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# Reticular chemistry guided function customization: a case study of constructing low-polarity channels for efficient C<sub>3</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>4</sub> separation†

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Guided by the principles of reticular chemistry, we have successfully presented the “bending-bridge” strategy, achieving an extraordinary function-targeted assembly by ingeniously redirecting the coordination direction of traditional SBUs. This led to the synthesis of a novel metal–organic framework (MOF), {[CH<sub>3</sub>NH<sub>3</sub>]<sub>2</sub>[InTPCA]·2H<sub>2</sub>O·NMF·DMF} (ZJNU-401). The smart design of bending branches within the ligand effectively transformed the tetrahedrally coordinated mononuclear In(III) into a square-planar configuration, thereby avoiding the introduction of open metal sites (OMSs) commonly associated with traditional ssb networks and creating a low-polarity pore surface environment. ZJNU-401 exhibits an optimal pore system that enhances its efficacy for high uptake of C<sub>3</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>6</sub> over C<sub>2</sub>H<sub>4</sub>. The remarkable selectivity ratio of C<sub>3</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>4</sub> reaches up to 15.45, alongside efficient one-step purification of C<sub>2</sub>H<sub>4</sub> (>99.95%) from the mixture of C<sub>3</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>4</sub>. DFT calculations revealed that multiple O active sites within nonpolar pores provide stronger interactions with both C<sub>3</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>6</sub> compared to those with C<sub>2</sub>H<sub>4</sub>.

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## Introduction

The methanol-to-olefin (MTO) process has become an important sustainable technology that allows non-petroleum resources to be converted into low-carbon olefins like ethylene (C<sub>2</sub>H<sub>4</sub>) and propylene (C<sub>3</sub>H<sub>6</sub>).<sup>1–4</sup> In the chemical industry, these olefins are essential raw materials, especially for the manufacture of polymers. The MTO method produces trace amounts of ethane (C<sub>2</sub>H<sub>6</sub>) impurities in addition to around 51 wt% C<sub>2</sub>H<sub>4</sub> and 21 wt% C<sub>3</sub>H<sub>6</sub>.<sup>5–7</sup> The purification of MTO products is crucial for obtaining high-purity C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>, which are necessary for the sustainability and effectiveness of the chemical manufacturing industry. The coexistence of these components in combination hampers downstream applications. However, it remains highly challenging to separate these gases due to their similar physical properties. Compared to traditional energy-intensive separation processes, physical adsorption technology based on porous materials offers a safer, more energy-

efficient, and environmentally friendly alternative, presenting significant potential for sustainable molecular separations, particularly in the purification of MTO products.<sup>8–10</sup>

The rapid development of reticular chemistry has allowed the integration of various building blocks into extendable frameworks *via* strong bonds, leading to the emergence of novel porous materials such as metal–organic frameworks (MOFs).<sup>11–17</sup> Furthermore, reticular chemistry serves as a powerful strategy for tailoring specific pore environments and structures to achieve targeted separations. For instance, in the context of MTO product purification, the design of low-polarity pore surfaces enables weak interactions with certain molecules, facilitating effective kinetic separations. This approach has proven highly effective for distinguishing molecules with similar physical properties, such as olefins and alkanes.<sup>18</sup> Therefore, employing reticular chemistry to design MOFs with precisely tuned pore environments is not only necessary but also a promising pathway to optimize separation efficiency and address the challenges of sustainable chemical manufacturing.

Not all nets are ideal targets for reticular chemistry, which is an important consideration in MOF design. As is known to all, transitivity [pqrs] refers to a structure that has p types of vertexes, q types of edges, r types of faces, and s types of tiles. Edge-transitive nets, which have only one type of edge (q = 1), are quite important.<sup>19,20</sup> In 2021, Eddaoudi *et al.* identified 53 three-dimensional (3D) nets within this category that are particularly suitable for practical applications in reticular chemistry, being considered ideal candidates for the design and

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construction of new structures.<sup>15</sup> One of the most important principles in constructing structures based on edge-transitive nets is building block selection, which includes the design of organic linkers as well as the selection of inorganic building units that are typically aligned with the desired functionality.<sup>21–23</sup> For example, the ssb net, which is a 4,4-c net formed by sql layers supported by pillars, has been realized using the Cu-paddlewheel and 4-c bulky organic linkers, as reported in NOTT-109 (ref. 24) and MMPF-1.<sup>25</sup> However, such designs pose challenges in creating low-polarity pore environments, as it is well known that Cu-paddlewheel SBUs provide abundant open metal sites (OMSs), which can be disadvantageous in certain separation applications, such as that of C<sub>2</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>4</sub>.<sup>26,27</sup>

Developing an effective and controlled design strategy for assembling commonly used secondary building units (SBUs) that satisfies the functional needs while fulfilling the geometric requirements of specific topologies remains one of the most significant challenges in reticular chemistry.<sup>28,29</sup> Here, abandoning paddlewheel type SBUs, like Cu or Zn-paddlewheel, complicates the selection of alternative 4-c inorganic SBUs that can achieve square-planar connectivity. Other highly connected polynuclear metal SBUs, although possessing four connections, still do not meet functional requirements due to the presence of OMSs. A straightforward alternative is to use mononuclear metal SBUs based on single metal ions.<sup>30,31</sup> For achieving 4-c connectivity with carboxylate groups, In(III) stands out as an optimal choice, forming tetrahedral structures that are representative SBUs in ZMOFs.<sup>32,33</sup> These materials highlight the versatility of indium in creating robust frameworks without the complications associated with OMSs.

The next challenge is to transform these tetrahedral nodes into the square-planar 4-c nodes required by ssb nets. This is where the “bending-bridge” strategy in ligand design becomes essential. By introducing a well-planned bend at a specific point in the ligand, the directionality of coordination can be effectively altered. This enables the transformation of tetrahedral 4-c nodes into square-planar 4-c nodes, allowing them to conform to the structural requirements of the ssb network.<sup>19,24</sup> This approach offers a flexible and innovative pathway to achieve the desired geometry of the ssb net without compromising the integrity or functionality of the framework. Specifically, considering that the bending of the ligand results in a reduction of effective connection lengths, it is necessary to incorporate redundant space in the design of the bending bridges (Scheme 1). A symmetry-reduced ligand, H<sub>4</sub>TPCA ([1,1':3',1'']terphenyl-3,4',6',3''-tetracarboxylic acid), has been employed in this system, taking into account two advantages: (1) the bending bridge can achieve large-angle rotations, thus adapting to the demands of the corresponding topology; and (2) the ligand integrates both the isophthalic acid part and the bending bridge part, allowing for a balance between rigidity and flexibility. Ultimately, as we anticipated, we truly succeeded in fabricating a low-polarity pore environmental compound (**ZJNU-401**) with the ssb network lacking OMSs. This facilitates the preferential selective adsorption of propylene and ethane (C<sub>3</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>4</sub>: 15.45 and C<sub>2</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>4</sub>: 1.75), thereby achieving efficient one-step

separation and purification of ethylene (>99.95%) in the MTO process.

## Results and discussion

### Synthesis of ZJNU-401

In(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O (8 mg, 0.021 mmol), H<sub>4</sub>TPCA (3 mg, 0.074 mmol), *N*-methylformamide (NMF) (0.5 mL), *N,N*-dimethylformamide (DMF) (0.5 mL), deionized water (H<sub>2</sub>O, 0.5 mL), and HNO<sub>3</sub> (500 μL, 2.2 mL of HNO<sub>3</sub> in 10 mL NMF) were mixed in a 20 mL vial and then placed in a precision oven for 12 h at 105 °C. After cooling to room temperature, colorless polyhedral crystals were collected and washed frequently with fresh NMF (yield 67.8%, based on H<sub>4</sub>TPCA). Elemental analysis (%) Calcd for **ZJNU-401** {[CH<sub>3</sub>NH<sub>3</sub>][InTPCA]·2H<sub>2</sub>O·NMF·DMF}: C, 46.86; H, 4.46; N, 5.86. Found: C, 47.01; H, 4.27; N, 5.80.

### Crystal structure

Herein, the solvothermal reaction of a well-designed ligand, H<sub>4</sub>TPCA, with In(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O, and HNO<sub>3</sub> in the DMF/NMF/H<sub>2</sub>O system, enabled the construction of the targeted ssb net by employing the “bending-bridge” strategy. Single-crystal X-ray diffraction structural analysis reveals that **ZJNU-401** crystallizes in the rhombohedral crystal system with the *Fmm2* space group where its asymmetric unit consists of eight In(III) ions, torsional deprotonated ligand TPCA<sup>4-</sup> and two [CH<sub>3</sub>NH<sub>3</sub>]<sup>+</sup> generated from the decomposition of NMF during solvothermal synthesis (Fig. S1†). As shown in Fig. 1a, the bending branch in the H<sub>4</sub>TPCA ligand features a wider coordination angle compared to the H<sub>4</sub>TPTA ligand, which can only rotate linearly. Additionally, the isophthalic acid part of the ligand coordinates with the metal In(III), occupying two of the four connectivities. The connections of the bending branches to the metal In(III), similar to a bending bridge, significantly alter the connection angle of the ligand, transforming the expected tetrahedrally coordinated mononuclear In(III) into a square-planar configuration. The asymmetric unit is illustrated by the crystal structure with a thermal ellipsoid diagram in Fig. S2.† This effective design strategy allows for the remarkable assembly of these two SBUs, which initially appear to be incompatible with the ssb topological node configuration, into the network. Moreover, in **ZJNU-401**, the introduction of open metal sites is effectively avoided, facilitating the formation of low-polarity pore surfaces. As shown in Fig. 1b and c, the bending branches of the ligand result in the straight channels being divided into a series of pockets, with a larger inner diameter of 11 Å and a smaller window size of 5 Å. Compared to the standard ssb network, **ZJNU-401** features a more diverse pore channel structure.

### Thermal and chemical stability

The experimental PXRD results show good agreement with simulation data on crystallographic information (Fig. S3†), verifying phase purity and stability of the synthesized sample. The chemical resistance of **ZJNU-401** to water, HCl (aq, pH = 3) and NaOH (aq, pH = 11) was evaluated over a 12-hours period while maintaining an unchanged PXRD pattern. These tests





Scheme 1 Illustration of the "bending-bridge" strategy, which modifies the original design approach of the ssb net by utilizing mononuclear metals and the tetracarboxylic acid ligand to construct low-polarity pore surfaces.

demonstrate the robust chemical stability of the skeleton in both aqueous and harsh environments. Additionally, TGA analysis was conducted on ZJNU-401 revealing an initial weight loss at 160 °C attributed to the removal of solvent molecules. Thermal decomposition commences when the temperature exceeds 300 °C resulting in the formation of corresponding oxides (Fig. S4<sup>†</sup>). These findings confirm the excellent chemical stability of ZJNU-401.

#### Gas adsorption of ZJNU-401

The permanent porosity of ZJNU-401 was investigated through nitrogen adsorption at 77 K, which exhibited a reversible type-I adsorption isotherm with a maximum saturated uptake capacity and Brunauer–Emmett–Teller (BET) values of 280 cm<sup>3</sup> g<sup>-1</sup> and 1224 m<sup>2</sup> g<sup>-1</sup>, respectively. Pore size distribution was determined using the density functional theory (DFT) method (Fig. S5<sup>†</sup>). Notably, JLU-MOF121 with twofold interpenetrated



Fig. 1 Structural description of ZJNU-401: (a) from the "bending-bridge" design of the ligand to the assembly with mononuclear In<sup>3+</sup> to form the 4-c node; (b) 1D pore channel of ZJNU-401; (c) low-polarity pore surface for effective MTO product purification.



and In-TPTAB with oversized pores did not exhibit any  $N_2$  adsorption behavior.<sup>34,35</sup> The unique pore environment characteristics of **ZJNU-401**, including uncoordinated O atoms, a saturated metal coordination mode, and an appropriate pore size, render it a promising candidate for investigating gas adsorption and separation properties.<sup>36,37</sup> Consequently, one-component adsorption isotherms for  $C_3H_6$ ,  $C_2H_4$  and  $C_2H_6$  were evaluated at 273/298/308 K under 1 bar. As illustrated in Fig. 2a–c and S6,† **ZJNU-401** demonstrates exceptional adsorption capacities of 5.38/4.53/4.28  $mmol\ g^{-1}$  for  $C_3H_6$  and 4.74/3.43/3.05  $mmol\ g^{-1}$  for  $C_2H_6$ , both significantly higher than that of 4.51/2.94/2.57  $mmol\ g^{-1}$  for  $C_2H_4$ . These results can be attributed to the smaller molecular size and fewer hydrogen atoms present in  $C_2H_4$ , leading to weaker host–guest interactions compared to the other gases studied.<sup>38–40</sup> In Fig. S5,† especially in the low-pressure region, the affinity of **ZJNU-401** for  $C_3H_6$ ,  $C_2H_6$  and  $C_2H_4$  shows a decreasing trend. This is consistent with the results of their respective adsorption enthalpies  $Q_{st}(C_3H_6) = 32\ kJ\ mol^{-1}$ ,  $Q_{st}(C_2H_6) = 29\ kJ\ mol^{-1}$ ,  $Q_{st}(C_2H_4) = 19\ kJ\ mol^{-1}$  as depicted in Fig. S7.†

### IAST selectivity and breakthrough testing of **ZJNU-401**

Remarkably, the adsorption capacity of **ZJNU-401** for  $C_3H_6$  and  $C_2H_6$  is significantly higher than that for  $C_2H_4$ , underscoring its suitability as an effective adsorbent material for the purification of  $C_2H_4$ , particularly in MTO processes. Consequently, we employed ideal adsorption solution theory (IAST) to calculate the separation of equimolar two-component gas mixtures at

temperatures of 273/298/308 K under 100 kPa. As illustrated in Fig. 2d and S8, S9,† **ZJNU-401** exhibited favourable selectivity values of 1.69/1.75/1.56 for  $C_2H_6/C_2H_4$ . This enhanced selectivity can be attributed to the slightly higher polarizability of  $C_2H_6$  ( $44.7 \times 10^{25}\ cm^3$ ) and more hydrogen atoms compared to that of  $C_2H_4$  ( $42.52 \times 10^{25}\ cm^3$ ). Furthermore, exceptional selectivity values of 11.81/15.45/13.96 were achieved for  $C_3H_6/C_2H_4$ , surpassing those reported for many well-known compounds in this field. Moreover, our calculations indicate that **ZJNU-401** holds significant promise for efficiently purifying  $C_2H_4$  from gas mixtures to yield polymer-grade olefin products. A comparison of **ZJNU-401**'s separation results at three different temperatures reveals that 298 K provides optimal purification conditions. Thus, a dynamic breakthrough experiment was conducted at this temperature and pressure using activated **ZJNU-401** to separate mixtures of  $C_3H_6/C_2H_6/C_2H_4$  (v/v/v, 1/1/1) and  $C_3H_6/C_2H_4$  (v/v, 1/1) (Fig. 2e and f). The carrier gas used was Ar with a total flow rate of  $2\ mL\ min^{-1}$ . Initially,  $C_2H_4$  elutes from the packed column at around 28 min while no detection of  $C_3H_6$  occurs until approximately 87 min. As a result, high-purity  $C_2H_4$  (>99.95%) can be continuously obtained over an extended duration lasting up to 59 min. Furthermore, while good adsorption is desirable, good repeatability is essential for the practical application of porous adsorbents. We performed multiple cycles of adsorption using  $C_2H_4$  gas and the breakthrough experiment after exposed to air for two months, and performed adsorption tests after six hours of immersion in different acid–base solutions (Fig. S10–S12†). The results indicate that **ZJNU-401** remains virtually unchanged, thereby confirming its excellent reproducibility. These findings underscore the



Fig. 2 (a–c) The adsorption isotherms of  $C_3H_6$ ,  $C_2H_4$  and  $C_2H_6$  at 273/298/308 K under 1 bar; (d) the selectivity of equimolar mixtures of  $C_2H_6/C_2H_4$  and  $C_3H_6/C_2H_4$  at 273/298/308 K; (e and f) the breakthrough curves of  $C_3H_6/C_2H_6/C_2H_4$  (v/v/v, 1/1/1) and  $C_3H_6/C_2H_4$  (v/v, 1/1) mixtures in an adsorber bed packed with activated **ZJNU-401** at 298 K and 1 bar; (g) comparison of selectivity for  $C_3H_6/C_2H_4$  and  $C_3H_6$  adsorption capacity at 10 kPa with other reported MOFs at 298 K.





Fig. 3 Calculation of the optimized adsorption sites for (a)  $C_3H_6$  and (b)  $C_2H_6$  and (c)  $C_2H_4$  within ZJNU-401, and comparison of the host–guest interactions among them.

potential applicability of ZJNU-401 as an excellent material for industrial MTO product separation. In Fig. 2g, we compare selectivity for both  $C_3H_6/C_2H_4$  and  $C_3H_6$  adsorption capacity at a pressure level of 10 kPa against other reported MOFs at 298 K.<sup>41–55</sup> Notably, ZJNU-401 demonstrates considerable advantages in addressing the recognized “trade-off” dilemma.

### Theoretical simulation

To gain further insights into the host–guest interactions between the framework and the adsorbate, the fixed loading task in the Sorption module based on the metropolis Monte Carlo method in MS 2020 was employed to determine the adsorption sites of acetylene, ethane and ethylene molecules at the MOF of ZJNU-401. Subsequently, binding energy between the adsorbates and framework was calculated for the low energy structure obtained from adsorption site calculation. As illustrated in Fig. 3 and S13,<sup>†</sup> the optimal adsorption sites for olefins are located near the  $[In(COO)_4]^-$  cluster within the channel, while alkanes tend to be surrounded by nonpolar aromatic rings. In ZJNU-401, we observed that all three gases interact with aromatic carboxylic acid backbones through multiple C–H $\cdots$ O/C hydrogen bonds and C–H $\cdots$  $\pi$  interactions. For  $C_3H_6$ , there are six short H $\cdots$ O/C distances ranging from 2.608 to 3.095 Å, which is significantly greater than those of  $C_2H_6$  and  $C_2H_4$ , resulting in a stronger binding affinity. This enhanced interaction can be attributed to the larger polarizability and size of the propylene molecule, which facilitates more extensive interactions with the framework (Fig. S14<sup>†</sup>). In contrast to  $C_2H_4$ , the saturated hydrocarbon  $C_2H_6$  has a higher number of hydrogen atoms. Thus, it is more likely to

be trapped by low-polarity benzene rings, forming approximately twice as many interactions at distances from 3.189 to 3.538 Å. Moreover, the host–guest binding energies are calculated as  $\Delta E$  ( $C_3H_6$ ) = 57 kJ mol<sup>-1</sup>,  $\Delta E$  ( $C_2H_6$ ) = 47 kJ mol<sup>-1</sup>, and  $\Delta E$  ( $C_2H_4$ ) = 40 kJ mol<sup>-1</sup>, respectively. These results indicate that both the low-polarity pore surface of ZJNU-401 and the intrinsic properties of the gases are conducive to the selective capture of  $C_2H_4$  from mixtures containing  $C_3H_6/C_2H_4$  and  $C_2H_6/C_2H_4$ . Finally, a comparison of the bond lengths of corresponding parts in the calculated structure and the host-crystal structure of ZJNU-401 was carried out. Since ZJNU-401 is a rigid framework, gas adsorption has a negligible influence on the host-crystal structures, resulting in insignificant bond-length changes (Fig. S15<sup>†</sup>).

### Conclusions

In summary, the introduction of a strategically designed bending angle at a specific point in the ligand facilitates the formation of square-planar 4-c nodes, providing a flexible and innovative pathway to achieve the desired geometry of the ssb net. The low polarity pore surfaces with accessible O active sites endow ZJNU-401 with preferential adsorption for  $C_3H_6$  and  $C_2H_6$  over  $C_2H_4$ , resulting in significant selectivity of  $C_3H_6/C_2H_4$  (15.45) and  $C_2H_6/C_2H_4$  (1.75). High-purity  $C_2H_4$  (>99.95% pure) was produced from  $C_3H_6/C_2H_4$  mixtures with a low-energy footprint. Multiple cycle experiments confirm its excellent reproducibility. DFT calculation results show that both the quantity and strength of host–guest interactions synergistically enhance the affinity of ZJNU-401 for  $C_3H_6$  and  $C_2H_6$  over  $C_2H_4$ .



This work establishes ZJNU-401 as a benchmark MOF for challenging binary separations involving C<sub>2</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>4</sub>, while also providing valuable insights to facilitate the design of ideal target nets based on advanced reticular chemistry for application in C<sub>2</sub>H<sub>4</sub> purification.

## Data availability

The authors confirm that the data supporting the findings of this study are available within the article [and/or its ESI†].

## Author contributions

Jiantang Li: writing – original draft, supervision; Zitong Song: preparation and synthesis of materials; Xia Zhou: experimental data analysis; Xue Wang: validation, visualization; Meng Feng: resources, software; Dongmei Wang: writing – review & editing, supervision, data curation; Banglin Chen: writing – review & editing, supervision.

## Conflicts of interest

There are no conflicts to declare.

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