A Rod-Packing Hydrogen-Bonded Organic Framework with Suitable Pore Confinement for Benchmark Ethane/Ethylene Separation

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Abstract: For the separation of ethane from ethylene, it remains challenging to target both high \( C_2H_6 \) adsorption and selectivity in a \( C_2H_6 \)-selective material. Herein, we report a reversible solid-state transformation in a labile hydrogen-bonded organic framework to generate a new rod-packing desolvated framework (ZJU-HOF-1) with suitable cavity spaces and functional surfaces to optimally interact with \( C_2H_6 \). ZJU-HOF-1 thus exhibits simultaneously high \( C_2H_6 \) uptake (88 cm\(^3\) g\(^{-1}\) at 0.5 bar and 298 K) and \( C_2H_6/C_2H_4 \) selectivity (2.25), which are significantly higher than those of most top-performing materials. Theoretical calculations revealed that the cage-like cavities and functional sites synergistically "match" better with \( C_2H_6 \) to provide stronger multipoint interactions with \( C_2H_6 \) than \( C_2H_4 \). In combination with its high stability and ultralow water uptake, this material can efficiently capture \( C_2H_6 \) from 50/50 \( C_2H_6/C_2H_4 \) mixtures in ambient conditions under 60% RH, providing a record polymer-grade \( C_2H_6 \) productivity of 0.98 mmol g\(^{-1}\).

Introduction

Ethylene (\( C_2H_4 \)) is a key feedstock for many chemicals and polymers in the chemical industry and is primarily derived from naphtha or ethane cracking.\(^{[1,2]}\) However, steam crackers do not produce pure \( C_2H_4 \) (\( \geq 99.95% \), polymer grade), in which ethane (\( C_2H_6 \)) is inevitably existed as a major byproduct. The separation of \( C_2H_6 \) from \( C_2H_4 \) is thereby a critical process to yield polymer-grade \( C_2H_6 \) for polymer production. At present, it is mainly accomplished by means of cryogenic distillation under harsh conditions (typically at 5–28 bar and 180–258 K), which represents one of the most energy-intensive processes. The energy consumption for such separation is estimated to be about 7.3 GJ per tonne of ethylene.\(^{[3,4]}\) To replace traditional cryogenic distillation, adsorptive separation technologies based on porous materials attract particular interest because of their great potential to provide tremendous energy savings.\(^{[5]}\) Such separation can be implemented by either ethane- or ethylene-selective adsorbents; however, ethane-selective materials are more desired because of the simplicity of being able to produce ethylene directly at the outlet.\(^{[6,7]}\)

Since ethane has a higher polarizability than ethylene, dispersion and induction interactions would make major contributions in \( C_2H_6 \)-selective adsorbents,\(^{[8]}\) so an adsorbent material with a pore structure enriched with nonpolar/inert surfaces (e.g., featuring aromatic or aliphatic moieties) may favor the preferential adsorption of \( C_2H_6 \) over \( C_2H_4 \). In this regard, the emerging hydrogen-bonded organic frameworks (HOFs) are of particular interest to be developed as \( C_2H_6 \)-selective adsorbents.\(^{[9,10]}\) HOFs are formed from purely organic building blocks through intermolecular hydrogen bonds (H-bonds).\(^{[11–14]}\) This metal-free nature endows HOFs with native nonpolar/inert pore surfaces to directly produce the desired \( C_2H_6 \)-selective materials. Owing to the soft and flexible H-bonds, HOFs hold some inherent advantages such as high solution processability, easy purification, and facile regeneration and healing by simple recrystallization. Moreover, HOF materials can be highly crystalline that benefits not only structural determination but also the investigation of structure–property relationship. These attractive merits make the exploitation of porous HOFs as \( C_2H_6 \)-selective adsorbents become very attractive. However, the major drawback of HOFs is their structural fragility because of the weak nature of H-bonds, making their frameworks oftentimes collapse upon removal of solvent molecules.\(^{[15]}\) It is also very difficult to precise control over pore size and functional sites in HOFs to strongly interact with gas molecules,\(^{[9,16]}\) which has always limited their separation performance. It is therefore not surprising that the research on robust HOFs for gas separation is still at the comparatively early stage.\(^{[16,17]}\) To date, only few porous HOFs have been established for the important hydrocarbon separations with quite limited separation per-
Despite a great challenge, we recently succeeded in realizing a robust HOF material (HOF-76a) for selective separation of \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \). While this material exhibits a moderate \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) selectivity, the large one-dimensional pores and the lack of strong \( \text{C}_2\text{H}_6 \) adsorption sites lead to a weak binding affinity and thus poor \( \text{C}_2\text{H}_6 \) uptake, largely delimiting the productivity of the desired \( \text{C}_2\text{H}_4 \) product.

A chemical separation benefits from both uptake capacity and adsorption selectivity and can be most efficient when a material excels in both aspects; however, it is very difficult to target a material with both high values (so-called trade-off). To realize both high gas selectivity and adsorption uptake for \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) separation, an ideal adsorbent should have suitable pore/cavity sizes and functional surfaces to simultaneously enforce the preferential adsorption of \( \text{C}_2\text{H}_6 \) over \( \text{C}_2\text{H}_4 \) but without sacrificing moderate pore volumes or surface areas to take up large amount of \( \text{C}_2\text{H}_4 \) molecules. However, from the structural point of view, there commonly exists a trade-off between pore dimensions and pore volumes in porous materials. For example, pore dimensions that match with small gas molecules often correlate to small pore volumes, which in turn result in low uptakes. Conversely, high pore volumes typically stem from large pores, which cannot discriminate the molecules with similar sizes. It is still a daunting challenge for the community to design and realize ideal adsorbents to meet the above mentioned criteria, especially for the immature HOFs. Herein, we report a unique rod-packing HOF material (ZJU-HOF-1, Figure 1) featuring the suitable cavity sizes (4.6 Å) and functional surfaces, which can meet those mentioned criteria for benchmark \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) separation. The activated ZJU-HOF-1 shows a relatively high BET surface area of 1465 m\(^2\)g\(^{-1}\) to secure enough pore spaces for high \( \text{C}_2\text{H}_6 \) uptake. Owing to the rod-packing configuration and threefold interpenetration, ZJU-HOF-1 features numerous small cage-like cavities decorated by multipoint functional sites that match better with the size/shape of \( \text{C}_2\text{H}_6 \) molecule and thus facilitate closer contacts with \( \text{C}_2\text{H}_4 \). This unique pore confinement thus results in a rare combination of simultaneously high \( \text{C}_2\text{H}_4 \) uptake (88 cm\(^3\)g\(^{-1}\) at 0.5 bar and 298 K) and \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) selectivity (2.25) observed in ZJU-HOF-1. Importantly, this material is also chemically stable and shows an ultralow water uptake at 60% RH to avoid co-adsorption of water. Breakthrough experiments confirmed that ZJU-HOF-1 exhibits the record-high \( \text{C}_2\text{H}_4 \) productivity of 0.98 mmolg\(^{-1}\) (or 21.9 Lkg\(^{-1}\)) for both dry and humid (60% RH) \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) mixtures at 298 K and 1.01 bar, a value higher than that of \( \text{Fe}(\text{O}_2)(\text{dobdc}) \) (0.86 mmolg\(^{-1}\)), the benchmark material for \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) separation in MOFs.

**Figure 1.** a) The structure of TMBTI. b) The single network constructed by TMBTI molecules. c) A rod-shaped H-bonded chain formed by meta-benzenedicarboxylic motifs along the \( c \) axis. d) The threefold-interpenetrated structure of JLU-SOF3. e) The modeled structure of ZJU-HOF-1 upon activation, revealing an obvious structural transformation between JLU-SOF-3 and ZJU-HOF-1. f) The acs topology of ZJU-HOF-1 (red dotted lines represent H-bonds). The CCDC number can be found in the Supporting Information.
Results and Discussion

The hexacarboxylate ligand 2,4,6-trimethylbenzene-1,3,5-triylisophthalate (TMBTI) was simply prepared through a multistep reaction procedure (Scheme S1, Supporting Information). Slow evaporation of an ethyl ether solution into a THF solution of TMBTI in two weeks afforded the colorless stick-like crystals. During our exploration of the activated ZJU-HOF-1, the structure of the as-synthesized HOF (JLU-SOF3) was independently reported for different properties.\[13c\] Single crystal X-ray diffraction analysis revealed that JLU-SOF3 crystallizes in a hexagonal $P\overline{6}2_1$ space group with a hydrogen-bonded 3D network (Figure 1). Due to the steric hindrance of methyl groups, the dihedral angle of each outer phenyl ring relative to the center phenyl ring in TMBTI molecule is about 90° (Figure 1a). This feature enables the adjacent meta-benzenedicarboxylate motifs from different TMBTI to form 1D infinite rod-shaped H-bonding chains along the $c$ axis (Figure 1c), which are further linked by the center phenyl ring to construct the 3D rod-packing framework (Figure 1b). The O–H···O distance and angle are 2.610/2.599 Å and 174.7°, respectively. If the TMBTI is considered as a six-connected node, JLU-SOF3 possesses the $acs$ topology (Figure S7). Closer inspection of the structure reveals that six discrete TMBTI molecules form a six-membered ring in a hexagon pore conformation with a large window size of 22.7 Å. This large pore nature of single network can lead to interpenetration, wherein three identical frameworks interpenetrate each other through the ring-like window along the $c$ axis (Figure 1d).

When the as-synthesized sample was desolvated in high vacuum to generate the activated sample (ZJU-HOF-1), we found that there exist obvious changes in the PXRD patterns between JLU-SOF3 and ZJU-HOF-1 (Figure S8). This clearly indicates that a structural transformation occurs during this activation, however, which was ignored in the reported literature. Great efforts have been made to elaborate investigate the new structure of the activated ZJU-HOF-1. Despite extensive attempts, we were not able to obtain high-quality single crystals of ZJU-HOF-1 for single-crystal X-ray diffraction studies (Figure S9) and thus structural determination was conducted by powder diffractometry. On the basis of the PXRD data, we first identified a new symmetry of hexagonal $P\overline{6}2_1$ space group for ZJU-HOF-1 crystal. With the symmetry and the overall network connection known, we thus modeled its structure straightforwardly and further optimized the structure based on DFT calculations (see Supporting Information for more details).\[24\] The structure model is shown in Figure 1c, which has different unit cell parameters with JLU-SOF3 (Table S4). The simulated PXRD pattern of this structural model agrees excellently with the experimental data (Figure S10), strongly supporting its validity. Detailed structure information of ZJU-HOF-1 is provided in Tables S3 and S4.

To further probe the structural transformation from JLU-SOF3 to ZJU-HOF-1, the nudged elastic band calculations were performed to find the minimum energy path of the structural transition. An animation consisting of structure snapshots along the minimal energy path shows clearly how the JLU-SOF3 framework evolves to the structure of ZJU-HOF-1 (see the movie in the Supporting Information). During this process, the different nets are obviously smoothing along the $ab$ plane to make the center phenyl rings of TMBTI molecules from adjacent nets coincide with each other, accompanying a slight rotation (15°) along the $c$ axis for every monomer molecular. This transformation induces a slight structure contraction (5.43% by volume), leading to a new symmetry and uniform pores in ZJU-HOF-1 (Figure 2a). The framework of ZJU-HOF-1 still holds a threefold interpenetration with the same $acs$ topology (Figure 1f and Figure S10, Supporting Information). The O–H···O distance (2.564 Å) on the rod-shaped H-bonded chains along the $c$ axis is slightly shorter than that in ZJU-HOF-1 (Figure 2c). As depicted in Figure 2b, ZJU-HOF-1 exhibits open triangular-

\[\text{Figure 2. a) The threefold-interpenetrated structure of ZJU-HOF-1. b) The triangular pore channel (7.0 Å) and three intercrossed small pockets around the corners of the triangular-like channel. c) View of the small pockets stacked along the c axis, with a diameter of 4.6 Å. d) Depiction of one pocket constructed by two stacked phenyl rings and four carboxylate groups (C, dark gray; O, red; H, white).}\]
like pore channels with a diameter of 7.0 Å along the c axis, which are large enough for both C₆H₆ and C₇H₈ molecules to enter the pores. Due to the rod-packing configuration and threefold interpenetration, there produces numerous small cage-like pockets around the corner of the triangular channels (Figure 2b,c). Each of such small pockets is constructed by two stacked phenyl rings and four carboxylate groups with a diameter size of 4.6 Å (Figure 2d), which matches better with the larger C₆H₆ molecule (4.4 Å) than C₇H₈ (4.1 Å). These optimized pocket sizes and pore surfaces of functional O atoms thus exhibit the potential to provide more suitable pore confinement effects toward C₆H₆ molecule.

The chemical stability and structural transformation between JLU-SOF3 and ZJU-HOF-1 were investigated at different conditions, monitored by PXRD patterns. As revealed in Figures S12 and S13, the framework of JLU-SOF3 can gradually transform to ZJU-HOF-1 under removal of solvent molecules upon air exposure, heating or vacuum degassing. Conversely, the framework of ZJU-HOF-1 can be reversibly converted to JLU-SOF3 when soaking the sample into the Et₂O or H₂O solution (Figure S14). To examine the chemical stability, the as-synthesized samples were treated in water, HCl (pH 1) and NaOH (pH 10) solutions at room temperature (RT). After two days, the framework can retain its structural integrity as evidenced by PXRD patterns and SEM images (Figures S15 and S16), revealing its highly chemical stabilities.

The permanent porosity of ZJU-HOF-1 was established by nitrogen (N₂) gas sorption experiments at 77 K. As shown in Figure 3a, ZJU-HOF-1 can adsorb a large amount of N₂ (386 cm³·g⁻¹) at 77 K and 1 bar. The BET surface area and pore volume of ZJU-HOF-1 were calculated to be moderate high of 1465 m²·g⁻¹ and 0.60 cm³·g⁻¹, respectively. The pore size distribution, determined by the Horvath–Kawazoe model, shows two types of pores in the range of 5–9 Å, consistent well with the results obtained from the crystal structure. After immersing in water, HCl and NaOH solutions for 2 days, the reactivated ZJU-HOF-1 samples show no obvious decrease on N₂ uptakes at 77 K (Figure S19).

Single-component adsorption isotherms of C₆H₆ and C₇H₈ for ZJU-HOF-1 were examined at both 273 K and 298 K up to 1 bar. As shown in Figures 3b and S20, ZJU-HOF-1 shows an obviously preferential adsorption of C₆H₆ over C₇H₈ at both temperatures. The uptake amount of C₆H₆ (109 cm³·g⁻¹) at 298 K and 1 bar is notably higher than that of C₇H₈. When compared with HOF-76a, ZJU-HOF-1 exhibits a much steeper and higher C₆H₆ uptake in the whole range of 1 bar (Figure 3c). At a partial pressure of 0.5 bar for 50/50 C₆H₆/C₇H₈ separation, ZJU-HOF-1 displays an extremely high C₆H₆ uptake of 88 cm³·g⁻¹, 2.3 times higher than that of HOF-76a (38 cm³·g⁻¹), indicating its significantly enhanced C₆H₆ capture capacity (Figure 3c). This can be well explicated by the experimental isosteric heat of adsorption (Qst), wherein the initial Qst value of C₆H₆ for ZJU-HOF-1 (31.5 kJ·mol⁻¹) is much higher than the 22.8 kJ·mol⁻¹ observed in HOF-76a (Figure S21). Further, we also investigated the time-dependent ads/desorption kinetics profiles of ZJU-HOF-1 at 298 K. As shown in Figure S23, ZJU-HOF-1 exhibits similar adsorption kinetics for C₆H₆ and C₇H₈ with fast diffusion rates and the adsorbed molecules can be completely removed under
a high vacuum quickly, which are probably attributed to its comparably large pore channels.

Ideal adsorbed solution theory (IAST) was employed to estimate the adsorption selectivity of ZJU-HOF-1 for C$_4$H$_6$/C$_6$H$_4$ mixtures at 298 K. As indicated in Figure 3d, ZJU-HOF-1 exhibits a high C$_4$H$_6$/C$_6$H$_4$ selectivity of up to 3.2 at low pressure and 298 K for C$_4$H$_6$/C$_6$H$_4$ (50/50) mixtures. With the increase of pressure, it gradually decreases down to 2.25 at 1 bar. This value is notably higher than that of HOF-BTB (1.4) and HOF-76a (2.0). It is worth to note that high C$_4$H$_6$ uptake capacity is also very important to determine the C$_4$H$_6$/C$_6$H$_4$ separation performance. As shown in Figure S25, ZJU-HOF-1 exhibits an extremely high C$_4$H$_6$ uptake (3.2 mmol g$^{-1}$) from an equimolar mixture of C$_4$H$_6$/C$_6$H$_4$ as a function of IAST selectivity, far exceeding that of HOF-76a (1.62 mmol g$^{-1}$) and HOF-BTB (1.67 mmol g$^{-1}$). When we put gas uptake and selectivity as concurrent objectives, ZJU-HOF-1 shows a rare balance of both very high C$_4$H$_6$/C$_6$H$_4$ selectivity and C$_4$H$_6$ adsorption from C$_4$H$_6$/C$_6$H$_4$ mixtures, outperforming most of MOF materials reported (Figure S25).

To elucidate the origin of the observed high C$_4$H$_6$ uptake and selectivity, we performed detailed modeling studies using first-principles dispersion-corrected density functional theory (DFT-D) method on ZJU-HOF-1. We found that, for both C$_4$H$_6$ and C$_6$H$_4$ molecules, the primary adsorption sites are located at the small cage-like pockets within the corner of the triangular pore channels (Figure 3e). The lowest-energy gas binding sites are shown in Figure 3f,g. For clarity, we only showed one pocket site that can trap one gas molecule. Within each unit cell, there exist 6 such binding sites, which are crystallographically equivalent (Figure S26).

The calculated static binding energies for C$_4$H$_6$ and C$_6$H$_4$ are 34.4 and 31.7 kJ mol$^{-1}$, respectively. The stronger C$_4$H$_6$–framework interactions are fully consistent with our experimental observations. This is partly because the nonplanar C$_4$H$_6$ molecule has more number of H atoms and sterically “matches” better to the pocket size/shape than the planar C$_6$H$_4$ molecule. As a consequence, each C$_4$H$_6$ molecule interacts with two stacked phenyl rings and four oxygen atoms originated from four carboxylic groups to form two C–H····π interactions (H····π, 3.226 and 4.060 Å) and seven C–H····O interactions (H····O, 2.605–4.060 Å; Figure S27). In contrast, the C$_4$H$_6$ molecule shows only one C–H····π interaction with one phenyl ring (H····π, 3.212 Å) and five C–H····O interactions (H····O, 2.552–3.811 Å). Evidently, the higher binding energy of C$_4$H$_6$ can be mainly attributed to the suitable size and functional surfaces of the pockets that match better with C$_4$H$_6$, thus leading to the more number of C–H····π and C–H····O interactions with the framework. A full occupancy of these binding sites would correspond to 4.91 mmol g$^{-1}$ gas uptake, which is very close to the experimental C$_4$H$_6$ uptake (4.82 mmol g$^{-1}$) at room temperature and 1 bar. In contrast, the much lower C$_4$H$_6$ uptake at room temperature and 1 bar suggests that only part of the binding sites are populated due to the weaker binding affinity with the framework. All of these results can explain the observed high C$_4$H$_6$ adsorption and separation performance at 1 bar qualitatively.

Transient breakthrough simulations were firstly conducted to preliminarily evaluate the feasibility of using ZJU-HOF-1 in a fixed bed for separation of C$_4$H$_6$/C$_6$H$_4$ (50/50 and 10/90) mixtures. As shown in Figure 4a, efficient separation...
can be realized by ZJU-HOF-1 for both 50/50 and 10/90 C$_2$H$_4$/C$_2$H$_6$ mixtures, wherein C$_2$H$_4$ breakthrough occurs first and then C$_2$H$_6$ passes through the fixed bed after a longer time ($t_{break}$). Next, experimental breakthrough studies were performed in a packed column of ZJU-HOF-1 for actual C$_2$H$_4$/C$_2$H$_6$ (50/50 and 10/90) mixtures with a total flow of 1.25 mL·min$^{-1}$ at 298 K. Figure 4c reveals that complete separation of C$_2$H$_4$ from C$_2$H$_6$ can be realized in ZJU-HOF-1. Ethylene was first eluted at 74 min to yield a pure gas with an undetectable amount of C$_2$H$_6$ (the detection limit of the instrument is 0.01%), whereas the adsorbent retained C$_2$H$_6$ until 92 min. During this breakthrough process, pure C$_2$H$_4$ production (>99.95%) from the outlet effluent for a given cycle was calculated to be 0.98 mmol g$^{-1}$ (21.9 L·kg$^{-1}$, Figure 4d), three times higher than HOF-76a (0.32 mmol g$^{-1}$ or 7.2 L·kg$^{-1}$)[38] and even outperforming that of the best MOF Fe$_2$(O$_2$)(dobdc) (0.86 mmol g$^{-1}$ or 19.3 L·kg$^{-1}$).[74] The C$_2$H$_4$ productivity of ZJU-HOF-1 can be further improved to 1.02 mmol g$^{-1}$ at a high pressure of 5 bar (Figure 4e). It is worth to note that Fe$_2$(O$_2$)(dobdc) shows a high regeneration energy ($Q_r = 66.8$ kJ·mol$^{-1}$), and is not stable in air/moisture and requires harsh handling under inert conditions, which largely hampers its real-world applications. In strong contrast, ZJU-HOF-1 shows highly chemical stability and low regeneration energy (31.5 kJ·mol$^{-1}$). This HOF can be easily regenerated to recover its separation capacity by the sweeping He gas at 323 K for 60 min, as evidenced by multiple breakthrough tests over five continuous cycles (Figure 4e).

In industrial C$_2$H$_4$/C$_2$H$_6$ separation, the feed gases typically contain water vapor, which could have negative effects on the uptake capacity and separation performance for many physisorbers. In this regard, many metal-containing materials such as MOFs and zeolites are sensitive to humidity or show high water uptake to result in competitive adsorption,[25] thus suffering from gas sorption capacity reduction or structure decomposition under high humidity.[74,21a] To effectively avoid the effect of water vapor, ideal adsorbents would have not only high water stability but also low water uptake to minimize the co-adsorption of water. As shown in Figure 4f, thanks to the hydrophobic nature of HOFs[38] we found that the water amount adsorbed in ZJU-HOF-1 is very low up to 60% RH, with a negligible uptake of only 0.011 g·g$^{-1}$. This could be highly favorable for C$_2$H$_4$/C$_2$H$_6$ separation under high humidity conditions. The breakthrough experiments on a wet C$_2$H$_4$/C$_2$H$_6$ mixture with 60% humidity confirm that the presence of water vapor has no effect on the separation capacity of ZJU-HOF-1 (Figure 4b), further rendering it an ideal adsorbent for C$_2$H$_4$ purification under real industrial conditions.

**Conclusion**

In summary, we have realized the reversible solid-state transformation of a labile HOF material to result in a rod-packing desolvated structure (ZJU-HOF-1). This structural transition gives rise to the optimized pore confinement with suitable cavity spaces and functional surfaces in ZJU-HOF-1 for benchmark C$_2$H$_4$/C$_2$H$_6$ separation. The moderate high surface area and unique pore architecture of ZJU-HOF-1 lead to a rare combination of both high C$_2$H$_4$ uptake capacity and excellent C$_2$H$_4$/C$_2$H$_6$ selectivity, both of which are higher than most of C$_2$H$_4$-selective materials. As revealed by DFT calculations, the suitable cage-like cavities and functional surfaces have collaborative roles for the preferential binding of C$_2$H$_4$ over C$_2$H$_6$. On account of the remarkable uptake and excellent selectivity, ZJU-HOF-1 exhibits the record polymer-grade C$_2$H$_4$ productivity of 0.98 mmol g$^{-1}$ (or 21.9 L·kg$^{-1}$) from 50/50 dry and humid (60% RH) C$_2$H$_4$/C$_2$H$_6$ mixtures at ambient conditions, even higher than the state-of-the-art Fe$_2$(O$_2$)(dobdc) reported so far. Combined with its extraordinary chemical stability and ultralow water uptake at high humidity, ZJU-HOF-1 embodies a new benchmark material that has the potential to be applied for C$_2$H$_4$/C$_2$H$_6$ separation in real-world applications. This work here not only reports the benchmark HOF material for C$_2$H$_4$/C$_2$H$_6$ separation, but also provides some guidance to design new porous HOFs with suitable pore confinement to address some other important and challenging gas separations.

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**Conflict of interest**

The authors declare no conflict of interest.

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