ and C₃H₆ were measured at 273 and 298 K (Figure 1e). The C₃H₄ sorption isotherm of ELM-12 exhibits type I character with a sharp increase at low pressure (<0.01 bar), and the uptake reaches 1.83 mmol/g (41 cm³/g) at 298 K and 0.01 bar (2.37 mmol/g, 53 cm³/g at 273 K and 0.01 bar). The corresponding isosteric heat of adsorption (Q_{st}) was calculated to be 60.6 kJ/mol at zero coverage (Figure S2), which is slightly higher than Q_{st} for C₂H₂ discovered in other MOFs with specific binding sites.^{2a} The high capacity and relatively strong binding affinity of ELM-12 for C₃H₄ at low pressure indicate that it could be a promising material for the capture of C₃H₄ as a trace component in C₃H₄/C₃H₆ mixtures. Furthermore, the C₃H₄ adsorption capacity of ELM-12 increases to 2.55 mmol/g at 0.1 bar, about 93% of the total uptake at 298 K and 1.0 bar, which is critical for C₃H₆ purification. In contrast, the C₃H₆ adsorption capacity of

ELM-12 is relatively low (0.67 mmol/g at 0.1 bar and 298 K) with a far smaller Q_{st} of 15.8 kJ/mol, which implies much weaker host-guest interaction compared with C₃H₄. These results suggest that high C₃H₄/C₃H₆ selectivity of ELM-12 for C₃H₆ purification is quite likely, breaking the stereotype that flexible porous materials are inferior for gas separation.

Next, to predict the adsorption selectivity of C₃H₄/C₃H₆ mixtures, ideal adsorbed solution theory (IAST) calculations were performed on both 1/99 and 50/50 C₃H₄/C₃H₆ mixtures at 298 K (Figures 1f and S3). As expected, ELM-12 exhibits very high C₃H₄/C₃H₆ selectivities, up to 84 for the 1/99 mixture and 279 for the 50/50 mixture, and its C₃H₄ uptake from the C₃H₄/C₃H₆ (1/99) mixture is 0.881 mmol/g (Figures S3 and S4). The calculated exceptional performance of flexible ELM-12 for C₃H₄ adsorption is rare, as indicated by the abnormally high capacity at low pressure, whereas common flexible MOFs typically exhibit negligible gas uptakes under similar conditions.

To determine the nature of C₃H₄ binding in this MOF structure, high-resolution neutron powder diffraction (NPD) measurements were carried out on a C₃D₄-loaded sample of ELM-12 at 298 K (Figures S5 and S6). Two preferential C₃H₄ adsorption sites were clearly identified from the data, as shown in Figure 1c,d. Two C₃D₄ molecules were found to be centrosymmetrically located in cavity I. Each C₃D₄ in cavity I binds to two OTf⁻ groups (from two different nets) through relatively short C–D···O hydrogen bonds (D···O, 2.31–2.36 Å; C–D···O, 2.80–3.16 Å), which is consistent with the large Q_{st} for C₃H₄ observed in ELM-12. Interestingly, hydrogen-bonding interactions between alkyne and sulfonate groups have also been observed in ionic liquids containing sulfonates.¹⁰ In cavity II, the C₃D₄ molecule shows a weaker binding affinity, as implied by its lower occupancy and longer hydrogen bond (D···O, 3.07 Å). Structure comparison reveals that the dynamic OTf⁻ adjusts its position/orientation accordingly upon C₃H₄ loading, while the overall crystal lattice stays nearly unchanged

(the average interlayer distance increases by only $\sim 2\%$). Also, the geometric pore volume ($0.145 \text{ cm}^3/\text{g}$) remains almost the same as that of guest-free ELM-12. In comparison, the fully opened ELM-12 has a pore volume of $0.287 \text{ cm}^3/\text{g}$, as observed from the N_2 -loaded structure (Table S2).^{7b} Thus, only the robust intermediate phase of guest-free ELM-12 is utilized for C_3H_4 adsorption under ambient conditions.

To further understand the mechanism of the selective $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$ adsorption in ELM-12, we conducted detailed first-principles dispersion-corrected density functional theory (DFT-D) calculations. The optimized C_3H_4 binding configurations agree well with the C_3D_4 -loaded structure determined from the NPD data. For the two binding sites, the DFT-D-calculated static binding energies (E_B) are ~ 53.5 and ~ 45.0 kJ/mol, respectively. In contrast, the binding affinity of C_3H_6 in ELM-12 is significantly lower than that of C_3H_4 , with calculated binding energies of only ~ 32.3 and ~ 25.6 kJ/mol for the two sites, respectively (Figure S7). All of these results from DFT-D calculations are fully consistent with those from the experimental studies, well supporting that the high $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$ adsorption selectivity originates from the strong binding of C_3H_4 with the polar OTf groups and the confinement of suitable pore geometry in ELM-12 for the sieving effects (Figure S8).

Next, to demonstrate the feasibility of $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$ separation, transient breakthrough simulations were conducted for ELM-12 in fixed-bed adsorption processes. C_3H_6 first eluted through the bed to yield a polymer-grade gas, and then C_3H_4 broke through from the bed at a long time τ_{break} (Figure S9). These simulation results indicate that ELM-12 can efficiently remove trace C_3H_4 from C_3H_6 gas (1/99 mixture).

In actual breakthrough experiments, 1/99 and 50/50 $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$ mixtures were used as feeds to mimic the industrial process conditions (Figures 2a and S10). The trace C_3H_4 was efficiently removed from C_3H_6 in the fixed bed to yield a polymer-grade gas. The purity of C_3H_6 monitored at the outlet was $>99.9998\%$, which indicated that the C_3H_4 impurity was completely removed by the ELM-12 material to a concentration below 2 ppm. Furthermore, ELM-12 also exhibited excellent separation performance for the 50/50 $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$ mixture, reducing the C_3H_4 impurity concentration to <10 ppm. In the practical production process of polymer-grade C_3H_6 , the feed gases are also contaminated by trace levels of C_3H_8 (<100 ppm), C_2H_4 (<50 ppm), and CO_2 (<50 ppm). Therefore, a breakthrough experiment with these impurities in the 1/99 $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$ mixture was also performed for ELM-12 (Figure S11). The results indicate that the presence of C_3H_8 , C_2H_4 , and CO_2 has nearly no effect on ELM-12 for the separation of C_3H_4 from C_3H_6 .

In the normal industrial environment, the adsorbent should also possess good regenerability and structural stability. To ensure the regenerability of ELM-12, C_3H_4 adsorption and 1/99 $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$ separation cycling experiments were further performed at 298 K (Figures 2b, S12, and S13). The experimental cycling results indicate that there was no noticeable loss in the C_3H_4 adsorption and separation capacity for ELM-12 after 20 cycles. Furthermore, in order to check the structural stability of ELM-12, an aged ELM-12 sample was measured by powder X-ray diffraction (PXRD), IR spectroscopy, C_3H_4 adsorption, and 1/99 $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$ separation at 298 K (Figure S14). Notably, ELM-12 can retain its structure, uptake capacity, and separation performance after 2 years of storage under ambient conditions.

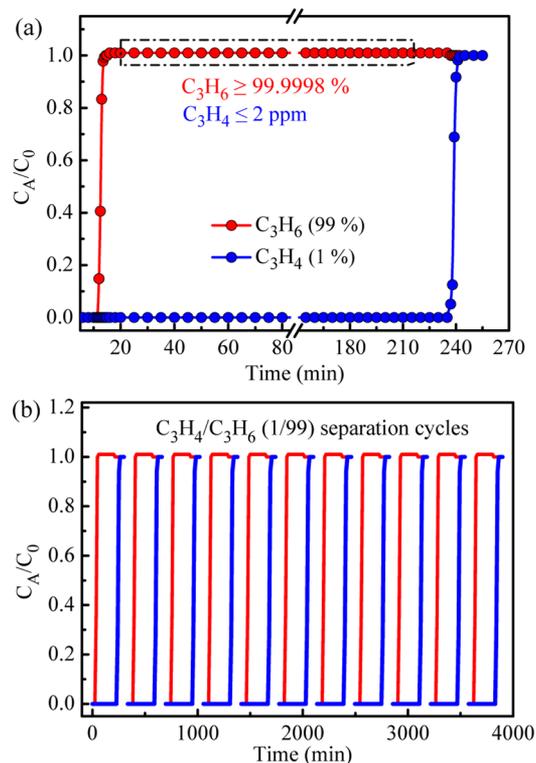


Figure 2. (a) Experimental column breakthrough curves for a $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$ mixture containing 1% C_3H_4 (298 K, 1.01 bar) in an adsorbent bed packed with ELM-12. (b) $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$ (1/99) separation cycles lasting for 4000 min. Each separation process was carried out at 298 K and 1.01 bar, while regeneration was performed using a He flow (100 mL/min) at 323 K for 30 min.

In summary, we have realized a flexible–robust porous MOF for the challenging task of $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$ separation/purification. The basic mechanism of this MOF for the specific recognition of C_3H_4 has been clearly demonstrated through neutron diffraction studies and theoretical calculations. The robust guest-free ELM-12 has suitable pore structure as well as strong binding sites to trap C_3H_4 molecules, similar to those revealed in robust MOFs for their recognition of small gas molecules. This work will initiate extensive interest in flexible–robust MOFs for their gas separation and purification properties and thus expand the dictionary of porous MOFs for these very important applications. The high efficiency of ELM-12 to remove the trace C_3H_4 from important raw $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$ mixtures under ambient conditions to produce high-purity C_3H_6 indicates that this MOF might be potentially useful for this industrially important separation. The realization of this unique porous MOF for the challenging $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$ separation has initiated the promise of porous MOFs for this very important industrial application. It is expected that extensive research on porous MOFs will eventually lead to some practically useful materials at a reasonable cost in the near future for important hydrocarbon separation and purification processes.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b04268.

Experimental procedures, PXRD patterns of ELM-12, crystallographic and refinement parameters for C₃D₄-loaded ELM-12, NPD data, heats of adsorption, adsorption selectivities of C₃H₄/C₃H₆ (1/99 and 50/50) predicted by IAST at 298 K, and regenerability and structural stability data for ELM-12 (PDF)

Crystallographic data for C₃D₄-loaded ELM-12 (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (21606163), the Natural Science Foundation of Shanxi (201601D021042), and the Welch Foundation (AX-1730).

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